The Separation of Alcohols

by

Traute Nieuwoudt

Dissertation submitted in partial fulfillment
of the requirements for the Degree

of

Master of Science in Engineering
(Chemical Engineering)

in the Department of Chemical Engineering
at the University of Stellenbosch

Supervised by

Prof. Izak Nieuwoudt

Prof. Leon Lorenzen

Stellenbosch
March 2002

DECLARATION

I, the undersigned, hereby declare that this dissertation is my own original work, except where specifically acknowledged in the text. Neither the present dissertation, nor any part thereof, has previously been submitted for a degree at any university.

Traute Nieuwoudt 13 December 2001

Group II experiments were performed in the format of a sensitivity analysis. The effects of various process parameters on the methanol breakthrough curves were individually assessed. Eighteen experiments were performed over a period of 8 days, with 86 samples drawn. The duration of an adsorption cycle was 30 minutes, allowing methanol breakthrough to occur. Water was preferentially adsorbed. Negative methanol bed loadings during high water loadings confirmed that water was able to displace methanol molecules. In the presence of water, molecular sieve 3A was capable of adsorbing 0.6 mg methanol/100mLAA, while in the absence of water with synthetically dosed methanol, molecular sieve 3A achieved a maximum loading of 12.3 mg methanol/100mLAA. The latter corresponded with a maximum methanol feed content of 1118 mg/100mLAA.

In general, quicker breakthrough occurred at higher flow rates and feed concentrations. Continuous breakthrough caused bed contamination and a 24-hour thermal regeneration was performed following experiment 12. The feed flow rate was increased from the theoretical 50 ℓ/hr to 70 ℓ/hr without any additional capital layout. Selected process conditions were found to be effective in continuously separating methanol from ethanol. Depending on the strategy of integration, profitability studies shows a Return on Investment of between 110.1% - 220.8% for the adsorption project.

Adsorption is superior to distillation in the separation of methanol. Due to the level of innovation involved, it is recommended that the contents of this study remain confidential and patent protection is to be extended. This dissertation speaks to both the wine making as well as the chemical engineering fraternity. It seeks to provide credibility to both parties, by clarifying the unknown issues fundamental to the respective disciplines.

SYNOPSIS

Pure primary alcohols are very valuable as raw materials and solvents. Close-boiling alcohol mixtures are produced as byproducts from the Fischer Tropsch synthesis. These byproducts include the mixtures 1-butanol+2-pentanol and 1-pentanol+2-hexanol. Due to the small difference in boiling points these alcohols cannot be separated from one another by using conventional distillation.

This study has been undertaken to determine whether primary and secondary alcohols may be separated by exploitation of their chemical properties. Esterification of the alcohols followed by distillation of the esters into cuts and hydrolyses of the esters, has been attempted to separate the alcohols. This however, was unsuccessful.

In this study the difference in dehydration rate of secondary and primary alcohols in acidic media has also been investigated. Several acidic resins and liquid catalysts have been used. The acidic resins gave no dehydration or extremely low dehydration rates in the liquid phase. The liquid catalysts H_2SO_4, Oxalic Acid, $NaHSO_4$ and H_3PO_4 were investigated. H_3PO_4 gave excellent results. Laboratory experiments were conducted at the boiling point of the reaction mixture at atmospheric pressure. The reaction mixture was sampled at varying time intervals and analysed. The secondary alcohol dehydrated rapidly to the corresponding alkene. The primary alcohol formed symmetrical ethers at a very low rate. The primary and secondary alcohol also combined to form small amounts of unsymmetrical ethers. After the dehydration reaction the organic products can be separated from the acid with a short path distillation unit. The primary alcohol can further be purified by conventional distillation. Conceptual process designs were done for the separation and purification of the reactor product streams of the alcohol mixtures 1-butanol+2-pentanol and 1-pentanol+2-hexanol.

On laboratory scale it was found that for the separation of 85% 1-butanol and 15% 2-pentanol (mass %), 90 % H_3PO_4 (mass %) at an acid:alcohol ratio of 1,5:1 results in suffcient dehydration of 2-pentanol. A reaction time of 70 minutes is required. A conceptual design on the purification of the 1-butanol predicted a product quality of 99,5 % 1-butanol (mass %) and a 1-butanol recovery of 75 %. The 1-butanol recovery is low, because a major part of the 1-butanol is lost in the purification as part of the ternary azeotrope with water and n-butylether.

On laboratory scale it was also found that for the separation of 85 % 1-pentanol+15 % 2-hexanol (mass %), 90 % H_3PO_4 (mass %) at an acid:alcohol ratio of 1,5:1 gives sufficient dehydration of 2-hexanol. A reaction time of only 35 minutes is required. A conceptual design on the purification of the 1-pentanol predicted a product quality of 99,9 % 1-pentanol and a 1-pentanol recovery of > 98 %. The 1-pentanol recovery is excellent, only the 1-pentanol that is converted to ethers is lost.

In this study it has been proven that a dehydration separation process can be applied successfully to remove secondary alcohols from a primary+secondary alcohol mixture. Especially the removal of 2-hexanol from a 1-pentanol+2-hexanol mixture gave promising results. In order to assess the economic viability of this dehydration process an economic evaluation should be done. This could be part of subsequent studies.

The dehydration separation process should be investigated further. It is believed that this dehydration separation process can be expanded to higher alcohols, e.g. 1-hexanol+2-heptanol. It would be extremely advantageous if a solid catalyst could be found for the separation. In this case the recovery of the organics from the reaction mixture would be very much easier. If a solid catatyst is not found, a continuous process using H_3PO_4 as liquid catalyst should be developed.

OPSOMMING

Suiwer primêre alkohole is baie waardevolle rou materiale en oplosmiddels. Alkohol mengsels, wat uit naby-kokende alkohole bestaan, word as newe-produkte in die Fischer Tropsch Sintese gevorm. Hierdie newe-produkte sluit alkohol mengsels soos 1-butanol+2-pentanol en 1-pentanol+2-hexanol in. Weens die klein verskil in kookpunte van hierdie alkohole kan die alkohole nie met konvensionele distillasie van mekaar geskei word nie.

Hierdie studie is onderneem om te bepaal of die chemiese eienskappe van alkohole benut kan word om primêre en sekondêre alkohole van mekaar te skei. 'n Poging is aangewend om die alkohole met behulp van esterifikasie te skei. Die alkohole is eers ge-esterifiseer, daarna met behulp van distillasie in verskeie snitte verdeel en die alkohol is vrygestel deur hidrolise van die esters. Dit was egter onsuksesvol.

Die verskil in dehidrasie tempo van sekondêre en primêre alkohole in suur mediums is ook ondersoek. Verskeie suur harse en vloeibare kataliste is ondersoek. Die suur harse het of geen dehidrasie of baie lae dehidrasie tempo's in die vloeistoffase gegee. Die vloeistof kataliste H_2SO_4, Oksaalsuur, $NaHSO_4$ en H_3PO_4 is ondersoek. H_3PO_4 het uitstekende resultate gelewer. Eksperimente is op laboratoriumskaal en onder atmosferiese druk uitgevoer. Monsters is van die reaksiemengsels by verskillende tydsintervalle geneem en geanaliseer. Die sekondêre alkohol het vinnig na die ooreenstemmende alkeen gedehidreer. Die primêre alkohole het simmetriese eters teen 'n lae tempo gevorm. Die primêre en sekondêre alkohole het ook gekombineer om gemengde eters te vorm. Kort-pad-distillasie kan gebruik word om na die dehidrase reaksie die organiese produkte van die suur te verwyder. Die primêre alkohole kan verder met konvensionele distillasie gesuiwer word. Konseptuele prosesontwerpe is uitgevoer vir die skeiding en suiwering van die alkohol mengsels 1-butanol+2-pentanol en 1-pentanol+2-hexanol nadat dehidrasie van die mengsels uitgevoer is.

Op laboratoriumskaal is dit gevind dat vir die skeiding van 85% 1-butanol en 15% 2-pentanol (massa %), 90 % H_3PO_4 (massa %) met 'n suur:alkohol verhouding van 1,5:1 effektiewe dehidrase van 2-pentanol lewer. 'n Reaksietyd van 70 minute word benodig. 'n Konseptuele ontwerp vir die suiwering van die 1-butanol het 'n produkkwaliteit van 99,5 % 1-butanol (massa %) en 'n 1-butanol opbrengs van 75 % voorspel. Die 1-butanol opbrengs is laag aangesien 'n groot deel van die 1-butanol verlore gaan as deel van die ternêre azeotroop wat 1-butanol met n-butieleter en water vorm.

Dit is ook op laboratoriumskaal vasgestel dat vir die skeiding van 85 % 1-pentanol+15 % 2-hexanol (massa %), 90 % H_3PO_4 (massa %) met 'n suur:alkohol verhouding van 1,5:1 effektiewe dehidrase van 2-hexanol lewer. 'n Reaksietyd van slegs 35 minute word benodig. 'n Konseptuele ontwerp vir die suiwering van die 1-pentanol het 'n produkkwaliteit van 99,9 % 1-pentanol en 'n 1-pentanol opbrengs van > 98 % voorspel. Die 1-pentanol opbrengs is uitstekend, en slegs die 1-pentanol wat omgeskakel word na eters gaan verlore.

In hierdie studie is dit bewys dat 'n dehidrasie skeidingsproses suksevol aangewend kan word om sekondêre alkohole uit 'n primêre+sekondêre alkohol mengsel te verwyder. Veral die verwydering van 2-hexanol uit 'n 1-pentanol+2-hexanol mengsel het belowende resultate gelewer. Om die ekonomiese lewensvatbaarheid van so 'n skeidingsproses te bepaal moet 'n ekonomiese evaluasie van die proses gedoen word. Dit behoort deel van verdere studies te vorm.

Die dehidrasie skeidingsproses behoort verder ondersoek te word. Dit word verwag dat die proses na hoër alkohol mengsels, bv. 1-hexanol+2-heptanol uitgebrei kan word. Dit sou baie voordelig wees indien 'n geskikte soliede katalis vir die skeiding gevind word. In so 'n geval sou die herwinning van die organiese produkte van die reaksiemengsel baie makliker wees. Indien 'n soliede katalis nie gevind word nie, behoort 'n kontinu proses waarin H_3PO_4 as vloeistof katalis gebruik word, ontwikkel te word.

Vir Izak, Stephan en Claudia

Index

LIST OF FIGURES

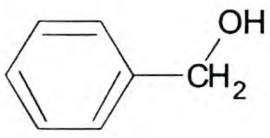
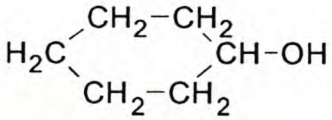
LIST OF TABLES

1 INTRODUCTION

1.1 What are alcohols ?

Alcohols are organic compounds that have a hydroxyl group (-OH) attached to a saturated carbon. This carbon may be a saturated carbon of a simple alkyl group, alkenyl group, alkynyl group or a carbon attached to an aromatic ring. The hydroxyl group may also be attached directly to an aromatic ring, in this case the alcohols are called phenols [1]. Examples of different alcohol types are given in Table 1.1.

Table 1.1: Different types of alcohols

Formula	Name	General type
$CH_3CH_2CH_2CH_2OH$	Butanol	aliphatic alcohol (saturated)
$H_2C{=}CH{-}CH_2{-}OH$	Allyl alcohol	aliphatic alcohols (unsaturated)
	Benzyl alcohol	aromatic alcohol
	Cyclohexanol	alicyclic alcohol

The hydroxyl group of an alcohol gives it specific characteristics. If this hydroxyl group is not attached to a carbon atom, which is attached with single bonds to other atoms, the alcohol will not have the general characteristics of an alcohol [2]. Alcohols are also named according to the number of hydroxyl groups that they contain, e.g. monohydroxy, dihydroxy, trihydroxy and polyhydroxy. In general one carbon atom cannot be attached to two hydroxyl groups, because water would be split out spontaneously. There are however, a few exceptions to this rule, e.g. chloral hydrate, $Cl_3CH(OH)_2$ [2].

Generally alcohols are classified into three groups, namely primary (1^o), secondary (2^o) and tertiary (3^o) alcohols. The condition of the carbon to which the hydroxyl group is attached, determines the classification. If this carbon is attached to one carbon, the alcohol is a primary alcohol. If this carbon is attached to two carbons it is a secondary alcohol and if this carbon is attached to three carbons, it is a tertiary alcohol, see Figure 1.1 [1].

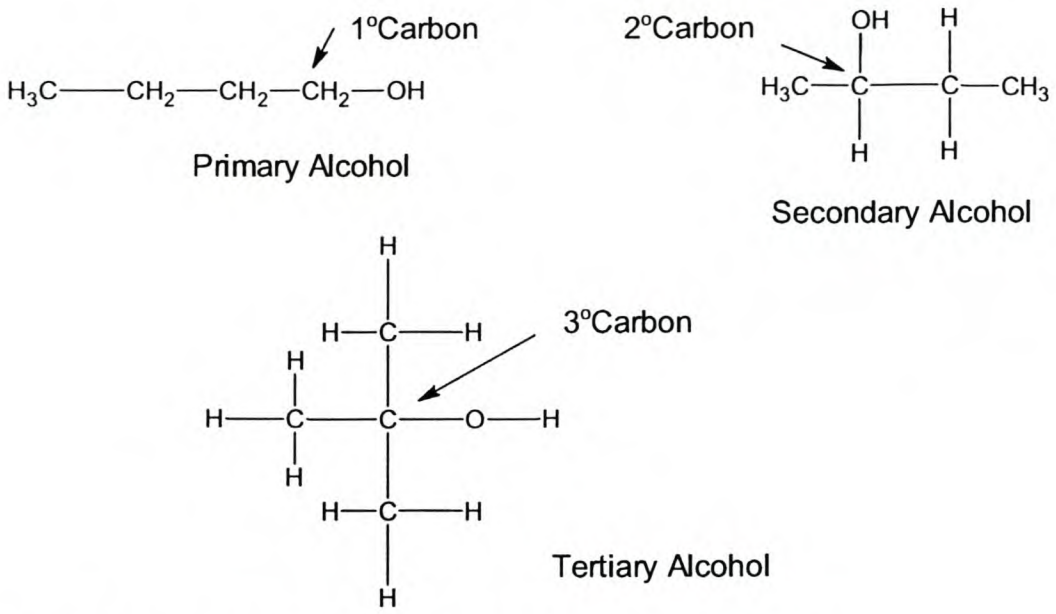


Figure 1.1: Schematic diagram of alcohol classification

Alcohols are clear liquids or colourless solids [2]. The density of most of the monohydroxy aliphatic alcohols is less than that of water. The viscosity of the monohydroxy aliphatic alcohols increases with molecular weight. The alcohols C_6 to C_{11} become increasingly viscous. At room temperature, n-Dodecyl alcohol is the first solid in the series of the normal primary alcohols [2].

Alcohols containing one to three carbon atoms are completely miscible in water. 1-Butanol, 2-butanol and pentyl alcohols have only limited solubility in water. The solubility in water decreases very rapidly with increase in molecular weight. Hexanol and higher alcohols are essentially insoluble in water. In alcohols with the same molecular weight increased branching increases the solubility in water [2]. This can be seen in Table 1.2 [3]. The solubility in water also increases from primary to secondary to tertiary alcohols. [2]. The solubility of water in butanols is given in Table 1.3 [3].

Table 1.2: Solubility of butanols in water [mass %]

Temperature	1-Butanol	2-Methyl-1-propanol	2-Butanol	tert-Butanol
20 °C	7,7	8,5	12,5	miscible
30 °C	7,08	7,5	18	miscible

Table 1.3: Solubility of water in butanols [mass %]

Temperature	1-Butanol	2-Methyl-1-propanol	2-Butanol	tert-Butanol
20 °C	20	15		miscible
30 °C	20,62	17,3	36	miscible

1.2 The commercial importance of alcohols

The commercial importance of the various alcohols differ significantly. The most important alcohols in industry are methanol, ethanol, 1-propanol, 1-butanol, 2-methyl-1-propanol (isobutylalcohol), the plasticizer alcohols (C_6 – C_{11}) and the fatty alcohols (C_{12} – C_{18}). Alcohols are used as solvents and diluents for paints (C_1 - C_6), plasticizers (C_6 – C_{11}) and in the manufacture of detergents (C_{12}- C_{18}). They are also used as intermediates in the manufacture of a range of organic products, e.g. esters, as flotation agents, as lubricants, and also increasingly as fuel or fuel additives, e.g. methanol, ethanol, *tert*-butyl alcohol [4].

Pure alcohols are very expensive. In order to cut costs, industry often prefers to use isomeric mixtures if possible. Mixtures of alcohols with different carbon numbers can also be used for certain purposes [4].

Because of periodical oil crises, environmental considerations and the aim to reduce energy consumption, the use of oxygenated compounds as fuels additives are considered [5]. Of all alcohols, ethanol is mostly used as a fuel. The main attractiveness to use ethanol as a liquid fuel, is that ethanol reduces the CO_2 emissions considerable in comparison to normal fossil fuels [6].

A further use for alcohols is as feedstock for the production of ethers. Olefins are reacted with alcohols to form ethers. These ethers (methyl *tert*-butyl ether, ethyl *tert*-butyl ether and methyl-*tert* amyl ether) are also used as fuels or fuel supplements [5].

The uses of 1-butanol in the USA in 1999 are shown in Table 1.4.

Table 1.4: Uses of 1-Butanol [7]

Uses of Butanol	**%**
Monomer component to produce butylacrylate and methacrylate and the corresponding esters	42
Monomer component to produce glycol ethers	25
Monomer component to produce butyl acetate	15
For direct solvent use	9
As plasticizer	3
To produce amino resins	2
Miscellaneous, incl. for the production of Butylamines	4

The esters are used in latex architectural paints, which is a growing market. The use of butanol to produce esters is growing at an annual rate of 4 to 5 %. This is higher than the growth (3%) of the 1-butanol market in general. The volume of the USA architectural surface coatings is only growing at 2 % per year, however, it is based on a huge volume, namely 700 million gallons per year. The use of 1-butanol as direct solvent for the production of butylamine and plasticizers is growing moderately. No growth is expected in the amino resin market [7].

The prices of alcohols as published in December 2000 are given in Table 1.5.

Table 1.5: Alcohol prices, USA, December 2000 [8]

Alcohol	Comments	Price in US $ per kg
1-propanol	Tanks, delivered	1,39 to 1,48
1-butanol	Synthetic, tanks, freight allowed	1,21 to 1,30
Sec-butanol	Synthetic, tanks, delivered	1,48 to 1,54
Tert-butanol	Synthetic, tanks, delivered	1,48 to 1,54
Amylalcohol (Pentanols)	Primary mixed isomers, tanks, Freight allowed	1,03
1-Hexanol	Synthetic, tanks, free on board	1,94

The future of the 1-butanol market is closely linked to its use for surface coatings. The demand for water-based coatings is growing. Analysts estimated that 70 % of interior paints and 85 % of exterior paints are already water based [7]. Due to environmental considerations, there is thus potential growth for 1-butanol in the surface coating industry world-wide.

The demand for 1-butanol in the USA is increasing: 1998, 0.82 million ton; 1999, 0.84 million ton; 2003, 0.91 million ton (including exports). The 1-butanol market has been growing annually, and is expected to grow in future. The historical growth (1989-1998) was 2.5 % per year. A future growth of 3 % per year through to 2003 is expected. The price of 1-butanol fluctuated between 0,36 US$ and 0,5 US$ per pound in 1999 [7]. According to Table 1.5 the price of 1-butanol fluctuated between 0,55 to 0,59 US$/pound in 2000.

Due to lower Asian export rates, higher energy costs and feedstock prices, the US markets (similar to the Europe Markets) for oxo alcohols decreased, especially the market demand for 1-butanol and 2-ethyl-hexanol. In January 2001 the oxo alcohol prices increased to keep up with the increase in propylene prices. Increases of between 2 and 7 % were announced. Several new oxo-plants are coming on-line in Asia. This causes an oversupply of oxo alcohols on the markets. Many producers are thus running at only 70 to 80 % of their plant capacity in order to match the demand for oxo alcohols. The oxo alcohol industry in the USA hopes that the domestic increase in demand for 1-butanol and 2-ethyl-hexanol will absorb the oversupply from Asia in the next 2 or 3 years [9].

1-Pentanol is used as a solvent and as an extracting agent. The solubility of 1-pentanol in water is very low, however, it has a high solvency for oily materials. It is used as diluent for hydraulic fluids, printing inks and laquers. It is also used as starting material for various chemicals. In the USA a high % of the primary amylalcohols are converted to amylacetate, which is used as a solvent or an extractant. Amylalcohols are also converted to a wide range of esters. The esters are used as plasticizers, solvents, perfumes and medicinals [10], [11]. The price of amylalcohols as given in Table 1.5 is the price of primary amylalcohol isomeric mixtures. The price of 1-pentanol is expected to be higher.

1-Hexanol is mainly used as a solvent, as plasticizer or as a basic material for the perfume industry [4]. According to Table 1.5, 1-hexanol is the most expensive of the primary C_3 to C_6 alcohols.

1-Heptanol has very little commercial application in its pure form. Isomeric heptanol mixtures are used as plasticizers [4].

The demand for fatty alcohols (C_{12}-C_{18}) to be used for alcohol-based surfactants is expected to grow globally. Shell Chemical Company is expanding its annual production of higher alcohols from 0.4 million tons to 0.56 million tons. This is an increase of 40 %. New plants are built and old plants are debottlenecked. The plants are expected to be on-line in mid 2002. The oxo-synthesis process is used in most of the expansions. (The oxo-synthesis is described in Chapter 2). In 1998 the demand for detergent alcohols was 1,5 million tons. It is expected that the global demand for detergent alcohols will increase at an annual rate of 3,1 % to 2,1 million tons in 2010 [12].

1.3 Commercial facts about Fischer-Tropsch alcohol products

Sasol sells a very wide range of alcohols as part of the Sasol Solvents Business. These alcohols vary from 99,9 % pure ethanol to C_5-alcohol mixtures. Many of the products are pure alcohols at varying grades. Several alcohol mixtures, ranging from C_2-isomers to C_5-isomers are also marketed as solvents. The costs of the alcohols and alcohol mixtures heavier than C_3-alcohols that are marketed by Sasol are given in Table 1.6 [13].

Table 1.6: Sasol commercial alcohols $\geq C_3$

Trade Name	Product Specification	Bulk Cost, May 2001 SA Rand per ton, ex. Johannesburg
Iso-Propylol	85 % iso-propylalcohol and 15 % ethanol	4205
1-Propanol	Pure	4910
Iso-Butylol	30 to 60 % iso-butylalcohol, the rest is 1-propanol and 2-butanol	Not available
Propylol	Minimum 85 % propanol and minimum 12 % 2-butanol	4000
1-Butanol	Pure	5235
Butylol	Minimum 75 % 1-butanol, The rest is iso-butylalcohol and secondary pentanol	3788
Sabutol	Minimum 60 % 1-butanol, The rest is iso-butylalcohol and secondary pentanol	3546
Sabutol Bottoms	C_4 and C_5 isomers, minimum 50 % C_5's	Not available
Pentylol	C_5 alcohol isomers	3150

Condea had the second largest market share in the European solvents (C_3 to C_5 alcohols) business in the year 2000. In the year 2000 Sasol sold about 100 kt per annum of detergent alcohols (>C_6-alcohols). Condea sold 250 kt per annum in 2000. With Sasol taking over Condea and if all the planned expansions of Sasol are realised, the Sasol Group will have the potential to be a major player in the global alcohol business [14].

A new 1-butanol plant is being built in Sasolburg. This plant should be in operation by 2002. This plant is a technology partnership between Sasol and the Japanese company Mitsubishi Chemical Corporation [15]. The production capacity of this plant will be 120 000 tons per year [16].

From Table 1.6 it is evident that the prices of the pure alcohols are considerably higher than those of the alcohol mixtures. The price of 1-propanol is 23 % higher than that of propylol and 1-butanol is 40 % more expensive than butylol. Assuming that the price of 1-pentanol is at least the same as 1-butanol, it will be 66 % higher than that of the Pentylol mixture. If these mixtures are separated into pure alcohol components, it could mean an increase in income for the Sasol Solvents Business.

Some alcohols boil close and cannot be separated easily from one another by conventional distillation. The mixture Propylol consists of 85 % 1-propanol and the rest is 2-butanol. The boiling points of these alcohols differ only with 2,3 ^{o}C. Sasol markets pure 1-propanol, the separation of 1-propanol and 2-butanol is achieved with extractive distillation.

Due to the anticipation that the 1-butanol market will increase in the future, Sasol is presently increasing their 1-butanol capacity by building a new plant. However, 1-butanol is still sold as a major part of the butylol mixture. The apparent reason that this mixture is sold, is that Sasol has no economic viable method to separate the components that are present in butylol. The same reason probably explains why pentylol is sold as a mixture.

1.4 Aliphatic close-boiling alcohols

The boiling points of alcohols rise with about 20 °C per added methylene group from ethanol to higher primary unbranched alcohols. For alcohols with a given molecular weight, the boiling point decreases with increasing branching and also decreases from primary to secondary to tertiary alcohol [2]. The physical properties of some monohydroxy alcohols are given in Appendix A, Table A1. From this table close boiling alcohols are identified. These close-boiling alcohols are summarised in Table 1.7.

Sasol produces typically some of these close-boiling mixtures as byproducts in the Fischer Tropsch Process (See Chapter 2).

Table 1.7: Close boiling alcohols (<C_7)

Type of aliphatic alcohol	Name	Boiling Point [°C]
Primary C_2	Ethanol	78,3
Secondary C_3	2-Propanol	82,3
Tertiary C_4	ter-Butanol	82,5
Primary C_3	1-Propanol	97,2
Secondary C_4	2-Butanol	99,5
Primary C_4	1-Butanol	117,7
Secondary C_5	3-Pentanol	115,3
Secondary C_5	2-Pentanol	119,9
Primary C_5	1-Pentanol	138
Secondary C_6	2-Hexanol	139,9
Secondary C_6	3-Hexanol	135,5
Primary C_6	1-Hexanol	156,5
Secondary C_7	2-Heptanol	157
Secondary C_7	4-Heptanol	155

The individual components in the mixtures as summarised in Table 1.7 cannot be recovered easily by conventional distillation. Physical properties, other than boiling points or the chemical properties of these components will have to be exploited to separate these components.

From Table 1.7 it is evident that the close-boiling alcohol mixtures consist of a primary alcohol with (n) carbons and one or more secondary alcohols with (n+1) carbons.

1.5 Project definition and aims

A new method will be developed to separate close-boiling primary and secondary alcohol mixtures. Typical mixtures as produced by the Fischer Tropsch synthesis will be used as feed material. The following mixtures will be used as case studies:

- 1-propanol + 2-butanol
- 1-butanol + 2-pentanol
- 1-pentanol + 2-hexanol

A primary:secondary alcohol mass ratio of 85:15 will be used.

The developed method will be evaluated and a conceptual design of a separation process will be done. The following steps will be performed to achieve this aim:

- A literature study, which summarises how alcohols are produced, separated and purified.

- It will be investigated whether the difference in chemical properties of primary and secondary alcohols can be utilised to achieve separation of these alcohols. Two approaches exploiting the chemical properties of alcohols will be tested:

  - esterfication of the alcohols, thermal separation of the esters and release of the alcohols
  - dehydration of the secondary alcohols to alkenes, removal of these alkenes during the reaction, recovering and purifying the remaining primary alcohols

- These separation methods will be tested experimentally. If the methods are found to be viable, the effect of process conditions will be evaluated and optimum process conditions will be determined.
- A conceptual design for the separation and purification process will be done.

2 THE PRODUCTION OF ALCOHOLS

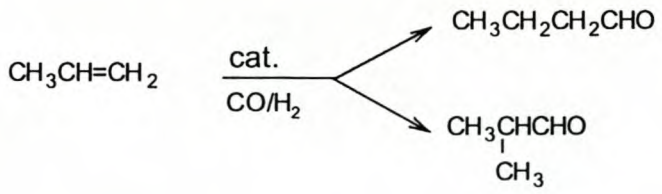
2.1 Introduction

Ethanol is mainly produced by fermentation of natural products. Industrially the other alcohols are produced mainly synthetically from hydrocarbon raw materials. Firstly a general description of the methods used for the commercial production of alcohols will be given. Thereafter a short description will be given of how the Fischer-Tropsch process produces alcohols.

2.2 General production methods of alcohols

The oldest method of producing ethanol is by **fermentation** of natural carbohydrate raw material. This method is still applied today to produce ethanol for human consumption and for industrial purposes. Pentanols are also recovered on a small scale from fusel oil [4]. Other alcohols have to be produced synthetically on an industrial scale.

The most widely applied process is the **oxo synthesis**, which produces alcohols in the range C_3 to C_{20}. In this process olefins react with synthesis gas ($CO + H_2$) in the presence of a homogenous catalyst to form aldehydes. Before 1970 the reactions were performed under pressures of 20 to 30 MPa and at temperatures of 100 to 180 °C. For olefins with more than two C-atoms, isomeric aldehyde mixtures are normally obtained. In the case of propylene these consist of 1-butanal and 2-methylpropanal:



(2.1)

The produced aldehydes are hydrogenated to form the corresponding alcohols [3].

Commercially this process was first used in 1963 to produce 1-butanol and 2-ethylhexanol. This process was developed further to produce higher alcohols [4].

The worldwide oxo production capacity for aldehydes and alcohols was 6.5×10^6 t/a in 1997. The C3 to C19 oxo products are the most important, of which Butanal presents 75 % [17].

There are several variations of the hydroformylation process. The differences are the catalysts used and the reaction conditions (temperature, pressure). Cobalt based and Rhodium based catalysts are used [3].

Until the mid 1970s only cobalt based catalysts were used. The more expensive rhodium catalysts were introduced in 1974. The rhodium catalyst improves the olefin efficiency and it has a higher selectivity. When using the rhodium catalyst cheaper construction material can be used. The oil crises in 1970 shifted the major expenses of the oxy synthesis to the raw materials, e.g. propene and synthesis gas account for about 75 % of the product value [17].

The process using a modified Rh-catalysts can give isomeric ratio's of 1-butanol and 2-methyl-propanol of about 92:8 or 95:5. Unmodified Rh-catalysts can produce up to about 50 % 2-methyl-propanol [3].

The Low-Pressure Oxo (LPO) Process is the most important of the oxo syntheses using rhodium-triphenylphospine as a catalyst on an industrial scale. A basic flow diagram of the LPO gas-recycle oxo synthesis process is given in Figure 2.1 [17].

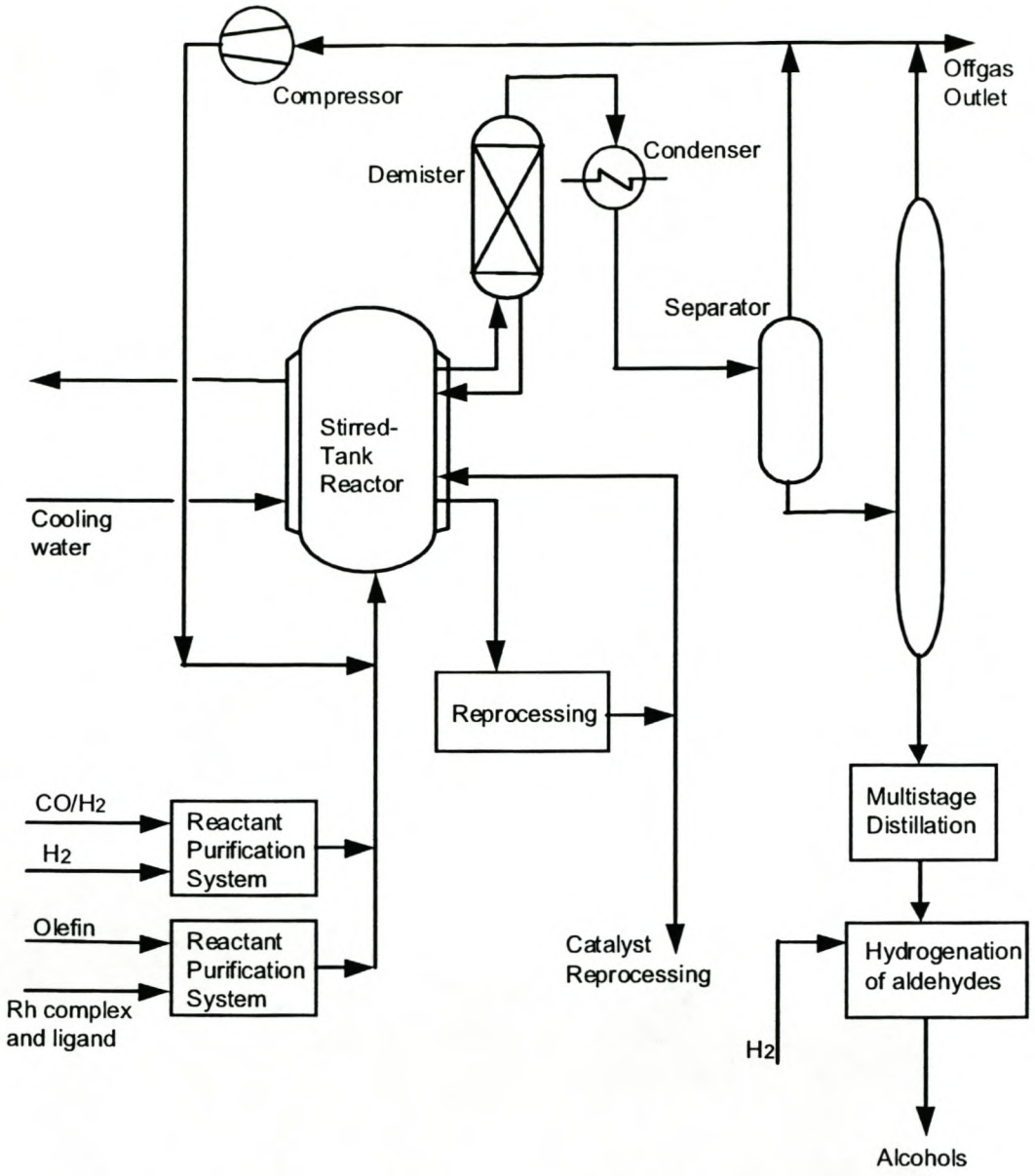


Figure 2.1: Schematic flowdiagram of Low-Pressure Oxo (LPO) Process

The reaction takes placed in a stainless steel stirred tank reactor. The reactants and make-up catalysts are fed from below. The reactants and catalysts have to be purified to prevent catalyst poisoning. The reactor is operated between 85 – 115 °C and at < 20 bar. A conversion of about 30 % per pass is achieved. The reaction is exothermic and the heat of reaction is removed with cooling water.

To maintain the catalyst activity a portion of the catalyst has to be reworked continuously. When the catalyst is deactivated, the catalyst has to be removed completely and reprocessed. The recycle gas forces the reaction products out of the reactor. The reaction products pass through a demister, condenser and separator. At the separator, unreacted starting materials and the hydrogenated olefin (e.g. propane if the olefin is propene) are recycled via a compressor back to the reactor. Part of the recycle stream is bled-off to avoid build-up of alkanes (e.g. propane) in the recycle stream to the reactor. Liquid-recycle variants of the LPO process are also in operation. The remaining olefins in the liquid stream after the separator are removed in a stripping column. The olefins are fed to the recycle stream. The crude aldehyde product is then processed further in multistage distillation processes. [17].

The pure aldehydes are then hydrogenated to the corresponding alcohols. Homogenous or heterogenous catalysts may be used for the hydrogenation. If the reactants contain sulphur or if the hydrogen contains carbon monoxide, a homogenous catalyst is used. Usually the heterogenous catalyst is preferred. Both catalysts are effective in the gas phase at about 25 bar and at temperatures between 90 to 180 °C. In the liquid phase the catalysts are effective between 80 and 220 °C and up to 300 bar. For continuous production of alcohols, the heterogenous catalyst in a fixed bed is used. The aldehyde and the hydrogen are mixed and fed together through the catalyst bed. The reaction is exothermic and the heat of reaction is removed by circulating the hydrogen through a heat exchanger. Mainly nickel and copper based catalysts are used, however zinc, chromium and combinations of these metals have been used successfully as catalysts [4].

The Shell Process is another version of the **oxy synthesis**. This process is used when the corresponding alcohol is the desired product and not the aldehyde. The strong hydrogenating activity of the catalyst, $HCo(CO)_3PR_3$, leads to the direct hydrogenation of the initially formed aldehyde in the oxo reactor [4].

$$R\text{-}CH{=}CH_2 + CO + 2\,H_2 \xrightarrow{\text{catalyst}} R\text{-}CH_2CH_2CH_2OH \qquad (2.2)$$

The Shell Process uses a modified Cobalt catalyst, which gives a favourable n-alcohol/iso-alcohol ratio (88:12) [17]. Very few plants are still using the first unmodified cobalt catalyst. This catalyst requires high reaction temperatures and pressures [17].

In 1989 the total world oxo capacity (aldehyde) was 8×10^6 t/a. The largest share in these productions were Germany (21 %) and USA (31 %) [17]. In 1999 the total USA 1-butanol capacity was $1{,}2 \times 10^6$ t/a [7].

Small amounts of alcohols are produced with **synthesis gas (CO and H_2).** Sasol produces alcohols as byproducts of the Fischer-Tropsch synthesis. The product range marketed by Sasol is discussed in paragraph 2.3.

Linear alcohols can be produced according to the **Ziegler process** [4]. Ethylene is added to triethylaluminium to produce a mixture of trialkylaluminium compounds with a higher molecular mass. The trialkylaluminum products can then be oxidized with air to form the corresponding aluminium oxides. These oxides are then hydrolysed to a mixture of linear primary alcohols with the same number of carbon atoms as the alkyl groups of the trialkylaluminium components:

ethylene addition: $\text{-Al-C}_2\text{H}_5 + x\,\text{C}_2\text{H}_4 \longrightarrow \text{-Al-(CH}_2\text{CH}_2)x\text{-C}_2\text{H}_5$

oxidation: $\text{-Al-(CH}_2\text{CH}_2)x\text{-C}_2\text{H}_5 + \text{O}_2 \longrightarrow \text{-Al-O-(CH}_2\text{CH}_2)x\text{-C}_2\text{H}_5$

hydrolyses: $\text{-Al-O-(CH}_2\text{CH}_2)x\text{-C}_2\text{H}_5 + \text{H}_2\text{O} \longrightarrow \text{HO-(CH}_2\text{CH}_2)x\text{-C}_2\text{H}_5 + \text{-Al-OH}$

(2.3)

Condea has developed a process known as the Alfol Alcohol Process (Conoco Process), which is based on the Ziegler process. The chain growth reaction is carried out at low temperatures to avoid alkene formation. The Alfol process produces practically 100 % linear alcohols. A very broad range of linear alcohols, from C_2 to C_{28} can be produced according to this method. The Ethyl Corporation developed a second industrial process that uses the Ziegler reactions. The alcohols produced are up to 95 % linear with the main fraction of alcohols being between C_{12} and C_{14} [4].

Oxidation of saturated hydrocarbons can be applied to produce alcohols. According to the Bashkirov Oxidation aliphatic hydrocarbons are converted to esters in the presence of boric acid and air. The esters are hydrolyzed to release the alcohols. Mainly secondary alcohols are produced. This process has two main disadvantages: the circulation of the hydrocarbons is very expensive and the market demand for secondary alcohols is very low [4].

Hydration of olefins is a further reaction for the production of lower alcohols. Secondary and tertiary alcohols are formed according to Markovnikov's rule. Primary alcohols cannot be formed according to this reaction if Markovnikov's rule is followed. This rule states that the hydrogen attaches to the carbon that has the highest number attached to it.

$$\text{R-CH=CH}_2 + \text{H}_2\text{O} \xrightarrow{\text{H}^+} \text{R-CHOH-CH}_3 \qquad (2.4)$$

"The rate of this reaction is determined by the stability of the intermediate carbenium ion (tertiary > secondary > primary). Therefore, the hydration of isobutene proceeds at room temperature in the presence of low H+ ion concentrations owing to the relative stability of the intermediate carbenium ion. The hydration of ethylene, in contrast, requires elevated temperatures and pressure" [4]. The *indirect process* (liquid-phase reaction) and *direct process* (gas-phase reaction) are applied in industry. The indirect reaction consists of two steps: the olefin reacts with sulphuric acid to form mono- and dialkylsulfates, thereafter the alkylsulfates are hydrolysed to the alcohol. In order to recycle the olefin, a costly reconcentration is required. In the direct process (gas phase) the alcohol formation is favoured by high pressure (2 moles form 1 mole) and low temperature. The conversion is incomplete and a gas recycle is required. Catalysts containing Phosphoric acid, e.g. celite are efficient catalysts. Ion exchangers have also been used recently. Hydration of olefins is primarily used to produce ethanol from ethylene, isopropylalcohol from propene, tert-butyl alcohol from isobutene and 2-butanol from 1-butene and 2-butene [4].

Carboxylic acids and esters can also be hydrogenated to produce alcohols. Natural fats and oils are used as starting materials. These fats and oils are then transesterified to the methyl esters and then reduced to alcohols. In this way unsaturated alcohols may be produced [4].

Limited amounts of highly branched isomeric alcohols, C_{16} to C_{18} are prepared by the **aldol condensation of lower aldehydes** (from the oxo synthesis) and hydrydrogenation of the alkenals [4].

2.3 The production of Alcohols in the Fischer Tropsch process

A schematic overview of the Sasol Fischer Tropsch process is given in Figure 2.2. The Sasol process uses coal as a raw material. The coal is converted into crude gas. This is done under pressure and at a high temperature in the presence of steam and oxygen. After the gasification the products are cooled. The main product of the gasification process is the synthesis gas (CO and H_2). The liquid products (co-products) are recovered. These co-products include tars, oils and pitches. Further co-products are recovered and processed further. These include ammonia, coke, phenol, cresol and xylenol and sulphur.

The purified synthesis gas is then converted, according to the Fisher Tropsch process, in either the Slurry Phase Distillate Reactor or the Advanced Synthol Reactor.

The Slurry Phase Distillate Reactor uses a low temperature conversion. This plant is situated at Sasolburg. The reactor produces linear-chained hydrocarbon waxes and paraffins. High-quality diesel can also be produced at the Sasolburg plant. The Slurry Phase Reactor also produces residual gas, which is sold as pipeline gas. A further product is ammonia, which is either sold or used downstream to produce explosives and fertilisers.

In Secunda the Sasol Advanced Synthol (SAS) reactors are used. Moderate-temperature conversion takes place in these reactors. The hydrogen and carbon monoxide react under pressure in a fluidised, iron-based catalyst. A very wide spectrum of hydrocarbons from C_1 to C_{20} are formed. These hydrocarbons include oxygenated hydrocarbons (e.g. alcohols). This technology gives Sasol a significant cost advantage. Sasol produces high value chemicals as a byproduct in their coal to synthetic fuel production.

Downstream of the SAS reactors, the products are cooled. The products are separated by distillation. The methane rich gas is converted to synthesis gas in the gas reforming unit. Part of the methane gas is sold as pipeline fuel gas. The C_2 stream is separated into ethylene and ethane. The ethane is further cracked to ethylene. Ethylene is utilised in further Sasol processes as a raw material or sold (e.g. to produce Vinyl Chloride Monomer). The Propylene is purified and used to produce polypropylene.

The C_4 to C_{20} are referred to as the "Heavy cut" or oil stream. The majority of this stream is routed to the refinery, to produce petrol, diesel, Liquid Petroleum Gas (LPG), Jet fuel, propane, butane, fuel oil and illuminating paraffin. The oil stream also contains very valuable olefins. The C_5 to C_8 olefins are recovered in the Alpha Olefins Plant. The C_9 to C_{11} olefins are routed to the fuel pool.

Oxygenated hydrocarbons in the exit of the SAS reactors are separated as an aqueous stream and purified in the Chemical Work-up Section. In this plant alcohols, acetic acid and ketones are produced [13].

The alcohol (C_2 +) and water are processed further. The water is removed form the alcohol stream by using benzene as an entrainer [18]. The dry alcohols are then separated further. Sasol markets a range of alcohols, including pure alcohols and alcohol mixtures. The pure alcohols include: ethanol, 1-propanol and 1-butanol. The trade names of the alcohol mixtures are Iso-Propylol, Iso-Butylol, Propylol, Butylol, Sabutol, Sabutol Bottoms and Pentylol.

After the production of alcohols they have to be purified before they can be used as raw materials or solvents. Several purification methods of alcohols will be discussed in the next chapter.

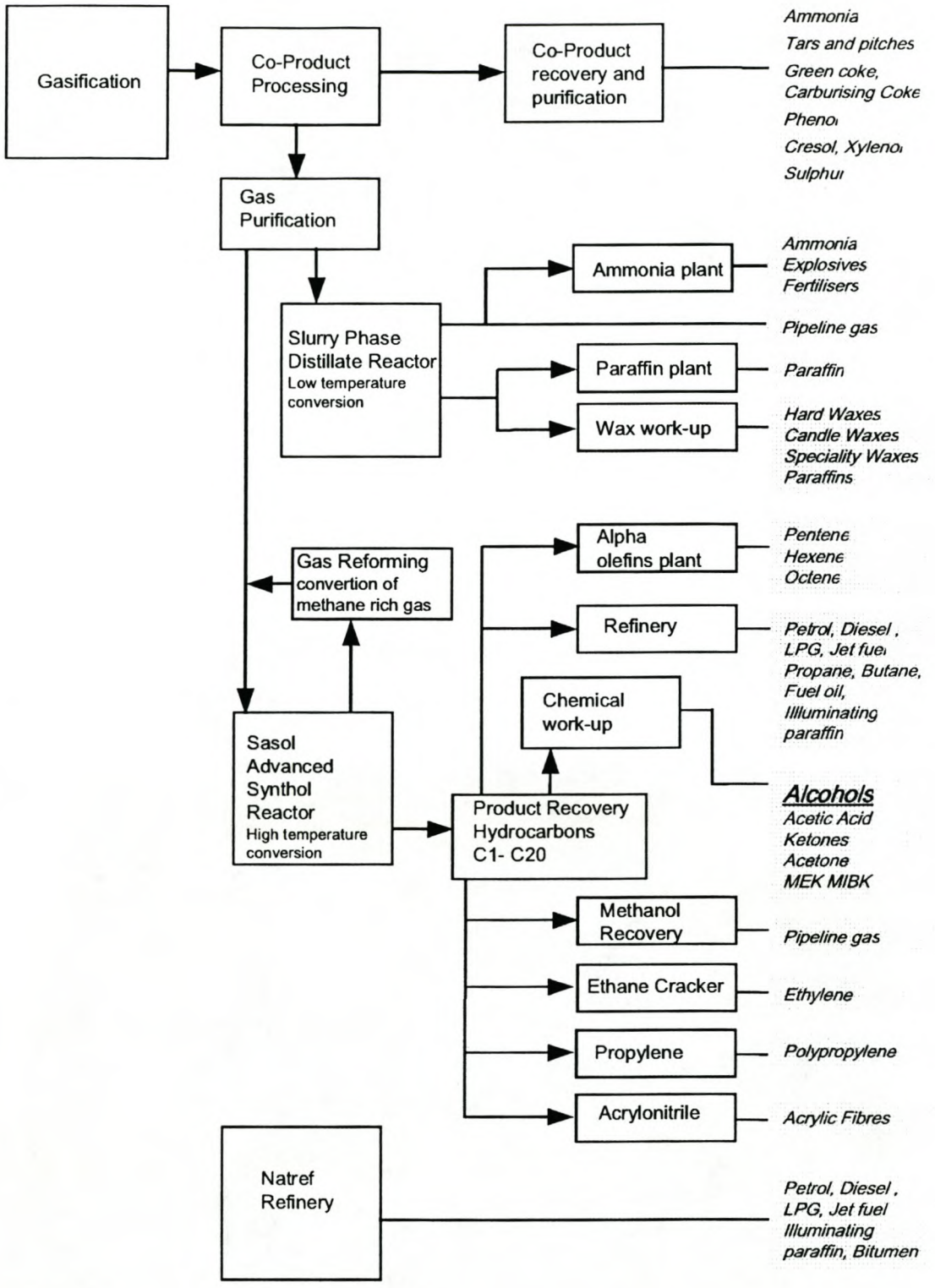


Figure 2.2: Schematic overview of the Sasol Fischer Tropsch Process

3 ALCOHOL SEPARATION AND PURIFICATION METHODS: THE STATE OF THE ART

3.1 Introduction

The techniques mainly used to separate alcohols from each other are distillation, extractive distillation and azeotropic distillation. Besides these techniques, several further techniques are also used to separate alcohols from other components. These techniques include extraction, reaction, film evaporation, pervaporation, osmoses, adsorption, crystallisation, stripping or combinations of these processes. They will all be discussed in this chapter.

3.2 Alcohol purification processes before World War II

The earliest patent publication for the purification of alcohols dates back to 1929. The problem to be solved was the purification of alcohols that were produced by the catalytic reaction of carbon monoxide with hydrogen. Several byproducts were formed. These byproducts included fatty acids, esters, unsaturated hydrocarbons, aldehydes, acetals, ketones, ethers, thiols and alkylsulphides. Although these byproducts were present in very small quantities they are responsible for the bad odour of the alcohols. The contaminated alcohols were not suitable for several technical applications [19]. The customary separation method applied was fractional distillation. However, the impurities interfered with the distillation process and pure alcohol cuts could not be produced [20].

Most of the purification processes consisted of subjecting the raw alcohol to a hydrogenation step and caustic wash step, followed by reaction steps during which the impurities are converted into non-volatile components. The final step is fractionation of the treated alcohol mixture wherein the alcohol is recovered in the distillate or side stream.

If the synthetic raw product (from the catalyzed reaction of CO and H_2) is distilled first, a caustic soda solution, sodium bisulphite or oxalic acid can be added to the mixture during distillation [20]. The free and combined acids, thiols and part of the free aldehydes are removed by treatment with the alkali [19]. The free aldehydes are polymerised to non-volatile bodies [21].

The raw alcohol product or the distillation fractions could also be treated with an oxidising agent. The oxidising agents, eg. potassium permanganate, hydrogen peroxide, persulphate, perborate, percarbonate, hypohalite are dissolved in water and

the synthetic product or the alcohol fractions are stirred with this solution. The purifying action begins immediately. The initial oxidisation can be supplemented by further oxidising with non-volatile organic bases, eg. aminophenols. It would be a further advantage to subject the raw alcohol to adsorption agents, eg. Fuller's earth, decolourising carbon, activated carbon or silica gel [20]. If the raw alcohol product contains ammonia or relatively volatile organic bases, these impurities may be made involatile by reaction with metallic halides before distillation [20].

Impurities which are not removed by treatment with an alkali could be removed by treating the raw alcohol (alcohols boiling below 100 °C) with chlorine or bromine. The halogen combines e.g. with the alkylsulphate impurities and the halogen also adds on to the other unsaturated compounds. Alkyl sulphide dihalides and halogenated hydrocarbons are formed, respectively. Other impurities are also chlorinated or brominated and the corresponding halogen acid is formed. The acids are removed with an alkali treatment. During batch distillation, after the alkali treatment, the modified impurities remain in the column. If a little water is present an azeotropic mitxture will be formed. The first cut will contain water, alcohol and halogenated hydrocarbons. Thereafter, the alcohol will be withdrawn and the alkyl sulphide dihalides remain in the still bottoms [19].

After the raw alcohol is subjected to a caustic treatment, the alcohol vapour may be subjected to an aniline and phosphoric acid treatment. Anilides of the ketones form during this treatment. The acetals that are not hydrolysed by the alkalies, are decomposed by the free acid and then condense with the aniline. The unsaturated bodies also combine with the excess acid [21].

If the raw alcohol is dry, water could be added and the hydrocarbons could be removed by azeotropic distillation. If propanol is produced by the catalytic reaction of CO and H_2, hydrocarbon byproducts are formed. Water, as entrainer is added to the raw alcohol before batch distillation. The first distillate will contain the hydrocarbon impurities, water and some of the alcohol. The propanol that is further removed contains water but is of superior quality in comparison with the raw alcohol. The alcohol will have to be dried downstream.

The alcohol may also still contain some unsaturated components. The following improvement is suggested: the removal of the hydrocarbon impurities could be achieved by the addition of an alcohol with a lower boiling point. The lower boiling alcohol and the hydrocarbons will leave the column as top product and the pure higher boiling alcohol will be the bottoms product. It is claimed that the alcohol with the higher boiling point will contain less hydrocarbon impurities [22].

3.3 Extractive Distillation

Distillation is the most obvious method of separation of alcohols from other components or to separate a specific alcohol from an alcohol mixture. Distillation can only be applied if the difference in volatility of the components to be separated is large enough so that a column with a reasonable amount of stages (< 100) may be used to effect the distillation [23].

If the difference in volatility between the components to be separated is very small, a solvent could be added to the feed mixture. This solvent increases the volatility difference between the two components to be separated. A column with several stages is then used to separate the components. This process is called *extractive distillation*.

Figure 3.1 shows a basic flow diagram for a general extractive distillation process. The solvent is fed near the top into the column, but not at the top, to ensure that none of the extractive agent is carried over to the condenser [24]. The solvent must be completely miscible with the liquid phase throughout the column. The solvent is usually less volatile than the components to be separated. The solvent is removed at the bottoms with one of the components. The solvent and the bottoms component are then purified in subsequent separation processes, usually distillation. The solvent is then recycled back to the column [23].

It is essential that there is a considerable difference in boiling point between the extracting agent and the bottoms component [24]. A high temperature difference will make azeotrope formation between the extractive agent and the components to be separated unlikely. A high temperature difference will also ensure that the extractive agent is not present in the distillates.

Berg [24, 26 to 51] has patented several extractive agents to separate alcohols from each other by extractive distillation. In Table 3.1 the extractive agents for several alcohol/alcohol separations are listed. Extractive agents for the separation of the typical Sasol components, namely 1-propanol and 2-butanol, 1-butanol and 2-pentanol are also listed.

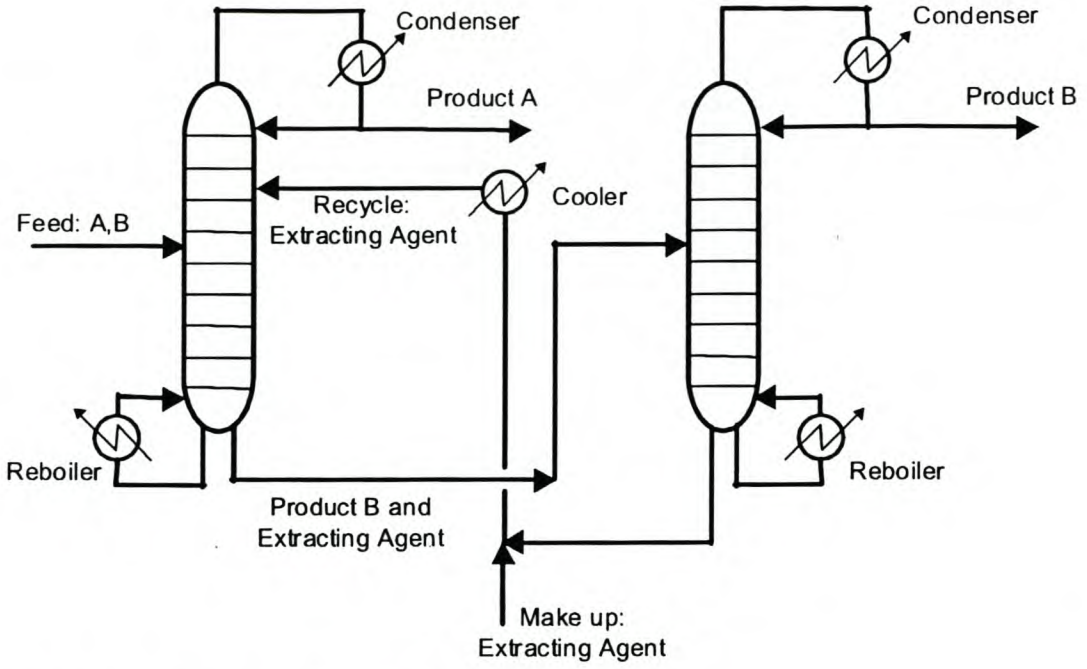


Figure 3.1: Extractive Distillation Flow Sheet [25]

Berg claims that extractive agents may be used to separate 1-propanol from 2-butanol. The relative volatility, $\alpha_{1\text{-propanol,2-butanol}}$ is 1,17. For a specific separation 78 plates are required if conventional distillation is used. For the same purity specifications only 28 actual plates are used if an extractive agent is used. If isobornyl methyl acetate is used as an extractive agent, the relative volativity, $\alpha_{1\text{-propanol,2-butanol}}$ is increased to 1,45. Some of the agents for this separation claimed by Berg are given in Table 3.1 [26], [24].

In one of the patent specifications [26] the following paragraphs are written: " The object of this invention is to provide a process or method of extractive distillation that will enhance the relative volatility of 1-propanol from 2-butanol in their separation in a rectification column. It is a further object of this invention to identify organic compounds: which in addition to the above constraints, are stable, can be separated from 1-propanol and recycled to the extractive distillation column with little decomposition".

Berg refers to extractive distillation, wherein the agent increases the relative volativity, $\alpha_{1\text{-propanol,2-butanol}}$ from 1,17 to 1,45. 1-Propanol will thus be the top product in the extractive distillation column and 2-butanol+the agent should be the bottoms product. Inexplicably Berg states that the agent should be separated from 1-propanol. The concentrations of the agents are not given in the vapour liquid equilibrium analyses that were presented in the patent.

Previous inventors (before 1950) claimed that 1,3 butanediol, ethylene glycol butyl ether, diethylene glycol ethyl ether and sulfolane are suitable extractive agents for the separation of 1-propanol and 2-butanol. Berg states that they cannot be used as extractive agents [24].

According to Berg, 1-butanol and 2-pentanol boil less than 1 °C apart. The relative volatility, $\alpha_{1\text{-butanol,2-pentanol}}$ is 1,08. This makes it impossible that they can be separated by conventional distillation. If an extractive agent is added, only 56 actual plates are required to separate 1-butanol and 2-pentanol. The relative volatility, $\alpha_{1\text{-butanol,2-pentanol}}$ can be increased to 1,25 if eg. anisole is added as extractive agent [27]. 1-Butanol and 2-pentanol actually boil 2,2 °C apart (at atmospheric pressure). One of the extractive agents that is claimed for the separation of 1-butanol and 2-pentanol is butylether. However, butylether forms an azeotrope with 1-butanol (see chapter 5). It is thus impossible to use butylether as an extractive agent for the separation of 1-butanol and 2-pentanol.

In a further invention it is claimed that for the same purity specifications in the separation of 1-butanol and 2-pentanol using conventional distillation, 160 actual plates are required in comparison to only 36 actual plates if an extractive agent is added. If d-limonene is added the relative volatility, $\alpha_{1\text{-butanol,2-pentanol}}$ can be increased to 1,4. A relative volatility, $\alpha_{1\text{-butanol,2-pentanol}}$ of 1,3 was determined when ethyl benzene is added to the alcohol mixture at the following ratio: 1-butanol:2-pentanol:ethyl benzene = 27:13:40 [28]. Ethyl benzene and 1-butanol form an azeotrope. The composition and boiling point of the azeotrope are given in Table 3.3. Ethyl benzene can thus not be used as an extractive agent to separate 1-butanol and 2-pentanol.

Several extractive agents for the separation of alcohols, which could be separated by conventional distillation, are also patented. For example the separation of t-amyl alcohol and 1-butanol could be achieved by conventional distillation. The boiling point difference of these components is 15.3 °C. According to the invention 55 actual plates are required using conventional distillation in comparison to 30 actual plates if an extractive agent is added, if 99 % purity is achieved in both cases [29]. However, if conventional distillation is used, only one column is needed, and if extractive distillation is used, the extractive agent has to be separated in a further distillation column from the 1-butanol. Whether the reduction from 55 to 30 actual plates in the first column, financially justifies the use of an extractive agent, is questionable.

It was not checked if the patents that are discussed in this chapter are still valid, have been withdrawn or are disclaimed.

Table 3.1: Extractive Distillation Agents for the Separation of alcohols from alcohols, patented by Berg.

Alcohol Mixture	Boiling Point [°C]*	Extractive Distillation Agents	Ref.
Sasol Mixture: 1-propanol 2-butanol ΔT = 2.3 °C	 97.2 99.5	isobutylacetate, isobornyl methyl acetate, ethylbutyrate; higher boiling oxygenated compounds and mixtures thereof, eg. methyl benzoate, benzoic acid, methyl benzoate and others.	[26], [24]
Sasol Mixture: 1-butanol 2-pentanol ΔT = 2.2 °C	 117.7 119.9	anisole, ethyl nonanate, butylether, ethylbenzene, d-limonene, terpinolene	[27], [28]
2-propanol t-butanol ΔT = 0.2 °C	82.3 82.5	Higher boiling oxygenated compounds and mixtures thereof, eg. Methyl benzoate, hexahydrophtalic anhydride, phthalic anhydride and mixtures thereof.	[30]
2-methyl-1-butanol 3-methyl-1-butanol ΔT = 1.9 °C	128.7 130.6	o-xylene, 3-carene, 1-methoxy-2-propanol	[31]
2-butanol t-amyl alcohol ΔT = 2.9 °C	99.5 102.4	methyl caproate, adiponitrile, cyclo-pentanone, higher boiling bezoate eg. methyl benzoate, salicyclic acid, cinnamic acid, hexanhydrophtalic anhydride and mixture thereof	[32], [33]
Ethanol Isopropanol ΔT = 4.0 °C	78.3 82.3	Higher boiling oxygenated compounds or mixtures thereof, eg. Methyl salicylate; salicyclic acid and hexahydrophthalic anhydride; salicylic acid, hexahydrophthalic anhydride and methyl benzoate; methyl caproate, cyclopentane and isobutyl acetate; dipentene, anisole and ethyl benzene.	[34], [35], [36]
Ethanol t-butanol ΔT = 4.2 °C	78.3 82.5	Higher boiling oxygenated compounds or mixtures thereof, eg. Methyl benzoate; benzyl benzoate and benzoic acid; methyl salicylate, hexahydrophtalic and salicylic acid.	[37]
3-methyl-2-butanol 1-butanol ΔT = 6.2 °C	111.5 117.7	ethyl n-valerate, dimethylacetamide and dimethylsulfoxide	[38]

Table 3.1, continued.

1-propanol t-amyl alcohol ΔT = 5.2 °C	97.2 102.4	dipentene, amylacetate and 1,4-dioxane; Higher boiling organic compound, or mixtures thereof: methylsalicylate; benzyl benzoate and hexahydrophtalic anhydride; methyl salicylate, benzoic acid and hexahydrophthalic anhydride.	[39], [40]
tert-amyl alcohol isobutanol ΔT = 5.6 °C	102.4 108.0	dimethylsulfoxide, N,N-dimethyl-acetamide, dimethylformamide, phthalic anhydride, and mixtures thereof. N,N-dimethylacetamide, cyclohexylamine and glycerol.	[41], [42]
3-methyl-2-butanol 2-pentanol ΔT = 8.4 °C	111.5 119.9	acetamide, 2,2,2-trichloroethanol	[43]
3-methyl-1-butanol 1-pentanol ΔT = 7.4 °C	130.6 138	butyl benzoate 2-undecanone diethylene glycol methyl ether	[44]
2-methyl-1-butanol 3-methyl-1-butanol from 1-pentanol ΔT ≈ 8.4 °C	128.7 130.6 138	3-carene, propylene glycol phenyl ether and dimethylsulfoxide	[45]
2-butanol isobutanol ΔT = 8.5 °C	99.5 108.0	propylene glycol ether, 2-methoxyethanol and ethyl acetate; hexyl acetate, dimethyl phthalate and p-xylene	[46], [47]
2-methyl-1-butanol 1-pentanol ΔT = 9.3°C	128.7 138	Mixture of aromatic carboxylic acids or aromatic carboxylic esters, eg. Benzoic acid, ethyl salicylate and salicylic acid; methyl benzoate, methyl p-hydroxy benzoate and phenyl salicylate.	[48]
2-methyl-1-propanol 1-butanol ΔT = 9.7 °C	108 117.7	ethyl benzene, amyl acetate and propoxypropanol	[49]
t-amyl alcohol 1-butanol ΔT = 15.3 °C	102.4 117.7	dimethylsulfoxide, N.N.dimethyl formamide and ethanolamine	[29]
2-methyl-1-propanol 2-methyl-1-butanol ΔT = 20.7 °C	108.0 128.7	hexyl formate, 2-heptanone and dipropyl amine	[50]
4-methyl-2-pentanol 3-methyl-1-butanol ΔT = 1.1°C	131.7 130.6	dodecane, dimethylformamide and dimethylsulfoxide	[51]

* at atmospheric pressure, 101.325 kPa

Byproducts are formed in the production of alcohols by the sulphuric catalysed hydration of olefins. Some of the byproduct formation is caused by the impurities in the olefin feed stream. The crude alcohol normally contains hydrocarbon impurities like ethers, ketones, higher boiling alcohols and sulphur compounds[52]. The quantitiy and variety of the high-boiling impurities both increase with the number of carbon atoms in the alcohol. The main byproduct that is formed, is the corresponding ether. In the case of hydration of propylene, 90 vol % isopropyl alcohol, 5 to 10 % di-isopropylether, and < 2 vol % hydrocarbons and oxygenated compounds are formed [53].

Extractive distillation can also be applied to remove organic impurities from alcohols or to dehydrate alcohols. Extractive distillation agents for the separation of non-alcohols from alcohols, found in the patent literature, are given in Table 3.2.

Table 3.2: Extractive distillation agents for the separation of alcohols from other components

Separation	Extractive Distillation Agent	Reference
iso-propanol and water	Polyethylene glycol	[54]
tertiary butanol and water	1,3-butanediol; triethylene glycol	[55]
methyl, ethyl and butyl esters from the corresponding alcohols	polyhydric alcohols: eg. Ethylene glycol; glycerine	[56]
n-propanol and allyl alcohol	higher boiling oxygenated, nitrogenous and/or sulphur organic compound, eg. dimethylsulfane, adiponitrile and others	[57]
ethanol and water	Phenol	[58]
Alcohols (C_2 to C_6) and corresponding ethers, oxygenated hydrocarbons	glycol and water mixture; ethylene glycol and water; glycol ether-ester and water; water	[52]

n-Butylether forms an azeotrope with ethylene glycol. The normal boiling point of the binary azeotrope is 139,5 °C and it consists of 6,4 mass % ethylene glycol [59]. It is thus not possible to use ethylene glycol as an extraction agent for the separation of butanol and n-butylether. According to Table 3.2 ethylene glycol can be used as extractive agent for the separation of butanol and n-butylether, however, this is not the case.

3.4 Azeotropic Distillation

Alcohols may also be separated and purified by *azeotropic distillation*. An entrainer is added which forms a minimum-boiling azeotrope with one or more of the components. After the vapour (including the entrainer and one of the components) is condensed, the condensate should split into two phases: entrainer phase and top product phase. The entrainer is recycled back to the column. The second component (or further components) is withdrawn at the bottom of the column [23].

Aliphatic alcohols form binary azeotropes with water. Water can thus not be removed from an aliphatic alcohol mixture by conventional distillation. Azeotropic distillation is used to remove water from alcohol. Sasol uses benzene as an entrainer to dehydrate a wet alcohol mixture. The alcohol mixture consists of lower aliphatic alcohols. A basic flow diagram of the Sasol Alcohol Dehydration system, which is based on azeotropic distillation, is given in Figure 3.2 [18]. A list of binary azeotropes are given in Table 3.3 and ternary azeotropes are given in Table 3.4.

As discussed in paragraph 3.2, azeotropic distillation was already used before World War II to purifiy alcohols.

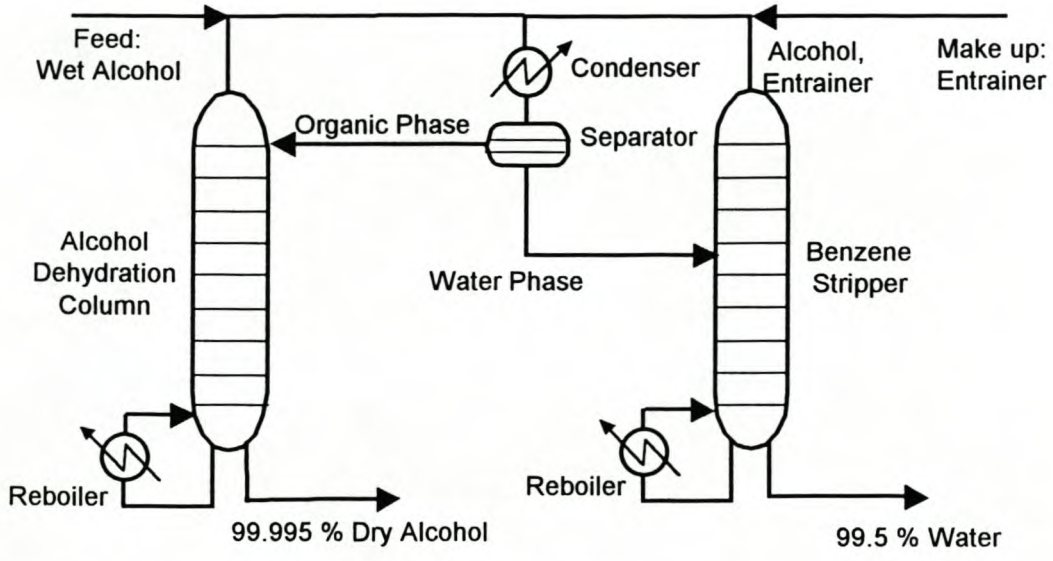


Figure 3.2: Sasol Alcohol Dehydration System

Table 3.3: Binary azeotropes of alcohols

Compounds	$T_{Boiling}$* [°C]	$T_{Boiling}$* [°C] Azeotrope	Azeotrope [Alcohol mass %]	Reference
Ethanol Water	78.3 100	78.15	23.2	[60]
1-Propanol Water	97.2 100	87.72	81.4	[60]
Isopropanol Water	82.3 100	80.37	60.5	[60]
1-Butanol Water	117.7 100	92.7 (2 phase)	57.5	[3]
2-Butanol Water	99.5 100	87	73.2	[3]
1-Pentanol Water	137.8 100	95.4	53.3	[61]
2-Pentanol Water	119.3 100	91.7	36.5	[10]
3-Pentanol Water	115.4 100	91.7	36.0	[10]
1-Propanol Di-n-propyl ether	97.2 90.5	85.8	32	[59]
2-Butanol Di-n-propylether	99.5 90.5	87	22	[59]
1-Butanol Di-n-butylether	117.7 142.4	117.6	82.5	[59]
1-Pentanol Di-n-butylether	138 142.4	134.5	50	[59]
1-Butanol Ethyl Benzene	117.7	115.5	68	[61]

* at atm. Pressure

Table 3.4: Ternary azeotropes of alcohols

Compounds	Compounds [mass %]	$T_{Boiling}$ * [°C]	$T_{Boiling}$ * [°C] Azeotrope	Reference
1-Propanol Water Di-n-propylether	20.2 11.7 68.1	97.2 100	74.8	[59]
1-Butanol Water Di-n-butylether	34.6 29.9 35.5	117.7 100	90.6	[59]
1-Butanol Water Di-n-butylether	24.6 31.2 44.2		45 (1.3 kPa)	[59]
2-Butanol Water Di-n-butylether	56.1 24.7 19.2	99.5 100	86.6	[59]
1-Pentanol Benzene Water	13.5 78.3 8.2	138 100	68.3	[60]
1-Propanol Benzene Water	7.0 84.2 8.8	97.2 100	68.48	[60]

* at atm. Pressure

Water-soluble alcohols may be separated from each other by adding water and an oxygenated compound, e.g. a ketone to the mixture. The ketone, water and higher boiling alcohol form a low boiling azeotrope. In the azeotropic distillation column, the lower boiling alcohol is removed as pure product from the bottoms. For example ethanol and iso-propanol can be separated by adding water and methyl ketone as an azeotropic agent. Pure ethanol is recovered as bottom product [62].

Several US patents have been issued to Berg for the separation of a specific alcohol from a mixture of alcohols by azeotropic distillation. These patents, filed by Berg, are summarised in Table 3.5.

In the separation of 1-butanol from 2-pentanol (a typical Sasol Mixture), conventional distillation cannot be used. The boiling points differ with only 2,2 °C. The relative volatility, $\alpha_{1\text{-butanol, 2-pentanol}}$ is 1,08. Berg has patented several entraining agents for the separation of 1-butanol and 2-pentanol. It is stated that if no entrainer is used, 160 plates are needed for a separation. If an entrainer is used that increases the relative volatility to 1,6, only 27 plates are required for the same separation specification. It is claimed that this increase in relative volatility may be achieved with methyl cyclohexane. The ratio 1-butanol:2-pentanol:methyl cyclohexane of 50:50:140 is needed. Several further entraining agents have been patented, including, 1-octene, hexane, cyclopentane [63].

1-Butanol boils at 118 °C and t-Pentanol boils at 134 °C. To obtain 99 % purity, 55 plates are required if conventional distillation is used. If an entrainer, e.g. dimethylbutane, cyclopentane, heptane (and many other possibilities) is used, only 30 actual plates are required for 99 % purification. The entrainer heptane at an 1:1 alcohol:heptane ratio increases the relative volatility, $\alpha_{1\text{-butanol, 2-pentanol}}$ to 1,5 [64]. If an entrainer is added, a second column and further equipment (pumps, heat exchangers, vessels) will be required to purify and circulate the entrainer. It should be much easier and cheaper to separate the t-pentanol and 1-butanol by conventional distillation with one column (55 trays) without the addition of an entrainer.

Berg has patented the use of several further entrainers for azeotropic distillation of alcohols, in cases where conventional distillation would be the appropriate method of separation. For the separation of 3-methyl-2-butanol (112 °C) and 2-Pentanol (Boling Point 118 °C) an entrainer was suggested. According to the invention 42 actual plates are required using conventional distillation, in contrast to 15 plates if an entrainer is added [65]. Once again, it is expected that it would be more economical to have one column with 42 plates, than 2 columns to enable recovery of the entrainer.

Table 3.5: Entrainers for the separation of alcohols from alcohols using azeotropic distillation

Alcohol Mixture	Boiling Point * [°C]	ΔT Boiling Point [°C]	Azeotropic Entrainer	Ref.
Sasol Mixture: 1-propanol 2-butanol	 97.2 99.5	2.3	t-butyl metyl ether, 1,4 dioxane and ethylformate	[66]
Sasol Mixture: 1-butanol 2-pentanol	 117.7 119.9	2.2	1-octene, hexane and methyl cyclohexane	[63]
2-butanol t-amyl alcohol	99.5 102.4	2.9	methyl acetate, ethyl propionate and octane; acetoacetate, nitroethane and 3-pentanone	[67] [68]
Ethanol Isopropanol	78.3 82.3	4.0	methyl ethyl ketone, cyclopentane, 2-pyrrolidinone; acetonitrile, methylene chloride; sec. butyl acetate, hexane-1 and 1,3-dioxolane.	[69] [70] [71]
3-methyl-2-butanol 1-butanol	111.5 117.7	6.2	methyl acetoacetate and dioxane	[72]
1-propanol t-amyl alcohol	97.2 102.4	5.2	heptane, ethyl acetate and tetrahydrofuran	[73]
Tert-amyl alcohol Isobutanol	102.4 108.0	5.6	triethyl amine, ethyl ether and acetone; butyl propionate, cyclo-hexane and 2,2-dimethoxypropane	[74] [75]
3-methyl-2-butanol 2-pentanol	111.5 119.9	8.4	2,2-dimethyl butane, ethyl acetate and dioxane; pentane	[65] [76]
2-pentanol 3-methyl-2-butanol 1-butanol	119.9 111.5 117.7	8.4 & 2.2 & 6.2	hexyl acetate, hexane, 3-methyl pentane	[77]
2-methyl-1-butanol and 3-methyl-1-butanol from 1-pentanol	128.7 130.6 138	ΔT ≈ 8.4	toluene, methyl acetate and tetrahydrofuran	[78]
2-butanol isobutanol	99.5 108.0	8.5	sulfolane, acetonitrile and acetal	[79]
2-methyl-1-propanol 1-butanol	108 117.7	9.7	isobutyl acetate, methyl cyclohexane and 2-nitropropane	[80]
t-amyl alcohol 1-butanol	102.4 117.7	15.3	propyl acetate, tetrahydrofuran and heptane	[75]
2-methyl-1-propanol 2-methyl-1-butanol	108.0 128.7	20.7	tetrahydrofuran, methyl acetate and toluene	[81]
4-methyl-2-pentanol 3-methyl-1-butanol	131.7 130.6	1.1	m-xylene and cumene	[82]

* at atmospheric pressure, 101.325 kPa

For the mixtures 2-propanol and t-butanol (ΔT = 0.2 °C), 2-methyl-1-butanol and 3-methyl-1-butanol (ΔT = 1.9 °C), ethanol and t-butanol (ΔT = 4.2 °C), 2-methyl-1-butanol and 1-pentanol (ΔT = 9.3°C), Berg has not filed patent applications (published before June 2001) for entrainers that could be used in azeotropic distillation to separate the components. However, Berg has filed agents for extractive distillation for the separation of these components.

Propylether is a byproduct in the production of propanol. Reaction water is formed when the propanol is dehydrated to form the ether. When the mixture undergoes distillation, the propylether is driven over with the water. The condensate forms two phases (lower phase = water). The upper phase contains propylether, propanol and water according to the ternary azeotrope. The water phase may be recycled. The bottoms product contains pure propanol. Usually the reaction water formed is adequate to achieve the separation [83].

Aliphatic alcohols (C_3 to C_5) which are produced by the catalyzed hydration of olefins, contain lower- and higher boiling contaminants. The higher boiling contaminants are called polymer oils (hydrocarbons and oxygenated compounds). Water may be used as an entrainer to remove the so-called polymer oils from the crude alcohol. The water alters the relative volatility of the alcohol and the other components to such an extent that the polymer oils are withdrawn from the column overheads or in a side stream. A dilute aqueous alcohol solution with a substantially reduced polymer content is withdrawn at the bottom [53], [84].

Table 3.6: Azeotropic distillation agents for the purification of alcohols

Alcohol Mixture	Azeotropic Entrainer	Ref.
Aliphatic Alcohols And Water	low boiling aromatics such as benzene, toluene, xylene and the like, paraffinic hydrocarbons of suitable boiling points, e.g. heptene and octane or olefinic materials such as diisobutylene	[85]
Tertiary butyl alcohol or propyl alcohol and water	Vinyl n-butyl ether; propylene glycol; dimethyl ether	[54]; [55]
Aliphatic Alcohols (C_2+) and Olefins and Paraffins	Methanol (forms azeotrope between olefin, paraffin and entrainer)	[86]
C_3 and C_4 alcohols and organic impurities, such as acetals and carbonyl compounds and organic oxides	Methyl Cyclohexane (forms azeotrope between alcohol and entrainer)	[87]
Lower aliphatic alcohols and Organic impurities, such as acetals and carbonyl compounds	Cyclohexane and water (ternary azeotrope between the alcohol, cyclohexane and water is formed)	[88]
Aliphatic Alcohols (C_3 to C_5) and polymeroils (hydrocarbons and oxygenated compounds)	Water (water forms azeotrope with polymer oils)	[53], [84], [22]
n-propanol and water	Benzene, trichloroethylene (entrainer forms azeotrope with water)	[89]
Alcohol and ethers	Glycols (glycols form azeotropes with ethers)	[90]
Alcohol and hydrocarbons e.g. cyclohexane, hexane, heptane, benzene. Example: t-butanol and cyclohexane	Anhydrous ammonia (the anhydrous ammonia and the hydrocarbons form an azeotropic mixture)	[91]
Paraffins (C_6 to C_{14}) and alcohols (C_4 to C_8)	Water and/or low boiling paraffins and/or low boiling alcohols	[92]

3.5 Extraction

Extraction may also be used to separate alcohols from other components. An example is the separation of alcohols and esters. In the production of alcohols according to the CO hydration process, esters are formed as byproducts. The reaction product is distilled and there is one fraction that contains alcohols (C_2, C_3, C_4) and their corresponding esters. Separation of this mixture into single components cannot be achieved by ordinary distillation, because azeotropes are formed. To separate this mixture into an alcohol and an ester phase, extraction may be used. The mixture is fed into the middle of an extractor. Water is fed at the bottom and an alkane (minimum boiling point of 120 °C) is fed at the top into the extractor. The water moves upwards through the column and the alcohol is extracted into the water phase. The esters leave the column at the bottom together with the alkane phase. n-Decane may be used as an extracting agent. The top-product, alcohol and water, is separated by conventional distillation methods. The bottom product, alkane and ester is also separated by conventional distillation. The alkane (extracting agent) is recycled to the extractor [93].

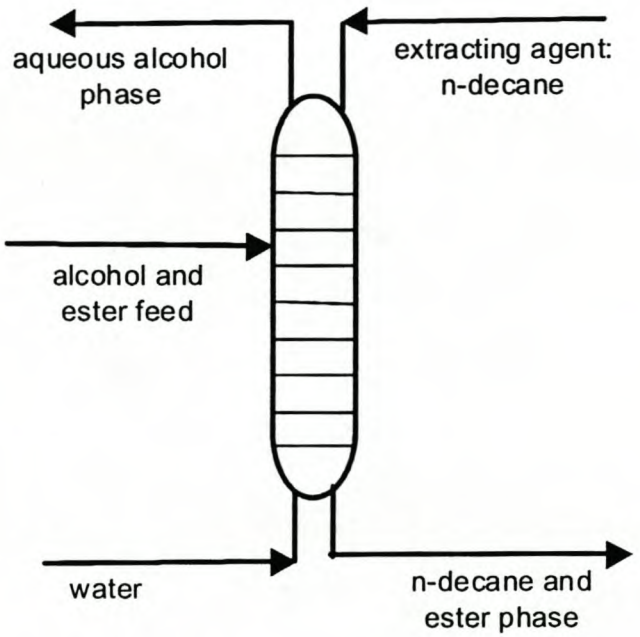


Figure 3.3: Extractive Process [93]

If one of the components is sensitive to high temperatures, extraction as a separation process is often preferred. Methanol and some enol ethers form azeotropes, and in some cases extractive distillation could be employed to achieve their separation. The enol ethers are very heat sensitive and are destroyed during the extractive distillation process. Extraction with a base at room temperature is recommended to separate the enol ethers from water soluble alcohols [94]. Several examples of patented extracting agents for the separation of alcohols from non-alcohols are given in Table 3.7.

Aliphatic alcohols which are produced by the catalyzed hydration of olefins, contain impurities. If the alcohol that is produced is water soluble, the water-insoluble impurities may be removed with a water wash. The alcohol will be extracted into the water phase and the insoluble oils will be in the organic layer [53].

Table 3.7: Extracting agents for the separation of alcohols from other organic components

Separation	Extracting Agents	Ref.
Alcohols from their esters, C_2,C_3,C_4	Alkane, eg. Decane	[93]
ethanol and water	Phenol	[58]
Water soluble alcohols and enol ethers	Aqueous solution of a base, eg. KOH, NaOH, $Ba(OH)_2$ $Ca(OH)_2$ or an amine	[94]
Lower alcohols and water	Flurocarbons	[95]
Lower alcohols from water	Phospine oxides, with or without alkali or alkaline earth metal salts	[96]
Aqueous aliphatic alcohols and carbonyl compounds	Primary amines under pressure	[97]
Alcohols (C_6 to C_{10}) and oxygenated organic compounds	Aminoalcohol, eg. monoethanol-amine, preferably a weak organic acid should also be present.	[98]

3.6 Reaction

Reaction and subsequent separation processes, e.g. distillation may be applied to separate alcohols from each other and to purify alcohols.

Aliphatic alcohols can be separated from a hydrocarbon-alcohol mixture by ***esterifying*** the alcohols with boric acid. Thereafter the esters are extracted with a solvent. The extract phase is separated. Thereafter the boric acid esters are decomposed with steam and the aliphatic alcohols are recovered by distillation. Suitable solvents for extraction are methanol, alcohols of higher molecular weight, glycol, aromatic and aliphatic amino-compounds [99].

A mixture of alcohols and hydrocarbons, containing eugenol and acetyleugenol, terpenes, ketones, aldehydes, esters, aliphatic alcohols or monohydric phenols can be separated by reaction. The mixture is ***treated with neutral esters of boric acid***. The heavier alcohols and phenols form borates. The other components are removed by distillation. The residual borates are decomposed and the alcohols and phenols are liberated. Separation of the different alcohols may be obtained if the reaction rates of the different alcohols vary. If only an adequate amount of boric ester is added to react the more readily reacting alcohol, the other alcohols may be removed with the other hydrocarbons by distillation from the borate [100].

A mixture of alcohols and organic compounds may be separated by adding an aldehyde to the mixture. The alcohols are ***converted to acetals***, which are high boiling components. The mixture is distilled and the residue of the distillation contains only the acetals. The acetals are hydrolised and the alcohols are liberated. The alcohol is then removed by distillation and may be recycled. The raw oxo-alcohols should first be treated and fractionated into different cuts and thereafter the conversion of the alcohols to acetals may be applied to each cut [101].

Alcohols may be separated from organic soluble impurities by ***treating the mixture with cyclic anhydrides***. The alcohols form half-esters with the anhydride. An aqueous base is added to the mixture and the half-esters form a water soluble salt. The water-soluble salt is extracted into the aqueous base and the impurities are in the organic phase. The half-ester substiuent is removed from the water-soluble salt and the purified parent alcohol is released. The impurities have to be inert to the reaction with cyclic anhydrides to ensure separation of the alcohol and impurities [102].

Alcohols (C_4 to C_{20}) can be produced via the oxo synthesis, which consists of the catalysed reaction of CO and H_2 and olefins and subsequent hydrogenation of the carbonyl groups. This oxo-alcohol may be contaminated with sulphur-containing impurities as well as with high-boiling impurities, which decompose if heat is applied during thermal separation. It is suggested that ***two distillation steps***, with a sulphur removing and hydrogen contacting step between the two distillation steps, could be applied. During the first distillation (alcohol stripping column) the crude alcohol is distilled at a temperature substantially above the normal boiling temperature of the alcohol to be recovered. Decomposition of some heavy components and sulphur containing components in the bottoms take place. The top product, which contains the alcohol, lights and some low-boiling-sulphur containing components is contacted with hydrogen and a solid contact material which removes the sulphur components. In the second column, the light boiling fractions are removed as top product, the alcohol is removed as a side stream and the bottom is recycled to the feed stream of the alcohol stripping column. The bottoms of the alcohol stripping column, which contains small amounts of alcohols, un-decomposed acetals, as well as thermally stable esters and ethers is removed from this column [103].

The raw oxo-alcohol product also contains aldehydes that have not been hydrogenated completely. These aldehydes are colour forming impurities that handicap the use of the alcohols to produce colourless ester plasticizers. It is suggested that after the first stripping distillation that follows the reaction, a ***second distillation with phosphoric acid solution*** could be introduced. Adding the phosphoric acid tends to alter the characteristics of the distillation. The colour forming compounds concentrate in the overhead stream and a cleaner alcohol stream is withdrawn as side stream. The overhead stream usually also contains unreacted reactants from the alcohol synthesis [104]. Aldehydes react with alcohols under conditions of acid catalysis to form acetals ("An acetal has two –OR groups attached to the same CH group" [1]). The acetal formation is favoured by excess alcohols [105]. The aldehydes must have been converted into compounds which form an azeotrope with the alcohol, unreacted hydrocarbons and/or water. The acetals probably are one of the azeotropic components.

The distillation with phosphoric acid can be performed in a batch distillation column. In this case sufficient contact time between the alcohol mixture and the acid is allowed. This is done under total reflux. Thereafter the total mixture is neutralised with an aqueous solution of caustic alkali. This treatment has to be done to prevent the alcohol from cracking and dehydration, which would occur during the distillation due to the increase in phosphoric acid concentration as the distillation proceeds [104].

Alcohols contaminated with carbonyl compounds may be purified by ***contacting them with a Lewis Acid*** for a sufficient period of time. The carbonyl compounds are converted to higher boiling materials. The process is useful to treat oxo-alcohols, containing 6 to 16 carbon atoms. Low quantities of Lewis Acids, e.g. aluminium chloride and boron trifluoride, are used. The Lewis acid in the treated mixture is neutralised and the mixture is treated with caustic. The organic layer is distilled to produce a pure alcohol free of carbonyl compounds [85]. Lewis acids are species that are electron-pair acceptors. They accept the electron pair just as a proton does [1].

If alcohols are produced according to the Ziegler process (see chapter 2), a wide range of alcohols, ranging from ethanol to about 1-triacontanol, and impurities are formed. These impurities include esters, paraffins, olefins and aldehydes. The low molecular weight alcohols are removed by fractional distillation. However, the impurities and high molecular alcohols have close boiling points and cannot be separated by fractional distillation. These high molecular weight alcohols contain 20 to 30 carbon atoms. The high molecular weight alcohols may be separated from these impurities by ***reacting the alcohol product with an aluminum alkoxide***:

$$3\,ROH + Al(OR_1)_3 \rightarrow Al(OR)_3 + 3R_1OH \qquad 3.1$$

The alcohols may also be reacted with an aluminum alkyl:

$$3\,ROH + Al(R_1)_3 \rightarrow Al(OR)_3 + 3R_1H \qquad 3.2$$

According to both the reactions the alcohols are converted to substantially non-volatile aluminum alkoxides. Only the alcohols are converted. The impurities may be removed from the nonvolatile aluminum alkoxides by volatilization. The purified alkoxides, which remain after the distillation, are hydrolyzed to regenerate the high molecular weight alcohols. Anorganic acids, water or organic basis may be used to effect the hydrolization. The hydrolization is perfomed between 50 and 100 °C. The high molecular alcohols are waxy at room temperatures. A solute, eg. benzol or isopropanol may be added during hydrolization [106]. No information is given on the recovery of the aluminum alkyls or aluminum alkoxides.

Alcohols (C_4+) produced according to the Oxo or Ziegler process may contain small amounts of diols after their treatments and purification. The ***diols***, which contain secondary OH-groups, may be ***catalytically dehydrated to unsaturated mono-alcohols***. These unsaturated mono-alcohols may be hydrogenated to saturated mono-alcohols. Suitable catalysts for the dehydration step are oxides of aluminium, zirkon and titan. Temperatures between 130 and 280 °C are applied. The dehydration is selective. Only the secondary OH-groups of the diols are dehydrated. Unsaturated mono-alcohols are formed. The dehydration may be performed in the fluid phase and the temperature and pressure are adjusted accordingly. Usually atmospheric pressure is used. The operating pressure has to be increased if lower molecular weight alcohols are processed [107]. This has to be done in order to keep the alcohol in the liquid phase. Very high molecular weight alcohols can be processed under vacuum pressure. A batch or continuous operation may be used. In the batch process, the solid catalyst is mixed with the alcohol to form a suspension. After sufficient time for dehydration of the diols, the catalyst is removed by filtration from the alcohol. In the continuous process the catalyst will be packed in a reactor. The alcohol contaminated with diols flows upwards through the reactor. A bubble reactor may also be used. All the examples of this patent are given in Table 3.8. Results of only alcohols with carbon numbers between 8 and 18 were reported [107].

An improvement of this invention was patented. A primary alcohol, contaminated with diols is contacted in the liquid phase between 170 and 275 °C with a calcium oxide on alumina catalyst. Selective conversion of the diol to a substantially lower boiling derivative thereof takes place. Exceptionally low levels of ether are produced. An acidic alumina catalyst, modified with calcium oxide gave significant results. Acid sites of sufficient strength are necessary to remove the diols at low temperature (e.g. 200°C). Ethers should not be formed before high temperatures (e.g. 300 °C) are reached. The inventor believes that ether formation is catalyzed by strong acid sites and that diol removal occurs on weak acid sites of the catalyst. High reaction temperatures will reduce the required contact time for the dehydration of the ethers. The reaction may be performed under vacuum, normal or elevated pressures. The reaction pressure depends on the volatility of the alcohols and the required reaction temperature. The derivative of the diol is removed by conventional thermal fractionation practices. The alcohol mixture may be subjected to mild hydrogenation. This is done to reduce the unsaturated and carbonyl content of the treated alcohol [108].

Table 3.8: Examples of diol removal from alcohols by dehydration of the diols [107]

Alcohol and diol mixture [mass %]	Catalyst	Reaction System Temperature and Time	End Diol Concentration [mass %]
C_{12} to C_{14} Diols = 1 %	1 % Zirconium-tetrahydroxyd	Batch System 230 °C 3 hours	< 0,05 %
C_{16} to C_{18} Diols = 1,2 %	1 % Titanium-tetrahydroxyd	Batch System 230 °C 6 hours	< 0,05 %
C_8 to C_{18} Diols = 0,8 %	2 % δ -Al_2O_3 as powder	Batch System 220 °C 6 hours	< 0,05 %
C_{12} to C_{14} Diols =0,85 %	2 % δ -Al_2O_3 as powder	Batch System 220 °C 6 hours	< 0,05 %
C_{12} to C_{14} Diols = 1 %	Packed solid 2 % δ -Al_2O_3	Continuous System 180 °C Flow Rate: 0,5 vol.alc./vol.cat./h Flow action: trickle	< 0,05 %
C_{12} to C_{14} Diols = 1 %	Packed solid 2 % δ -Al_2O_3	Continuous System 200 °C Flow Rate: 0,5 vol.alc./vol.cat./h pumped upwards through packed bed	< 0,05 %

Close boiling alcohols may be separated through ***selective etherification with isobutylene***. Ion exchange resins are used. The ethers have a larger difference in boiling point and can easily be separated. After the separation the ethers are easily cracked at high temperatures in the presence of an acid catalyst, to release the corresponding alcohol. If the mixtures ethanol ($T_{boiling}$=78,3 °C) + isopropanol ($T_{boiling}$=82,3 °C) and isopropanol + tert-butanol ($T_{boiling}$=82,5 °C), in the presence of an acidic catalyst, are etherified with isobutylene, the following ethers are formed: ethyl tert-butylether ($T_{boiling}$=72 °C), isopropyl tert-butyl ether ($T_{boiling}$=87,6 °C) and di-tert-butyl ether ($T_{boiling}$ =106,5 °C). The experiments were carried out at 3,5 atm abs. at temperatures ranging between 40 and 70 °C. The resin catalysts Amberlyst-15, SPC-228 and K-2631 achieve an adequate conversion of ethanol. The local concentration and the nature of the solvent, influence the acidity of the catalyst. The reactivity of ethanol was much higher than that of isopropanol. This was attributed to the lower basicity of ethanol than that of isopropanol. Furthermore, because ethanol is more polar than isopropanol, the ethanol would distribute more in the resin. More ethanol will thus be in contact with the active resin sites. In the etherification of a 50:50 mixture ethanol + isopropanol, 70 % conversion of ethanol [catalyst loading:10 % mass/mass, Temperature= 60 °C, Pressure= 3,5 atm abs.] was obtained after 6 hours. The conversion of isopropanol was only 32 % [109].

In the etherification of the mixture isopropanol and tert-butanol, the conversion of isopropanol was 48 % after 9 hours [catalyst loading:10 % mass/mass, Temperature= 40 °C, Pressure= 3,5 atm abs.]. The tert-butanol did not etherify at all. Adding a nonpolar solvent, namely toluene, increased the reactivity of isopropanol. This is attributed to the higher distribution of the isopropanol and the isobutylene in the resin phase. An increase in temperature from 40 to 60 °C increased the conversion of both ethanol and isopropanol, but with further increase to 70 °C the conversion was decreased (Pressure=3,5 atm abs.) [109]. No information is given on how the unreacted alcohols are separated from the ethers.

An alpha, omega-alkanedial is used to ***precipitate linear alcohols*** from a mixture of C_7 to C15 alcohols. The linear alcohol is subsequently liberated from the crystal [110]. An alcohol may be separated efficiently from an alcohol mixture by adding the alcohol mixture to a specific dissolved complexing substance. After the resulting crystals are filtered, the alcohol is liberated [111]. The patent was written in Japanese and only the abstract was available in English. No further information, besides the abstract, was available.

3.7 Short Path Distillation

Crude alcohols such as those obtained by Oxo synthesis can be separated from thermally unstable higher boiling non-alcohol impurities by vacuum distillation [112]. Operating under vacuum, reduces the boiling temperature of the mixture. Thermal decomposition is not a function of temperature only, but also a function of time. Film evaporators, specifically *Short Path Distillation* apparatuses reduce the time the distillate is exposed to high temperatures. The distillate flows as a thin film by gravity over a vertical surface [113]. The vapours are transported with no throttling losses from the evaporating surface to the condensation surface. The surfaces are arranged a very short distance from each other. A "short path" with a large flow area is thus available for the vapours [114]. If the distillate is viscous, gravity flow could be too slow and the distillate could decompose. To increase the gravity flow, the distillate could flow over a moving surface, e.g. rotating surface [113]. In wiped film evaporators highly viscous, high boiling liquids are applied to a heated wall and the liquid is distributed mechanically on the wall by rotating wipers. A continuous thin liquid layer is produced which is renewed continuously so that local overheating is avoided. The vapours that are formed flow directly from the product film to the condensing surface. In a wiped film evaporator pressures of only a few mbar (abs) are applied and the residence time is only a few seconds [115].

Sugars and an excess amount of aliphatic alcohols, usually fatty alcohols, are reacted to form alkyl glycosides. The unreacted aliphatic alcohols have to be separated from the alkyl glycosides (to < 1% weight alcohol in the alkyl glycoside). Distillation temperatures of 140 °C may not be exceeded. Entraining agents, e.g. glycol may be added to remove the alcohol. Adding the entraining agent has the disadvantage that the product comes into contact with an additional compound, which can reduce the quality of the product. Secondly it is costly (capital costs) to recycle the entraining agent. Wiped film evaporators operating under vacuum could be used to remove the alcohols from the reaction mixture [115].

3.8 Adsorption

Alcohols containing impurities may be purified by *adsorption* of the impurities onto an adsorbing agent. Alcohol may also be recovered from an organic stream by adsorption of the alcohol and subsequent release of the alcohol. Adsorption agents may also be used to dry alcohols.

Alcohol (eg. methanol, ethanol, n-propanol, n-butanol etc.) may be removed from a low concentration aqueous alcohol solution, by adsorping the alcohol onto a crystalline aluminosilicate [116].

Raw alcohol that is produced according to the indirect hydration of olefins in the presence of sulphuric acid catalyst contains impurities (The process is briefly described in paragraph 2.1). By contacting the neutralized raw alcohol with cuprous oxide, the alcohols are purified and the odour thereof is improved [117]. Alcohols produced by the catalytic hydration of olefins have an off-odour that reduces their value. Some of the impurities causing this off-odour are aldehydes. Due to the odour of the alcohol, some of the impurities are referred to as "sulphurous, polymeric or ethereal". It has been determined that the odour of the alcohol can be improved by contacting the alcohol after fractional separation with one or more ion-exchange resins. Amberlite is mentioned as a possible commercial cation ion exchanger [118].

Water may be removed from a water/ethanol mixture by contacting the mixture with a molecular sieve in the presence of supercritical CO_2. The water is adsorbed and the ethanol is separated from the CO_2 [119].

Alcohols may be separated from an organic compound by adsoprtion of the alcohol ($<C_8$) on an strongly acidic cation-exchange resin which has a sulfonic group [120]. Sugar alcohols may be separated from each other by selective adsorption on molecular sieves [121].

Small amounts of isoproyl alcohol may be removed from tertiary butyl alcohol by selective adsorption of the isopropyl alcohol on a carbonaceous adsorbent. An adsorbent produced by Rohm and Haas has proved to be efficient, namely Ambersorb.RTM.XE-347. The adsorbent has asymetric apertures which are larger than 5 Angstroms in length and less than 5 Angstroms in width [122].

3.9 Membranes

If thermal separation, which is based on the separation of components into different phases, cannot be used to separate components, the use of membranes could be attempted. If membranes are used to separate components from each other, the difference in speed at which each component moves through the separation film is used to separate the components [123]. Membranes may be used to remove water or impurities from alcohols. Some alcohols may also be separated from each other or from other organic components by pervaporation.

Aqueous alcohols may be dehydrated by permeation of the water through a membrane. Several membranes and the production of the membranes for the dehydration of lower alcohols are patented [124], [125], [126].

A specific alcohol may be separated by pervaporation from a mixture of water and several alcohols. The use of transmission films that transmit the specific alcohol to be recovered faster than water and much faster than the other alcohols are patented. The other alcohols are thus transmitted later than water. Only the abstract of the patent application was available in English. No examples of which alcohols can be separated were described in the abstract [127].

Alcohols, C_1 to C_{10}, but mainly C_1 to C_4 may be separated from an alcohol/ether/non-linear hydrocarbon mixture using a membrane. If the mixture is contacted with the membrane under pervaporation conditions, the alcohol permeates selectively through the membrane. With this method alcohols can be removed effectively from a ether/alcohol mixture, to produce high value ethers, e.g. methyl-tertiary butyl ethers or tertiary-amyl methyl ethers. These ethers can be used as octane enhancers in motor fuels [128],[129].

C_1 to C_3 alcohols may be separated from organic mixtures by pervaporation of the alcohols through a membrane [123]. A heat resistant gas separating membrane may be used to permeate a lower alcohol, e.g. ethanol selectively from a vapour of a mixture containing ethanol and an organic compound [130].

Reverse osmosis may also be used to remove water from an aqueous low molecular weight alcohol solution. The water is removed through the membrane. The desired substance is further extracted with an extracting agent from the solution [131].

3.10 Other Separation Processes

The water content of an ethanol/water mixture may also be reduced by *freezing* some of the water out. The mixture is sprayed as droplets into a refrigerated process vessel. The process vessel is cooled by a contained heat transfer fluid. Some of the sprayed ethanol/water droplets form ice and are separated from the mixture. The process may be repeated until the water content has been reduced to 8 % in the ethanol/water mixture [132]. A dilute aqueous solution of a lower alcohol (C_1 to C_5) may be concentrated by simultaneously chilling part of the water out and by extracting the alcohol into an aromatic organic solvent. The alcohol and the solvent are separated by distillation [133].

Alcohols containing at least 8 carbon atoms may be purified by *crystallisation*. These alcohols may be produced according to the Ziegler process (described in Chapter 2). The alcohol with the impurities is dissolved in an alkane/ether mixture. This is done at the boiling temperature of the mixture. The total mixture is cooled to 20 – 40 °C and the alcohol is allowed to crystallise out. The crystals may be washed with the alkane/ether mixture and thereafter they are dried [134]. Alcohol mixtures containing more than 8 carbon atoms, can be separated into components of different melting point. The mixture is allowed to solidify incompletely and the solid and liquid components are then separated by pressing. Organic impurities may also be separated from the alcohols by allowing the alcohol to solidify and thereafter removing the liquid by pressing [135].

Methanol may be removed from an isobutyl alcohol/methanol mixture by *stripping* the methanol out of the mixture. A gas (free or poor in methanol) that is used as synthesis gas in the reaction step wherein the alcohol is produced, may be used [136].

No references were found where the dehydration of secondary alcohols was applied to purify primary alcohols. A reference on the esterification of alcohols to achieve their separation has been found. The difference in esterification rate of the alcohols was used to achieve separation [100]. In the next two chapters the experimental results of this study on esterification and dehydration of the alcohols to achieve their separation will be discussed.

4 ESTERIFICATION OF ALCOHOLS

4.1 Introduction

In the past, esterification of alcohols has been used to separate aliphatic alcohols from an alcohol/hydrocarbon mixture [99]. Phenols and higher alcohols may also be recovered by esterification [100]. However, esterification has not been used to separate close-boiling alcohols from each other.

One aim of this investigation is to determine whether esterification may be used to separate the alcohols of a close-boiling primary and secondary alcohol mixture. One way for this method to work, is if only pure boric esters (esters containing only the primary or the secondary alcohol) and not mixed boric acid esters are formed if the alcohol mixture is reacted with boric acid.

Formation of pure boric acid esters can be presented by the following reaction:

$$2H_3BO_3 + 3ROH + 3R'OH \rightleftharpoons B(OR)_3 + B(OR')_3 + 6H_2O \qquad (4.1)$$

R represents the primary alcohol and R' represents the secondary alcohol.

The reaction water will be removed by azeotropic distillation by adding a solvent [137]. It is anticipated that the formed esters will have different boiling points and could be separated by vacuum distillation after completion of the reaction. Thereafter each ester cut will be hydrolysed with water. Only boric acid and the resulting alcohol(s) will be formed. The boric acid powder will be filtered from the mixture and the corresponding alcohol(s) will be recovered.

For this first method to work, it is imperative that only pure boric esters will be formed.

A second possibility is that one of the alcohols, preferably the one that is in lesser amount and that has to be removed, esterifies at a much higher rate than the other alcohol. If the secondary alcohol (alcohol in lesser amount) has to be removed from the primary alcohol, only enough boric acid should be added to ensure complete esterification of the secondary and only part of the primary alcohol. After the boric acid has been used completely, the remaining primary alcohol will be distilled over. The primary alcohol can then be recovered from the distillate. This method has been part of a patent published in 1931 [100]. It is described in paragraph 3.6.

4.2 Esterification of alcohols

Boric esters [$B(OR)_3$] can be prepared by the reaction of alcohols with boric acid [$B(OH)_3$]:

$$B(OH)_3 + 3ROH \rightleftharpoons B(OR)_3 + 3H_2O \qquad (4.2)$$

This equilibrium reaction favours the hydrolysis products, boric acid and ROH. It is displaced to the right by removing the reaction water by azeotropic distillation with a hydrocarbon solvent, eg. benzene or toluene [137].

No catalyst is needed and the reaction is endothermic. The amount of boric acid may be varied to control the fraction of the alcohols that will be esterified.

The alcohols may be released from the esters by adding water. Thereby the above reaction is displaced to the left. The boric acid is a powder and can be filtered off from the mixture.

Low molecular weight esters, methyl- and ethylborate, form a low boiling azeotrope between the borate and one molar equivalent of the alcohol [137]. The alcohol would thus be removed continuously from the reaction mixture and the yield of esters (based on the alcohol) would be low. This method can thus not be used for the separation of low alcohol mixtures, namely those that contain methanol and/or ethanol.

4.3 Experimental set-up and procedures

The experiments were performed in glass equipment, under atmospheric pressure, on laboratory scale.

Alcohols, boric acid and an entrainer were added in a round ball flask. The mixture was heated and the reaction water and the entrainer were continuously removed by azeotropic distillation. The water and the entrainer form two phases at room temperature. The phases were separated and the reaction water was weighed. See Figure 4.1.

It was assumed that the reaction was completed at the time when no further water was removed from the system. After completion of the reaction, the remaining entrainer was removed. After cooling, the esters were separated by batch vacuum distillation. The different ester cuts were hydrolysed in round ball flasks. The resulting boric acid (solid) was removed by filtration and the final product was weighed and analysed to determine the alcohol distribution.

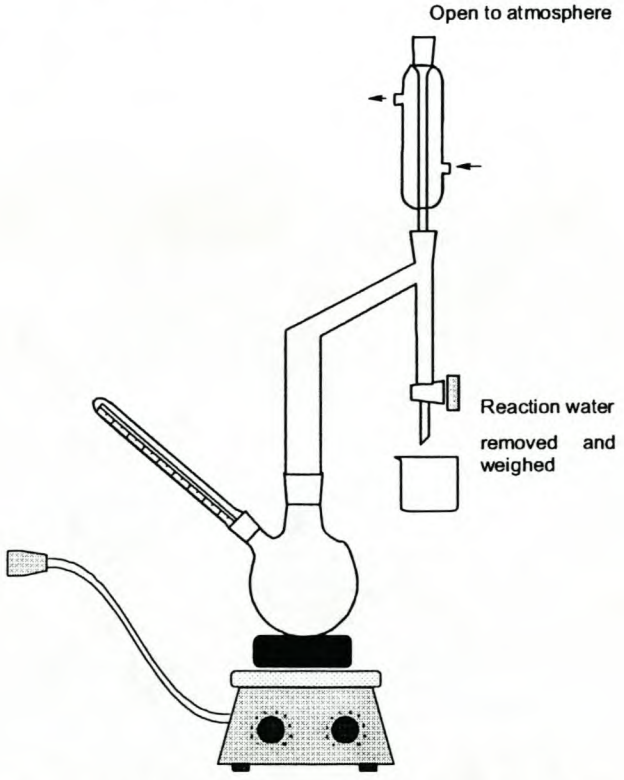


Figure 4.1: Esterification system experimental set-up

If the reaction was performed with an excess amount of alcohol, the unesterified alcohol was removed after the reaction water has been removed. Analysis of the alcohol product mixtures were done with a Gas Chromatograph.

4.4 Results of esterfication experiments

Firstly pure 1-propanol and 2-butanol were reacted separately with boric acid (Appendix A&B - Experiments 1 & 2 respectively). These experiments were performed to determine whether 1-propanol and 2-butanol are esterified at the same rate. Cyclohexane was added as an entrainer. Cyclohexane and water form a low boiling heteroeneous azeotrope, that boils at 69,4 °C [61]. The reaction water was removed continuously by azeotropic distillation. After completion of the reaction, the remaining cyclohexane was distilled off. The boric ester formed was weighed and hydrolysed to form the corresponding alcohol. The boric acid powder was filtered off.

In the esterification experiments with pure alcohols (Appendix C&D -Experiments 1 and 2) it was found that reaction water formed at the same rate if 1-propanol or 2-butanol are esterified separately with boric acid, see Figure 4.2.

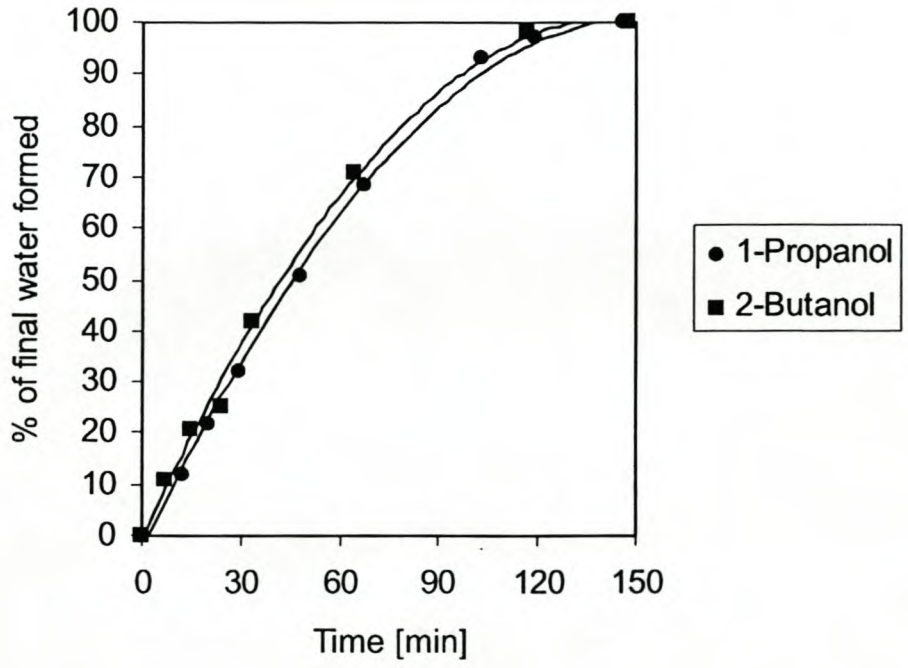


Figure 4.2: Rate of water formation in esterification of alcohols

Due to the similar reaction rate, it was anticipated that the 1-propanol and 2-butanol esters would form at the same rate. In further experiments it should be determined if pure esters or mixed esters will be formed.

A 3:3:2 mol mixture of 1-propanol:2-butanol:boric acid was reacted (Appendix C&D: Experiment 3). This experiment was done to determine if the esters could be separated. Cyclohexane was added as a solvent. Cyclohexane and water form a low boiling heterogeneous azeotrope that boils at 69,4 °C at atmospheric pressure [61]. The reaction water was removed continuously by azeotropic distillation. The reaction is completed when no further reaction water is formed. After completion of the reaction, the remaining cyclohexane was distilled off. The ester product was then batch distilled under vacuum conditions with a high reflux ratio. A 28 mm diameter packed glass column, packed to a height of 1 meter with random gauze packing, was used. The resulting alcohol was analysed.

The analyses of the different cuts are shown in Figure 4.3. It is clear that each cut contained mixed boric acid esters. Cuts 1 and 5 contained high amounts of 1-propanol. The original esters in cut 1 and 5, could have been a mixture of $B(OR)_3$ and $B(OR)_2(OR')$, with R and R' representing 1-propanol and 2-butanol respectively. Esters containing both 1-propanol and 2-butanol were thus formed. These reaction conditions are thus not appropriate to form pure esters (esters which contain only primary alcohols or only secondary alcohols).

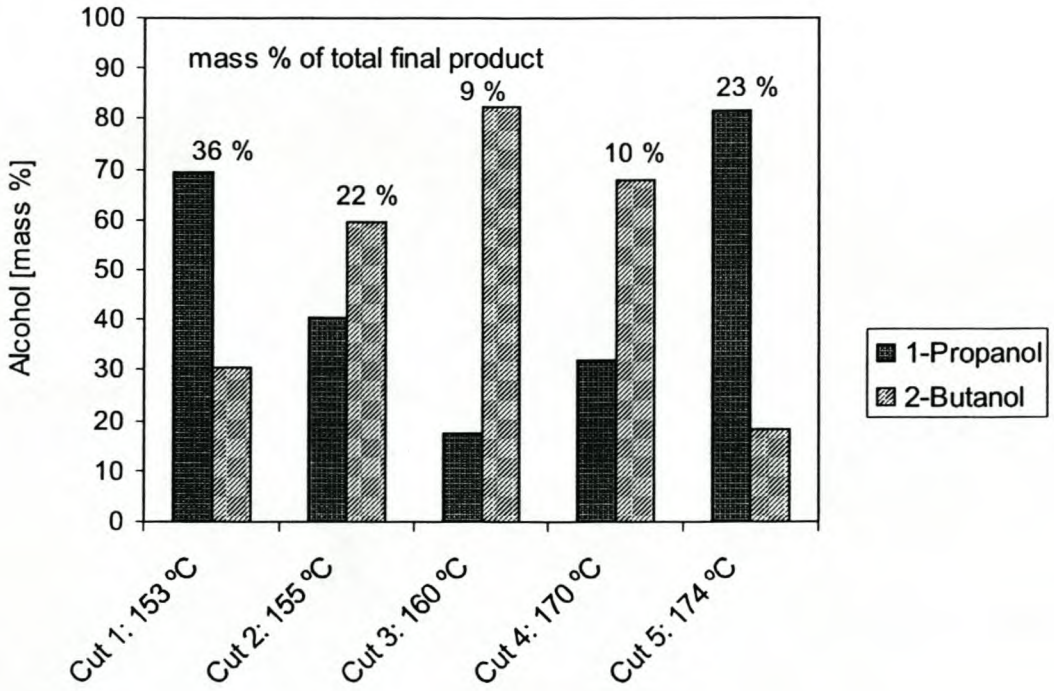


Figure 4.3: Alcohol distribution after hydrolysis of each ester cut

In the last two esterification experiments (Appendix C&D: Experiments 4 and 5) a typical industrial Sasol alcohol mixture, 85 % (mass) 1-propanol and 15 % 2-butanol was reacted with boric acid. Less than the required amount of boric acid for the complete esterification of the alcohols was used. These experiments were performed to determine if the secondary alcohol, being in a lesser amount, would be esterified completely before the primary alcohol was esterified. If this was the case, the primary alcohol could be distilled off and the secondary alcohol and part of the primary alcohol would remain in the reaction mixture as esters. The remaining primary alcohol that had been distilled off, could then be purified from the solvent and water. 15 % and 50 % of the stoichiometric required amount of boric acid was used, in experiments 4 and 5 respectively. DIPE (Di-iso-propyl-ether) was added as solvent. DIPE and water form a low boiling heterogeneous azeotrope that boils at 63 °C at atmospheric pressure [61]. The water was removed continuously. Thereafter the DIPE and the remaining alcohols were boiled-off. The boric esters formed were hydrolysed and the boric acid was filtered off. The resulting alcohol was analysed.

From Table 4.1 it can be seen that the alcohols esterify in the same ratio as they are present in the feed mixture.

Table 4.1: Esterification of alcohol mixtures, alcohol analysis

Experiment	Reaction Mixture [mass %]		Boric Acid	Product [mass %]	
	1-Propanol	2-Butanol	[% of stoichiometric required for esterification of total alcohol]	1-Propanol	2-Butanol
4	85	15	15	86	14
5	85	15	50	84	16

The small difference in product composition and reaction mixture composition can be attributed to analytical errors. Esterification of alcohols is thus not an appropriate method to separate the secondary alcohol from the primary alcohol.

4.5 Conclusion on esterfication of alcohols for the separation of close boiling alcohols

The following was found if a mixture of 1-propanol and 2-butanol is subjected to esterification with boric acid in the liquid phase and at atmospheric pressure:

- 1-propanol and 2-butanol are esterified according to their amount in the alcohol mixture, and
- only mixed boric acid esters are formed

It is thus not possible to use esterification of alcohol mixtures with boric acid and subsequent separation of the boric acid esters and thereafter releasing the alcohols, to separate close-boiling alcohols.

It is expected that a mixture of 1-butanol and 2-pentanol, and a mixture of 1-pentanol and 2-hexanol, will give equivalent results.

5 DEHYDRATION OF ALCOHOLS

5.1 Introduction

Under acid catalysed reaction conditions alcohols may be dehydrated to alkenes. The aim of this part of the investigation was to determine whether the secondary alcohol, of a close-boiling primary and secondary alcohol mixture, would dehydrate faster than the primary alcohol. The alkene of the secondary alcohol will continuously be flashed out of the reaction system. Only the primary alcohol, heavy byproducts and catalyst should remain in the reaction system. The secondary alcohol will thus be removed from the close-boiling primary and secondary alcohol mixture.

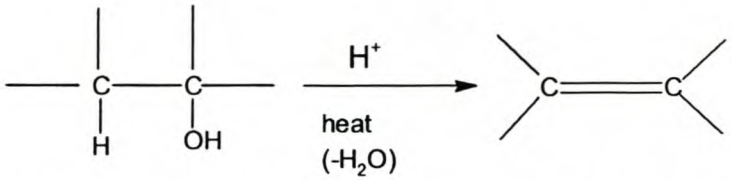
Theoretical background on dehydration of alcohols and relevant byproduct formation will be given. Applicable patents in which dehydration reactions are applied to achieve purification of alcohols will be discussed.

It will be determined experimentally whether selective dehydration of the secondary alcohol may be applied to remove the secondary alcohol from a primary+secondary alcohol mixture. The alcohol mixtures 1-propanol+2-butanol, 1-butanol+2-pentanol and 1-pentanol+2-hexanol will be subjected to dehydration conditions.

It will be established first whether solid catalysts can be used for the liquid phase dehydration of alcohols. If solid catalysts cannot be used, the use of various liquid catalysts will be investigated. For a successful catalyst, the influence of reaction conditions on the time of dehydration, selectivity and byproduct formation will be determined. An optimum catalyst system will be suggested.

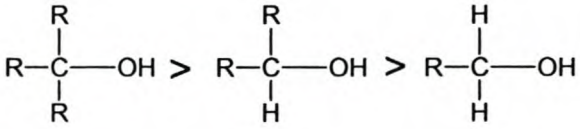
5.2 Background on the dehydration of alcohols to alkenes

Most alcohols, when heated with a strong acid, will lose a water molecule and ***dehydrate*** to form an alkene.



(5.1)

The reactivity for dehydration of alcohols is in the following order [1]:



3°Alcohol 2°Alcohol 1°Alcohol

The degree of dehydration of alcohols is mostly dependent on the reaction conditions and on the structure of the alcohol [138].

Some alcohols dehydrate to give several products. The formation of the more stable alkene is the general rule in the acid-catalyzed dehydration reactions of alcohols [1].

Alcohol dehydration is regioselective. The Zaitsev rule is followed: *1,2-elimination reactions of alcohols yield the most highly substituted alkene as the major product.* The most stable alkene will be formed predominantly.

The dehydration is not only regioselective, but also stereoselective. A single alcohol, when dehydrated can yield two or more stereoisomeric products. The more stable alkene is formed predominantly. When 3-Pentanol is dehydrated by concentrated H_2SO_4, *cis*-2-Pentene (minor product: 25%) and *trans*-2-Pentene (major product: 75%) is formed [105].

The dehydration of 1-butanol illustrates the regioselectivity and stereoselectivity of alcohol dehydration. When 1-butanol is dehydrated at 170 °C catalysed by concentrated H_2SO_4, three products are formed: *trans*-2-butene, *cis*-2-butene and 1-butene [1].

During dehydration, some primary and secondary alcohols also undergo rearrangements of their carbon skeleton [1]. If rearrangement has taken place, the arrangement of atoms in the alkene is different from that in the alcohol. If 3,3-dimethyl-2-butanol is dehydrated, a mixture of alkenes, some with rearranged structures are formed [105]. Dehydration may be achieved in the vapour or liquid phase [139].

In the ***vapour phase***, temperatures in the region of 250 to 400 °C are needed to split off water from the alcohols. For tertiary and secondary alcohols, temperatures of 200 to 350 °C are sufficient. The formation of ethers will be predominant if the reaction is carried out with low molecular weight primary alcohols at too low a temperature. At temperatures below 260 °C, di-ethylether is almost exclusively formed from ethanol. The tendency to form ethers decreases with an increase of the molecular weight of the alcohol. Addition of phenol or acetic acid may suppress the formation of ethers, however, phenolether or phenolic esters may be formed as byproducts. If aluminiumoxide is used, no ethers are formed from secondary and tertiary alcohols [139]. Reactions for the dehydration of alcohols to ethers are discussed below.

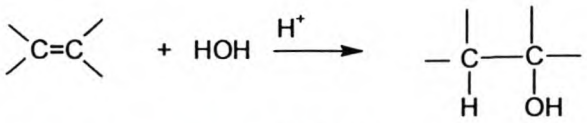
It is very difficult to dehydrate primary alcohols in the ***liquid phase***. To dehydrate primary alcohols in the presence of a dissolved acid catalyst, severe conditions, e.g. high temperature, are needed. The dehydration of primary alcohols to alkenes is mainly achieved in the presence of heterogeneous catalysts. Secondary alcohols dehydrate substantially easier to olefins than primary alcohols [138]. The dehydration of secondary and tertiary alcohols in the liquid phase is mainly accomplished with acid catalysts. Sulphuric acid, oxalic acid, phosphoric acid, acetanhydride and potassiumhydrogensulphate are possible catalysts. Potassiumhydrogen-sulphate is used most and is the safest to use. Lewis acids, inorganic and organic acids may also be used for the dehydration of alcohols. [140]

In order to avoid side-reactions and to shift the equilibrium in the desired direction, it is important to distill the olefin off as it is formed. The temperature must be chosen to ensure that the alcohol is not distilled off. However, care must be taken that the minimum temperature for dehydration is exceeded [139].

Sulphuric acid in an aqueous solution of 15 to 98 % is used for the production of olefins. The risk of coking and the contamination of the product with sulphur dioxide is high when the acid is too concentrated. There is a risk that ethers can be formed when low molecular weight alcohols are brought into contact with sulphuric acid [139]. 2-Pentene was produced on a laboratory scale as follows: 176 g 2-Pentanol was added to a cold mixture of 200 ml H_2O and 200 ml H_2SO_4. The mixture was heated on a water bath, 2-Pentene was distilled off. A 80 % yield of pentene can be expected [139].

Cyclo alcohols e.g. cyclohexanol, are easily dehydrated in the liquid phase. For the dehydration of cyclohexanol, a 67 % H_2SO_4 solution is suitable [138].

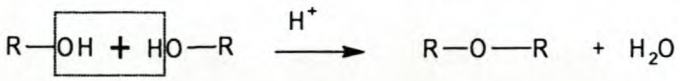
Alkenes are easily hydrated to secondary and tertiary alcohols in an acidic medium. Mainly sulphuric acid and phosphoric acid are used. The addition of water to the double bond follows Markovnikov's rule. This rule states that the hydrogen attaches to the carbon that has the higher number of hydrogens attached to it. In general the reaction is as follows [1]:



(5.2)

The ***formation of ethers*** when alcohols are subjected to acid catalysts will be discussed next. Ethers between aliphatic alcohols are mainly produced with the assistance of hydrogen sulphate acids or phosphoric acids, at a higher acid strength and at a lower temperature than when olefins are produced [141].

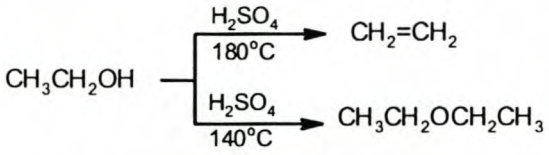
Ethers can be produced by intermolecular dehydration of alcohols. Primary alcohols can dehydrate to form ethers and/or alkenes [1].



(5.3)

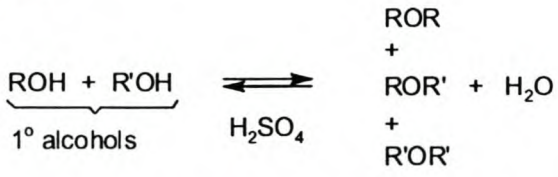
An ether is called a simple or symmetrical ether if the two R groups are the same. If the two R groups differ, the ether is called a mixed or unsymmetrical ether [142]. Generally ethers are pleasant smelling, neutral and volatile compounds. Their density is lower than the density of water. They are insoluble in water but easily soluble in organic liquids. Ethers boil at temperatures lower than the corresponding alcohol, if the R is less than butyl. If the R is butyl or greater, the ether boils at a higher temperature than the alcohol [142].

The dehydration of primary alcohols to ethers usually takes place at a lower temperature than dehydration of the alcohols to alkenes. The dehydration to the ether will be aided, if the ether is distilled off as it is formed. Diethyl ether is made commercially by dehydration of ethanol. Ether is the main product at 140 °C and ethylene is the main product at 180°C [1]. One mole of water is formed for each mole of ether that is formed. The presence of water in the reaction mixture will suppress the formation of ethers.



(5.4)

This method of preparing ethers is not very useful. When secondary alcohols are dehydrated, alkenes are mainly formed and ethers are not successfully synthesized with this method. Tertiary alcohols form only alkenes. This method cannot be used to form only unsymmetrical ethers from primary alcohols, because the reaction leads to a mixture of products [1].



(5.5)

One of the oldest methods to produce ethers is by catalytic dehydration. Sulphuric acid, phosphoric acid, phosphorous pentoxide, boric acid and hydrochloric acid are effective dehydration catalysts [142]. With sulphuric acid as catalyst, the dehydration takes place as follows

Step 1 $ROH + HOSO_2OH \rightarrow ROSO_2H + H_2O$

Step 2 $ROSO_2OH + ROH \rightarrow ROR + H_2SO_4$

Step 3 $ROSO_2OH + ROH \rightarrow ROSO_2OR + H_2O$

Step 4 $ROSO_2OH + ROH \rightarrow ROR + ROSO_2OH$

(5.6)

Ethers can thus be formed via steps 1,2 or 1,2,3 or 1,4. This process can be used commercially to produce lower simple ethers. It does not give satisfactory yields above propyl, because the higher-molecular-weight alcohols, particularly if secondary or tertiary, are readily dehydrated to the corresponding olefin [142]. This however, does not exclude the possibility that ethers could be formed in small amounts as byproducts from these higher alcohols.

If one of the alkyl groups is tertiary, mixed ethers may be produced, by the reaction of olefins, e.g. isobutylene, with alcohols in the presence of sulphuric acid [142].

$$(CH_3)_2C{=}CH_2 + C_2H_5OH \xrightarrow{H_2SO_4} (CH_3)_3COC_2H_5 \qquad (5.7)$$

Ethers can be converted to the corresponding alkyl hydrogen sulphates. These hydrogen sulphates can be further hydrolysed to the alcohol [142]:

$$ROR \xrightarrow[Heat]{H_2SO_4} ROSO_3H + ROH \xrightarrow{H_2SO_4} 2\,ROSO_3H + H_2O$$

$$ROSO_3H + H_2O \longrightarrow ROH + H_2SO_4 \qquad (5.8)$$

Ethylether is produced commercially according to the following reactions [142]:

$$C_2H_5OH + H_2SO_4 \rightarrow C_2H_5HSO_4 + H_2O$$

$$C_2H_5OH + C_2H_5HSO_4 \rightarrow C_2H_5OC_2H_5 + H_2SO_4 \qquad (5.9)$$

Although tarry products are formed via side reactions, the sulphuric acid has to be recharged after several months only [142].

Secondary and tertiary ethers can be formed by the direct alkylation of olefins with alcohols, using an acidic catalyst. The reaction proceeds as follows [143]:

$$R_2C{=}CH_2 \longrightarrow R_2\overset{+}{C}\text{-}CH_3$$

$$R_2\overset{+}{C}\text{-}CH3 + R'\text{-}OH \rightleftharpoons R_2C(O\text{—}R')\text{—}CH_3 + H^+ \qquad (5.10)$$

The reactivity of the olefin decreases as its molecular weight increases; thus isobutene reacts more favourably than 2-methyl-2-butene, and diisobutylene does not react at all. The reaction is further restricted to olefins containing tertiary carbon atoms since secondary olefins require higher temperatures and catalyst concentrations. Primary alcohols react easier than secondary alcohols while tertiary alcohols are found to react only slightly with olefins to form ethers. In the presence of sulphuric acid the reaction proceeds most favourably at 60 °C. Higher temperatures lead to alcohol dehydration and olefin polymerisation, while lower temperatures give unacceptable slow rates.

At 180 °C and under pressure, in the presence of alcohols, acetylene can react as follows:

$$ROH + CH{\equiv}CH \longrightarrow ROCH{=}CH_2 \qquad (5.11)$$

This reaction can be expanded to olefins and mixed ethers may be formed according to the reaction [144]. Properties of some ethers are given in Table 5.1 [142].

Table 5.1: Properties of ethers [140]

Compound Name	Boiling Point	Solubility and azeotropes	Comments
$C_2H_5OC_2H_5$ Ethyl ether	34.5 °C	Soluble in e.g. ethanol, benzene, chloroform	Wide range of industry uses, very volatile, highly flammable, forms explosive peroxides when exposed to air and light.
$C_3H_7OC_3H_7$ n-Propylether	90.5 °C	Slightly soluble in water, soluble in alcohol and ethers.	Highly volatile & flammable, forms explosive peroxides when exposed to air and light, should not be allowed to evaporate to dryness.
$(CH3)_2CHOCH(CH3)_2$ Isopropylether	68.5 °C	Solubility in water: 0.94 %; forms azeotropes with: e.g. water, isopropylalcohol, ethanol.	Moderately volatile, flammable liquid, forms explosive peroxides.
Butylethers:		Insoluble in water, soluble in ethanol and ether; Forms azeotropes with e.g. water, butanol.	
$CH_3(CH_2)_3O(CH_2)_3CH_3$ n-Butylether	142 °C		Used as solvent. Forms explosive peroxides which should be removed before distillation.
$[C_2H_5CH(CH_3)]_2O$ sec-Butyl ether			Not available commercially, but can be prepared by dehydration of sec-butyl alcohol
Amyl Ethers:		Insoluble in water, soluble in ethanol and ethyl ether; forms azeotropes with water.	
$CH_3(CH_2)_4O(CH_2)_4CH_3$ n-Amyl ether, (n-pentyl ether)	187.5 °C		
$[(CH_3)_2CHCH_2CH_2]_2O$ isoamyl ether, (isopentyl ether)	173.2 °C	Extremely insoluble in water, miscible with e.g. alcohols and ethers	Not commercial. Can be prepared in laboratory by the sulphuric acid method.
$[C_3H_7CH(CH_3)]_2O$ *sec*-amyl ether	166 °C		Not commercial. Can be prepared in laboratory by the sulphuric acid method.
Higher Alkyl Ethers:		Extremely insoluble in water (< 0.01 mass %)	Mild odored stable liquid, much less volatile than the lower ethers. Used as solvent for chemical reactions requiring an anhydrous medium.
$CH_3(CH_2)_5O(CH_2)_5CH_3$ Hexyl ether	226.2 °C		
$CH_3(CH_2)_6O(CH_2)_6CH_3$ Heptyl ether	259 °C		Commercially available

No reference could be found to any process where the dehydration of secondary alcohols was used to remove the secondary alcohol from an organic mixture. However, as discussed in chapter 3, processes wherein ***diols*** with secondary OH-groups are removed from an alcohol mixture by dehydration of the secondary OH-group have been patented. The inventors have found that the dehydration is very selective. The diols contain mainly OH groups on the 1 and 3 carbon position. Only the secondary OH-groups of the diols are dehydrated to form unsaturated mono-alcohols. In further steps, these unsaturated alcohols are hydrogenated to alcohols. It is claimed that extremely low amounts of ethers are formed. Examples are only given for an diol content of < 0,5 mass % and alcohols with more than 8 carbon atoms. The reaction pressure is varied to keep the alcohol in the liquid phase. Suitable catalysts for the dehydration step are oxides of aluminium-, zirconium and titanium. Temperatures between 130 and 180 °C were applied. The pressure was adjusted to keep the reaction mixture in the liquid phase [107]. For the same dehydration of diols, the use of catalysts which form even less ethers have been patented. The use of an acidic alumina catalyst, modified with calcium oxide, gave good results. The diol is converted to a substantially lower boiling derivative thereof and removed by conventional distillation without further hydrogenation [108].

It is thus evident that no secondary alcohol dehydration process for the purification of primary alcohols has been developed yet. The experimental results of such dehydration studies will be discussed next.

5.3 The use of solid catalysts for the liquid phase dehydration of secondary alcohols

5.3.1 Introduction

Solid catalyst can be applied in a continuous or batch reaction system. In this section various acidic resins were tested as catalysts. Continuous and batch configurations were tested.

The use of a solid catalyst would make the separation of the alcohol product from the catalyst very easy. In a continuous system the catalyst would remain fixed in the reactor bed. In a batch system, the catalyst would be filtered out from the catalyst/alcohol suspension. In a batch system the alcohol product could also be decanted from the solid catalyst. In this experimental investigation various acidic resins at varying catalyst:alcohol ratio's were tested.

In all the references found, acidic solid catalyst were only used successfully in the vapour phase dehydration of alcohols. However, solid catalyst were used for the selective dehydration of diols in the liquid phase at high temperatures (>130^{o}C). The diols had to be removed from an alcohol mixture. The selective dehydration of diols is discussed in paragraph 3.6. The alcohol mixtures contained only primary high molecular mass alcohols (>C_8). These alcohols did not dehydrate to alkenes or ethers at the reaction conditions.

5.3.2 Experimental set-up using solid catalysts

Firstly the use of a continuous system was attempted. A glass column (diameter = 20 mm, height = 300 mm, packed height = 200 mm) was packed with 75 gram acidic resin. The alcohol mixture and a small amount of water was first pumped through a preheating section and then it flowed upwards through the column. An average flowrate of 100 ml/hour was maintained. A positive displacement pump was used to pump the alcohol mixture. The alcohol composition at the inlet and exit was determined.

In the batch system, the alcohol and resin were mixed in a round ball flask. The alcohol:resin ratio was varied from 1:1 to 10:1. Water was added to suppress ether formation. The reaction system is illustred in Figure 5.1. The reaction mixture was heated under reflux. The condenser temperature was maintained to ensure removal of the alkenes of the secondary alcohol in the reaction mixture. After a specific time the mixture was allowed to cool off. Thereafter the solid catalyst was filtered out of the suspension. The organic content of the liquid product was determined by Gas Chromatography (GC) analysis. Details on the GC analysis, column and temperature program are given in Appendix G.

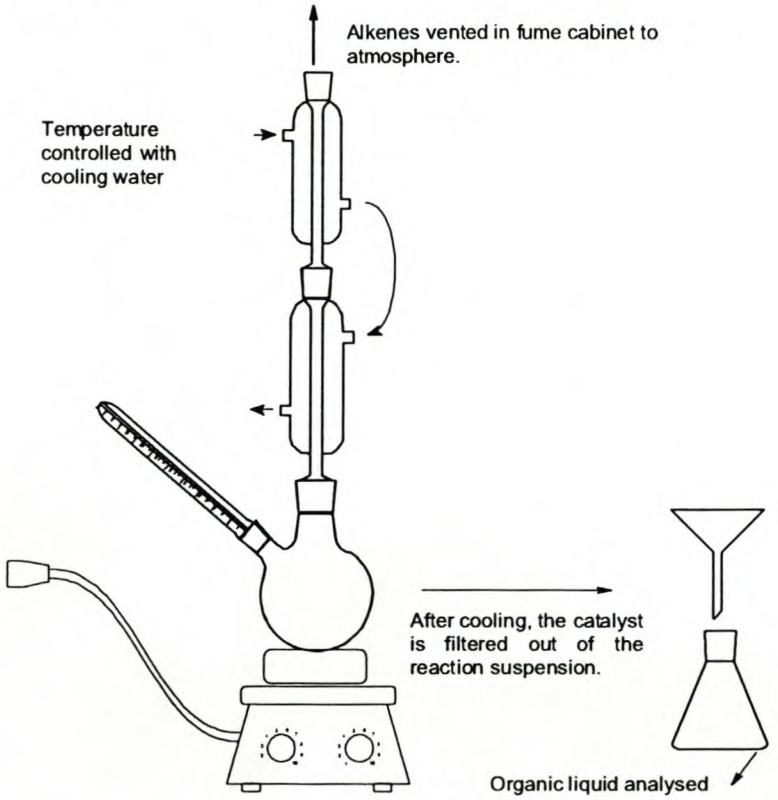


Figure 5.1: Batch reaction system used for solid catalysts

The condenser temperatures were controlled as prescribed in Table 5.2. These settings were used for the reactions performed at atmospheric pressure.

Table 5.2: Condenser Temperature used for atmospheric pressure reactions

Alcohol Feed Mixture	Condenser Temperature [°C]
1-propanol & 2-butanol	~ 40
1-butanol & 2-pentanol	~ 50
1-pentanol & 2-hexanol	~ 80

5.3.3 The liquid phase dehydration of secondary alcohols with solid acidic resin

In the continuous system, the alcohol mixture 85 % 1-propanol + 15% 2-butanol was preheated (~ 80 °C) and then passed upwards through the column. The column was packed with Dowex Macroporous (MSC-1). The system was unsteady and bubbles were observed. These bubbles could have been butene. However, analysis of the liquid exit stream showed that the 2-butanol content only reduced to 14,8 % (based on alcohols only). Almost no dehydration of the secondary alcohol was thus achieved. The original readings and results are given in Appendix D and E: Experiment 7. The alcohol flow through the system could be reduced to reduce the catalyst loading. However this would also increase the contact time between the alkenes (if formed from the secondary alcohol) and the catalyst. The alkenes could thus react further to form byproducts. The alkenes have to be removed from the reaction system as fast as possible.

The use of resins was further investigated at atmospheric pressure in a batch system as illustrated in Figure 5.1. Two alcohol mixtures, namely 85 % 1-propanol+15 % 2-butanol and 85 % 1-butanol+15 % 2-pentanol were used. The alcohol:resin ratio was varied from 3:1 to 10:1. Small amounts of water were added to suppress the formation of ethers. The resins Amberlyst 131 Wet, Amberlyst 15, Dowex MSC1 and Dowex Macroporous were tested. Almost no dehydration of the secondary alcohol occurred with any of the resins.

The dry alcohol:resin mass ratio decreased to 2:1. 8 % H_2O (based on alcohol and water) was added. Slight dehydration of the secondary alcohol occurred (See Appendix E: Experiment 10B). With a dry alcohol:resin ratio of 2:1, the resin was poorly wetted. Industrial application on batch scale of such alcohol:resin ratio's or smaller ratio's will be difficult. The 1-propanol quality (based on alcohol only) also only increased from 85 to 86,6 %. The reaction times were varied between 120 and 180 minutes. Tabulated readings and results are given in Appendix D&E: Experiments 8,9 and 10.

Pure 2-pentanol was also heated with the varying resins for 2 hours. The alcohol:resin ratio varied between 2,8:1 and 5:1. The % mass loss of 2-pentanol varied from 1 % to 11 %. If these losses are only contributed by the formation of alkenes, the dehydration rate of 2-pentanol was very slow in comparison with the use of liquid catalysts (as described in the next paragraphs).

All the resins tested proved not to be useful as catalysts in the liquid phase dehydration of secondary alcohols at atmospheric pressure. Other catalyst systems had to be investigated.

5.4 The use of liquid catalysts for the selective dehydration of alcohols.

5.4.1 Introduction

Several examples were found in the literature (paragraph 5.2) where liquid catalysts have been used for the dehydration of alcohols in the liquid phase. Among others, sulphuric acid, oxalic acid, phosphoric acid and potassiumhydrogensulphate were mentioned as possible catalysts.

In this investigation the use of these catalysts was tested experimentally. The experimental set-up and experimental procedures will be described. The reactions were performed using pure alcohols and alcohol mixtures. For an efficient catalyst the influence of the following reaction variables had to be investigated.

- Alcohol feed mixture
- Catalyst concentration
- Catalyst:Alcohol ratio
- Reaction time
- Stripping of reaction products
- Pressure/Temperature

An optimum batch reaction system for the selective dehydration of the secondary alcohol will be suggested. The byproduct formation will be qualified and quantified. Finally the reliability of the experimental results will be discussed.

5.4.2 Experimental set-up and procedures

The experimental set-up is illustrated in Figure 5.2.

The alcohol mixture, catalyst and water were heated together in a round ball flask (250 ml). The condenser cooling water temperature was kept stable. To ensure good removal of the alkenes, this temperature was set a few degrees higher than the boiling point of the alkene of the secondary alcohol (condenser temperatures are given in Table 5.2).

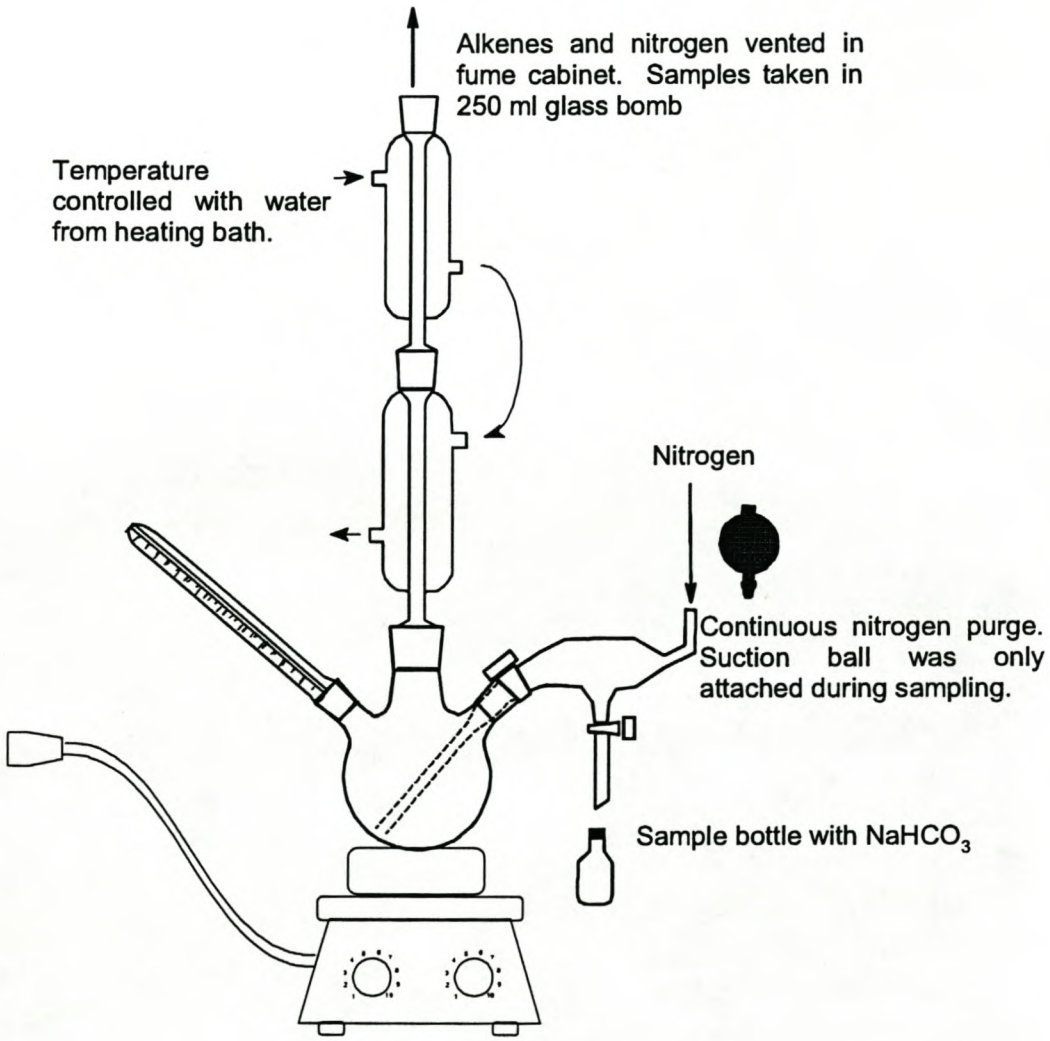


Figure 5.2: Experimental set-up of dehydration experiments

A special sample point had to be constructed to ensure good sampling. The sample point is illustrated in Figure 5.2. The sample point was purged continuously with 99,9 % nitrogen, to ensure that no dead legs were formed in the sample point. The sample point was also flushed with a little reaction mixture before taking each sample. Small samples of the reaction mixture were removed during the reaction at different time increments. An air-suction-ball was used to withdraw a sample. Each sample was neutralised immediately with an excess amount of sodiumbicarbonate. The reaction was thus quenched immediately. The remaining organics and water were washed out of the solid salt with dichloromethane. The alcohol/dichloromethane mixture was analysed. Details on the neutralisation of the samples and analysis are given in Appendix G.

The moment when the first droplets started to condense was logged as time zero. To reduce the error in logging of the reaction time, the time from heating up to boiling was reduced. In most experiments the catalyst and water was preheated to about 80 °C before the alcohol mixture was added.

A block flow diagram of the experimental procedure with neutralisation is given in Figure 5.3.

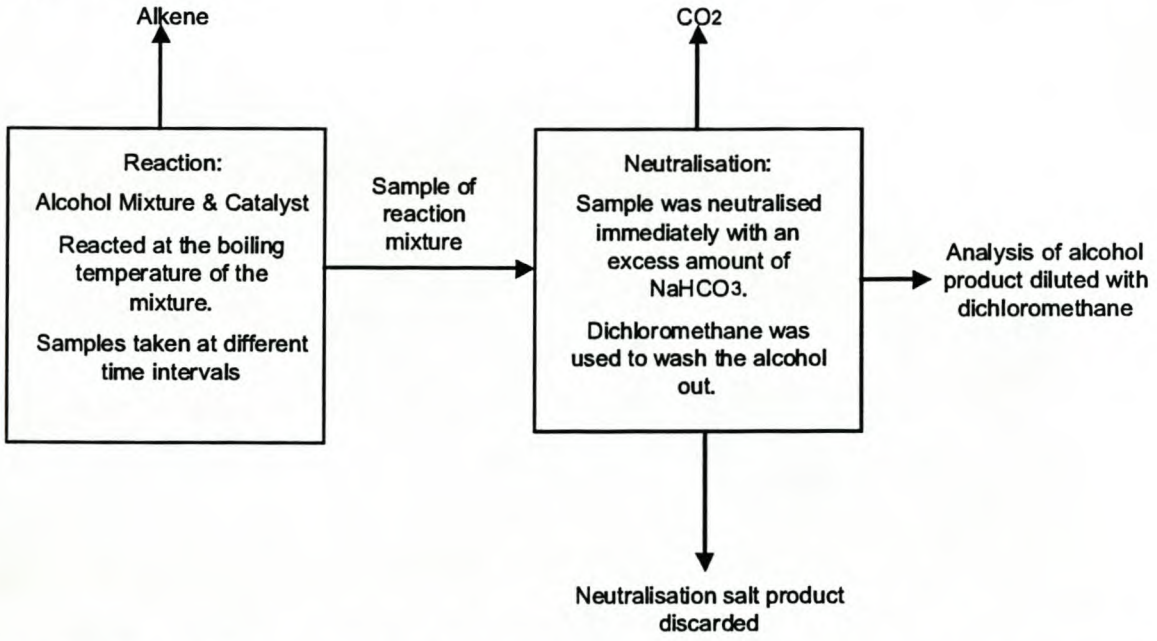


Figure 5.3: Block flow diagram of experimental procedure with neutralisation of reaction mixture samples

Some experiments were performed before the sample point was constructed. In these experiments each batch reaction was allowed to proceed for a specific time. Thereafter the reaction system was allowed to stand to cool off. The organic product was batch distilled with a Liebig Cooler set-up. The distillate was collected and analysed. The time for the distillation was not added to the reaction time. Further details on the batch distillations are given in chapter 6. The experimental steps that were followed are illustrated in Figure 5.4.

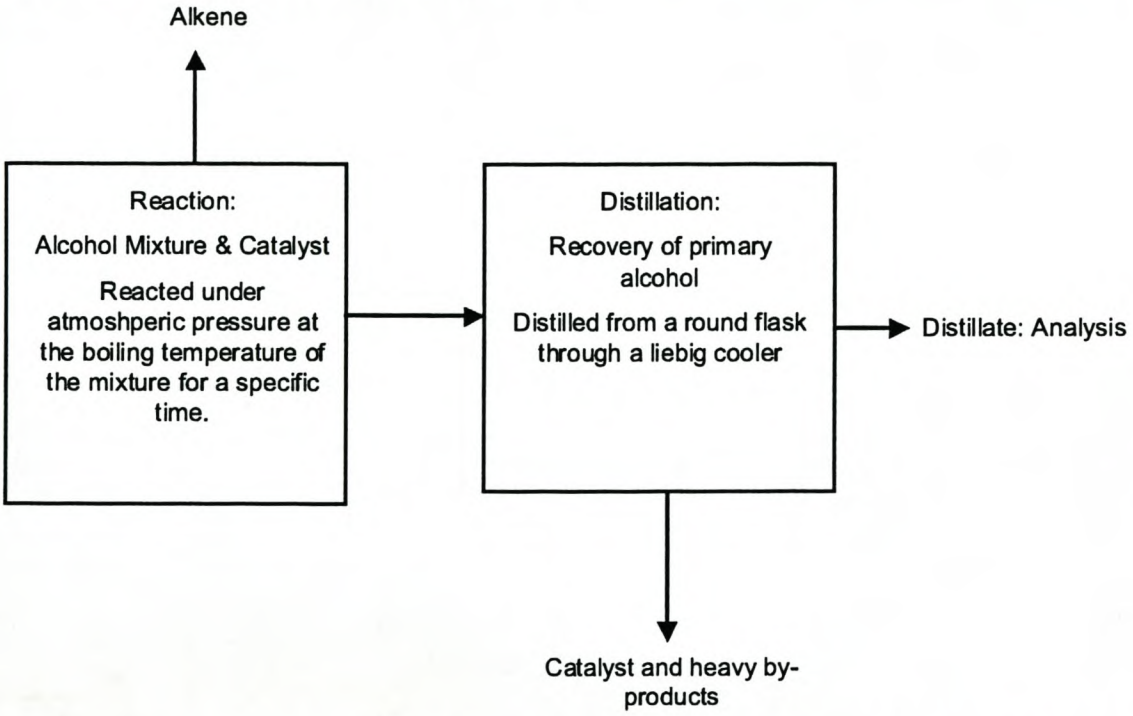


Figure 5.4: Basic diagram of experimental steps followed by batch distillation

5.4.3 Comparison of the liquid phase dehydration rates of primary and secondary alcohols

After the first liquid phase dehydration experiments using liquid catalysts, it was determined that selective dehydration takes place. As expected from the theory it was found that the secondary alcohol of a close boiling alcohol mixture dehydrates much faster than the primary alcohol.

H_2SO_4, with a concentration of 67 % was added - at an acid/alcohol ratio of 1:2 - to pure 1-propanol and pure 2-butanol respectively (Appendix D: Experiments 1,2 & 3). The mixtures were heated for various time periods. After a specific time, the reaction mixture was allowed to cool off and was weighed. The weight losses of the 2-butanol mixtures were much higher. According to the theory (see par.5.2) only secondary alcohols are dehydrated to their corresponding alkenes. Butene thus forms as light product from 2-butanol. The butene was flashed off to atmosphere during the reaction. The experimental set-up is illustrated in Figure 5.4. According to Figure 5.5 the amount of dehydration of the secondary alcohol was directly proportional to the reaction time.

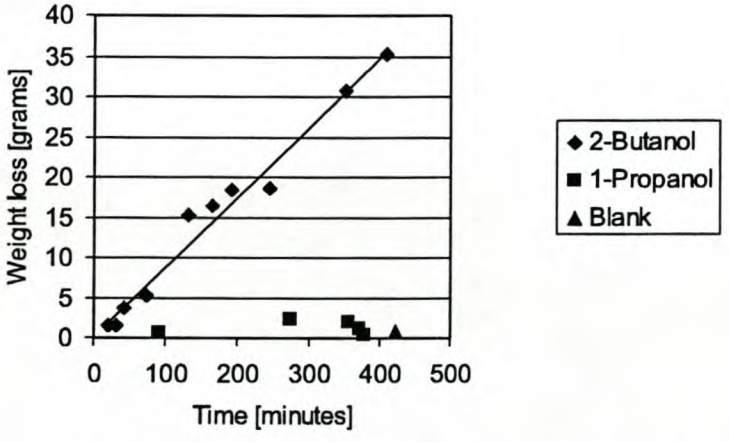


Figure 5.5: Rate of formation of alkenes; Catalyst: 67 % H_2SO_4, Pure Alcohols.

A blank run, with 1-propanol and without catalyst, was performed to determine whether any alcohols are lost through the vents. Less than 1 % of the 1-propanol was lost after 400 minutes. The time that it took to cool the reaction mixture was not added to the reaction time. However, during this time the dehydration reaction could still proceed. The reaction mixture was not always weighed at the same temperature. There is thus definitely a variation in the logged reaction times. This contributes to the deviation of the dehydration of 2-butanol from the line. As can be seen from Figure 5.5, the weight loss of the 1-propanol was extremely low and negligible in comparison to the weight loss that the 2-butanol experienced. The remaining reaction mixture was not analysed for byproducts.

5.4.4 Liquid catalysts

The liquid catalysts H_2SO_4, H_3PO_4, Oxalic Acid and potassium hydrogen sulphate were tested.

Firstly the use of H_2SO_4 was investigated. High acid concentrations with a low acid:alcohol ratio were used. A fixed amount of alcohol mixture (85 % 1-propanol + 15 % 2-butanol) was reacted with varying amounts of 80 % H_2SO_4 The reaction time was varied in the various experiments. The organics were recovered by batch distillation before analysis. It was found that the purity of 1-propanol (based on 1-propanol and 2-butanol only) varied between 88,1 and 99,8 %. A negative result was that very high amounts of heavy byproducts (ranging from 9 to 65 %) were formed. The highest amount of byproducts were formed at the highest acid:alcohol ratio.

Although very long reaction times were allowed, the secondary alcohol did not dehydrate completely. The results are given in Table 5.3. Due to the incomplete dehydration and high amounts of heavy-byproducts, it is clear that the use of a high concentration of H_2SO_4, at a low acid:alcohol ratio, is not a viable option for the removal of 2-butanol from 1-propanol (Original readings and results are given in Appendix D&E: Experiment 4).

The exact amounts of heavy byproducts could not be determined. For the GC analyses it was assumed that the response factor of all the heavies were the same and equal to 1. The structures of the heavy byproducts were not known. However, a comparison between the amounts that were formed can be made.

Table 5.3: Dehydration results using 80 % H_2SO_4; Alcohol Feed: 1-propanol+2-butanol

Experiment	Acid:Alcohol [mass ratio]	Reaction Time [minutes]	1-propanol in reaction product based on alcohol only [mass %]	Heavy Byproducts [%]
04:A	15:100	563	88.1	9
04:B	45:100	689	96.3	56
04:C	50:100	357	96.4	52
04:D	100:100	294	99.8	65

In order to attempt to reduce the byproduct formation, the use of lower concentrations of H_2SO_4 at higher acid:alcohol ratio's were investigated. A 85 % 1-propanol + 15 % 2-butanol mixture was reacted with 55 % and 67 % H_2SO_4 (Appendix D&E: Experiments 5 and 6). Acid:alcohol ratio's between 0,5:1 to 2,5:1 were used. From Table 5.4 it can be seen that almost all the 2-butanol can be removed from the alcohol mixture. Analyses between 90 to 99,9 % 1-propanol, based on alcohol only in the final distillate, were obtained. When lower % H_2SO_4 concentrations were used, the amount of heavy byproducts were less. However, a large acid:alcohol ratio, namely 2,5:1 was needed to achieve complete dehydration of the secondary alcohol. The byproducts that were formed, were not analysed quantitatively, however, from the theory it can be assumed that the heavy byproducts will consist of mainly ethers. The theory on ether formation is discussed in par 5.3.

Table 5.4: Dehydration of secondary alcohol using H_2SO_4 as catalyst; Reaction system: 1-propanol+2-butanol, varying acid concentrations and varying acid:alcohol ratio's.

Catalyst	Acid:Alcohol [mass ratio]	Reaction Time [minutes]	1-propanol in reaction product based on alcohol only [mass %]	Heavy Byproducts [%]
55 % H_2SO_4	2,5:1	120	99,9	8
67 % H_2SO_4	1:1	127	99,0	18
55 % H_2SO_4	1,5:1	120	94,2	7
67 % H_2SO_4	0,5:1	127	90,5	16

H_2SO_4 can be used to remove the secondary alcohol from a primary+secondary alcohol mixture. A rather big disadvantage is that large amounts of heavy byprouct are formed.

The use of oxalic acid and potassiumhydrogensulpate as catalyst were also tested.

The system 85 % 1-propanol + 15 % 2-butanol was used as alcohol feed system. The use of oxalic acid produced a distillate that improved the 1-propanol % from 85 to 88,7 % only. An oxalic acid concentration of 94,7% and an acid:alcohol ratio of 1,1:1 was used. The reaction was allowed to proceed for 120 minutes.

Potassiumhydrogensulphate reduced the amount of 1-propanol from 85 to 82 %. A potassiumhydrogensulphate concentration of 93,5 % and an acid:alcohol ratio of 1,3:1 was used.

Many byproducts were also formed with both these acids. It is clear that neither oxalic oxide nor potassiumhydrogensulphate can be used at atmospheric pressure for the liquid phase dehydration of 2-butanol (see results in Appendix E: Experiments 13C and 13D).

The next acid that was tested was orthophosphoric acid. Orthophosphoric acid produced very promising results. Initially acid concentrations between 55 % and 88 % were used. A high ratio of orthophosphoric acid to alcohol was used. The alcohol system 1-propanol+2-butanol was subjected to dehydration. In a reaction followed by batch distillation, a distillate which contained 99,5% 1-propanol, based on alcohol only, was produced. 88 % H_3PO_4, at an acid:alcohol mass ratio of 1,6:1 and a reaction time of 150 minutes was used (see Appendix E – Experiment 11D).

The use of orthoposphoric acid was compared to the use of sulphuric acid.

Experiments with sampling of the reaction mixture at various time intervals were performed using 67 % H_2SO_4 or 90 % H_3PO_4 as liquid catalyst. The alcohol system 85 % 1-butanol and 15 % 2-pentanol was investigated. An acid:alcohol ratio of 2,2:1 was used for the H_3PO_4 system. The acid:alcohol ratio for the H_2SO_4 was calculated to obtain the same % of water in the wet alcohol product (excluding the acid) as for the H_3PO_4 system. The 67 % H_2SO_4 acid:alcohol ratio was 0,65:1. For both cases the reaction mixtures contained about 18 % water based on organics and water only (see Appendix D & E: 67 % H_2SO_4 = Experiment 92 and 90 % H_3PO_4 = Experiment 89).

From Figure 5.6 and Figure 5.7 it can be seen that the secondary alcohol using 67 % H_2SO_4 as catalyst dehydrates unacceptably slowly in comparison to the system were 90 % H_3PO_4 is used.

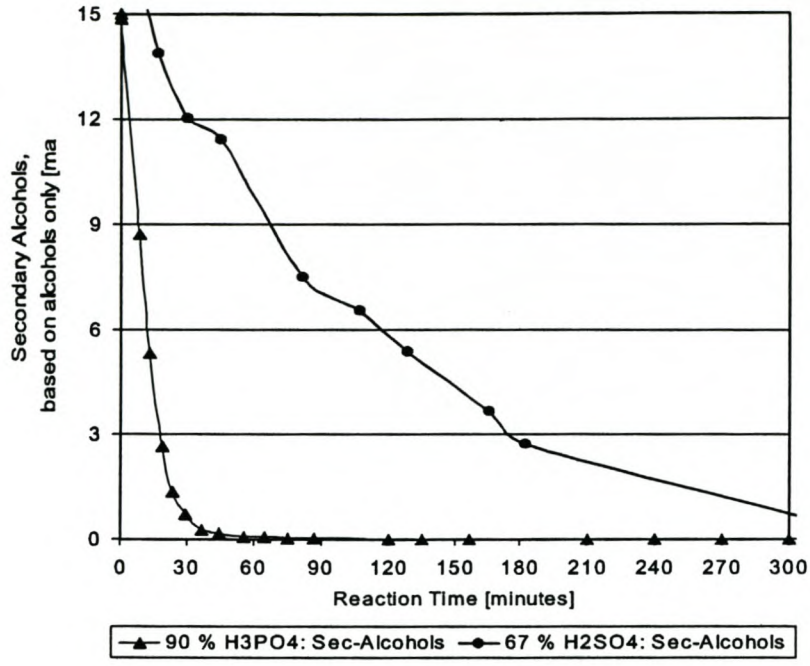


Figure 5.6: **Comparison of the dehydration rate of secondary alcohol using H_2SO_4 or H_3PO_4 as catalyst; Reaction System: 1-butanol+2-pentanol, 67 % H_2SO_4 with acid:alcohol = 0,65:1 or 90 % H_3PO_4 with acid:alcohol = 2,2:1.**

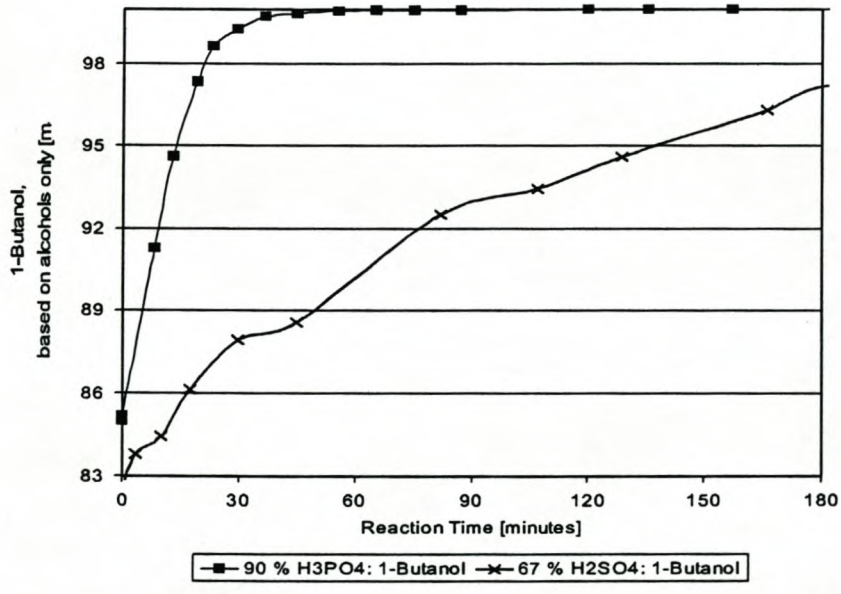


Figure 5.7: **Comparison of the 1-Butanol quality based on alcohols only using H_2SO_4 or H_3PO_4 as catalyst; Reaction System: 1-butanol+2-Pentanol, 67 % H_2SO_4 with acid:alcohol = 0,65:1 or 90 % H_3PO_4 with acid:alcohol = 2,2:1.**

Furthermore the rate of ether formation using H_2SO_4 or H_3PO_4 was compared. As can be seen from Figure 5.8 and Figure 5.9 it was found that the rate of ether formation is unacceptably high using H_2SO_4 as catalyst.

Descriptions of the ether byproduct formations for the various alcohol systems are given in paragraph 5.5.

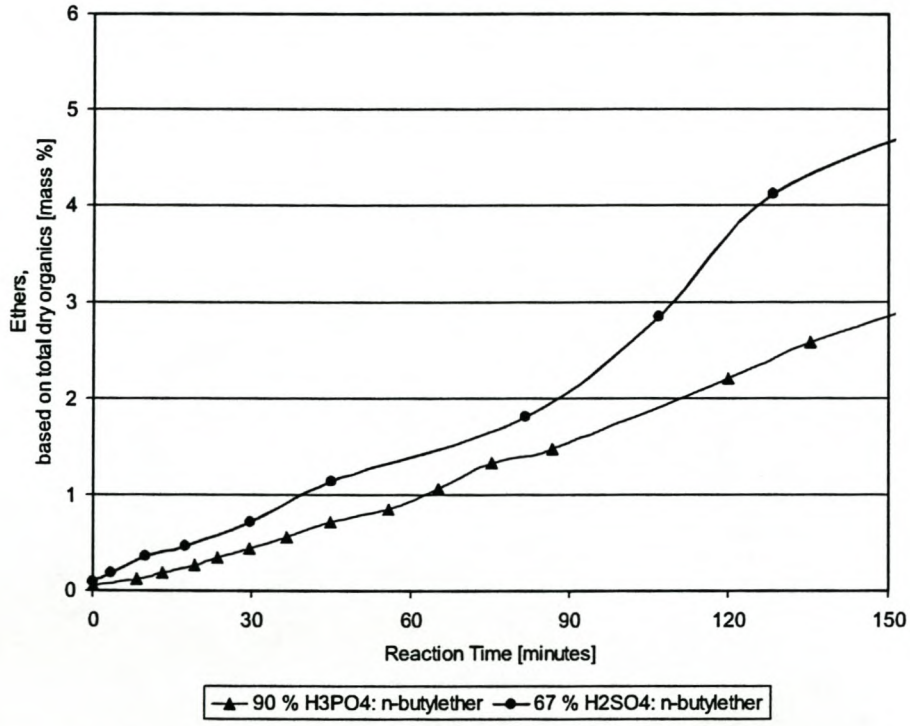


Figure 5.8: n-Butylether formation versus reaction time using H_2SO_4 or H_3PO_4 as catalyst; Reaction System: 1-butanol+2-pentanol, 67 % H_2SO_4 with acid:alcohol = 0,65:1 or 90 % H_3PO_4 with acid:alcohol = 2,2:1.

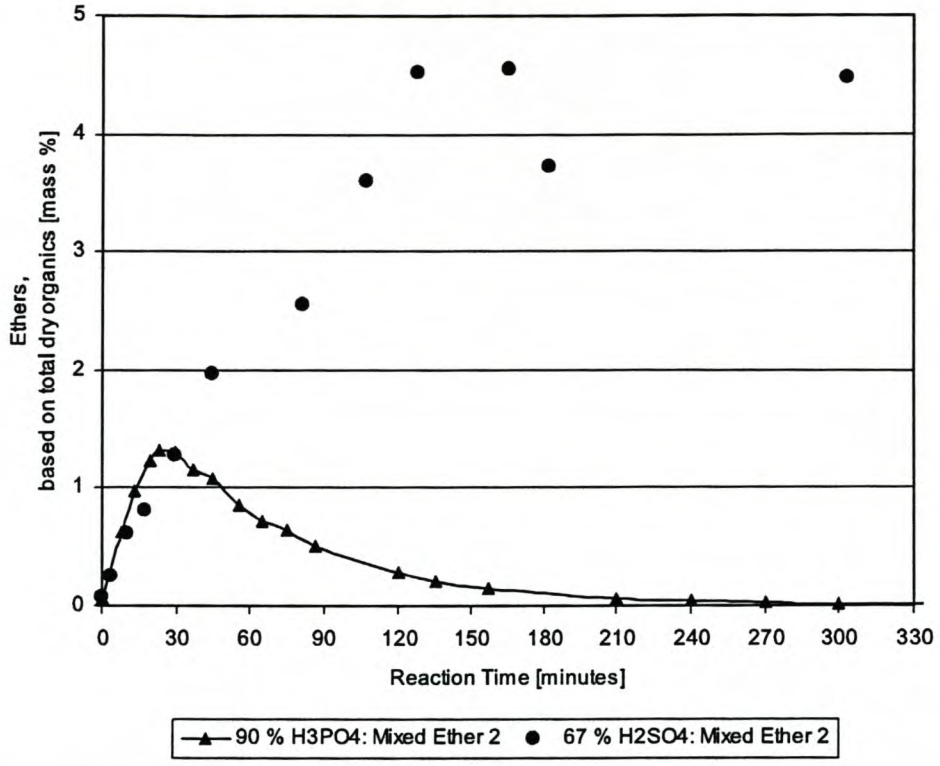


Figure 5.9: Mixed ether formation using H_2SO_4 or H_3PO_4 as catalyst; Reaction System: 1-butanol+2-Pentanol, 67 % H_2SO_4 with acid:alcohol = 0,65:1 or 90 % H_3PO_4 with acid:alcohol = 2,2:1 and 1-butanol+2-pentanol

Although H_3PO_4 and H_2SO_4 can both be used to achieve dehydration of the secondary alcohol, H_3PO_4 is the preferred catalyst, because

- it is less corrosive than H_2SO_4 and safer to use,
- it can be used at higher concentrations than H_2SO_4. The alcohol product will contain less water and the subsequent purification will be easier, and
- the ether formation, if H_3PO_4 is used, is lower.

Of all the liquid catalysts tested it is thus clear that H_3PO_4 is the best catalyst for the removal of the secondary alcohol from a close-boiling primary and secondary alcohol mixture.

The influences of various reaction conditions on systems where H_3PO_4 is used as catalyst will be discussed next.

5.4.5 The influence of time on the dehydration of the secondary alcohol if H_3PO_4 is used as catalyst.

The three alcohol systems 1-propanol+2-butanol, 1-butanol+2-pentanol and 1-pentanol+2-hexanol were subjected to H_3PO_4 catalysed dehydration conditions. Similar trends in the composition of the organics were obtained for all three systems.

The trends of the organic compositions for the various alcohol systems at various acid:alcohol ratio's and acid concentrations are illustrated in Figure 5.10 to Figure 5.13.

The effect of reaction time on the system 85 % 1-butanol + 15 % 2-pentanol, using 90 % H_3PO_4 as catalyst, at an acid:alcohol ratio of 2,2:1 is given in Figure 5.10 (Tabulated results are given in Appendix E: Experiment 89). Several runs were done on the butanol+2-pentanol system. This run (Experiment 89) is used to illustrate the typical trends that were determined.

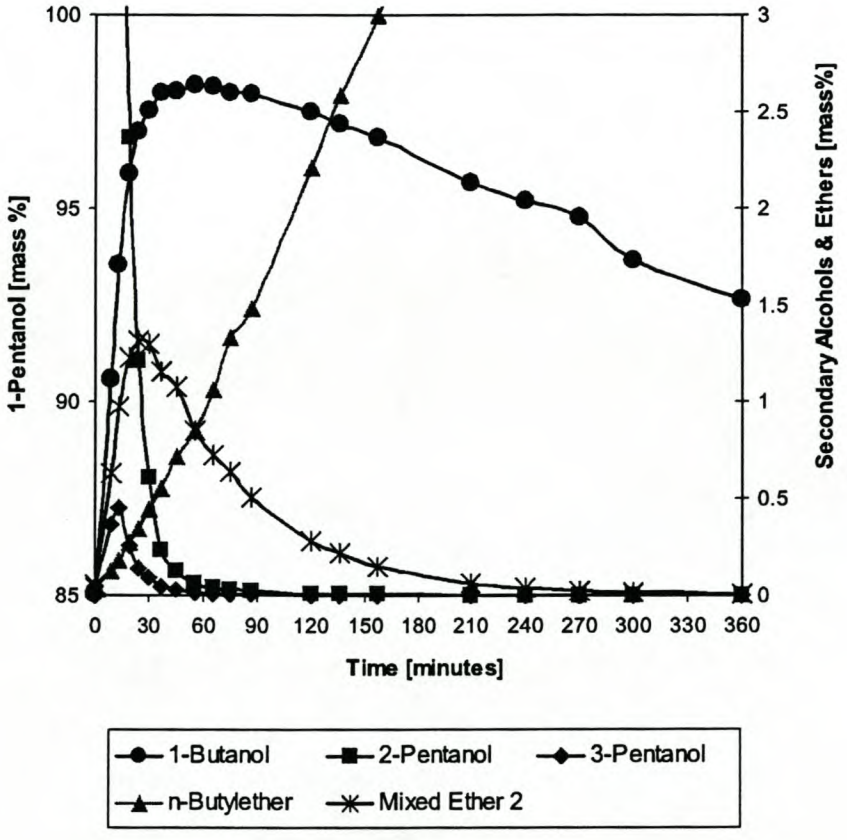


Figure 5.10: Effect of time on the alcohol mixture 1-butanol + 2-pentanol; Reaction system: 90 % H_3PO_4, acid:alcohol = 2,2:1

The main results were the following:

- adequate reaction time to reduce the secondary alcohol content < 0,1 % (based on alcohol only) = 55 minutes
- product quality based on alcohol only = > 99,9 % 1-butanol
- composition of organics at 55 minutes (mass %):
  1-butanol = 98,211 %
  3-pentanol = 0,017 %
  2-pentanol = 0,065 %
  n-butylether = 0,853 %
  mixed ether 2 = 0,853 %
- rate of increase of n-butylether at 55 minutes
  ~ 0.0207 g/g organics.min

Further increase in reaction time has the following effect:

- primary alcohol content reduces,
- secondary alcohol content reduces further,
- n-butylether content increases, and
- mixed ether content decreases.

The % of primary alcohol (based on dry organics) in the reaction mixture increases with time. After a certain time the amount of primary alcohol decreases due to the formation of ether byproducts. For a specific catalyst system and alcohol mixture there is thus an optimum reaction time to achieve adequate secondary alcohol removal and minimum total ether formation.

Although there was no 3-pentanol in the feed mixture, it was detected in the organic product. The 2-pentanol dehydrated to form 2-pentene. This 2-pentene was hydrated to form 3-pentanol. After most of the 2-pentanol was removed, the amount of 3-pentanol also started to decrease. The 3-pentanol also dehydrated to pentene and flashed off.

From Figure 5.11 it can be seen that the initial rate of dehydration of 2-pentanol was very high. After 40 minutes this rate reduced. With less 2-pentanol in the reaction mixture, the driving force for dehydration reduced.

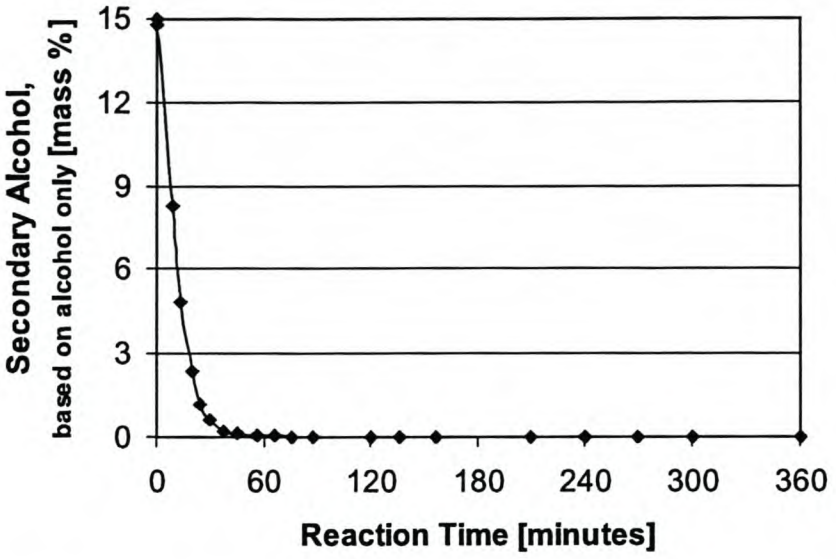


Figure 5.11: Secondary alcohol concentration vs reaction time; Reaction system: 1-Butanol + 2-Pentanol, 90 % H_3PO_4, acid:alcohol = 2,2:1.

The effect of time was the same for all three systems, independent of catalyst concentrations and acid:alcohol ratio's. Graphs showing the effect of time for the alcohol systems 1-propanol+2-butanol and 1-pentanol+2-hexanol are given in Figure 5.12 and Figure 5.13 respectively. (The original readings and grapical results are given in Appendix D&E: Experiments 76 and 88).

Either symmetrical ethers of the primary alcohol or unsymmetrical ethers (=mixed ethers) of the primary and secondary alcohols were formed. Possible structures for the mixed ethers are given in paragraph 5.5. For the system 1-pentanol+2-hexanol the symmetrical ether n-pentylether was formed. The concentration of this ether increased with time during the reaction. Initially the concentration of unsymmetrical ethers started to increase, but after the secondary alcohol was removed, these ethers started to disappear.

For the system 1-propanol+2-butanol the symmetrical ether n-propylether was formed. Very small amounts of unsymmetrical ethers were formed and no clear trends in their concentration were observed. The trends of the organic composition of the reaction mixture is given in Figure 5.12. Only one run using the continuous sampling experimental set-up was done in the 1-propanol+2-butanol system (Appendix E: Experiment 76). A detailed investigation on the system 1-propanol+2-butanol was thus not performed.

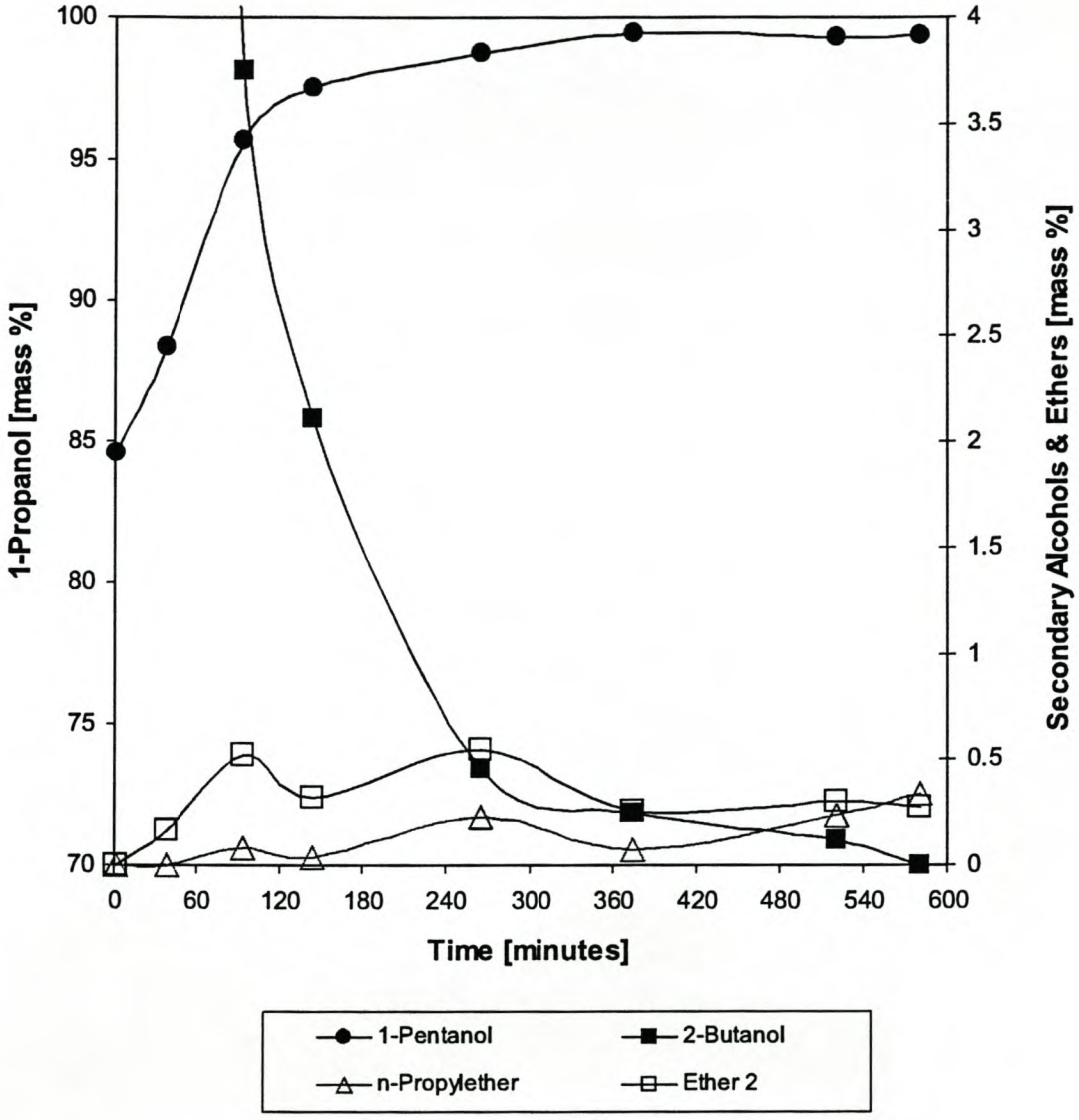


Figure 5.12: Effect of time on the system 85 % 1-propanol+ 15 % 2-butanol; Reaction System: 85 % H_3PO_4 and acid:alcohol = 2,2:1

A detail investigation was done on the dehydration of the secondary alcohol in the system 1-pentanol+2-hexanol. The trends of the organic composition of the reaction mixture were similar to those obtained with the system 1-butanol+2-pentanol. Only one symmetrical ether, n-Pentylether was formed. Two unsymmetrical ethers, probably 3-hexyl pentyl and 2-hexyl pentyl ether were formed. The identification of the ethers is discussed in paragraph 5.5. The trends of one 1-pentanol+2-hexanol dehydration run are illustrated in Figure 5.13.

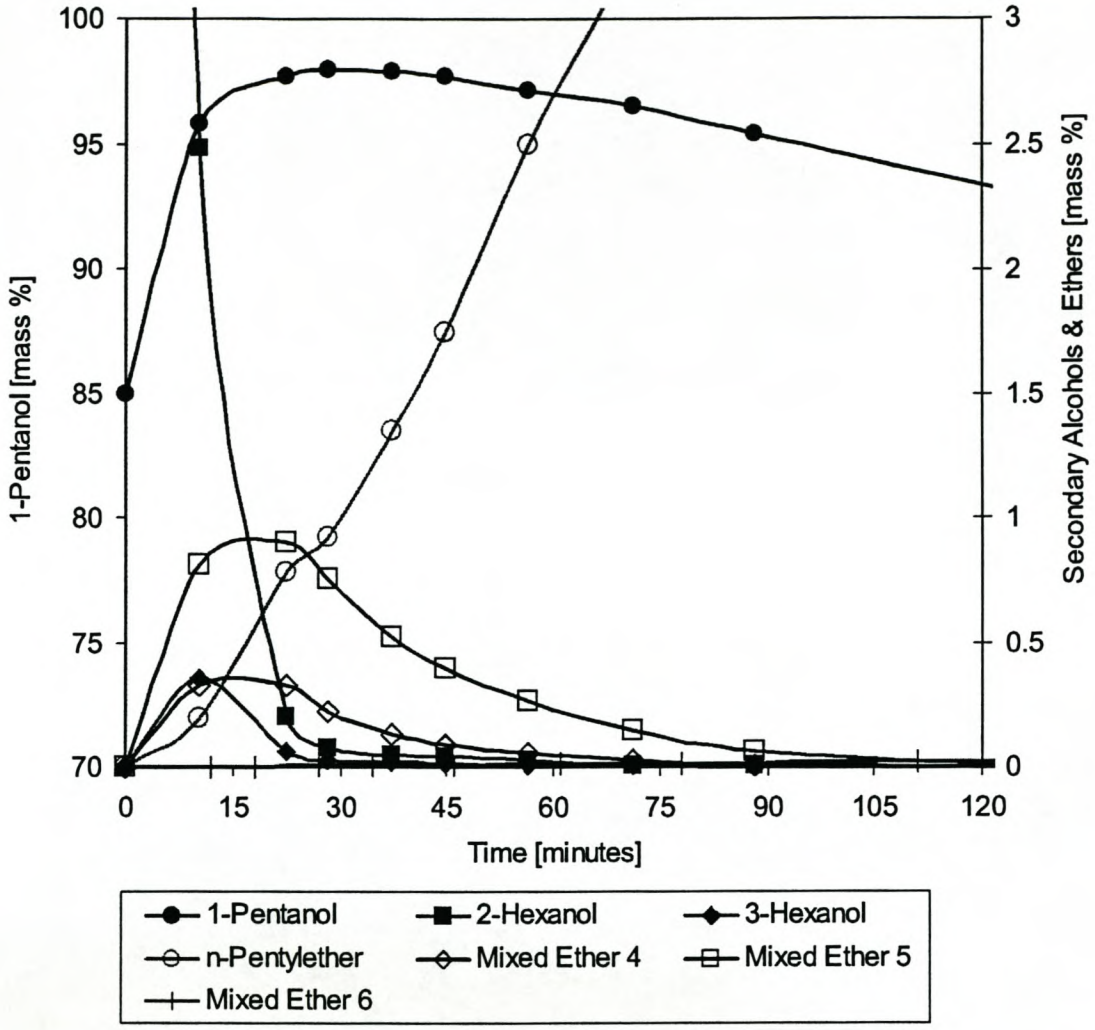


Figure 5.13: Effect of time on reaction composition; Reaction system: 85 % 1-pentanol + 15 % 2-hexanol, 90 % H_3PO_4, acid:alcohol = 2,2:1

The influence of varying H_3PO_4 concentrations and acid:alcohol ratios on required reaction time and ether formation will be discussed next.

5.4.6 The influence of H_3PO_4 concentration and acid:alcohol ratio on the dehydration rate and ether formation rate

The effect of H_3PO_4 concentration as catalyst on the increase in 1-butanol concentration of the system 1-butanol and 2-pentanol is illustrated in Figure 5.14. For the higher concentrated H_3PO_4 as catalyst (at the same acid:alcohol ratio, namely 2,2:1) less time is needed to obtain 100 % 1-butanol (based on alcohol only). The dehydration rate of the secondary alcohol thus increases with an increase in H_3PO_4 concentration. The times required to reduce the secondary alcohol content to < 0,1 mass % are given in Table 5.5. The increase in dehydration rate is not linear with the increase in catalyst concentration. A small increase in catalyst concentration achieves a high reduction in time required for the complete dehydration of the secondary alcohol. The original data and graphical results of these experiments are given in Appendix D and E: Experiments 64, 89, 62 and 65.

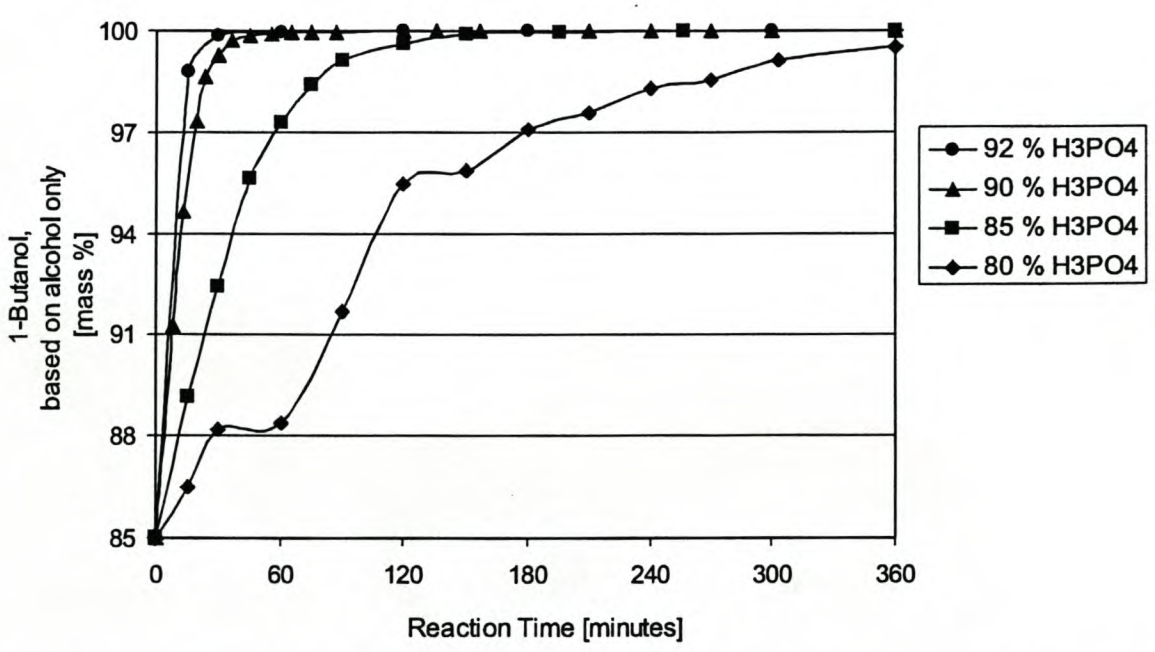


Figure 5.14: Effect of catalyst concentration on 1-butanol quality; Reaction system: 1-butanol+2-pentanol, H_3PO_4 at acid:alcohol=2,2:1.

Table 5.5: Effect of H_3PO_4 concentration on required reaction time and total ether formation; Reaction system: 1-butanol+2-pentanol, H_3PO_4 at an acid:alcohol ratio of 2,2:1.

	Reduction of the secondary alcohol content to < 0,1 mass % (based on alcohols only)			
H_3PO_4 concentration [mass %]	92,3 %	90 %	85 %	80 %
Time Required [minutes]	40	55	150	500
Total ether content [mass %]	2,25	1,71	1,72	0,29

From Figure 5.15 it can be seen that the amount of ethers increased more rapidly in the systems wherein the higher acid concentrations were used. The water present in the reaction system reduces the formation of ethers. The equilibrium of the ether formation reaction is shifted to the left if water is present in the reaction mixture.

The total amount of ethers formed (mass %) and time required - if the reaction is stopped - after the secondary alcohol content is reduced to < 0,1 mass % are given in Table 5.5.

Although the ethers increase the slowest using a low concentration acid, it is not an option to use low acid concentrations. The reaction times required for adequate removal of the secondary alcohol are too high (> 500 minutes). A high water % also means added separation costs. Long reaction times and high water contents would make a commercial production plant very expensive. It is doubtful whether the increase in required reaction time and the additional removal of the water would justify the lower formation of ethers.

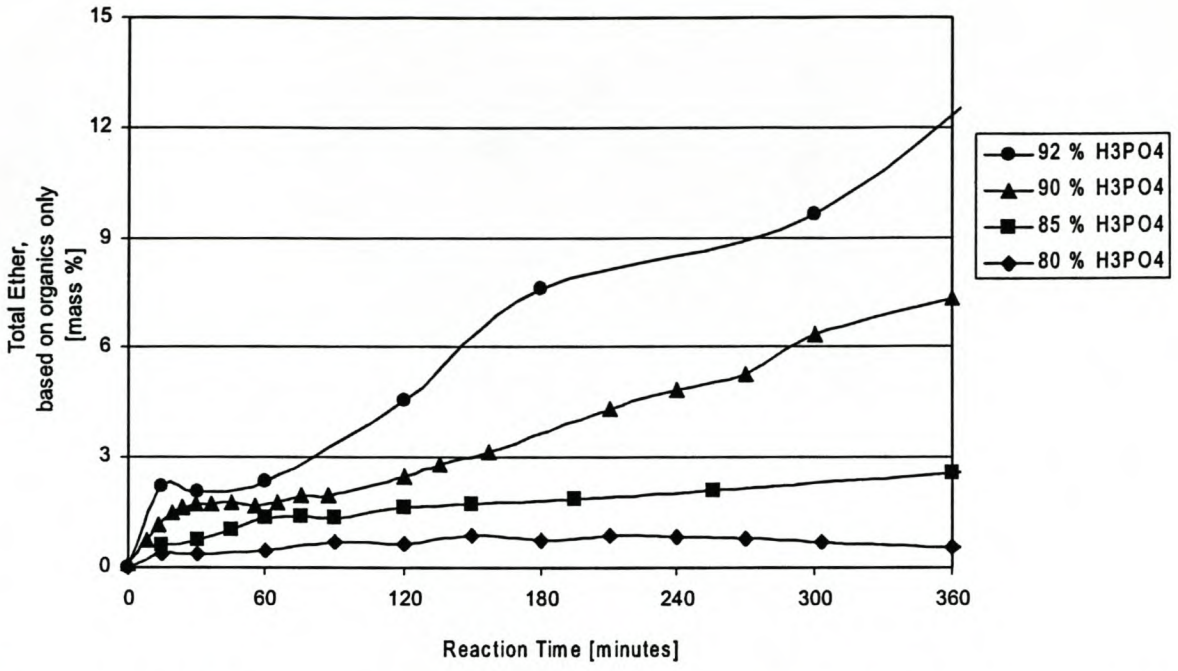


Figure 5.15: Effect of catalyst concentration on ether formation, 1-Butanol+2-Pentanol, acid:alcohol=2,2:1

The effects of acid concentrations on the dehydration of the secondary alcohol of the mixture 1-pentanol+2-hexanol was also determined. The acid:alcohol ratio of the starting reaction mixture was 1,5:1. The results are graphically presented in Figure 5.16 and Figure 5.17 (Experimental data is given in Appendix D: Experiments 80, 81 and 86). As expected, the effect was the same as was observed for the 1-butanol+2-pentanol system. The higher the alcohol concentration, the faster the dehydration and the higher the ether formation rate. The effect of acid concentration on the dehydration and ether formation rate is very high.

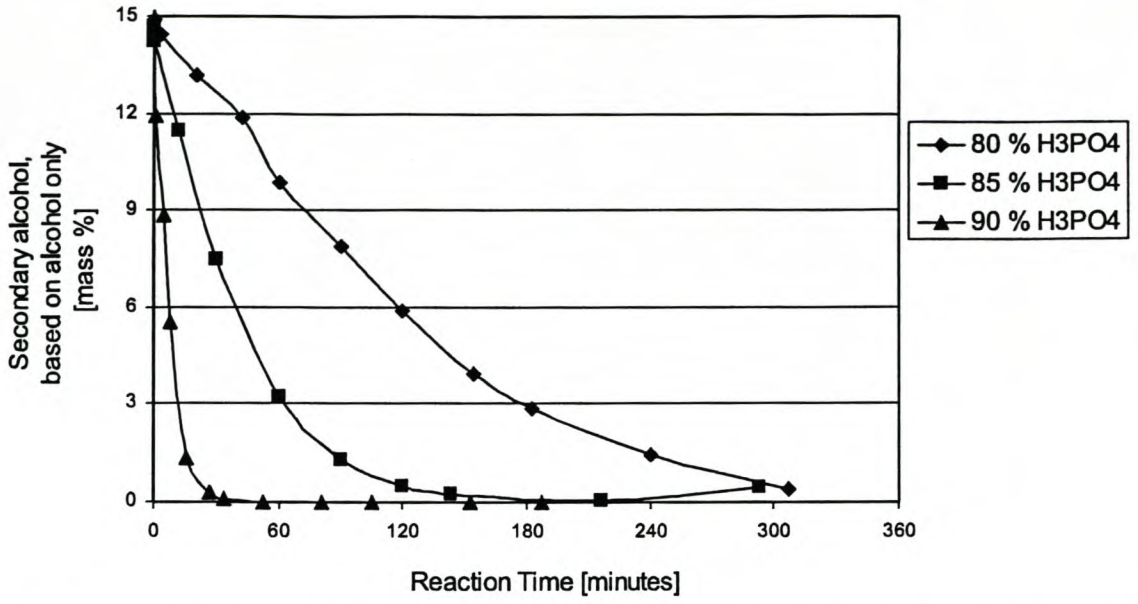


Figure 5.16: Effect of acid concentration on secondary alcohol dehydration, 1-pentanol+2-hexanol, acid:alcohol = 1,5:1

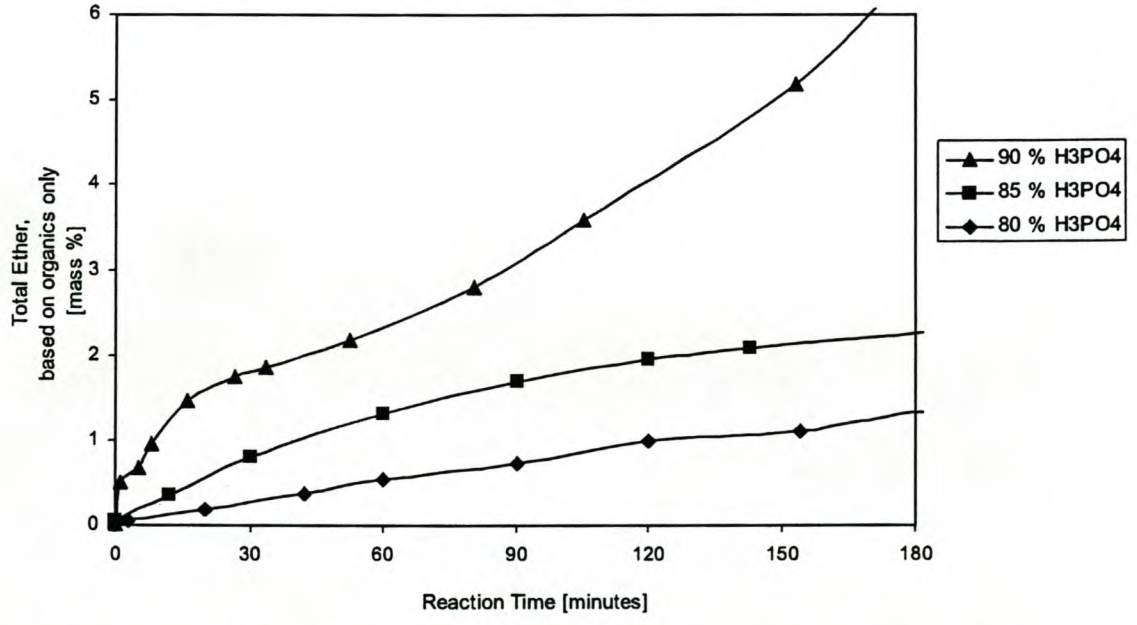


Figure 5.17: Effect of acid concentration on ether formation; Reaction system: 1-pentanol+2-hexanol, acid:alcohol=1,5:1

The effect of acid concentration for an acid:alcohol ratio of 1,5:1 for the alcohol systems 1-butanol+2-pentanol are presented in Figure 5.18 and Figure 5.19 (The experimental results are given in Appendix D: Experiments 72, 69 and 73). The same trends in dehydration rate and ether formation as observed for an acid:alcohol ratio of 2,2:1, were observed for the 1,5:1 system.

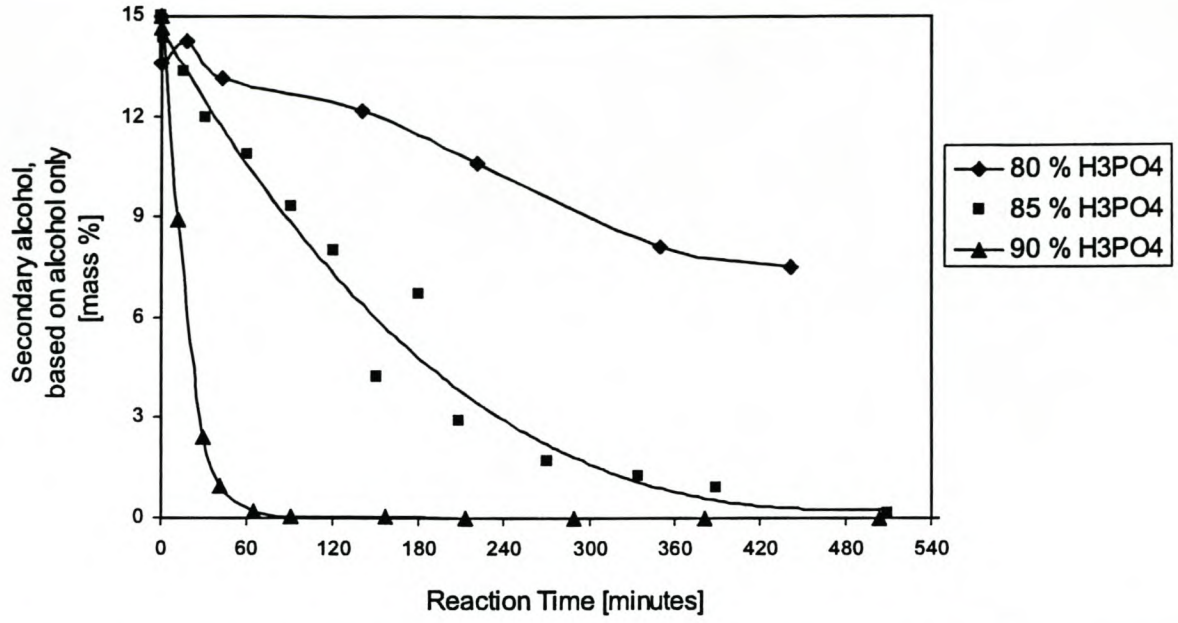


Figure 5.18: Secondary alcohol dehydration for varying acid concentrations; reaction system: 1-butanol+2-pentanol, acid:alcohol = 1,5:1

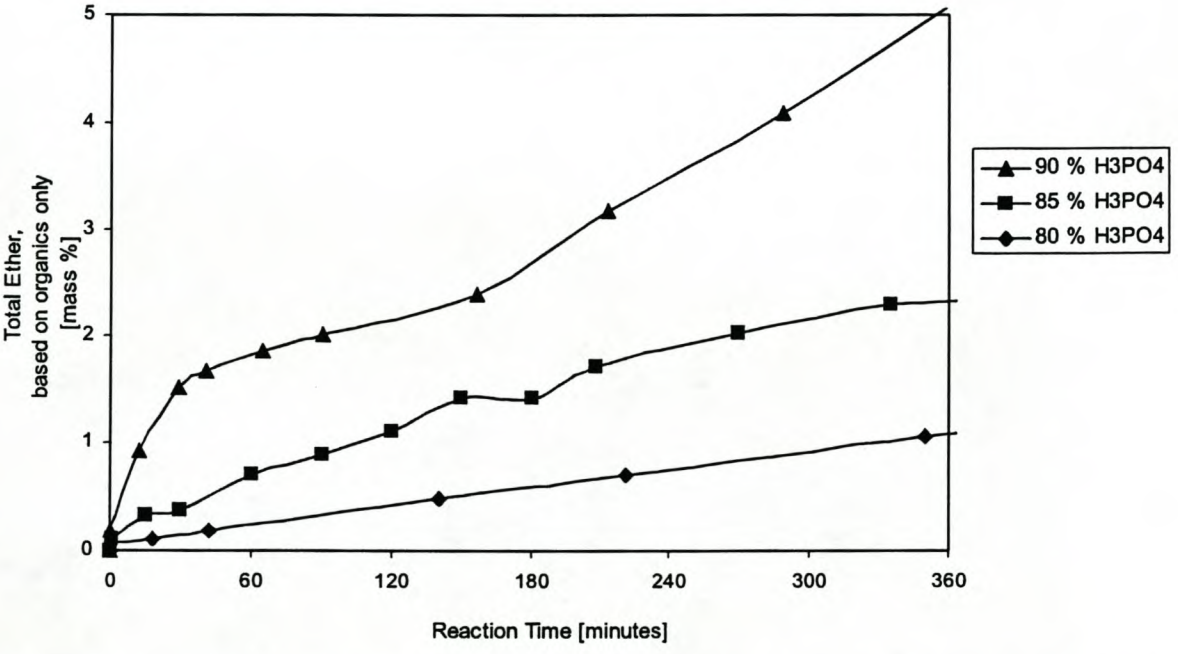


Figure 5.19: Ether formation for varying acid concentrations; reaction system: 1-butanol+2-pentanol, acid:alcohol = 1,5:1

The acid:alcohol ratio was also varied to determine the effect thereof on the dehydration and ether formation rate. Acid:alcohol ratio's of 1,5:1 , 2,2:1 and 3:1 for varying H_3PO_4 concentrations were used.

For the system 85 % 1-Butanol + 15 % 2-Pentanol, 90 % H_3PO_4, the effect of acid:alcohol ratio's of 1,5:1 , 2,2:1 and 3:1 on 1-butanol quality is illustrated in Figure 5.20 (Orginal data and results are given in Appendix E: Experiments 73, 89, 66).

For higher acid:alcohol relations, less time is needed to obtain 100 % 1-butanol (based on alcohol only). Thus, less time is needed to dehydrate the 2-pentanol and 3-pentanol to pentenes.

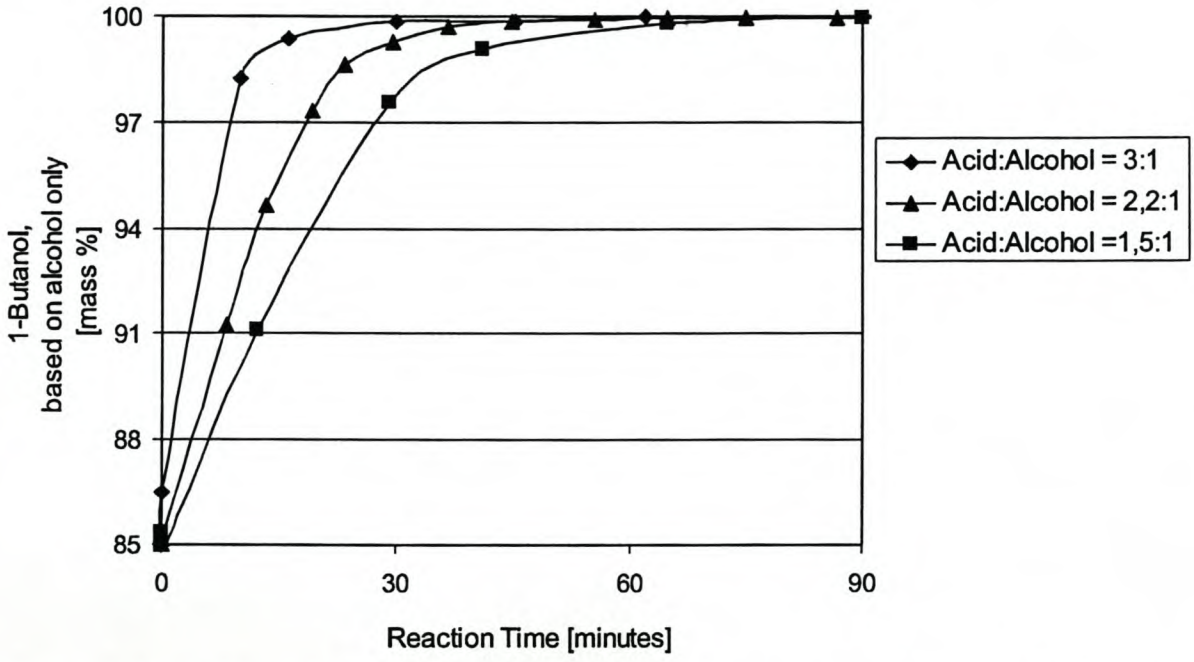


Figure 5.20: Effect of acid:alcohol ratio on product quality; reaction system: 1-butanol+2-pentanol alcohol feed mixture, 90 % H_3PO_4.

From Figure 5.21 the conclusion can be made that higher acid:alcohol ratio's increase the formation of ethers. The ethers plotted in the graphs, are the total ethers formed. For the system with a ratio of 3:1 the total ethers formed are higher at reaction times of 10 and 16 minutes. These high amounts were found because mixed ether 2 was very high in both these samples. The mixed ether content at 10 minutes was 3,6 % and at 16 minutes it was 3,0 % in comparison to the symmetric n-butylether which was 0,4 and 0,7 % respectively. According to Figure 5.22 the amount of mixed ethers decreased after 16 minutes, however, the n-butylether and total ether increased.

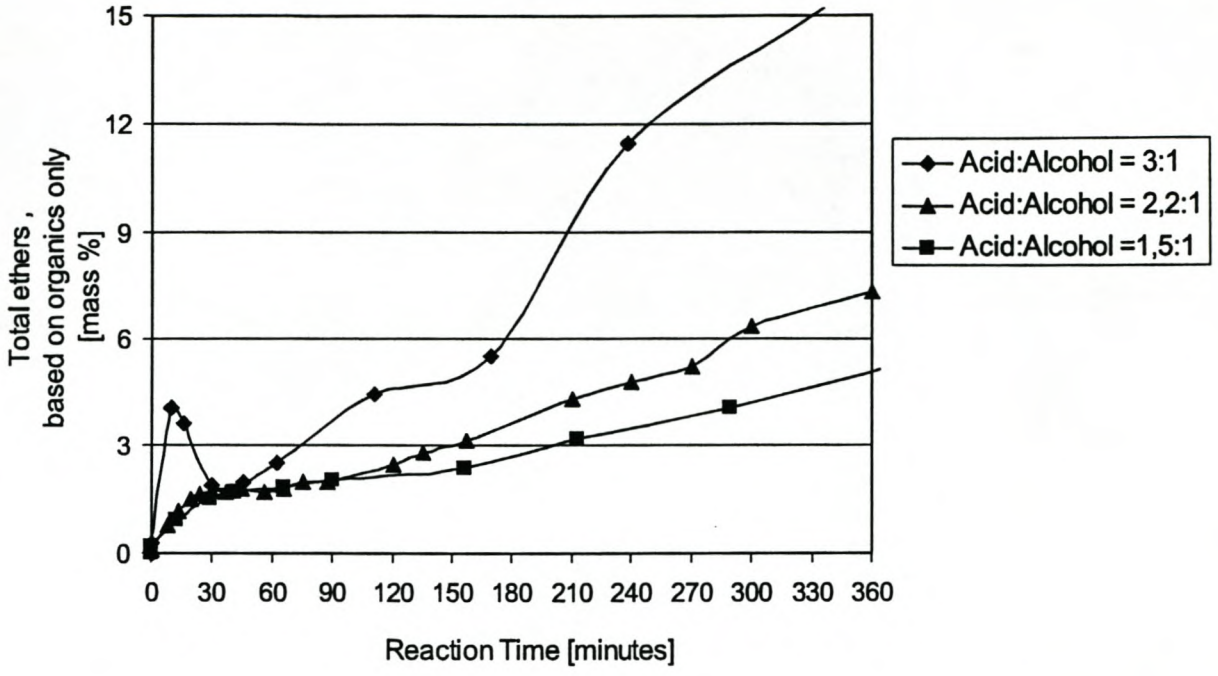


Figure 5.21: Effect of acid:alcohol ratio on ether formation; reaction system: 1-butanol+2-pentanol, 90 % H_3PO_4

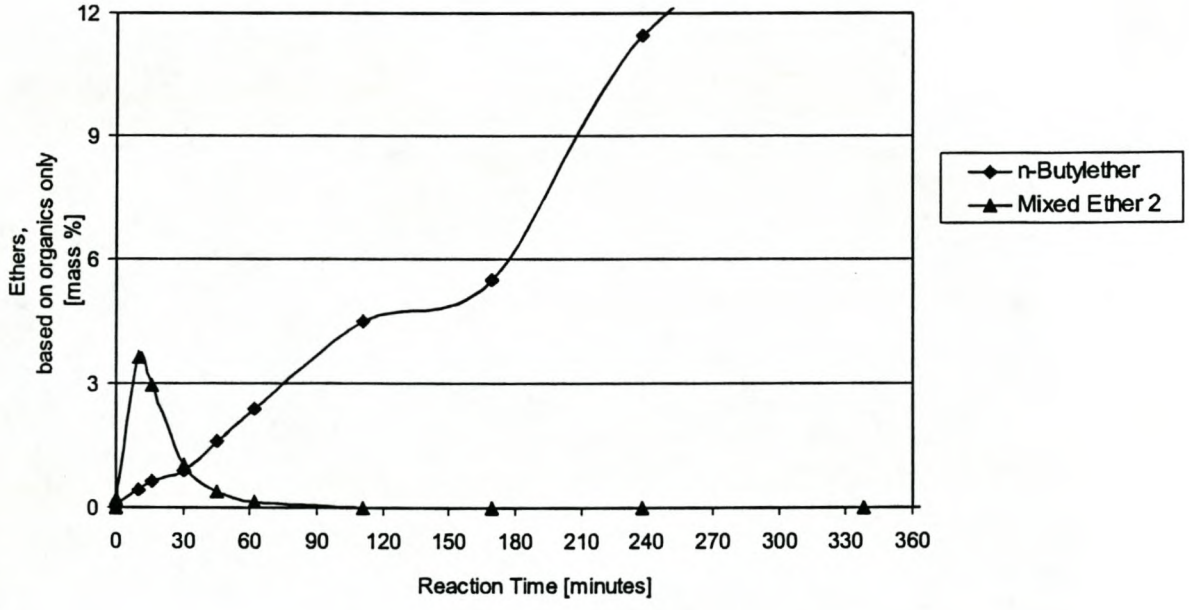


Figure 5.22: Ether formation; reaction system: 90 % H_3PO_4 at acid:alcohol ratio of 3:1, 1-butanol +2-pentanol alcohol feed mixture

Similar results were obtained if the acid:alcohol ratio is varied in the dehydration reactions of 1-pentanol+2-hexanol. It was also found that the rate of dehydration of the secondary alcohol reduced with a reduction in acid:alcohol ratio. This is shown clearly in Figure 5.23. However, the amount of ethers formed were not influenced significantly by the acid:alcohol ratio, this can be seen in Figure 5.24.

In varying the acid:alcohol ratio's in the dehydration of 1-butanol+2-pentanol, using 80 % or 85 % H_3PO_4 as catalyst, the same was found. The increase in the rate of secondary alcohol dehydration is shown in Figure 5.25. The rate of ether formation is shown in Figure 5.26 and Figure 5.27.

The conclusion can be made that the rate in dehydration of the secondary alcohol definitely increased with the acid:alcohol ratio. However, the rate of ether formation is not very sensitive to the acid:alcohol ratio if H_3PO_4 with an concentration of < 85 % is used. Only at high acid concentrations, as shown for 90 % H_3PO_4, the rate of ether formation increased significantly with an increase in acid:alcohol ratio.

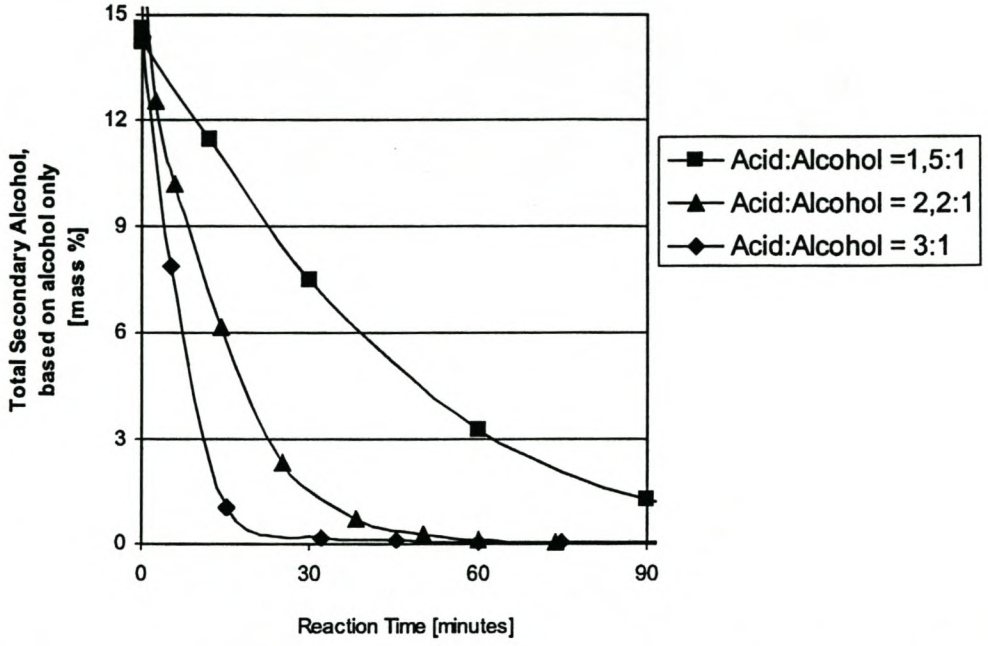


Figure 5.23: Secondary Alcohol vs time for varied acid:alcohol ratio's; reaction system: 85 % H_3PO_4 and 1-pentanol + 2-hexanol

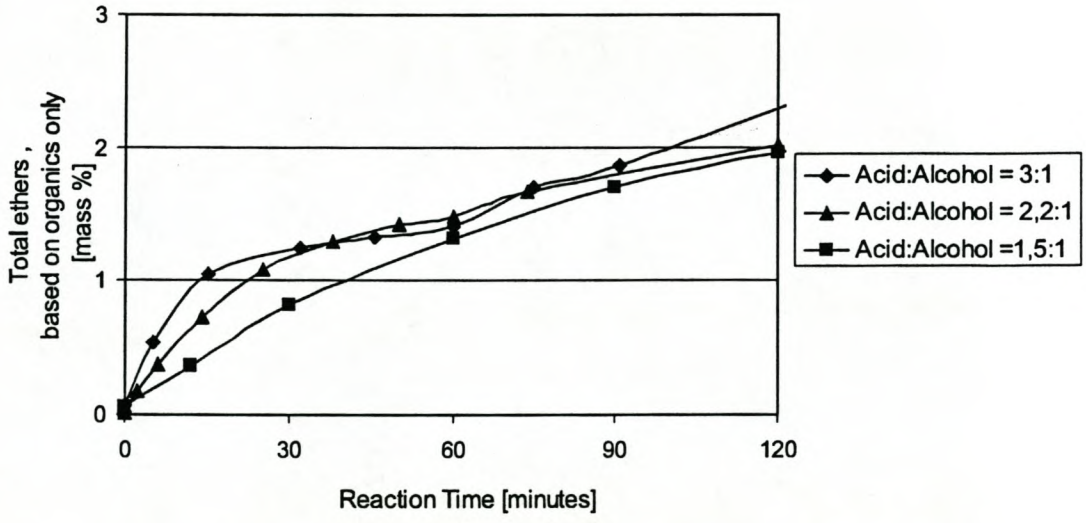


Figure 5.24: Total ethers vs time for varied acid:alcohol ratio's; reaction system: 85% H_3PO_4 , 1-pentanol+2-hexanol

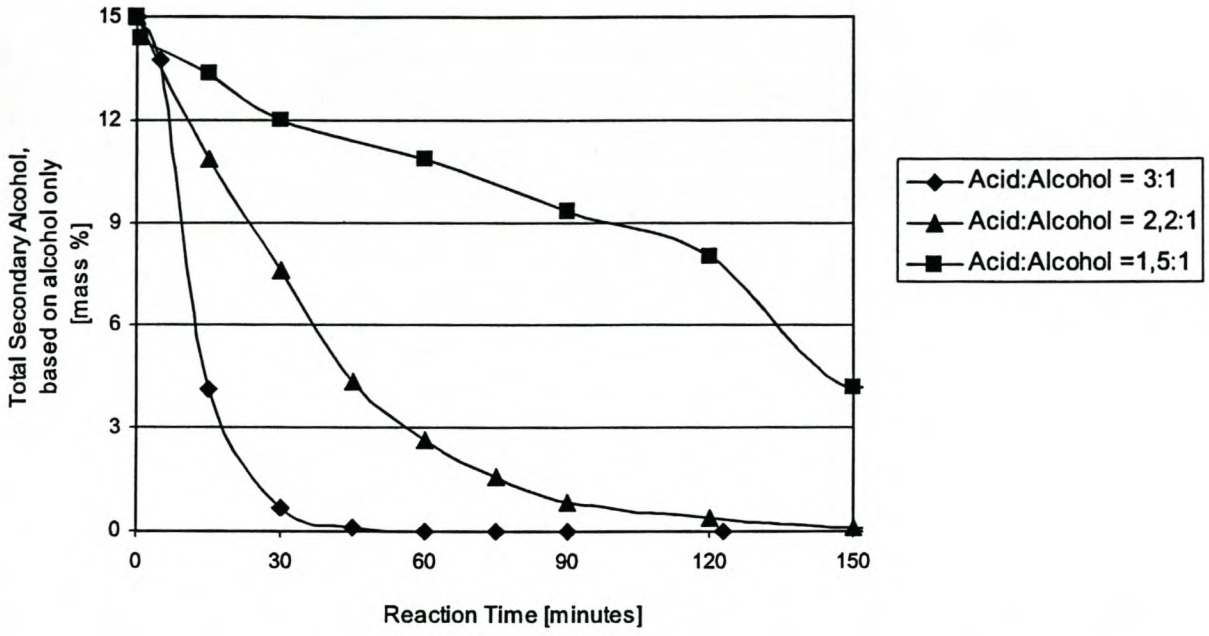


Figure 5.25: Secondary alcohol vs time for varied acid:alcohol ratio's; reaction system: 85 % H_3PO_4, 1-butanol+2-pentanol

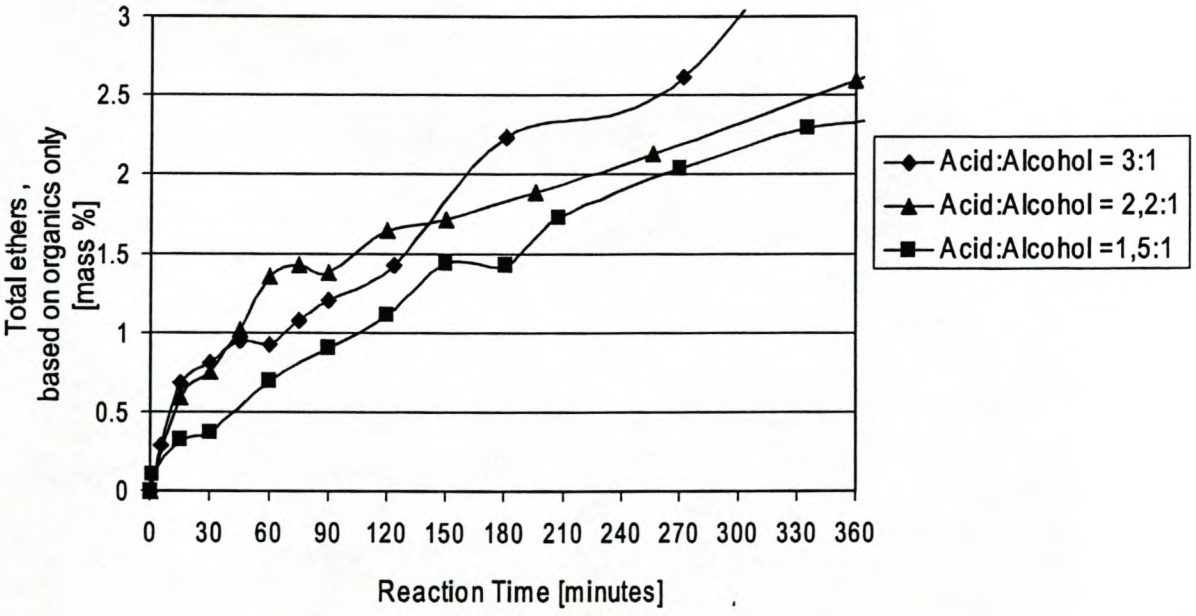


Figure 5.26: Ether vs time for varied acid:alcohol ratio's; reaction system: 85% H_3PO_4, 1-butanol+2-pentanol

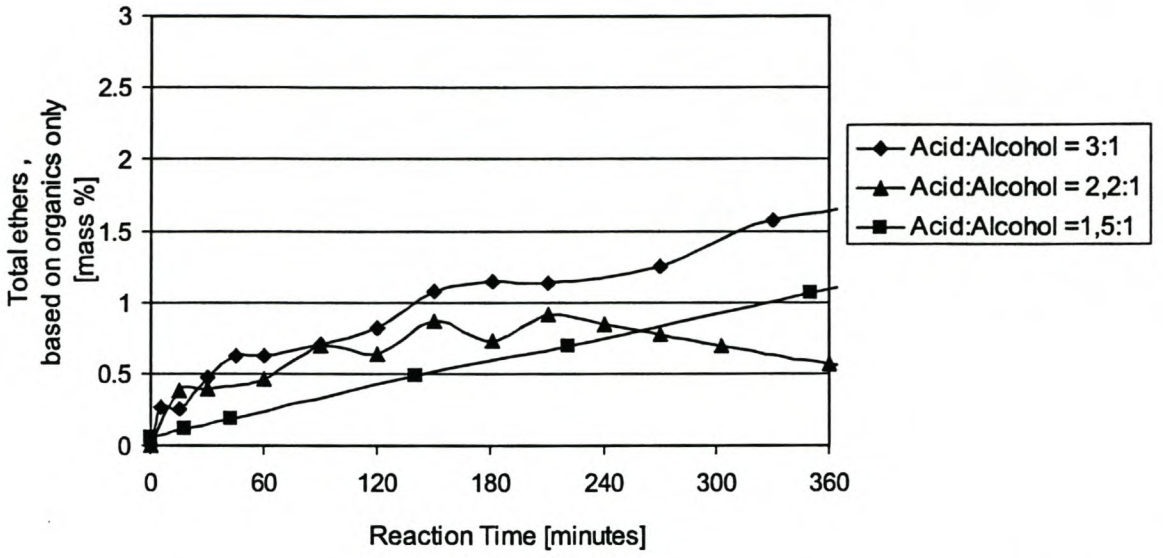


Figure 5.27: Total ethers vs time for varied acid:alcohol ratio's; reaction system: 80 % H_3PO_4, 1-butanol+2-pentanol

It was shown that the dehydration rate of the secondary alcohol and ether formation rate is sensitive to the H_3PO_4 concentration. If the effect of acid concentration is compared to the effect of acid:alcohol ratio, the conclusion can be made that the acid concentration is the stronger determining variable of the two. The effect on secondary alcohol dehydration is illustrated clearly in Figure 5.27. The effect on the ether formation if the acid concentration and acid:alcohol ratio is compared, was not as strong as the effect on the dehydration rate. This is shown in Figure 5.28.

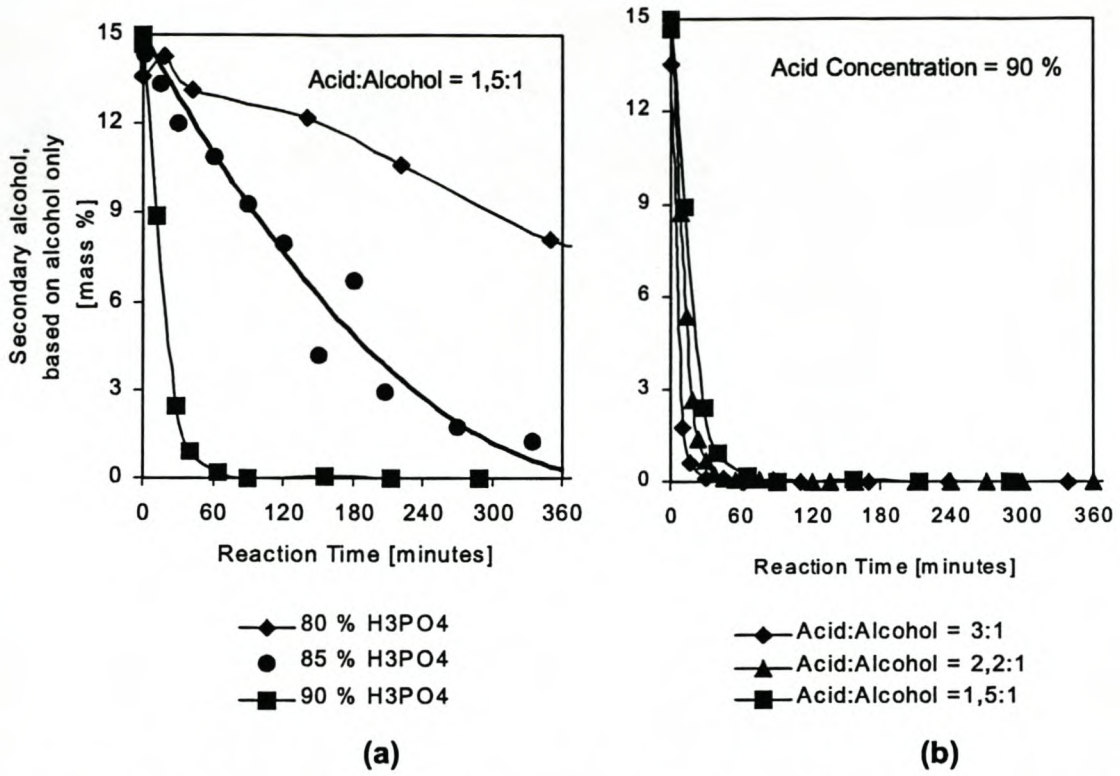


Figure 5.28: Comparison of the effect of H_3PO_4 concentration and the effect of acid:alcohol ratio for the system 1-butanol+2-pentanol

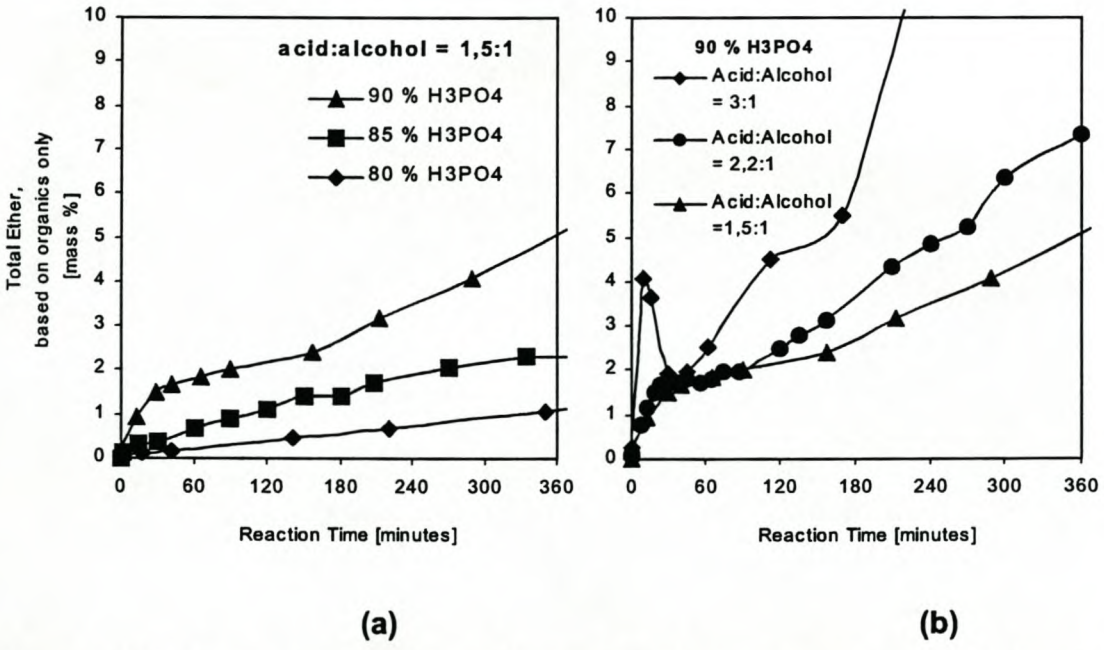


Figure 5.29: Comparison of the effect of H_3PO_4 concentration and the effect of acid:alcohol ratio on ether formation; reaction system: 1-butanol+2-pentanol

5.4.7 Influence of the feed composition on the dehydration time and ether formation rates.

It was found that if the alcohol composition was changed to 50 % 1-butanol + 50% 2-pentanol that the time required to dehydrate the secondary alcohol to <0,1 % in the alcohol product remained the same. This is illustrated in Figure 5.30 (The graphical results of the complete analysis are given in Appendix E - Table E7: Experiments 89 and 96). 90 % H_3PO_4 at an acid:alcohol ratio of 2,2:1 were used. The higher rate of dehydration in the 50/50 mixture is caused by the higher secondary alcohol concentration. The driving force for dehydration of the secondary alcohol is thus higher. For both mixtures a reaction time of about 50 minutes should be adequate to reduce the secondary alcohol content to < 0,1 mass %, based on the alcohols only.

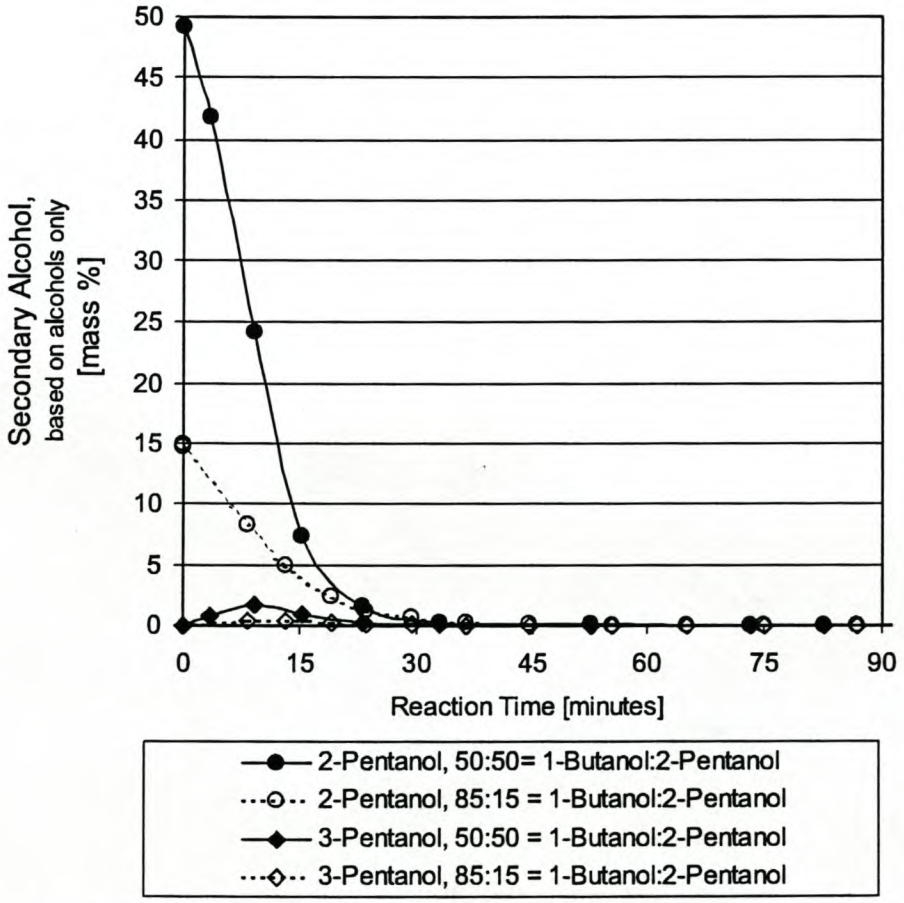


Figure 5.30: Effect of feed composition on dehydration rate of Secondary Alcohols; reaction system: 90 % H_3PO_4, acid:alcohol = 2,2:1, 1-butanol+2-pentanol

The increase in 1-butanol quality is compared for the feed systems 85/15 and 50/50 in Figure 5.31.

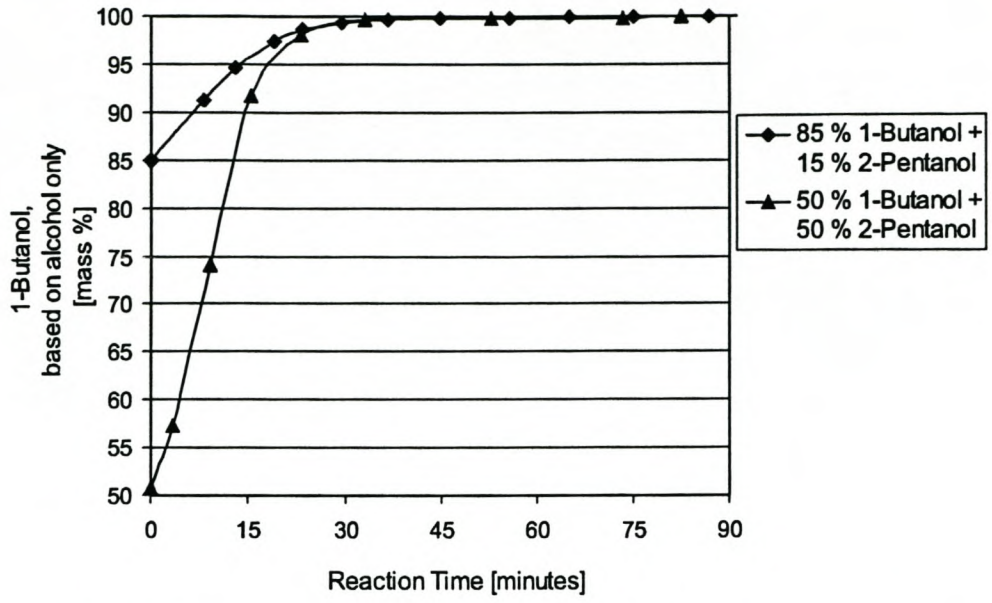


Figure 5.31: Effect of feed composition on 1-butanol quality; reaction system: 90 % H_3PO_4, acid:alcohol = 2,2:1, 1-butanol+2-pentanol

The rate of formation of n-butylether was the same for the 50/50 and 85/15 alcohol systems. This is showed clearly in Figure 5.32. The rate of Mixed Ether 2 formation was significantly higher in the 50% 1-butanol + 50 % 2-pentanol mixture. This result was used to justifiy that Mixed Ether 2 could be 2-pentyl butyl ether. The identification of the ethers is discussed in paragraph 5.5 .

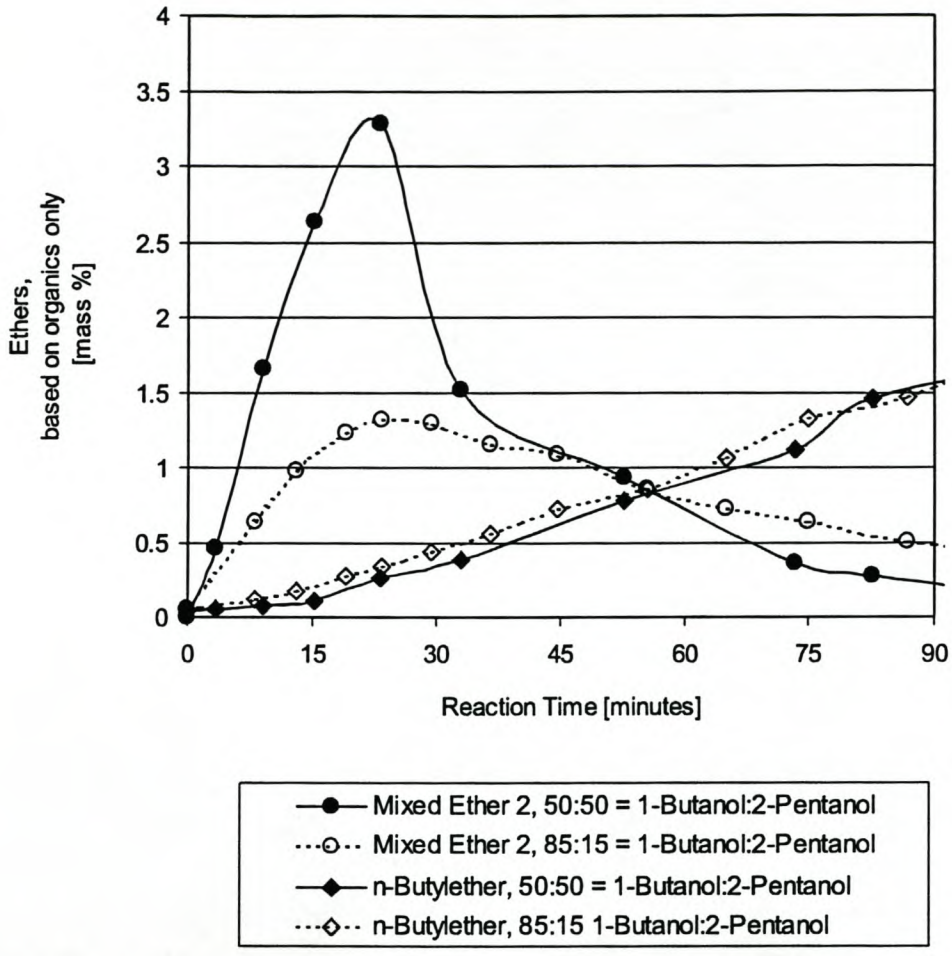


Figure 5.32: Ether formation vs time for varying feed composition; reaction system: 90 % H_3PO_4, acid:alcohol = 2,2:1, 1-butanol+2-pentanol

A reaction was carried out where n-butylether was added to the feed mixture. The organic feed mixture consisted of 82,4 % 1-butanol + 14,5 % 2-Pentanol +3,1 % n-butylether. 90 % H_3PO_4 was added as catalyst at an acid:alcohol ratio of 2,2:1 (Appendix D&E: Experiment 91). The results are compared with a similar experiment where no n-butylether was added (Appendix E: Experiment 89).

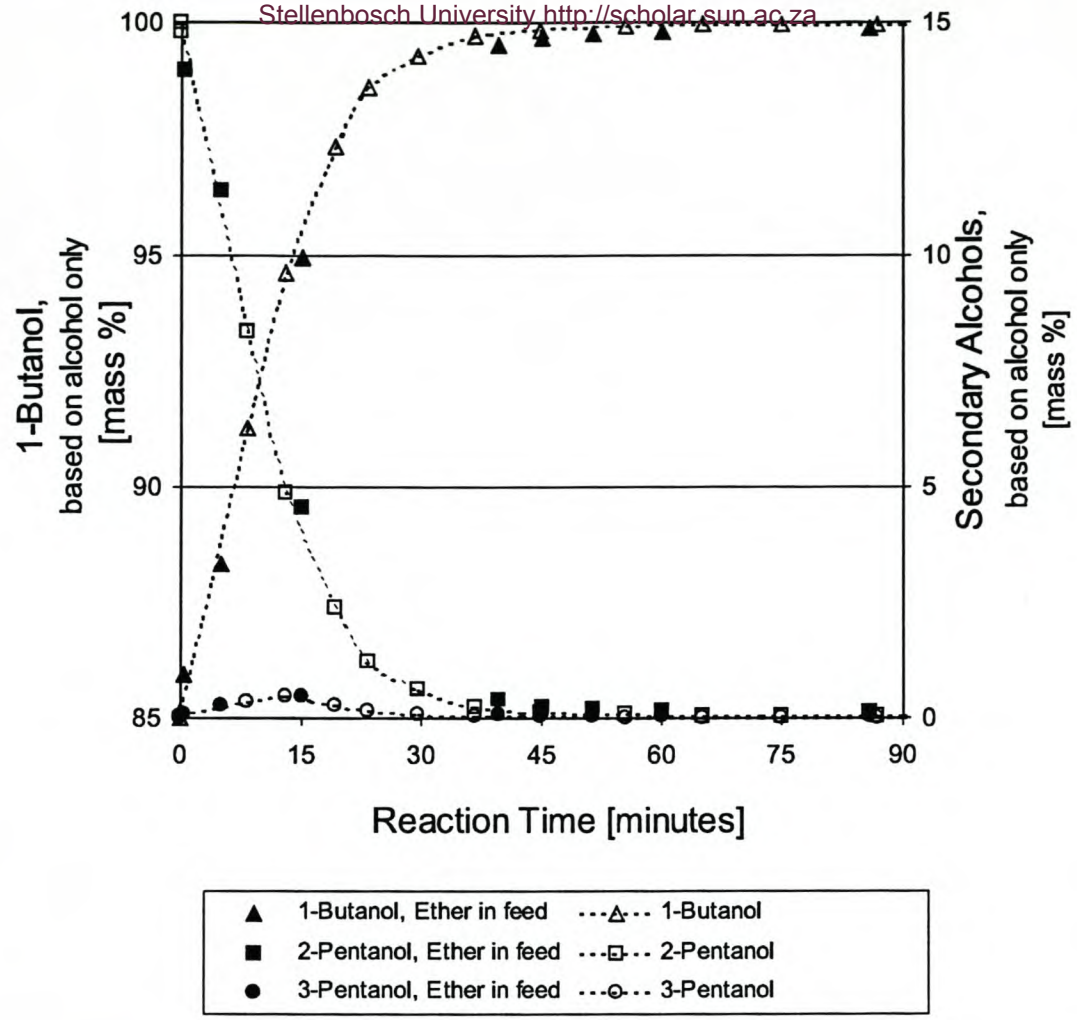


Figure 5.33: Effect of n-butylether in feed on alcohol quality; reaction system: 90 % H_3PO_4, acid:alcohol = 2,2:1, 1-butanol+2-pentanol

The ether in the feed did not influence the initial rate of dehydration of the secondary alcohol substantially. At 50 minutes, the total secondary alcohol content was already reduced to 0,25 %. However, further reduction of the secondary alcohol was very slow. At 50 minutes it was 0,19 % and at 60 minutes it was 0,13 %. The time required to reduce the secondary alcohol to < 0,1 mass % based on the alcohols was 120 minutes. The usual time it took to dehydrate an adequate amount of secondary alcohol, at the acid:alcohol ratio and acid concentration, if no n-butylether was present in the feed, was less than 60 minutes (See Appendix E: Experiments 63 and 89).

The rate of formation of n-butylether in the feed mixture containing n-butylether was the same as in the alcohol feed mixture without n-butylether. However, according to Figure 5.34 the concentration of the mixed ether 2 was slightly higher when n-butylether was present in the feed.

The reason why these experiments were done was to determine whether all the ethers have to be removed from the acid catalyst, before the catalyst is recycled to the reactor. Further investigations are needed to determine the influence of ethers in the reactor feed system.

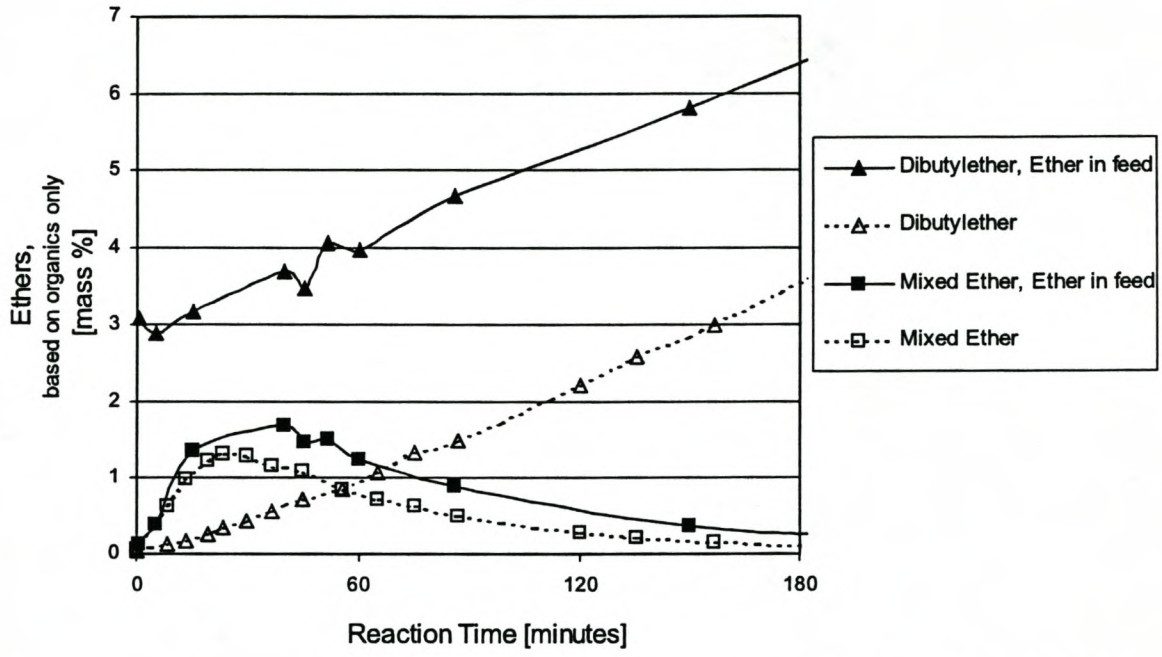


Figure 5.34: Formation of ether with ether present in feed; reaction system: 90 % H_3PO_4, acid:alcohol = 2,2:1, 1-butanol+2-pentanol

5.4.8 Comparison of the dehydration rates of the various alcohol mixtures

Three close-boiling alcohol systems, namely 85 % 1-propanol + 15 % 2-butanol, 85 % 1-butanol + 15 % 2-pentanol and 85 % 1-pentanol and 15 % 2-hexanol were compared with each other. 85 % H_3PO_4 at an acid:alcohol ratio of 2,2:1 was used for all three systems. (Appendix D: Experiments 76, 62, 77 and Appendix E: Experiments 76, 62, 77).

According to Figure 5.35 and Figure 5.36 the dehydration rate of the secondary alcohol increases with an increase in the molecular mass of the alcohol mixture. 2-Hexanol dehydrates faster than 2-pentanol and 2-pentanol dehydrates much faster than 2-butanol for the same acid concentrations and acid:alcohol ratios in the mixture. The boiling point of the acid/alcohol mixture increases with molecular weight. The higher boiling temperature could offer one explanation of why the secondary alcohols of the higher molecular weight mixture dehydrate faster. The approximate boiling temperatures of the three reaction mixtures were as follows: 1-propanol+2-butanol = 113 °C,; 1-butanol+2-pentanol = 121 °C ; 1-pentanol+2-hexanol = 134 °C.

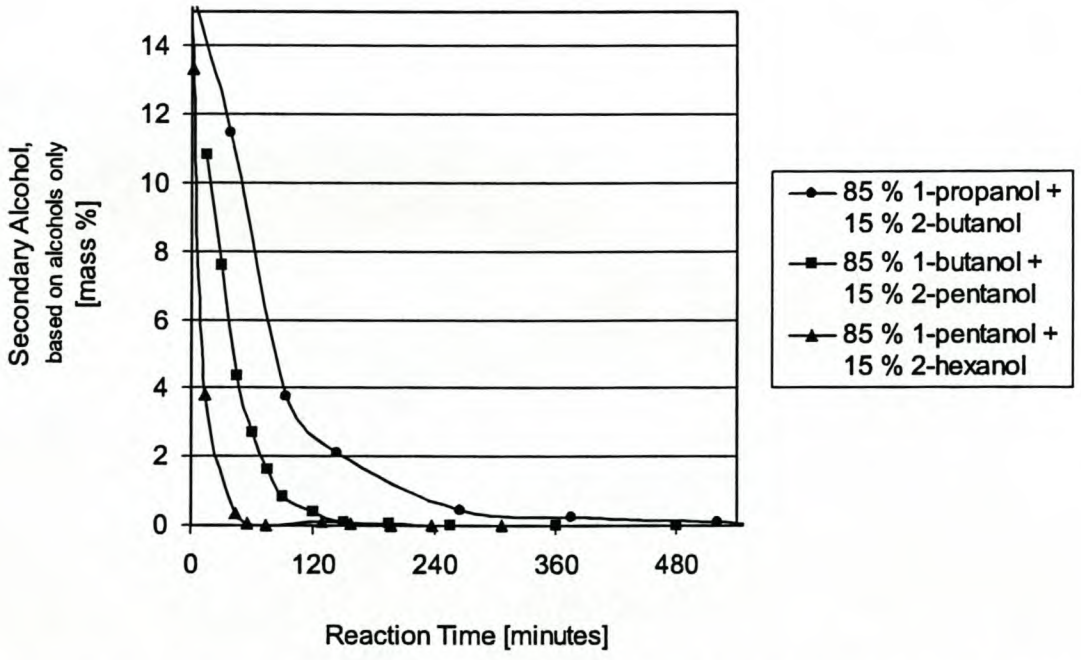


Figure 5.35: Comparison of the dehydration rate of the secondary alcohol in various alcohol mixtures; catalyst system: 85 % H_3PO_4, acid:alcohol=2,2:1.

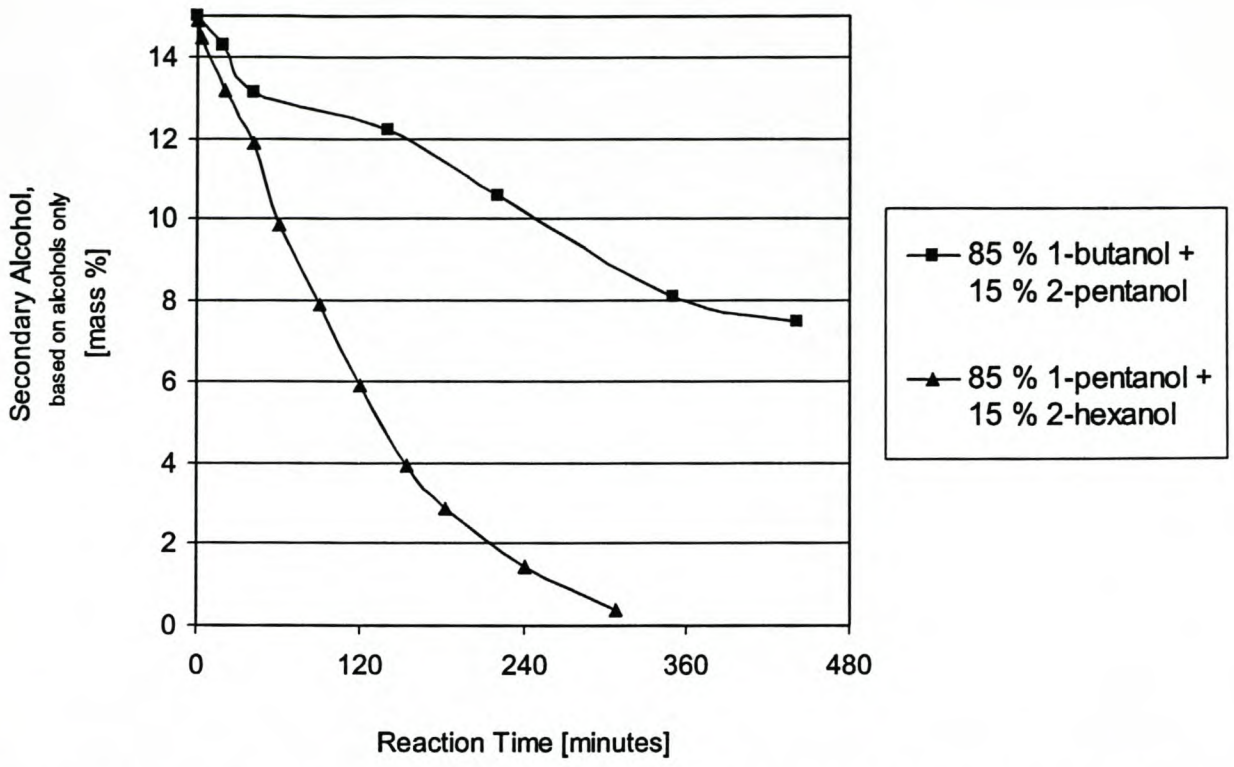


Figure 5.36: Secondary alcohol dehydration vs time for varying alcohol systems; catalyst system: 80 % H_3PO_4 and acid:alcohol = 1,5:1

As can be seen from Figure 5.36 the difference in the secondary alcohol dehydration rate of the two alcohol systems at the lower H_3PO_4 concentration (80 %) was rather pronounced. From Figure 5.37 and Figure 5.38 it can be seen that at the higher acid concentrations (90 %) this difference in secondary alcohol dehydration was less. When 90 % H_3PO_4 with an acid:alcohol ratio of 3:1 is used, there is almost no difference in the secondary alcohol dehydration rate for the systems 1-butanol+2-pentanol and 1-pentanol+2-hexanol. In Figure 5.38 the secondary alcohol dehydration rate using 90 % H_3PO_4 at a low acid:alcohol ratio (1,5:1) is illustrated. The secondary alcohol dehydration rate of the 1-butanol+2-pentanol system is only slightly lower than the dehydration rate of the secondary alcohol of the 1-pentanol+2-hexanol system.

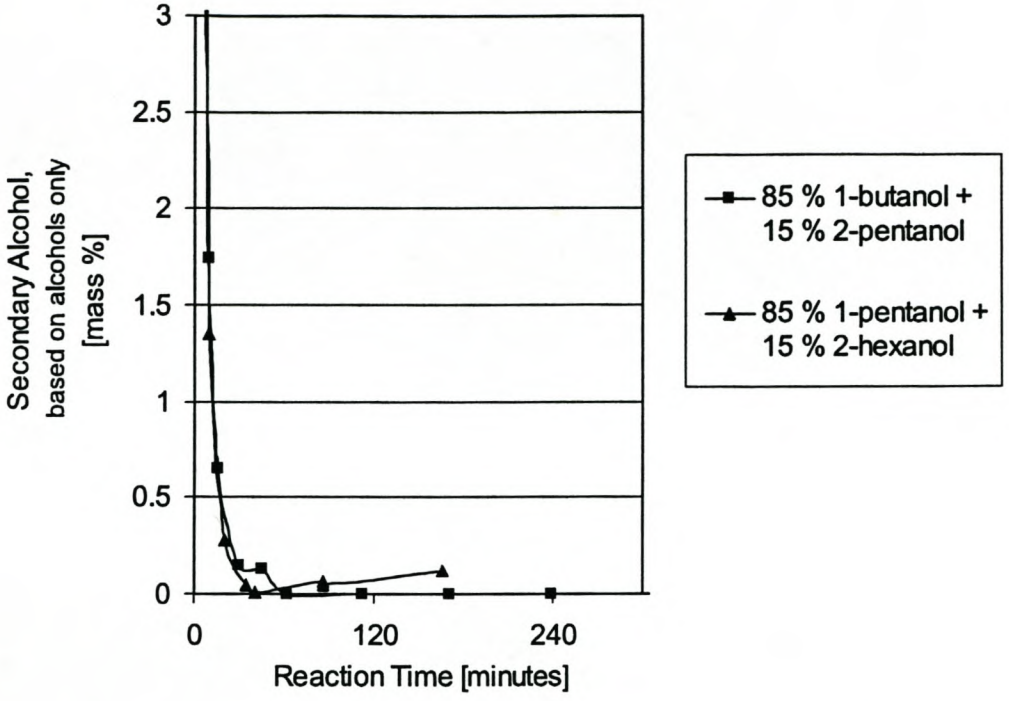


Figure 5.37: Secondary alcohol dehydration vs time for varying alcohol systems; catalyst system: 90 % H_3PO_4, acid:alcohol=3:1

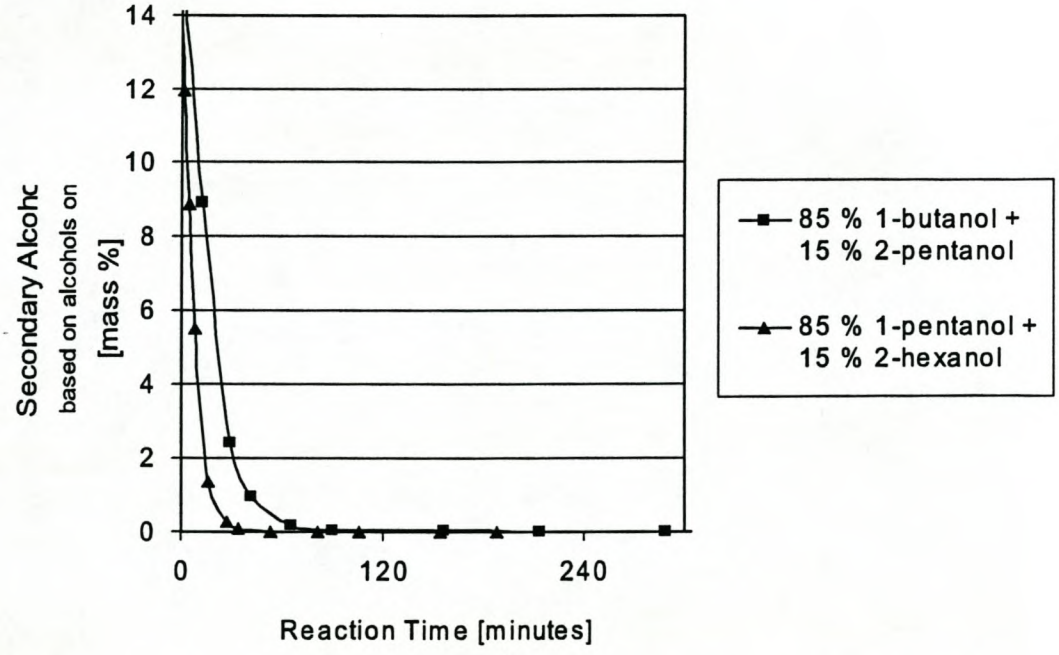


Figure 5.38: Secondary alcohol dehydration vs time for different alcohol systems; catalyst system: 90 % H_3PO_4, acid:alcohol = 1,5:1

The rate of ether formation of the different alcohol systems was also compared. It was found that the rate of ether formation increases with the molecular weight of the close boiling alcohol mixtures. The ether formation for the various alcohol mixtures at specific H_3PO_4 concentrations and acid:alcohol ratio's are graphically presented in Figure 5.39, Figure 5.40, Figure 5.41 and Figure 5.42. The higher molecular weight close-boiling alcohol mixtures are more easily dehydrated, however more care must be taken not to produce large quantities of ethers. The higher dehydration rate, thus higher presence of olefines in the reaction mixture can attribute to the higher ether formation of the higher molecular weight alcohol mixtures.

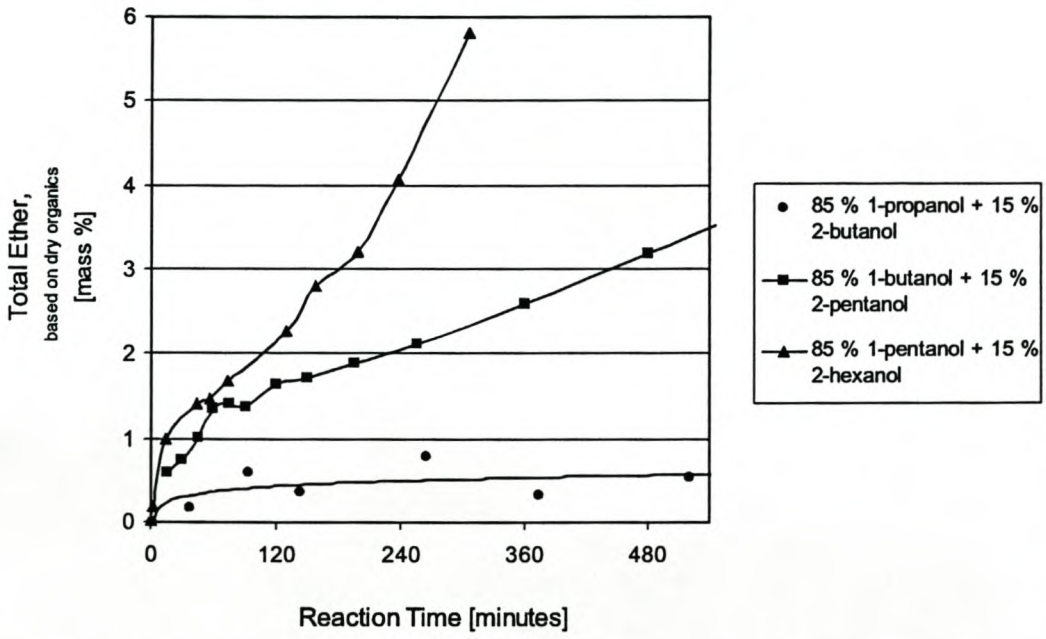


Figure 5.39: Total ether formation vs time for various alcohol systems; catalyst system: 85 % H_3PO_4 and acid:alcohol = 2,2:1

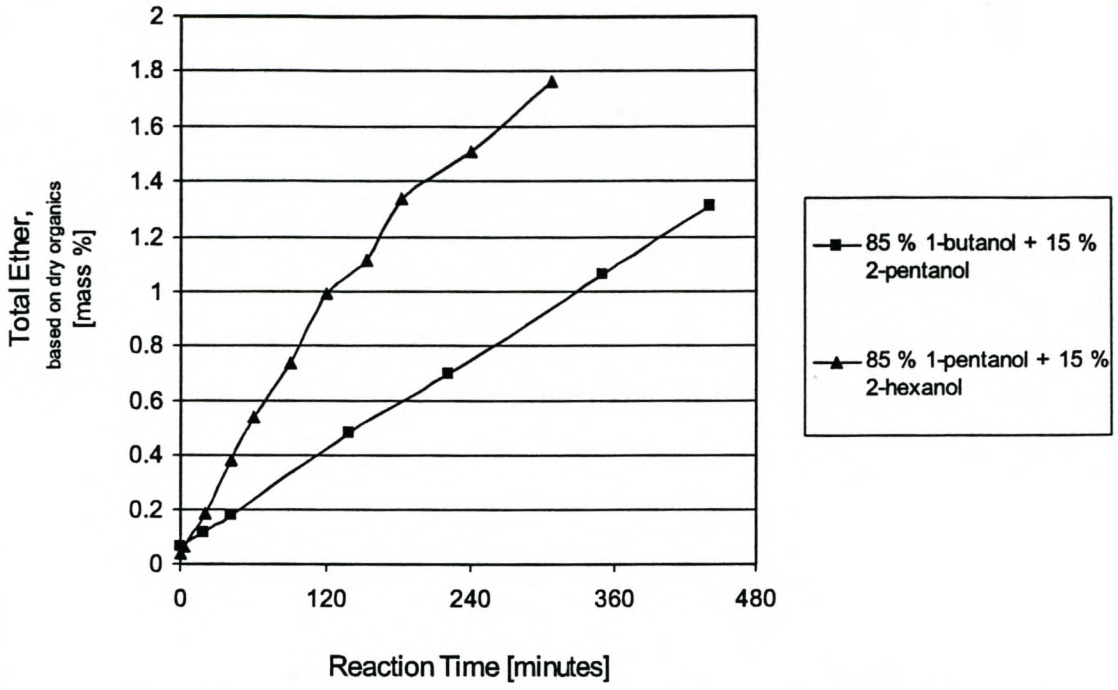


Figure 5.40: Ether formation for varying alcohol systems; catalyst system: 80 % H_3PO_4, acid:alcohol = 1,5:1

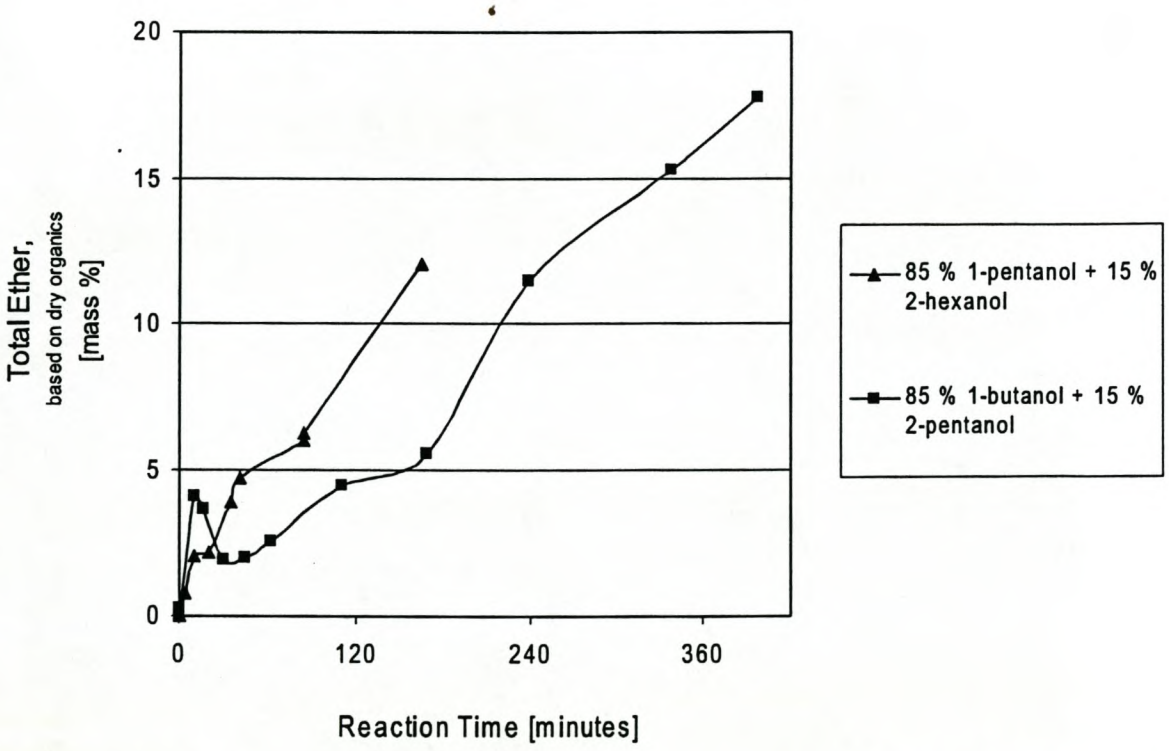


Figure 5.41: Ether formation for varying alcohol systems; catalyst system: 90 % H_3PO_4 and acid:alcohol = 3:1

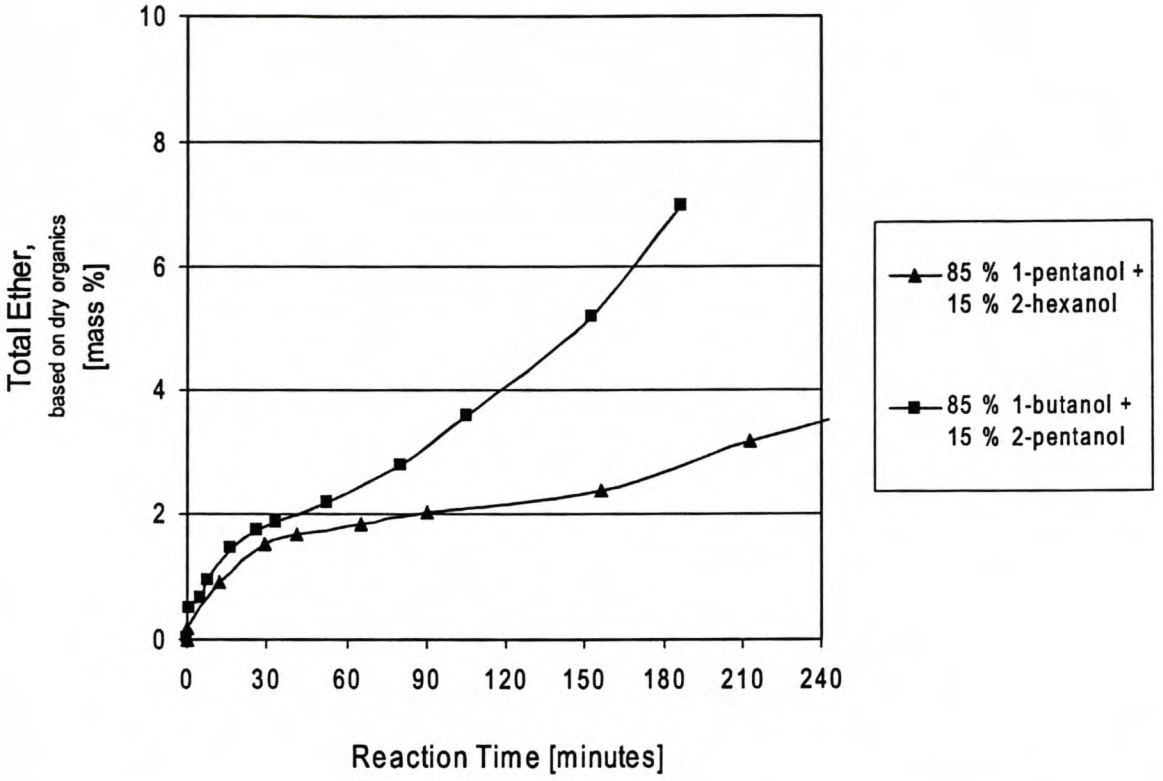


Figure 5.42: Total ethers vs time for varying alcohol systems; catalyst system: 90 % H_3PO_4, acid:alcohol = 1,5:1

It should be investigated whether a 1-butanol+2-pentanol+1-pentanol+2-hexanol alcohol mixture if subjected together to acid catalysed reaction conditions would give sufficient dehydration of the secondary alcohols and produce an acceptable level of ethers. If this can be achieved, the initial alcohol mixture will not have to be fractionated into close-boiling cuts before subjected to dehydration conditions. The dehydration reaction would be performed on the entire range of alcohols. Thereafter the primary alcohols would be separated in the downstream fractionation units. The nature of the ethers will also influence the downstream purification of the primary alcohols. It could be that if all the ethers are present in the same dehydrated alcohol feed stream, that downstream purification of the alcohols will not be achieved.

5.4.9 The influence of nitrogen stripping on the secondary alcohol dehydration rate and the rate of ether formation

In the atmospheric continuous sampling experiments a small constant nitrogen flow was always maintained through the sample point. This nitrogen flow had to pass further through the reaction system. During sampling the flow was stopped. The duration of sampling was less than 20 seconds. The nitrogen flow could not be controlled precisely but was maintained at a low flowrate. However in the following set of experiments the flow was varied between low, normal and high to determine the effect of nitrogen stripping.

It is anticipated that if the nitrogen flow is increased, the alkenes that are formed will be stripped out of the reaction system and this will reduce the mixed ether formation. Part of the light boiling azeotropes between the water/alcohols/ethers could also be stripped out of the system.

The effects of nitrogen flow on the dehydration rate and ether formation are illustrated in Figure 5.43, Figure 5.44 and Figure 5.45.

The 1-butanol+2-pentanol alcohol system, using 90 % H_3PO_4 at an acid:alcohol ratio of 2,2:1 was subjected to varying nitrogen flows (see Appendix D&E: Experiment 93-Low Nitrogen Flow, Experiment 89-Normal Nitrogen Flow, Experiment 94-High Nitrogen Flow). Approximate nitrogen flowrates are given in Table 5.6.

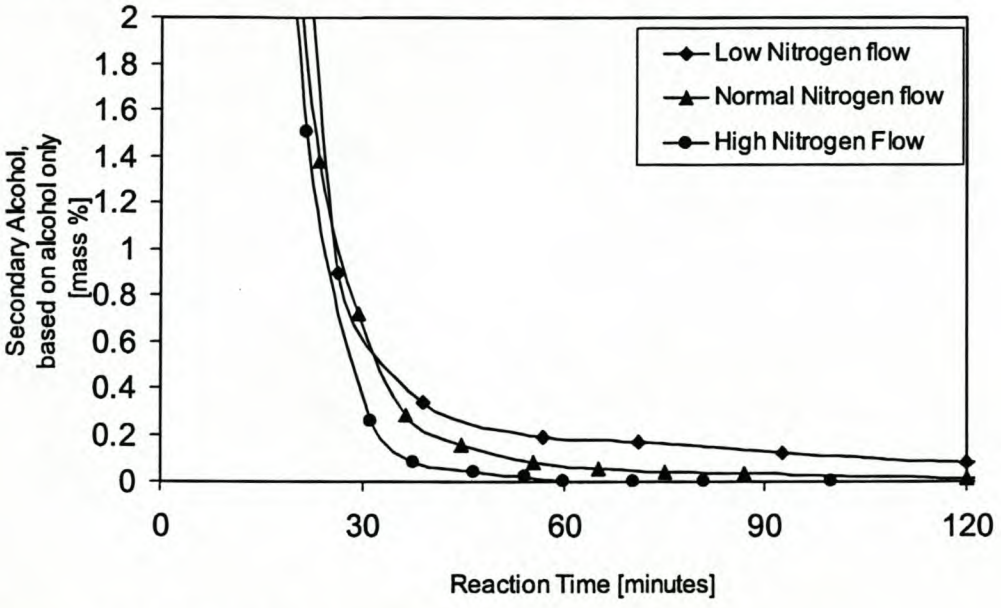


Figure 5.43: Effect of nitrogen purge on dehydration rate

According to Figure 5.43 the initial dehydration rate of the secondary alcohol did not vary substantially between the three systems (Low, Normal and High Nitrogen flow). However, after 30 minutes a clear trend can be seen. The system subjected to the lowest nitrogen purge had the lowest reduction rate in secondary alcohol.

The times for dehydration of the secondary alcohols to < 0,1 mass % based on alcohol only are given in Table 5.6. The amount of ethers formed after dehydration of the secondary alcohol are also given in Table 5.6.

Table 5.6: Reaction time required for dehydration

Nitrogen Setting	Nitrogen Flow [ml/s.mg reaction mixture]	Time [minutes]	n-butylether [mass %]	Mixed Ether 2 [mass %]	Total Ether [mass %]
Low	0.1	105	2.61	0.46	3.07
Normal	0.8	55	0.85	0.85	1.70
High	12	38	0.46	0.62	0.76

The formation of Mixed Ether 2 was slightly lower at high Nitrogen flows, see Figure 5.45. In paragraph 5.5 the formation of Mixed Ether 2 is explained. It is assumed that Mixed Ether 2 is formed by a combination of 1-butanol with 2-pentene. With nitrogen stripping, the removal of the 2-pentene out of the alcohol mixture will be improved and thus less mixed ether 2 will be formed.

The amount of n-butylether was drastically less in the system with high nitrogen flow. The total ether was also less. Maintaining a nitrogen purge through the reaction system would thus reduce the amount of byproducts formed, and it reduces the reaction time required for adequate dehydration of the secondary alcohol.

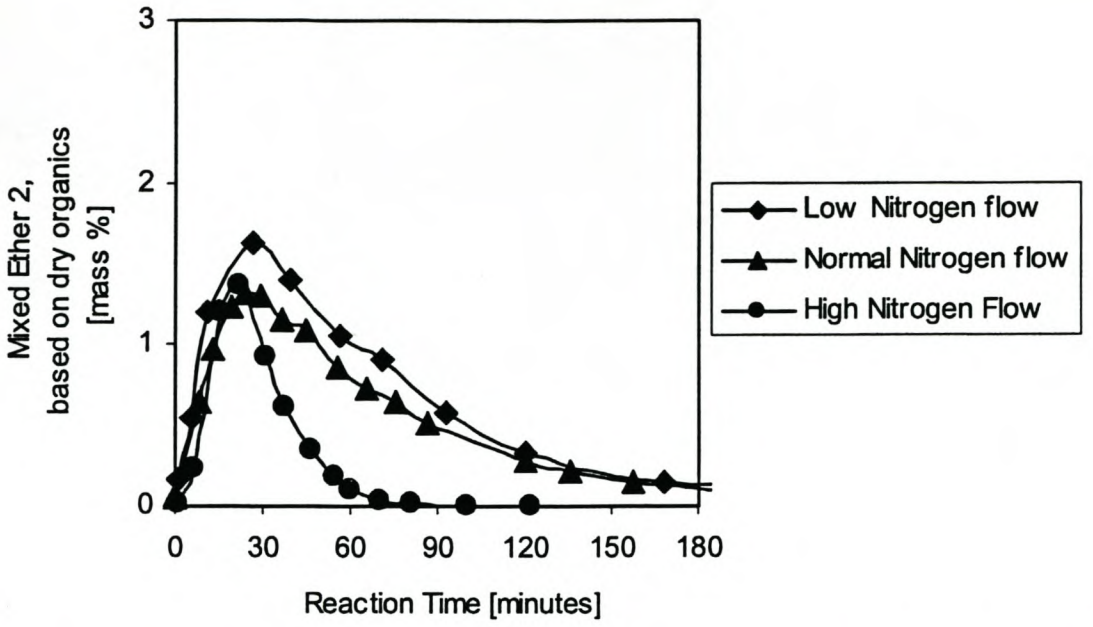


Figure 5.44: Mixed Ether 2 vs time for varying Nitrogen flows; reaction system: 1-butanol+2-pentanol, 90 % H_3PO_4, acid:alcohol ratio = 2,2:1

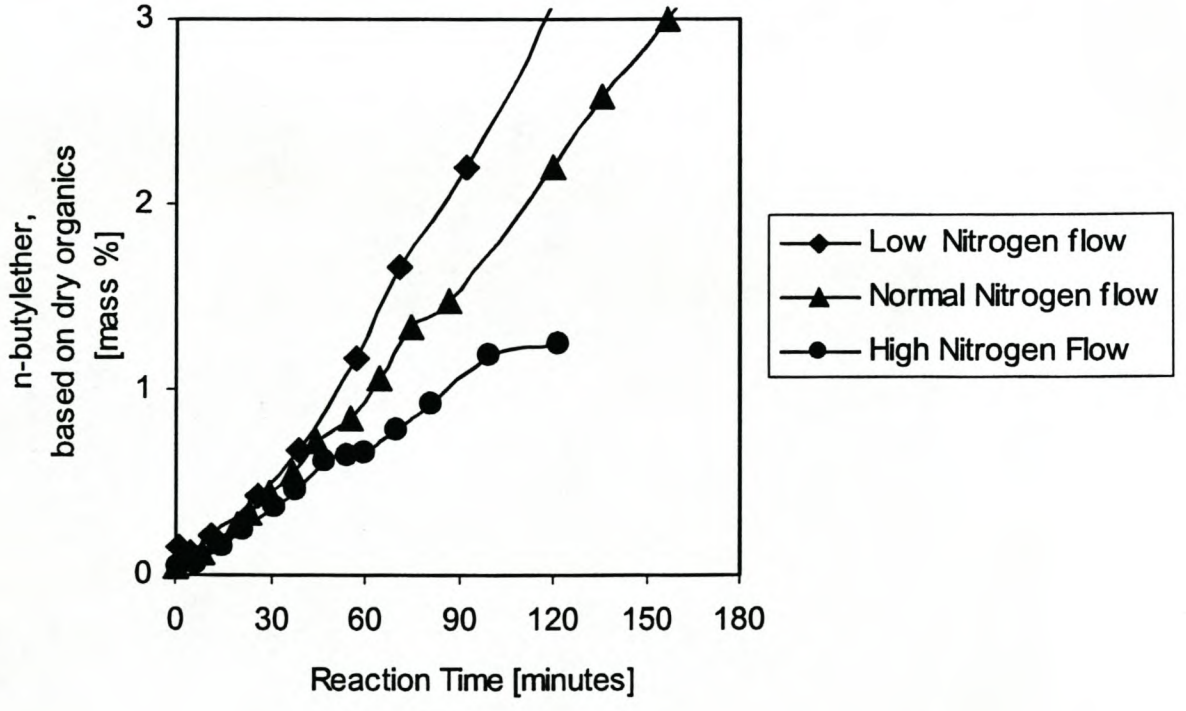


Figure 5.45: n-Butylether vs time for varying Nitrogen flows; reaction system: 1-butanol+2-pentanol, 90 % H_3PO_4, acid:alcohol ratio = 2,2:1

5.4.10 Effect of reaction pressure and temperature

With reduction in reaction pressure, the reaction system temperature would also be decreased. According to the theory (see par. 5.3) lower temperatures could lead to higher symmetrical ether formation.

In Figure 5.46 the effect of pressure on the dehydration rate of the secondary alcohol is illustrated. The alcohol system 85 % 1-butanol and 15 % 2-pentanol was subjected to dehydration under vacuum with the following catalyst system: 90 % H_3PO_4 at an acid alcohol ratio of 2,2:1. The results of the reaction performed under vacuum are compared to the results of a reaction performed under atmospheric pressure (Appendix D: Experiments 99 & 89 and Appendix E: Experiments 99 & 89).

For the vacuum system the pressure varied between 540 and 660 mbar (abs.). During sampling the vacuum had to be interrupted. After 15 minutes reaction time, the nitrogen purge was closed. With the purge stream open, it was too difficult to maintain the vacuum pressure. The sampling point was clear of any reaction liquid during the reaction. The condenser temperature was maintained at 41 °C. The boiling point of 2-pentene (cis) at 0,5 bar (abs) is 18 °C. At atmospheric pressure the boiling points of the 2-pentene stereoisomers vary between 36 and 37 °C (the condenser temperature was maintained at 50 °C during atmospheric reactions). The removal of the alkenes should thus have been efficient in the vacuum system.

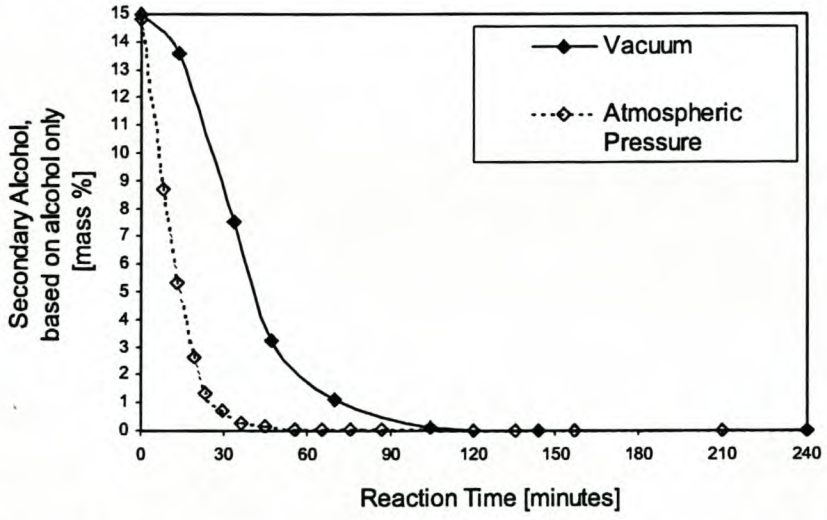


Figure 5.46: Effect of pressure on dehydration of secondary alcohols; reaction system: 1-butanol+2-pentanol, 90 % H_3PO_4, acid:alcohol=2,2:1.

The rate of dehydration of the secondary alcohol decreased substantially with a decrease in pressure. To obtain dehydration of the secondary alcohol to < 0,1 mass %, based on alcohol only, a reaction time of at least 105 minutes is needed if a system pressure of about 500 mbar(abs.) is maintained. The required reaction time is substantially higher than the time required if the system is operated at atmospheric pressure, which is 55 minutes.

The vapour space temperature of the reaction mixture, which was kept under vacuum, varied between 118 and 126 °C (reaction time < 140 minutes). The vapour space temperature of the reaction which was operated under atmospheric presssure was about 132 °C after 60 minutes.

The lower reaction temperature during vacuum operation could explain the lower rate of dehydration of the alcohol.

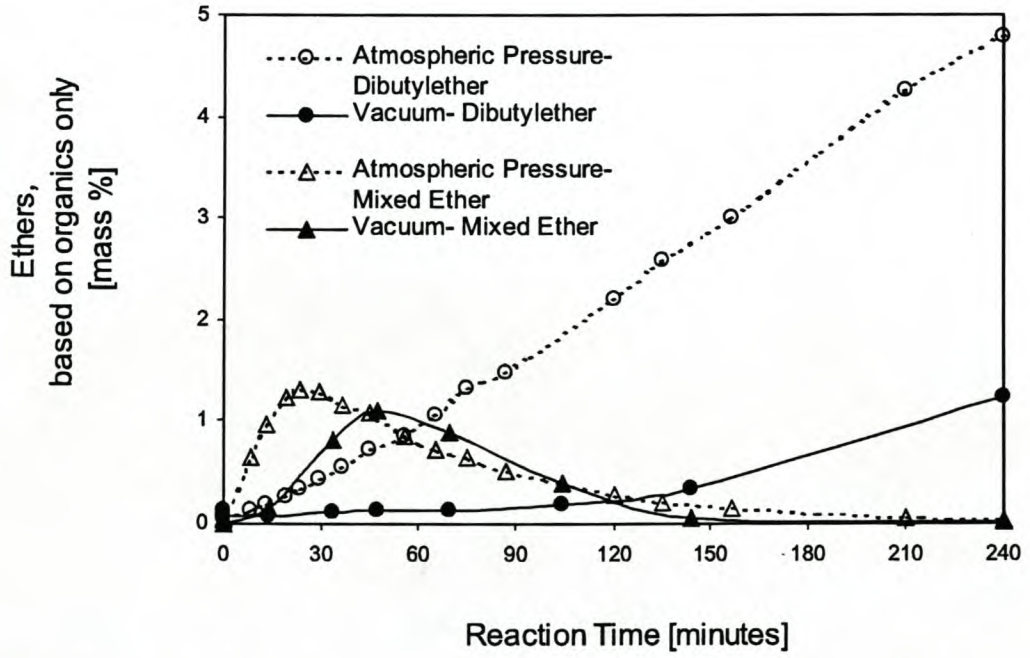


Figure 5.47: Effect of reaction pressure on ether formation; reaction system: 1-butanol+2-pentanol, 90 % H_3PO_4, acid:alcohol = 2,2:1

The effect of pressure on ether formation is illustrated in Figure 5.47. A surprising result for the system 1-butanol+2-pentanol was that the reduction in operating pressure also decreased the rate of ether formation, both that of n-butylether and the mixed ether. After dehydration of the secondary alcohol content to < 0,1 mass %, based on alcohol only, far less ethers were formed in the reaction system which operated under vacuum. A summary of the amount of ethers that are formed is given in Table 5.7.

A reason why lower amounts of ether were detected was that a large % of the ethers were lost through the vent stream during the unstable operation of this run. Later in this section the analysis of the vent stream is given and discussed.

A further ether, named mixed ether 1 was also detected (not indicated on Figure 5.47 – the ether is referred to as mixed ether 1 because it elutes before mixed ethers 2 and 3 on the GC column). The amount of mixed ether 1 increased up to about 0.23 % and decreased to < 0,1 %. This ether was not detected in these amounts in the other experiments performed on the 1-butanol+2-pentanol systems.

Table 5.7: Ether formed after completion of dehydration for vacuum system; reaction system: 1-butanol+2-pentanol, 90 % H_3PO_4, acid:alcohol=2,2:1

	Reaction Time for dehydration to < 0,1 mass % sec-alcohol [minutes]	**n-butylether** [mass %]	**Total Mixed Ether** [mass %]	**Total Ether** [mass %]
Vacuum ~ 500 mbar(abs.)	105	0,2	0,40	0,60
Atmospheric Pressure	55	0,85	0,85	1,70

The system pentanol + hexanol was also subjected to dehydration under vacuum conditions. The reaction pressure was reasonably stable, it varied only between 600 and 630 mbar (abs). The condenser temperature was maintained at 61 °C. The boiling point of 2-hexene (cis) is 48 °C at 0,5 bar(abs) and about 68 °C at atmospheric pressure. Good removal of the alkene from the reaction mixture should thus have been achieved.

The rate of dehydration of the secondary alcohols under vacuum conditions was the same as during atmospheric reaction conditions. The dehydration rates are compared in Figure 5.48.

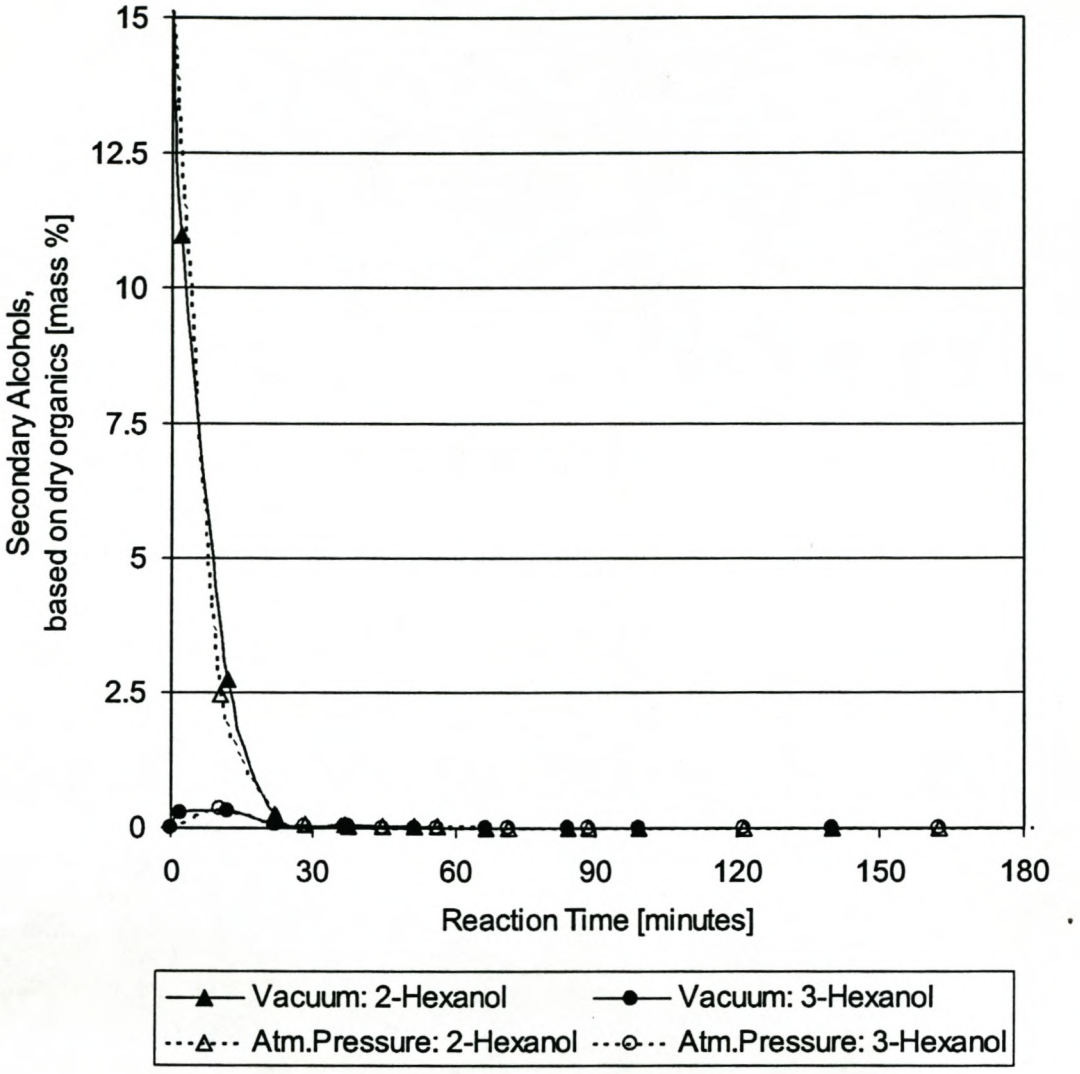


Figure 5.48: Dehydration of secondary alcohol vacuum system compared with atmospheric reaction system; reaction system: 1-pentanol+2-hexanol, 90 % H_3PO_4, acid:alcohol=2,2:1.

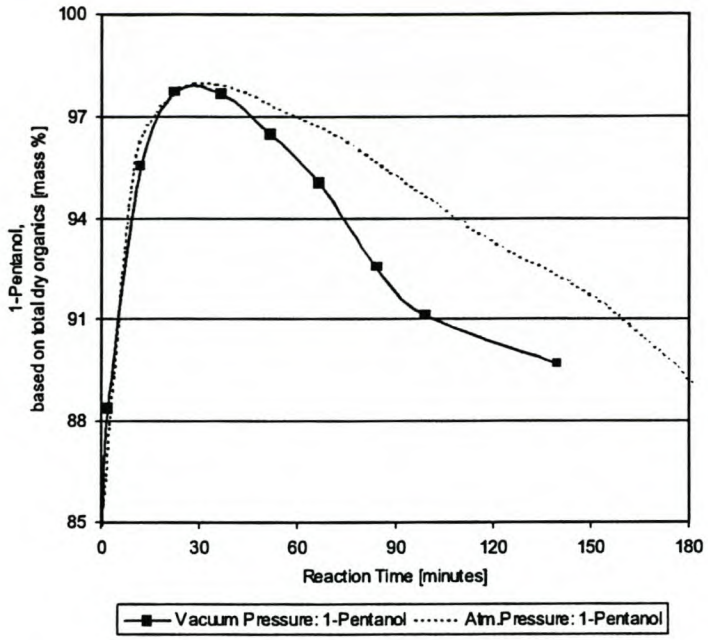


Figure 5.49: 1-Pentanol vs time for reaction under vacuum and atmospheric conditions; reaction system: 1-pentanol+2-hexanol, 90 % H_3PO_4, acid:alcohol=2,2:1.

The amount of the 1-pentanol decreased more rapidly during vacuum operation after the secondary alcohol has been removed, see Figure 5.49. This could have been due to high losses of water through the vents. The water forms an azeotrope with the ethers and alcohol. The acid concentration and the acid:alcohol ratio increased over time and this could have caused higher ether formation. The amount of Mixed Ethers 4 and 5 are given in Figure 5.51. The rates of formation of these ethers under vacuum conditions were very similar to the ether formations in experiments performed under atmospheric pressure.

Reducing the reaction pressure from atmospheric pressure to 600 mbar (abs) thus did not effect the removal of the secondary alcohol from the pentanol+2-hexanol system substantially, however, it had a substantial effect on the 1-butanol+2-pentanol system.

An interesting result was that as in the butanol+pentanol system another mixed ether was formed. This ether was named Mixed Ether 3. The n-penthylether and Mixed Ether 3 contents are given in Figure 5.50.

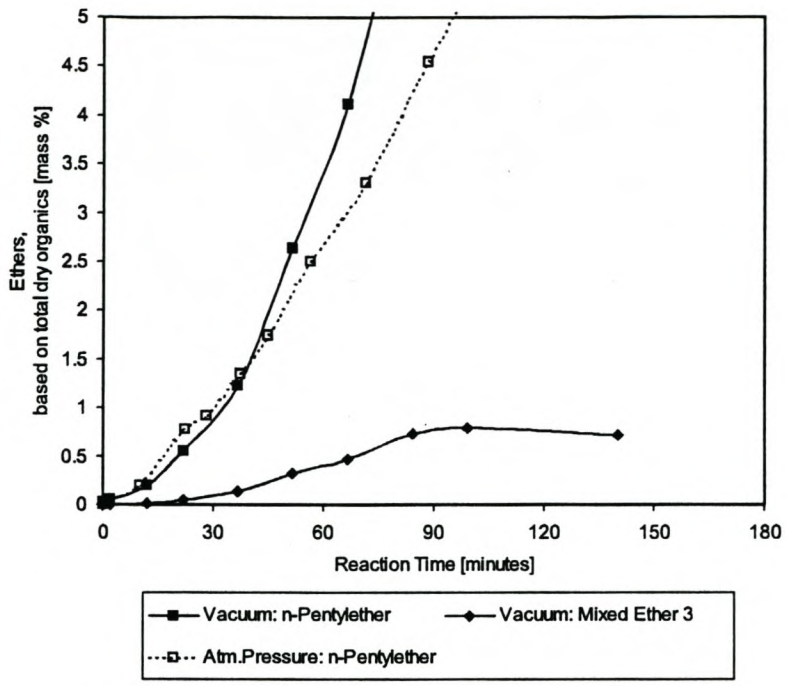


Figure 5.50: n-Pentylether and Mixed Ether 3 for reaction under vacuum and at atmospheric conditions; reaction system: 1-pentanol+2-hexanol, 90 % H_3PO_4, acid:alcohol=2,2:1.

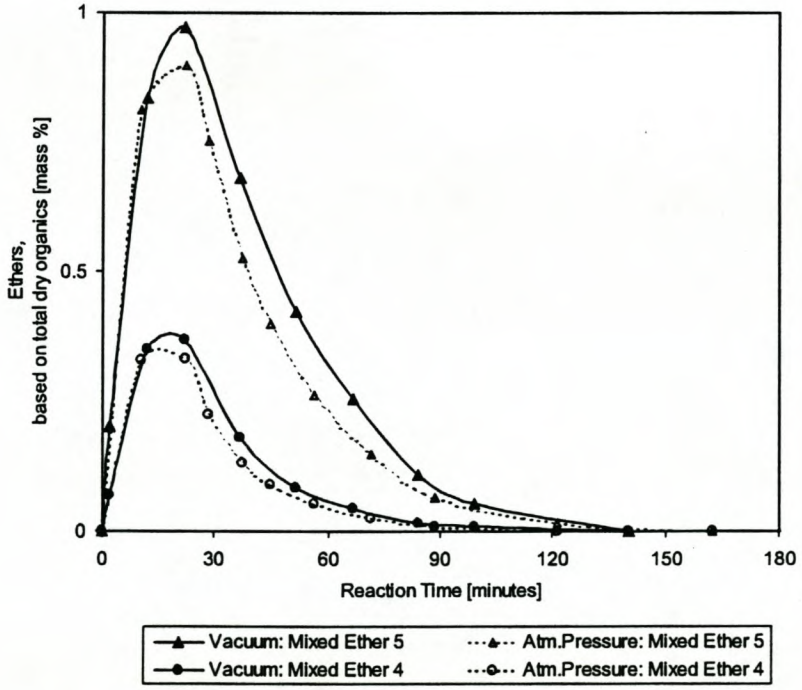


Figure 5.51: Mixed Ethers, reaction under vacuum and atmospheric conditions; reaction system: 1-pentanol+2-hexanol, 90 % H_3PO_4, acid:alcohol =2,2:1.

The vent stream was collected during the dehydration reactions under vacuum conditions for the alcohol mixtures 1-butanol+2-pentanol and 1-pentanol+2-hexanol. The following catalyst system was used for both alcohol mixtures: 90 % H_3PO_4 with an acid:alcohol ratio of 2,2:1, (Appendix D: Experiments 99 and 100). In both systems the vents formed two phases, an organic and a water phase. Some components were lost to atmosphere through the vents. The vents were collected at about 20 °C. However, in both runs secondary alcohol was present in the vents. This means that losses of the organics to atmosphere from the reaction mixture from the start of the reaction must have occurred. The analyses of the vents are given in Table 5.8. Especially in the 1-butanol+2-pentanol systems there were losses - 28 grams of vents have been collected. This represented 15 % of the total organics and water in the feed. Large amounts of the ethers were thus lost through the vents and were not present in the reaction mixture. This could be the reason why it seems that a reduction in pressure, reduced the ether formation as illustrated in Figure 5.47. The 1-butanol+2-pentanol reaction proceeded for 4 hours, thus a high amount of total ethers was formed. The 1-pentanol+2-hexanol system was only allowed to react for 140 minutes. During the start-up of the 1-butanol+2-pentanol experiment under vacuum, the nitrogen purge was open and this must have contributed to the losses. The nitrogen purge was closed after 15 minutes. During the reaction of the 1-pentanol+2-hexanol system the nitrogen purge was kept close.

Table 5.8: Composition of organic phase of vent streams of reactions performed under vacuum

Alcohol feed mixture	**1-butanol+ 2-pentanol**	**Alcohol feed mixture**	**1-pentanol + 2-hexanol**
Catalyst System	90 % H_3PO_4 acid:alcohol = 2,2:1	Catalyst System	90 % H_3PO_4 acid:alcohol = 2,2:1
Reaction Time [minutes]	240	Reaction Time [minutes]	140
Component	[mass %]	Component	[mass %]
1-butanol	92,7	1-pentanol	99.895
3-pentanol	0,1	3-hexanol	0.002
2-pentanol	1,3	2-hexanol	0.032
Mixed Ether 1	0,0	Mixed Ether 3	0.007
n-butylether	2,9	n-pentylether	0.056
Mixed Ether 2	2,9	Mixed Ether 4	0.003
		Mixed Ether 5	0.006
		Mixed Ether 6	Not detected

At this stage no definite conclusions can be drawn on the effect of pressure on the dehydration reactions. However, there are indications that reduced pressures could reduce the rate of dehydration of the secondary alcohol. Although the run with 1-butanol+2-pentanol was unstable and there were considerable losses of the organic mixture, the ratio between the 1-butanol:2-pentanol could not have been influenced by these losses. They would be lost in the same ratio as they are present in the reaction mixture. However, the acid:alcohol ratio could have increased. This would have increased the rate of dehydration. This, however, was not the case. The rate of dehydration was reduced considerably.

There is also no clarity on the effect of a reduction in pressure on the ether formation. However, due to the lower temperature of the reaction mixture it is expected that the amount of ethers should increase. This was not found for the 1-butanol+2-pentanol system as explained above. However, an increase in ether formation was observed for the 1-pentanol+2-hexanol system, which was a more stable run.

5.4.11 Optimum reaction conditions if H_3PO_4 is used as catalyst for the liquid phase dehydration of the secondary alcohol under atmospheric pressure.

To keep capital costs, running costs and losses of primary alcohol as low as possible, the criteria as set out in Table 5.9 have to be met.

Table 5.9: Criteria for optimum reaction conditions

Factors to minimize	Reason
Water in reaction mixture	To ease downstream purification and to minimise capital costs therof
Ether production	To ease downstream purification and to minimise capital costs thereof; to maximise primary alcohol recoveries
Reaction time	To minimise capital costs

From Figure 5.52 the conclusion can be made that the following systems could be used for the 85 % 1-butanol and 15 % 2-pentanol system:

90 % H_3PO_4 at an acid:alcohol ratio of 1,5:1 to 2,2:1

When these catalyst systems are used, the increase in n-butylether, after removal of the secondary alcohol, varies between 12 and 21 g/kg of reaction mixture. The disadvantage of using the 90 % H_3PO_4 is that after completion of the reaction, the reaction mixture will have to be quenched immediately to avoid an unnecessary increase in n-butylether. The quantity of Mixed Ether 2 reduces as the reaction proceeds. However, n-butylether is formed continuously. The rate of n-butyl ether formation is compared in Table 5.10.

The acid:alcohol ratio of 1,5:1 has the advantage that the amount of water in the reaction system is 15 % lower and the rate of n-butylether formation is 40 % lower than for the 2,2:1 system. The system 90 % H_3PO_4, acid:alcohol = 1,5:1 will be used as a design basis for the separation of 85% 1-butanol+ 15 % 2-pentanol (See chapter 7).

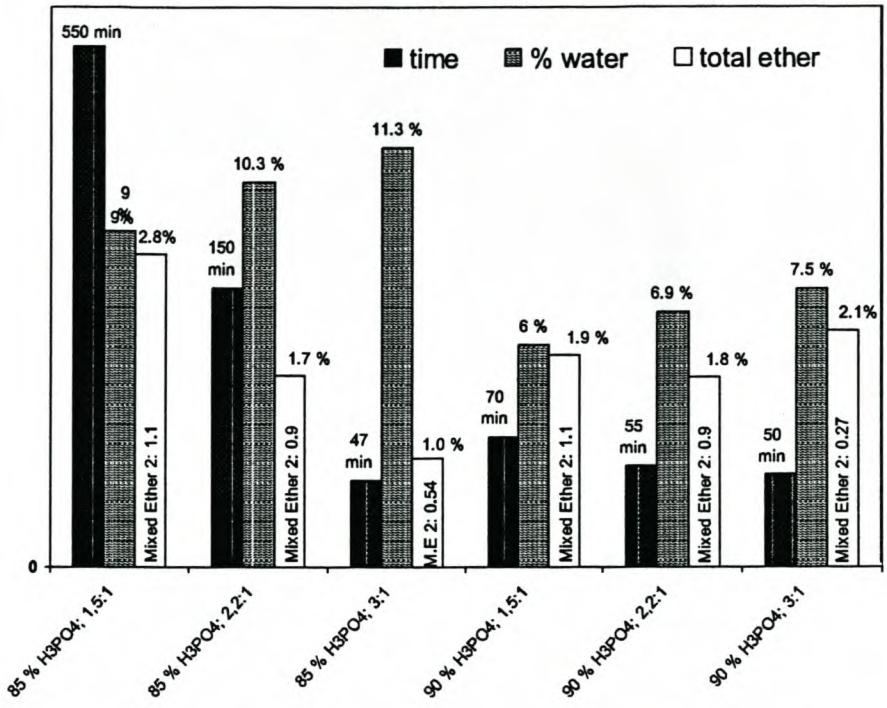


Figure 5.52: Comparison of H_3PO_4 as catalyst for the alcohol mixture 85 % 1-butanol and 15 % 2-pentanol; catalyst system: H_3PO_4 at varying concentrations and varying acid:alcohol ratio's.

Table 5.10: Comparison of reaction systems for the separation of 1-butanol+2-pentanol (see Appendix E: Experiments 73, 89, 95)

	85 % 1-butanol+ 15% 2-pentanol 90 % H_3PO_4	
Acid:Alcohol	1,5:1	2,2:1
Reaction Time required for dehydration of the secondary alcohol to <0,1 mass % (based on alcohols only)	70	55
Water in feed system [mass %]	6	6,9
Total Ethers	1,9	1,8
Rate of n-butylether formation	0,012 g /g organics.minute	0,021 g /g organics.minute

If it is difficult to remove the mixed ether 2 from the reaction mixture, the dehydration could be allowed to continue until all the mixed ether 2 has dehydrated. In this case n-butylether would be the only contaminant in the primary alcohol product after the water and acid have been removed. From Figure 5.52 it can be seen that the ethers were mostly present in a 50:50 ratio after sufficient dehydration of the 2-pentanol. However, using 90 % H_3PO_4 at an acid:alcohol ratio of 3:1 produced an organic product in which the mixed ether 2 represented < 15 % of the ethers. If only the reaction time is increased, an organic product may be produced that contains only n-butylether as organic byproduct. This design basis was used for the first conceptual process design in chapter 7.

Similar results for the optimum reaction conditions were obtained for the 1-pentanol+2-hexanol system.

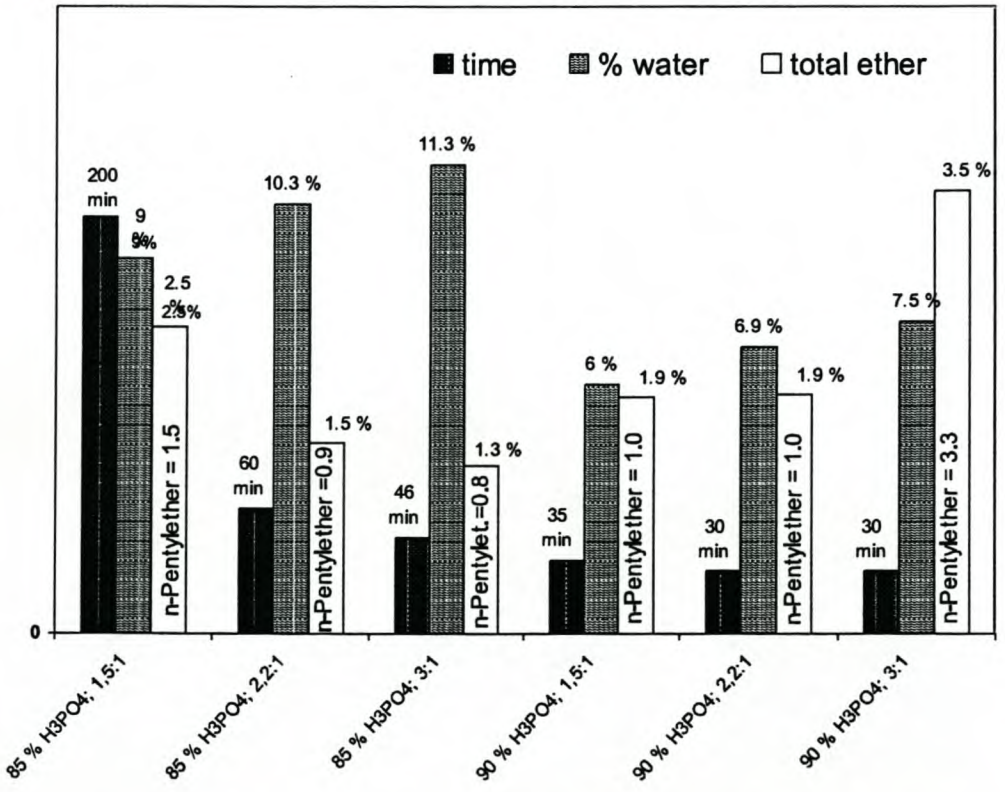


Figure 5.53: Comparison of H_3PO_4 as catalyst for the alcohol mixture 85 % 1-pentanol and 15 % 2-hexanol; catalyst system: H_3PO_4 at varying concentrations and varying acid:alcohol ratio's.

From Figure 5.53 the conclusion can be made that the following systems are the most suitable to use for the dehydration of the secondary alcohol for the 85 % 1-pentanol and 15 % 2-hexanol system:

90 % H_3PO_4 at an acid:alcohol ratio of 1,5:1 or 2,2:1

The two reaction systems are compared in Table 5.11. The acid:alcohol ratio of 1,5:1 has the advantage that the amount of water in the reaction system is 15 % lower and the rate of n-pentylether formation is about 50 % lower than for the 2,2:1 system. The required reaction time is only increased from 30 to 35 minutes (Appendix E: Experiments 83 and 86). The system 90 % H_3PO_4, acid:alcohol = 1,5:1 will also be used as design basis for a conceptual design process to separate the mixture 85% 1-pentanol + 15 % 2-hexanol.

Table 5.11: Comparison of reaction systems for the separation of 1-pentanol+2-hexanol

	85 % 1-pentanol+ 15% 2-hexanol 90 % H_3PO_4	
Acid:Alcohol	1,5:1	2,2:1
Reaction Time, required for dehydration of the secondary alcohol to <0,1 mass % (based on alcohols only)	35	30
Water in feed system [mass %]	6	6,9
Total Ethers	1,89	1,92
Rate of n-pentylether formation	0,028 g /g organics.minute	0,057 g /g organics.minute

If the mixed ethers prove to be a problem in the purification of the primary alcohol product, the reaction time could be increased up to the point when all the mixed ethers have dehydrated. In this case high amounts of n-pentylether, but only n-pentylether would be present as organic byproduct in the primary alcohol product. High acid concentrations and high acid:alcohol ratio's would be required. This can also be seen from Figure 5.53.

For the system 85 % 1-propanol+ 15 % 2-butanol only one run using continuous sampling of the reaction mixture and one run where the reaction was followed by short path distillation (discussed in chapter 6) was done. The following proved to be conditions that would achieve dehydration of the secondary alcohol to < 0,1 mass %:

88 % H_3PO_4 & 120 minutes & acid:alcohol = 2,2:1
In total less than 2,7 % ethers were formed.

The system 1-propanol + 2-butanol was not investigated further, because it is known to the writer that SASOL has developed and successfully applies an extractive distillation process for the separation of 2-butanol from 1-propanol.

5.5 Which ethers were formed ?

Analytical grade symmetrical ethers were bought and used as internal standards in Gas Chromatographic analysis. These ethers were n-propylether, n-butylether and n-pentylether. These ethers were also identified with Mass Spectrometry (MS) Analysis. However, not one of the unsymmetrical ethers could be purchased. Only some of the unsymmetrical ethers could be identified with an MS Analysis.

Firstly the byproducts of the 1-propanol+2-butanol alcohol systems were determined. 1-Propanol+2-Butanol runs, using H_3PO_4 or H_2SO_4 as catalysts, were used for the ether identification (for original data and GC results, see Appendix E – Experiments 12D and 14's). MS analyses were performed on some of the distillates. It was found that for the system 1-propanol + 2-butanol, three ethers were formed irrespective of whether H_3PO_4 or H_2SO_4 was used as catalyst. These ethers were:

- 1-(1-methylethoxy)-propane
- n-propylether
- 2-butyl-propyl-ether

From the structure of the ethers it is clear which alcohols combined to form them. However, to confirm that the MS ether identification is correct, the pure alcohols were heated separately with the catalyst (Appendix E5– Experiments 19). 100 % 1-Propanol was heated with 88 % H_3PO_4. It was found that both 1-(1-methylethoxy)-propane and n-propylether were formed. Small amounts of 2-propanol were also present in the distillate. The 2-propanol probably formed propene and the propene was hydrolised to 2-propanol, as described in paragraph 5.2.

100 % 2-Butanol was heated with 88 % H_3PO_4. It was found that no ether byproducts were present in the distillate.

The compound 2-butyl-propyl ether thus has to be a combination of a 1-propanol molecule and a 2-butanol molecule. This ether is probably formed by the reaction of 1-propanol with butene, the reaction is described in paragraph 5.2. A second possiblity is that 1-propanol and 2-butanol combined according to the alkylsuphate formation as described in paragraph 5.2.

n-Propylether (=1,1'-Oxybis-propane) is formed according to the alkylsulphate formation as described in paragraph 5.2. To form 1-(1-methylethoxy)-propane, some of the 1-propanol must have been dehydrated to propene. The propene then combined with 1-propanol to form 1-(1-methylethoxy)-propane.

For analytical purposes an attempt was made to produce large amounts of ethers and to isolate these ethers from each other. This, however, was not successful (Appendix D – Experiment 16). This should have been expected, because of the azeotropic nature of an alcohol+ether+water mixture.

Only n-propylether and 2-butyl propyl ether were detected in the continuous sampling reactions (see Appendix D&E: Experiment 76). The ether 1-(1-methylethoxy)-propane probably formed during the batch distillation process.

The combination of the alkenes with the alcohols in the 1-propanol+2-butanol system will be used to attempt to understand the structure of the mixed ethers that were formed in the 1-butanol+2-pentanol and 1-pentanol+2-hexanol system.

For the alcohol systems 1-butanol+2-pentanol and 1-pentanol+2-hexanol further alcohols - other than present in the feed system - were formed during the dehydration experiments. The secondary alcohols dehydrated to form secondary alcohols with a different structure. 2-Pentanol formed 3-pentanol. When using the non-polar capillary column for GC analysis, the 3-pentanol could not be separated from the 1-butanol or 2-pentanol. The amount of 2-pentanol was reported as total secondary alcohols. In the 1-pentanol+2-hexanol system, the 2-hexanol was converted to 3-hexanol. Both 3-pentanol and 3-hexanol were identified by MS Analyses.

For the system 1-butanol+2-pentanol the symmetrical ether n-butylether and two unsymmetrical ethers were formed. They were named Mixed Ether 1 and Mixed Ether 2. Mixed Ether 2 was formed in every dehydration experiment. The amount thereof increased until the 2-pentanol was reduced to a small amount, thereafter the amount of Mixed Ether 2 also decreased. The same trend was observed in all the dehydration experiments. Mixed Ether 1 was only present in small amounts in the reaction mixture that was subjected to vacuum (see Appendix D&E: Experiment 99). The definite structure of both Mixed Ether 1 and Mixed Ether 2 could not be determined analytically. Several MS Apparatuses have been used (Department of Chemical Engineering, US; Department of Organic Chemistry US; Sastech).

Experiments were performed to attempt to clarify the structure of the mixed ethers.

100 % 1-Butanol was reacted with 90 % H_3PO_4 at an acid:alcohol ratio of 2,2:1 (Appendix E- Table E7: Experiment 55). It was found that only n-butylether was produced as byproduct. Even after allowing the reaction to proceed for more than 1200 minutes, no other ethers were formed. The formation of the n-butylether is presented in Figure 5.54. Mixed Ether 2 could thus not be a combination of two butanol molecules.

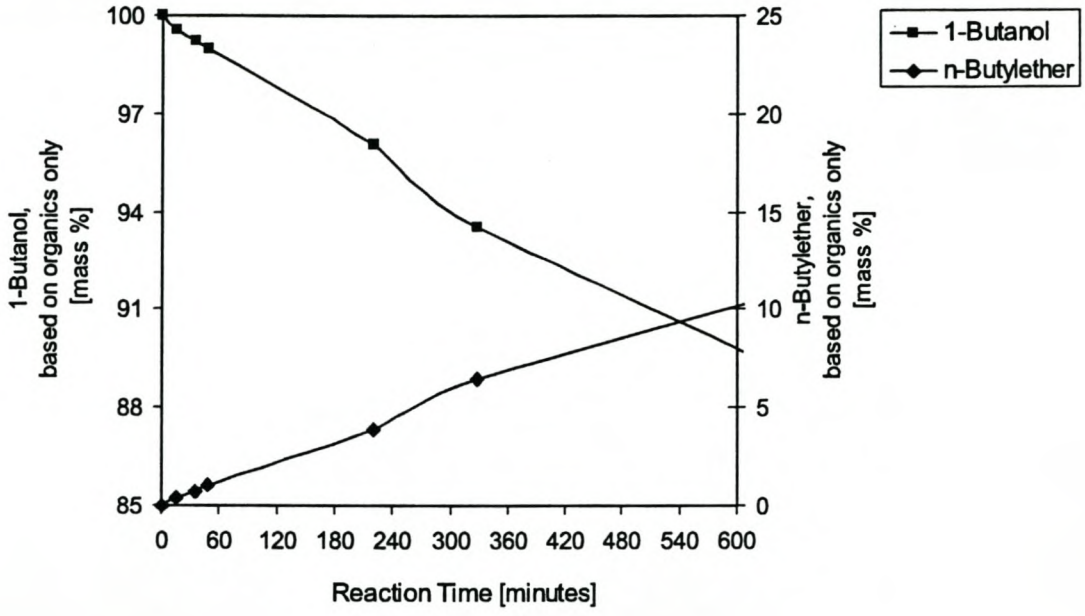


Figure 5.54: Formation of n-butylether in the reaction of pure 1-butanol

100 % 2-Pentanol was reacted with 90 % H_3PO_4 at an acid:alcohol ratio of 2,2:1 (Appendix D – Table D7:Experiment 53 and Appendix E-Table E7:Experiment 53). A summary of the results are given in Table 5.12.

Table 5.12: 100% 2-Pentanol reacted with 90 % H_3PO_4 at an acid:alcohol ratio of 2,2:1

Reaction Time (minutes)	0	2	7.3	15.5	20.5	1200 *
Component	Mass %, dry basis					
3-Pentanol	0.0	0.0	0.000	6.3	10.1	0.0
2-Pentanol	100.0	99.6	98.6	89.9	85.4	0.0
Byproduct A	0.0	0.3	1.1	2.8	3.3	70.0
Byproduct B	0.0	0.1	0.4	1.0	1.2	30.0
Alcohols Only						
3-Pentanol	0.0	0.0	0.0	6.5	10.5	0.0
2-Pentanol	100.0	100.0	100.0	93.5	89.5	0.0

*Standing, not heated after 28 minutes

The reaction was extremely vigorous. After 25 minutes the reaction mixture turned to milky white. This was an indication that all the 2-pentanol and water have been removed and the H_3PO_4 started to solidify. Samples were taken at various time intervals as indicated in Table 5.12. There were no traces of n-butylether or the mixed ethers in any of the washed samples. Traces of other byproducts, named byproduct A and B were present in the organic product. Only extremely small amounts of alcohol were left to be analysed. From the GC analysis it was clear that byproducts A and B could not have been Mixed Ether 1 nor Mixed Ether 2. It is thus unlikely that Mixed Ether 1 and 2 are combinations of two pentanol groups. 3-Pentanol was also present at 15 and 20 minutes, however, the 3-pentanol dehydrated thereafter and the pentene was flashed off.

An alcohol mixture containing 50 % 1-butanol and 50 % 2-pentanol was reacted with 90 % H_3PO_4 at an acid:alcohol ratio of 2,2:1. The ether formation is graphically presented in Figure 5.55. The ether formation and the amount of secondary alcohol is compared with a 85 % 1-butanol and 15 % 2-pentanol system which was subjected to similar catalyst conditions.

The initial rate of formation of mixed ether 2 is higher in the 50/50 (=50 mass % 1-butanol + 50 mass % 2-pentanol) alcohol system than in the 85/15 (=85 mass % 1-butanol + 15 % 2-pentanol) alcohol system. The maximum amount of mixed ether was also considerably higher for the 50/50 alcohol system. This justifies the argument that Mixed Ether 2 must be a combination of 2-pentanol and 1-butanol. This ether is thus an unsymmetrical ether. The reaction probably progresses as follows: The 2-pentanol forms 2-pentene. The 2-pentene combines with 1-butanol to form 3-pentyl butyl ether as shown in the reactions below.

$$CH_3CH_2CH_2CHOHCH_3 \xrightarrow{H_3PO_4} CH_3CH_2CH{=}CHCH_3 + H_2O$$

2-Pentanol → 2-Pentene

$$CH_3CH_2CH{=}CHCH_3 + CH_3CH_2CH_2CH_2OH \xrightarrow{H_3PO_4} (CH_3CH_2)_2CHOC_4H_9$$

2-Pentene + 1-Butanol → Mixed Ether 2
3 Pentyl Butyl Ether

(5.12)

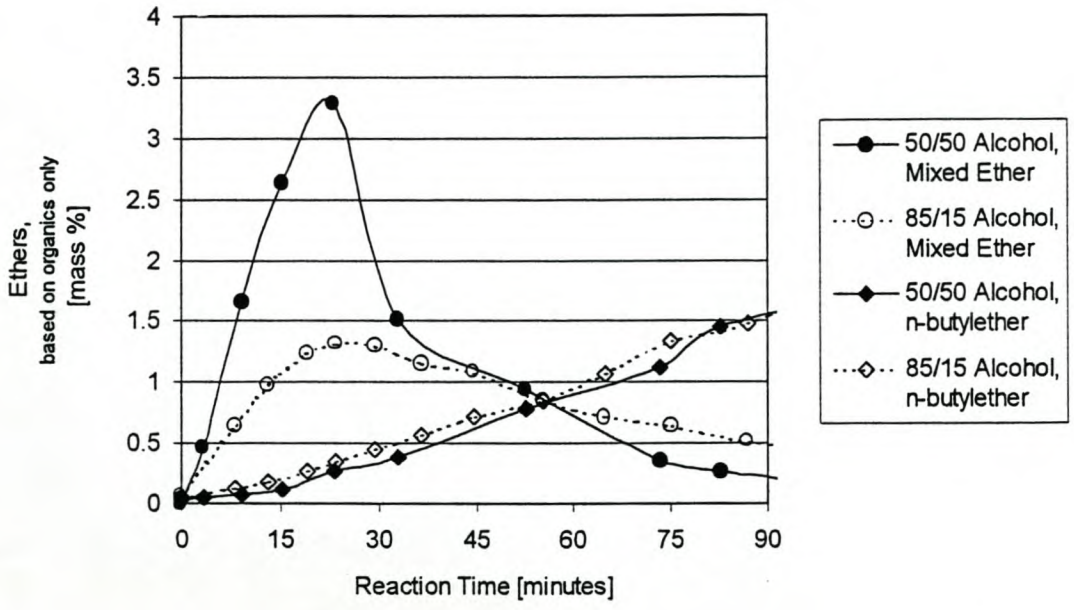


Figure 5.55: Effect of feed composition on ether formation; reaction system: 1-butanol+2-pentanol, 90 % H_3PO_4, acid:alcohol = 2,2:1

The 3-pentanol that forms is also dehydrated to form 2-pentene. The combination of the 2-pentene with 1-butanol will give the same mixed ether as described above. No further mixed ethers could thus have formed from the 3-pentanol.

In the reaction of 1-butanol and 2-pentanol under acidic catalysis, part of the gas vents were accumulated and analysed. It was found that the vents consisted mainly of 2-pentene. Small amounts of 1-pentene, 1-butene and 2-butene were also present (see Appendix F1). Of these alkenes, the majority present was 1-pentene.

Some of the 2-pentanol thus also dehydrated to form 1-pentene, and this pentene could have formed a mixed ether by combining with 1-butanol. The small amounts of 1-butene that were formed could have combined with 1-butanol to form 2-butyl butyl ether. These ethers could only have formed in very small amounts. If present, these amounts were similar to the impurities detected in the alcohol feed stream. Trends of increase or decrease of these ethers could also not be detected.

In the reaction performed under vacuum, small amounts of Mixed Ether 1 were detected (See results given in Appendix E: Experiment 99). This ether could have formed because of the change in reaction condition during sampling. However, after the secondary alcohol was removed, Mixed Ether 1 has also been reduced to <0,01 %. Mixed ether 1 thus probably also consisted of a combination of 1-butanol and 2-pentanol.

The system 1-pentanol and 2-hexanol gave n-pentylether and Mixed Ethers 3, 4, 5 and 6 as byproducts. This system was also subjected to several experiments to determine the structure of the Mixed Ethers, as it could not be determined by an MS analysis.

Mixed Ether 4 and Mixed Ether 5 were detected in substantial quantities in all the experiments performed on the mixture 1-pentanol+2-hexanol. Mixed Ethers 4 and 5 both increased until the secondary alcohol was considerably reduced, thereafter these ethers started to decrease until they disappeared. This trend of Mixed Ethers 4 and 5 was detected clearly in all the dehydration experiments and the trend was similar to the trend of Mixed Ether 2 as detected in the 1-butanol+2-pentanol alcohol reaction system.

Mixed Ether 3 was only detected in the dehydration of the 1-pentanol+2-hexanol alcohol system which was subjected to vacuum conditions.

Only small amounts of Mixed Ether 6 were detected in some of the experiments where 1-pentanol+2-pentanol have been subjected to dehydration.

For the 1-butanol+2-pentanol system it was argued that the mixed ether that was formed and disappeared again, was a combination of the secondary alcohol and the primary alcohol. The same reasoning can be followed to state that Mixed Ether 4 and Mixed Ether 5 are combinations of 1-pentanol and 2-hexanol.

Part of the accumulated reaction vents of a 1-pentanol+2-hexanol dehydration experiment were analysed on a MS. It was found that from the hexanol mainly 1-hexene, 2-hexene and 3-hexene were formed. The distribution was about 1-hexene:2-hexene:3-hexene = 8:80:12. 2-Pentene and 1-pentene were also present in the vent stream (see Appendix F2). The amount of 2-pentene was substantially higher than that of the 1-pentene.

All of these alkenes could thus have combined with 1-pentanol to form unsymmetrical ethers. 1-Pentanol was throughout present in excess. It is anticipated that Mixed Ether 5, which was present in the largest amount (of all the mixed ethers) is formed by combination of 2-hexene or 3-hexene and 1-pentanol, to give 3-hexyl pentyl ether.

Mixed Ether 4 was present in a lesser amount than Mixed Ether 5. It is anticipated that Mixed Ether 4 is formed by the combination of 1-hexene or 2-hexene and 1-pentanol to give 2-hexyl pentyl ether.

Mixed Ether 3 was only detected in the experiment performed under vacuum. In comparison to Mixed Ethers 4 and 5, it continuously increased. It kept on increasing after all the hexanol has been removed. It is thus anticipated that Mixed Ether 3 was a combination of 1-pentene or 2-pentene and 1-pentanol.

Mixed Ether 6 which was detected in most of the atmospheric experiments, only started to appear after the content of Mixed Ether 4 and Mixed Ether 5 started to reduce. The amount of this ether increased throughout the reaction, however it increased extremely slowly. In an experiment where 85 % 1-pentanol + 15 % 2-hexanol were reacted with 85 % H_3PO_4 at an acid:alcohol ratio of 2,2:1, Mixed Ether 6 represented only < 2 % of the total ethers at the time when the secondary alcohol was reduced to < 0,1 % (based on alcohols only). The results are given in Appendix E: Experiment 88. In all the experiments the amount of Mixed Ether 6 was very small, and in some cases not even detected. In all the reactions where Mixed Ether 6 was detected, it continued to increase. It is expected that Mixed Ether 6 is a combination of 1-pentene and 1-pentanol, e.g. it could be 3-pentyl pentyl ether.

For the purpose of this study, it is not absolutely necessary to determine the exact structures of the ethers. After complete dehydration of the secondary alcohol the organic products and water will be removed from the reaction mixture. Thereafter the wet organic mixture will be subjected to fractionation to produce pure primary alcohol. For a conceptual design of the separation process the composition of the feed stream to the fractionation units has to be determined. Only the structures of those ethers present in substantial amounts after completion of the reaction have to be determined.

In the systems that are recommended as design basis, the symmetrical ethers represented > 50 % of the total ethers. The total ethers are less than 2% of the total organics in the reaction mixture. The structures of Mixed Ethers 2, 4 and 5 have been determined with reasonable confidence as 3-pentyl butyl ether, 3-hexyl pentyl ether and 2-hexyl pentyl ether, respectively. These structures will be used to obtain thermodynamic data for the conceptual designs.

A summary of the detected and reported ethers in this study is given in Table 5.13.

Table 5.13: Summary of ethers that were detected

Alcohol System	Ethers (in sequence as they occurred on GC analysis using a capillary column)	Positive identification with GC Retention Times and MS Analysis	Assumed structure
1-propanol+ 2-butanol	n-propylether	Yes	N/A
	2-butyl propyl ether	Yes	N/A
	1-(1-methylethoxy)-propane	Yes	N/A
1-butanol + 2-pentanol	Mixed Ether 1	No	No structure assumed, only present in vacuum system
	n-butylether	Yes	N/A
	Mixed Ether 2	No	3-pentyl butyl ether
1-pentanol + 2-hexanol	Mixed Ether 3	No	No structure assumed, only present in vacuum system
	n-pentyl ether	Yes	N/A
	Mixed Ether 4	No	2-hexyl pentyl ether
	Mixed Ether 5	No	3-hexyl pentyl ether
	Mixed Ether 6	No	Combination of two pentanol molecules, e.g. 2-pentyl pentyl ether

5.6 The reproducibility and reliability of the experimental results

Quantitative analyses of the organic mixtures were performed with GC analysis. Pure components, if available were used as internal standards. However, as discussed in paragraph 5.5, the mixed ethers were not available as pure components.

It was assumed that the response factors, as determined for the symmetrical ethers can be used for the Mixed Ethers of the respective alcohol systems. For the system 1-propanol+2-butanol the response factor of n-pentylether was used as response for 1-(1-methylethoxy)-propane and 2-butyl-propyl-ether.

For the system 1-butanol+2-pentanol, the response factor of n-butylether was used for Mixed Ethers 1 and 2.

For the system 1-pentanol +2-hexanol, the response factor of n-pentylether was used for Mixed Ethers 3,4,5 and 6.

Furthermore, it was assumed that the response factor of 3-pentanol is the same as that of 2-pentanol. It was also assumed that the response factor of 3-hexanol was the same as that of 2-hexanol.

In the experiments where various catalysts were evaluated, total light and heavy byproducts were reported. These were only relative indications. However, the analytical results of the alcohols, based on alcohols only, should be very reliable for all the experiments.

The analytically determined quantity of symmetrical ethers should also be very reliable, however the amounts of Mixed Ethers are only estimated quantities. The same discrepancies would have occurred in every series of analyses. The trends and the comparisons of the analytical results between the different catalyst systems should be reliable.

Experiments and analysis were repeated to determine the reproducibility and reliability of the results.

The system 85 % 1-pentanol + 15 % 2-hexanol was subjected to dehydration using 90 % H_3PO_4 at an acid:alcohol ratio of 2,2:1 (see Appendix D,E: Experiment 88). Many samples were taken at different time intervals. All the samples were neutralised immediately with sodiumbicarbonate, however, the analyses were done at different time intervals after sampling. Set 1 was analysed one day after the experiment was performed and set 2 was analysed 2 days after the experiment was completed. From Figure 5.56, Figure 5.57, and Figure 5.58 it can be seen that the time delay in analysis of the samples had no effect on the analysis of neither the alcohol nor the ether content.

In some of the other experiments several days could have passed before the GC analysis of the diluted alcohol mixture was done.

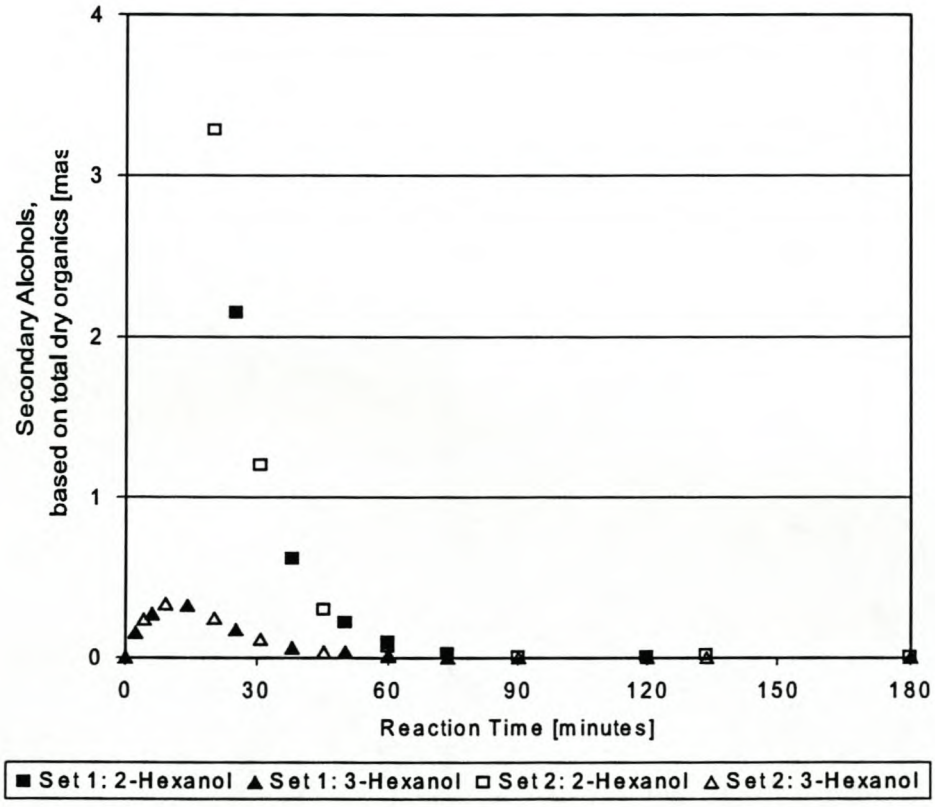


Figure 5.56: Secondary alcohol content analysed 2 days apart; reaction system: 1-pentanol + 2-hexanol, 85 % H_3PO_4, acid:alcohol = 2,2:1

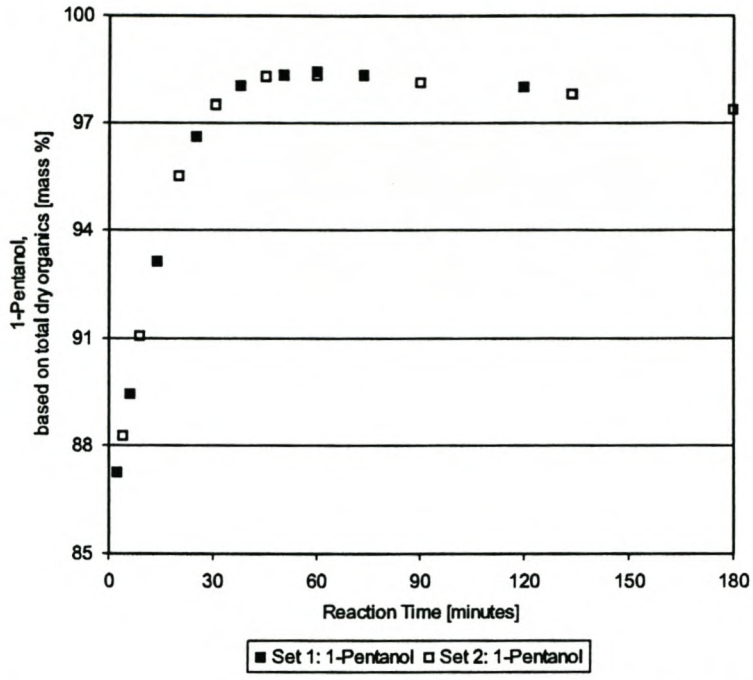


Figure 5.57: 1-Pentanol content analysed 2 days apart; reaction system: 1-pentanol + 2-hexanol, 85 % H_3PO_4, acid:alcohol = 2,2:1

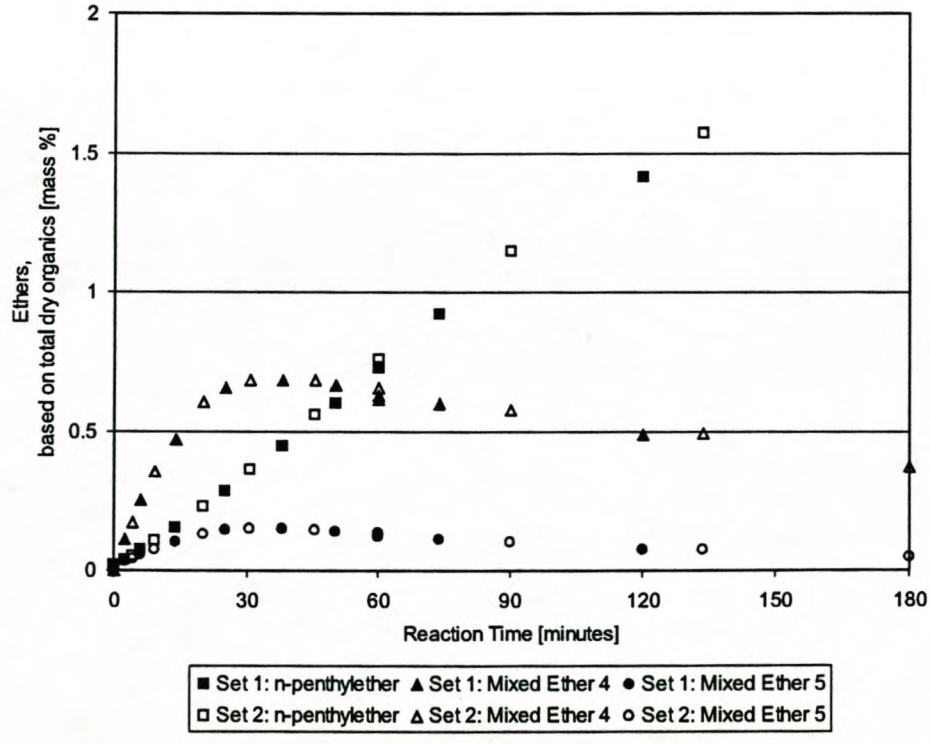


Figure 5.58: Ether content analysed 2 days apart; reaction system: 1-pentanol + 2-hexanol, 85 % H_3PO_4, acid:alcohol = 2,2:1.

Some experiments have also been repeated. The system 85 % 1-pentanol + 15 % 2-hexanol was subjected twice to the same reaction conditions, namely 85 % H_3PO_4, acid:alcohol = 2,2:1 at atmospheric pressure. The analytical results of the repeated experiments are given in Appendix D: Experiments 77 & 88. The experiments were conducted about 2 months apart from each other. The GC analyses were done on the same GC Column. According to Figure 5.59, Figure 5.60 and Figure 5.61 it can be seen that the results were very similar. There is almost no discrepancy in alcohol composition.

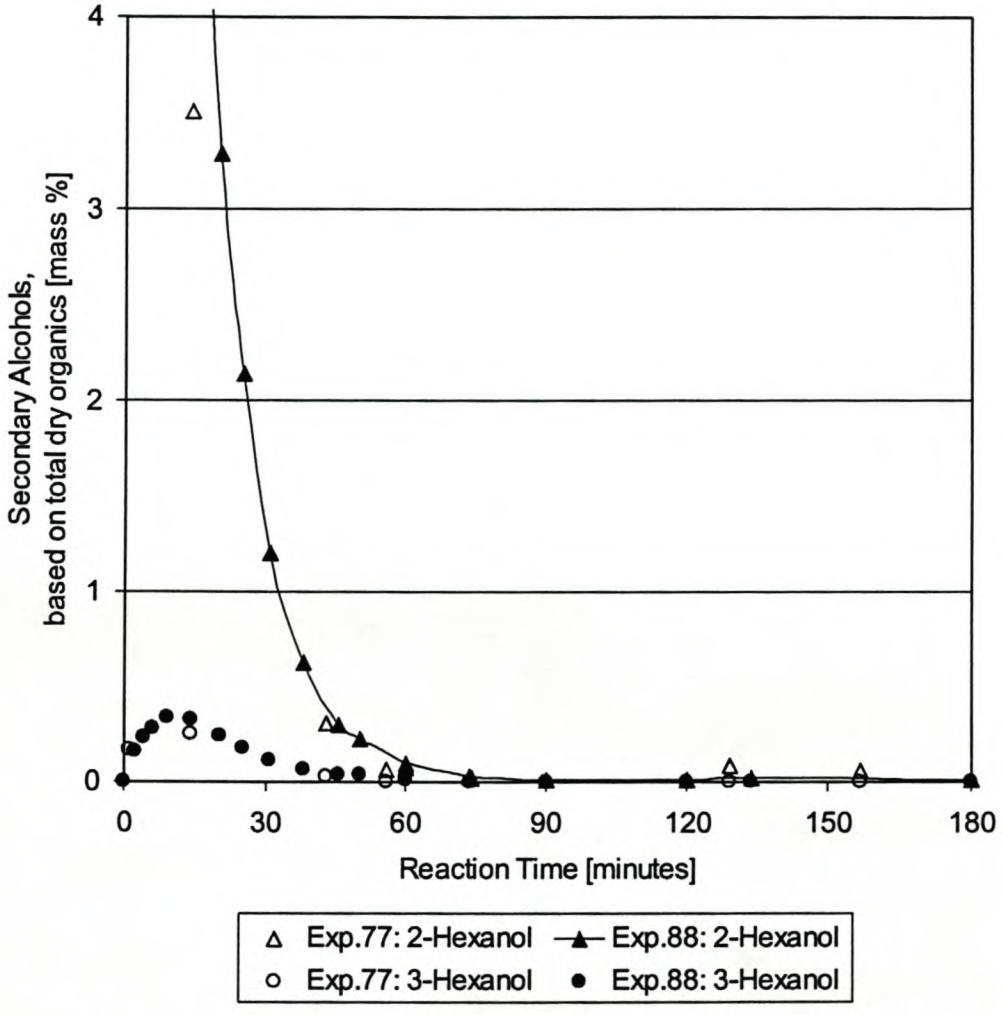


Figure 5.59: Secondary alcohol content for repeated experiments; reaction system: 1-pentanol+2-hexanol, 85 % H_3PO_4, acid:alcohol=2,2:1

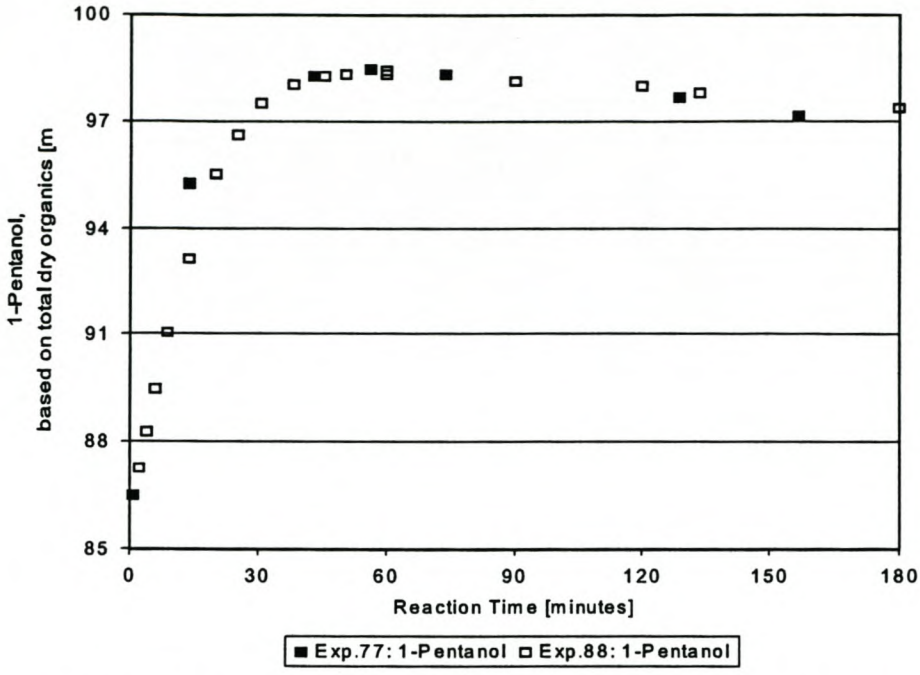


Figure 5.60: 1-Pentanol content of repeated experiments; reaction system: 1-pentanol+2-hexanol, 85 % H_3PO_4, acid:alcohol=2,2:1.

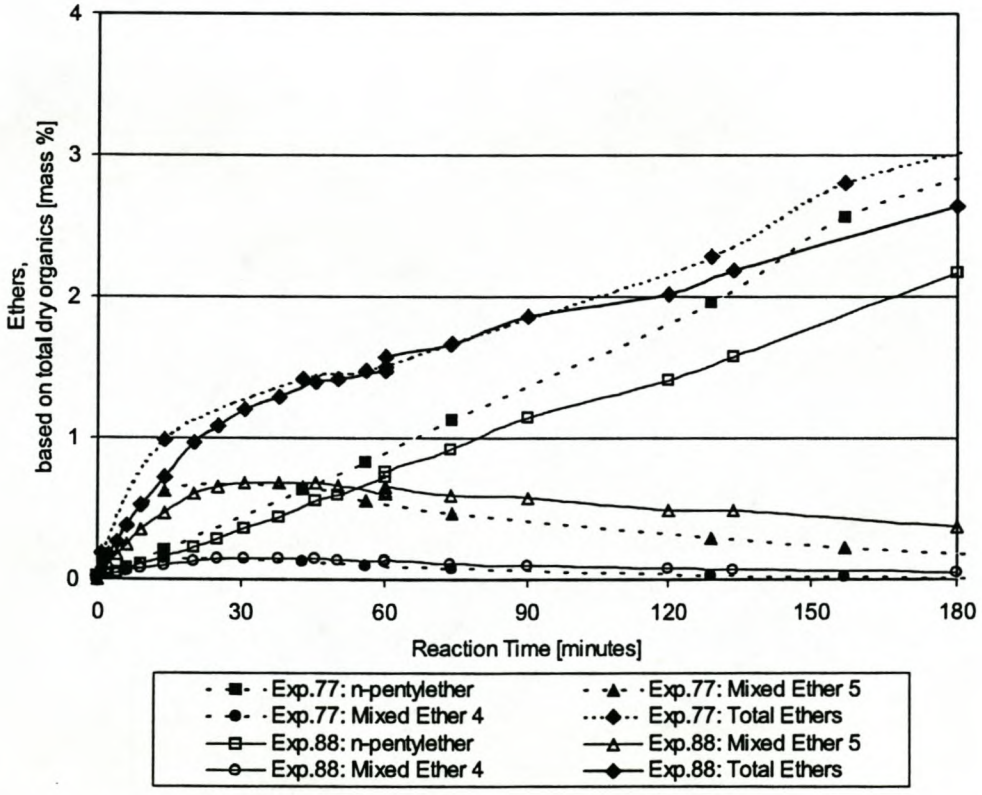


Figure 5.61: Ether quantities of repeated experiments; reaction system: 1-pentanol+2-hexanol, 85 % H_3PO_4, acid:alcohol=2,2:1.

From Figure 5.61 it can be seen that the amounts of ethers were not exactly the same for the two experiments. One of the reasons for this deviation could be that the logged starting times of the reactions were probably not exactly the same for the two runs. Also according to the alcohol compositions it seems as if the time logged for Experiment 88 was a few minutes later than the times logged for Experiment 77.

The nitrogen flow through the two reactor set-ups could also have differed. Slight deviations in acid concentrations as bought from the supplier could also lead to some deviations. The slight difference in acid:alcohol ratio could have contributed to the difference in ether formation (experiment 88 : acid:alcohol = 2,18:1 and experiment 77 : acid:alcohol = 2,16:1).

For this study the analytical results up to the time where the secondary alcohol is removed from the reaction mixture, are the most important. The analysis (not interpolated) of the reaction mixture at the time when an adequate amount of secondary alcohol was removed, is given in Table 5.14. As can be seen from Table 5.14 the total amount of ether is approximately the same.

Table 5.14: Comparison of analysis of repeated experiments; reaction system:1-pentanol+2-hexanol;85%H_3PO_4, acid:alcohol=2,2:1

	Experiment 77	Experiment 88
Reaction Time:	56 minutes	60 minutes
Components	Mass %	Mass %
Secondary alcohol based on alcohols only	0,064	0,108
1-Pentanol	98,456	98,413
2-Hexanol	0,000	0,016
3-Hexanol	0,064	0,090
n-Pentylether	0,832	0,725
Mixed Ether 4	0,094	0,123
Mixed Ether 5	0,554	0,612
Mixed Ether 6	Not detected	0,021
Total Ethers	1,48	1,48

The alcohol mixture 1-butanol+2-pentanol was also subjected to the same reaction conditions during 3 different runs. The analytical results are graphically presented in Figure 5.62, Figure 5.63, Figure 5.64 and Figure 5.65

From Figure 5.62 and Figure 5.63, it can be seen that the quantities of 1-butanol and secondary alcohols for the system 1-butanol+2-pentanol were repeatable. There was however, a discrepancy in the ether quantities that were analysed in the three equivalent runs. This discrepancy is illustrated in Figure 5.64 and Figure 5.65. The reason for the deviation in ether quantities (of Experiment 63 and 89 & 95) is that different GC Columns were used for the analysis. The slightly polar capillary GC column used for experiments 89 and 95 should give the more reliable results. The column gave very good component separations and peak forms.

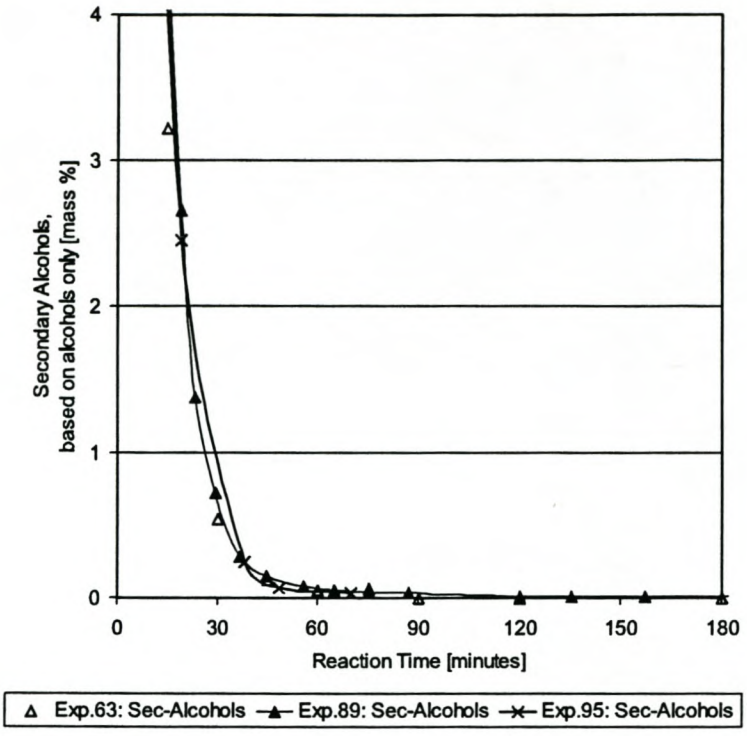


Figure 5.62: 2-Pentanol content for repeated experiments; reaction system: 1-butanol+2-pentanol, 90 % H_3PO_4, acid:alcohol = 2,2:1.

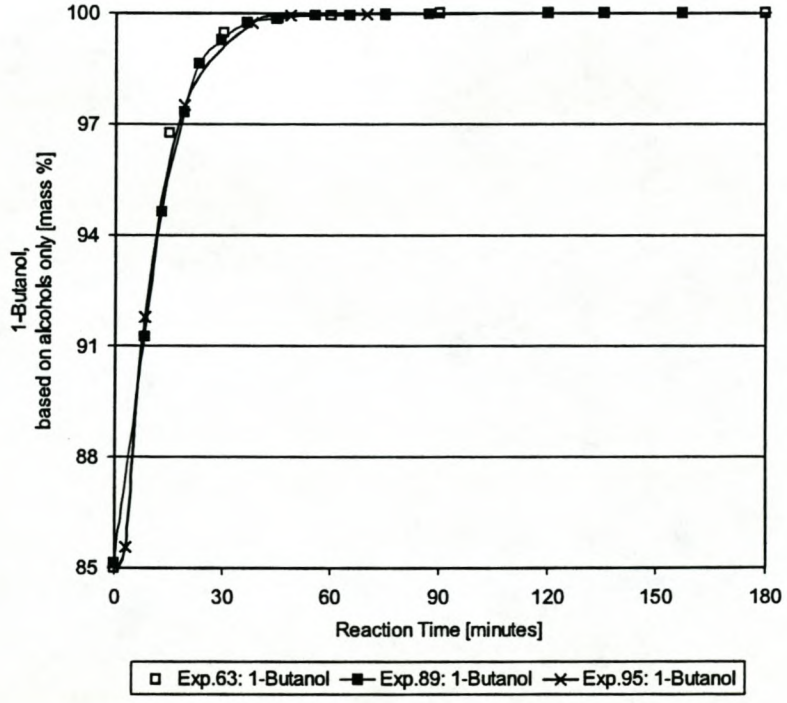


Figure 5.63: 1-Butanol content for repeated experiments; reaction system: 1-butanol+2-pentanol, 90 % H_3PO_4, acid:alcohol = 2,2:1.

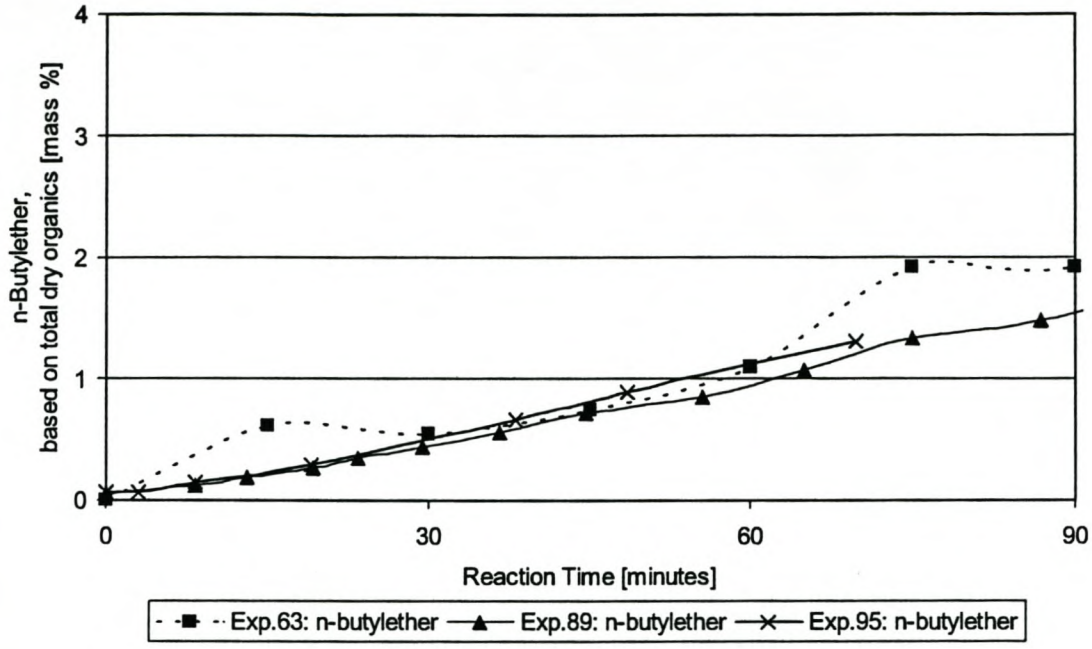


Figure 5.64: n-Butylether content for repeated experiments; reaction system: 1-butanol+2-pentanol, 90 % H_3PO_4, acid:alcohol = 2,2:1

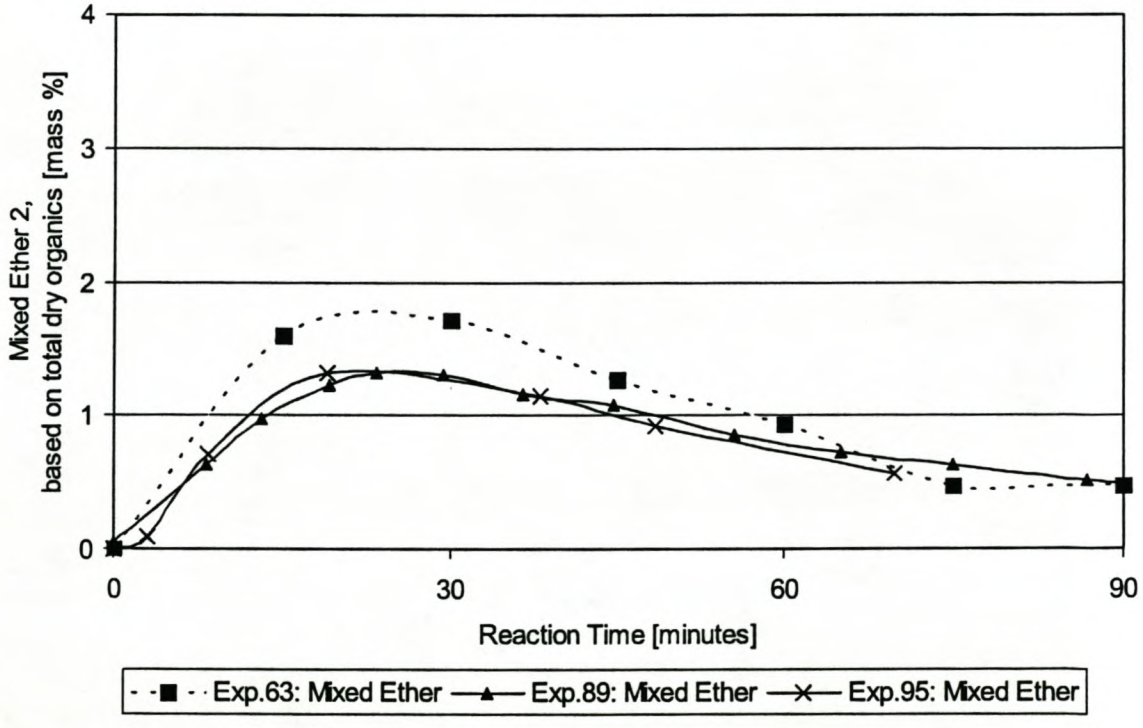


Figure 5.65: Mixed Ether 2 content for repeated experiments; reaction system: 1-butanol+2-pentanol, 90 % H_3PO_4, acid:alcohol = 2,2:1

To summarize, the following reaction variables could have caused some discrepancies:

- the H_3PO_4 concentration,
- the Nitrogen flow through the sampling system,
- heat input setting to reactor, and
- atmospheric conditions.

CP (Chemically Pure) grade 85 % H_3PO_4 was used in all the experiments. The H_3PO_4 was concentrated by boiling off some water. The new acid concentration was calculated. For every experiment the acid was diluted with distilled water or with a lower concentration acid to obtain the correct acid concentration. Only two H_3PO_4 samples were analysed by titration. One sample of the purchased 85 % H_3PO_4 gave an analysis of 86,18 %. A 88 % H_3PO_4 sample made-up by boiling off the water, gave an analysis of 88,50 %. Once again, even if the H_3PO_4 concentrations were not 100 % correct, any deviation would have occurred in all the experiments. The trends in concentration of the various components as influenced by varying acid concentrations and ratio's should thus be correct. It can be assumed that the purchased CP grade H_3PO_4 had the same concentration because it came from the same batch.

The effect of nitrogen flow through the system was discussed in paragraph 5.4.9. It can be seen that the flow does have an effect on the ether formation and the secondary alcohol dehydration rate. High flow reduced the time for the complete removal of the secondary alcohol and reduced the ether formation. During all the experiments it was attempted to keep the nitrogen flow constant and only high enough to keep the sample point clear of reaction fluid. This setting is referred to as "normal" nitrogen flow.

The heat setting of the heating mantle was usually set on maximum heat input. The amounts of alcohol loaded into each system also varied. The reaction system was kept open to atmosphere and the temperature of the reaction fluid must have been the same for similar systems. The amount of organics in the vapour space could have differed between the various reactions because of the heat input. The fraction of the alcohols in the vapour space compared to the total alcohol in the reaction mixture was always very low. The acid:alcohol ratio's in the reaction mixture could thus have been slightly influenced by the amount of alcohol in the vapour phase.

It is expected that the influence of change in atmospheric conditions on the dehydration rate and ether composition is negligible.

5.7 Conclusions on the use of liquid catalyst for the dehydration reaction

The primary alcohols in the close boiling primary+secondary alcohol mixtures can be purified. The purification of the alcohol systems 1-propanol + 2-butanol, 1-butanol + sec-pentanol and 1-pentanol + sec-hexanol have been investigated. The secondary alcohols are removed from each alcohol system by conversion of only the secondary alcohol to the corresponding olefin in an acid catalysed reaction. The alkene is continuously flashed off from the reaction mixture. The removal of the primary alcohol from the reaction mixture and the purification thereof is discussed in chapter 6.

Conclusions on the liquid catalysts systems:

- The best catalyst that was identified for the liquid phase dehydrations of secondary alcohol was H_3PO_4.
- The following solid resins proved to be unsuccessful as catalysts for the dehydration of the secondary alcohol in the liquid phase: Amberlyst 131 Wet, Amberlyst 15, Dowex MSC1 and Dowex Macroporous.
- The following liquid catalysts proved to be unsuccesful for the liquid phase dehydration of secondary alcohols: H_2SO_4 (byproduct formation too high), oxalic oxide and potassium hydrogen sulphate.

The effect of several reaction variables have been investigated for the use of H_3PO_4 as liquid phase dehydration catalyst for the separation of 1-propanol+2-butanol, 1-butanol +2-pentanol, 1-pentanol+2-hexanol. The following was found:

- An increase in acid:alcohol ratio increases the rate of formation of ethers and decreases the required reaction time for dehydration of the secondary alcohol.
- Lower H_3PO_4 concentrations at the same acid:alcohol ratio reduce the rate of formation of ethers, however increase the required reaction time for complete dehydration of the secondary alcohol.
- The dehydration rate of the secondary alcohol and ether formation is more sensitive to acid concentration than to acid:alcohol ratio.
- Varying secondary alcohol contents and ethers in the alcohol feed system, did not substantially influence the time required for complete dehydration of the secondary alcohol.
- Stripping of lighter components from the reaction mixture with an inert gas improves the product quality of the primary alcohol. The stripping also reduces the time required for dehydration of the secondary alcohols.
- Reducing the reaction pressure reduces the dehydration rate of the secondary alcohol. No definite conclusion can be made on the effect of pressure reduction on ether production.

Close boiling alcohol mixtures with different molecular weights were subjected to the dehydrations reactions. The secondary alcohols of the higher molecular weight systems are more easily removed by dehydration than the secondary alcohols of the lower molecular weight systems. The rate of ether formation is also higher for these higher molecular weight systems. However, the total amounts of ethers formed up to the time when all the secondary alcohol is dehydrated, was similar for the alcohol systems that were investigated.

The suggested reaction conditions for the varying alcohol systems are summarized in Table 5.15.

Table 5.15: Suggested batch reaction conditions and estimated ether formation for the removal of secondary alcohols from an alcohol mixture

Alcohol System	**85 % 1-propanol + 15 % 2-butanol**	**85 % 1-butanol + 15 % 2-pentanol**	**85 % 1-pentanol + 15 % sec-hexanol**
Catalyst [mass %]	88 % H_3PO_4	90 % H_3PO_4	90 % H_3PO_4
Acid:alcohol ratio	2,2:1	1,5:1	1,5:1
Reaction time [minutes]	120 min	≥ 70 min	≥ 35 min
Main estimated ethers [mass %]	n-propylether < 0,25 2-butyl propylether < 2,0	n-butylether = 0,85 3-pentyl butyl ether = 0,85	n-pentylether =0,97 3-hexyl pentyl ether = 0,75 2-hexyl pentyl ether = 0,15
Estimated total ethers [mass %]	< 2,25 %	1,7	1,89
Appendix E	Experiment 51	Experiment 89	Experiment 86

6 PURIFICATION AND RECOVERY OF DEHYDRATION REACTION PRODUCTS

6.1 Introduction

In chapter 5 it has been shown that the secondary alcohol of a primary + secondary alcohol mixture can be removed by dehydration of the secondary alcohol. The secondary alcohol is dehydrated to an alkene that is flashed off from the reaction mixture. It was found that the acidic liquid catalyst H_3PO_4 is suitable for the removal of the secondary alcohols. The primary alcohols have to be removed from the catalysts and organic byproducts. The lowest possible temperatures should be used during the purification of the products, to avoid the formation of byproducts. The liquid catalyst has to be recovered to enable recycling thereof. Two methods of removal of the alcohol from the reaction mixture have been investigated, namely batch distillation and short path distillation. The use of conventional distillation for the purification of the primary alcohol product has been investigated.

6.2 Removal of alcohols from reaction mixture

6.2.1 Removal by batch distillation

Dehydration experiments were performed as described in paragraph 5.4.2. No samples were taken during the reaction. After a specific time the heat input to the batch reaction system was cut off. The mixture was allowed to cool off to about 80 °C. This was done to enable handling of the glassware. The condenser was replaced by a simple liebig cooler set-up, see Figure 6.1. The organics were then distilled off by batch distillation. Tap water was used for cooling. The organics were collected and analysed. If two phases are formed, the organic phase and water phase were separated before analysis. The organic phase was analysed. The experimental steps that were followed are illustrated in Figure 6.2.

Initially many experiments were performed according to the experimental steps as illustrated in Figure 6.2. Only the most important results are given below. Original readings and detail results of all the experiments are given in appendix D and E (reaction followed by batch distillation was used for experiments 1 - 5, 14 - 19, 30 - 33).

During the batch distillation where H_2SO_4 was used as catalyst, the reaction mixture decoloured to dark black. This could have been due to the decomposition of the reaction mixture. The temperature of the reaction mixture increased as the light products were removed from the catalyst. Unpleasant fumes were also observed (Appendix E: Experiments 04C, 04D, 05B).

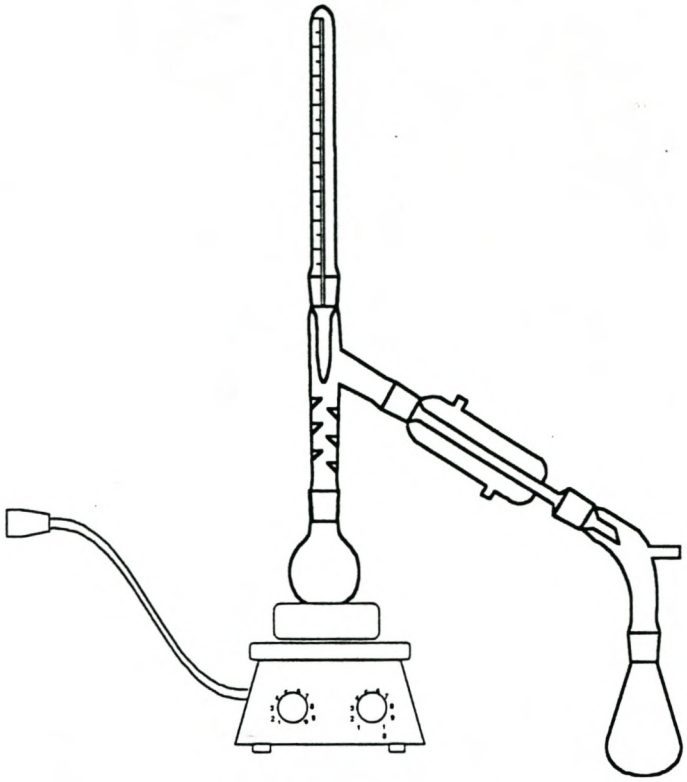


Figure 6.1: Experimental set-up of batch distillation

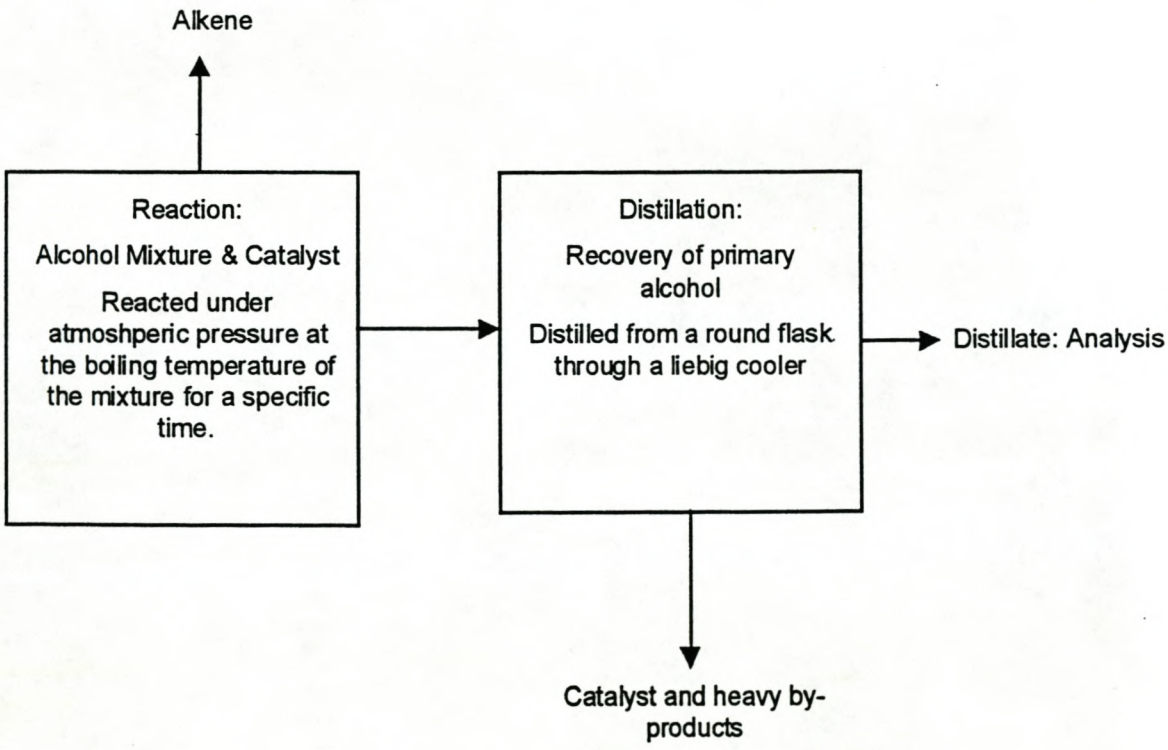


Figure 6.2: Basic diagram of experimental steps

In the experiments where H_3PO_4 was used as catalyst, the decolouring was less. However, high amounts of light products (lighter than the alcohols) were also detected in the distillate. Some of the results of the alcohol system 1-propanol+2-butanol are given in Table 6.1.

Table 6.1 : Results of dehydration reaction followed by batch distillation; reaction system: 1-propanol+2-butanol, H_3PO_4 as catalyst.

Alcohol Mixture	**85 % 1-Propanol + 15% 2-Butanol**			
H_3PO_4 concentration [mass %]	72 %	88 %	88 %	88 %
Acid:alcohol ratio	1:1	1,6:1	1,3:1	2,2:1
Reaction Time [minutes]	160	150	120	120
Batch Distillation Temperature – Botttoms [°C]	Not logged	128	140	120
1-Propanol quality, based on dry alcohols only [mass %]	86 %	99,5 %	93,0 %	99,4 %
Distillate Composition [mass %]				
Lights	1,4	0,9	4,4	1,7
1-Propanol	84,6	93,0	84,6	92,7
2-Butanol	13,8	0,5	6,4	0.6
Heavies/Ethers	0,2	5,7	4,6	5,0
Appendix E – Experiment	11B	11D	12A	12D

During the batch distillation the water and organics are distilled off from the reaction mixture. As the alcohol is removed the acid:alcohol ratio increases continuously. As the water is removed, the acid concentration also increases continuously. From paragraph 5.4.6 it can be seen that high acid:alcohol ratio's will lead to high ether formation. From the literature study (chapter 3) it is known that if H_2SO_4 is present in an alcohol/acid mixture, the decomposition of the reaction mixture will take place if the mixture is subjected to high temperatures.

From Table 6.1 the conclusion can be made that the amount of lights do not depend on the amount of dehydration of the secondary alcohol. Even if almost no dehydration of the secondary alcohol was achieved, a high amount of lights were present. The lights were not identified. The lights must have formed during the batch distillation because of the decomposition of the reaction mixture.

For the 1-butanol+2-pentanol mixture a summary of the results are given in Table 6.2 (Original readings and results are given in Appendix D&E, Experiments 30-32). To try to prevent decomposition of the reaction mixture, the alcohol was only distilled off to a bottoms temperature of about 120 to 160 °C. A high amount of alcohol remained in the reaction mixture and this caused very low primary alcohol recoveries.

Table 6.2 : Results of dehydration reaction followed by batch distillation; reaction system: 1-butanol+2-pentanol, H_3PO_4 as catalyst.

Alcohol Mixture	**85 % 1-Butanol + 15% 2-Pentanol**			
Acid concentration [mass %]	H_3PO_4 85 %	H_3PO_4 75 %	H_3PO_4 80 %	H_3PO_4 85 %
Acid:alcohol ratio	2,1:1	2,2:1	2,2:1	1:1
Reaction Time [minutes]	120	120	90	150
Batch Distillation Temperature – Botttoms [°C]	150	140	130	161
1-Propanol quality, based on dry alcohols only [mass %]	100 %	92 %	96,9 %	92 %
1-Butanol recovery	72 %	81 %	81 %	87 %
Distillate Composition [mass %]				
Lights	5,7	7,4	7,2	13,1
1-Butanol	87,6	82,6	86,4	76,4
2-Pentanol	0	7,2	2,6	6,2
Heavies/Ethers	6,7	2,8	3,8	4,2
Appendix E - Experiment	30B	30C	30D	32B

From Table 6.2 it can be seen that the amount of lights present in the distillate does not depend on the amount of dehydration of the 2-pentanol. The lights are probably formed during the batch distillation.

A further experiment was performed to determine how the batch distillation changes the composition of the recovered product. The alcohol mixture 85 % 1-butanol + 15 % 2-pentanol was subjected to dehydration using 85 % H_3PO_4 as catalyst. The reaction mixture was split after 120 minutes. One part was batch distilled, and the other part was partly neutralised with Na_2CO_3 before distillation. The results are given in Table 6.3 (See Appendix D&E: Experiment 33).

Table 6.3: Treatment of reaction mixture with Na_2CO_3 before GC analysis

Reaction System	**1-Butanol+2-Pentanol, 85 % H_3PO_4 acid:alcohol = 2,2:1, reaction time = 120 min**	
Treatment	Na_2CO_3 used to neutralise the reaction mixture partly before distillation.	Alcohol removed from reaction mixture by batch distillation, bottoms Temperature = 180 °C.
Composition of Organic phase [mass %]		
Lights	Not detected	5
1-Butanol	98,1	88,9
2-Pentanol	Not detected	Not detected
Heavies/Ethers	1,9	6,1

Only the neutralised mixture contained no lights in the distillate. The neutralised mixture also contained by far less heavies than the other mixture. There is thus no doubt that decomposition of the reaction mixture took place during all the batch distillation experiments.

Batch distillation at atmospheric pressure can thus not be used to recover the primary alcohol from the reaction mixture.

6.2.2 Removal of alcohols from reaction mixture with short path distillation

The batch distillation step was replaced by a short path distillation step to try to eliminate the decomposition of the reaction mixture during the alcohol removal step.

A stainless steel pilot plant short path distillation unit was used. A glycol/water mixture was used for heating and tap water was used for cooling.

Reactions and distillations were performed for the systems 1-propanol+2-butanol, 1-butanol+2-pentanol, 1-pentanol+2-hexanol (see Appendix D – Experiments 36, 51 and 70). The main results are given in Table 6.4.

Table 6.4: Results of dehydration followed by short path distillation

Alcohol System	**85 % 1-propanol + 15 % 2-butanol**	**85 % 1-butanol + 15 % 2-pentanol**	**85 % 1-pentanol + 15 % 2-hexanol**
Catalyst acid:alcohol Reaction time [min]	88 % H_3PO_4 2,2:1 120	88 % H_3PO_4 2,2:1 120	88 % H_3PO_4 2,2:1 120
Short Path Distillation Pressure & Heating Temperature	0,09 – 0,12 bar abs 80 – 93 °C	0,09 – 0,11 bar abs 84 – 100 °C	0,095 bar abs 108 °C
Primary alcohol quality, based on alcohols [mass%]	99	100	100
Distillate runs	One	Two	Two
Ethers in organic phase of distillate [mass%]	n-propylether = 0,7 2-butyl propylether = 2,0	Cut 1 n-butylether = 2,2 mixed ether 2 = 2,2	n-pentylether = 3,3 total mixed ethers = 1,4
		Cut 2 n-butylether = 0,7 mixed ether 2 = 0,7	

The processing of the 85 % 1-propanol + 15 % 2-butanol mixture (88 % H_3PO_4, acid:alcohol = 2,2:1, 120 minutes reaction time) gave a product quality of 99 % 1-propanol (based on alcohols only). In total 2,7 % ethers were in the distillate. The distillate was homogeneous. In earlier experiments where batch distillation for the alcohol recovery was used the product quality exceeded 99 % if a reaction time of 120 minutes at the same catalyst conditions as above was used (e.g. Appendix E - Experiment 12D). During the batch distillation the dehydration of the 2-butanol continued and the reaction time was thus > 120 minutes. The total ether content was 5 %. The reactions (dehydration and ether formation) thus probably did not continue during the short path distillation.

The processing of the 85 % 1-butanol + 15 % 2-pentanol mixture (85 % H_3PO_4, acid:alcohol = 2,2:1, 120 minutes reaction time) gave a product quality of ~ 100 % 1-butanol (based on alcohols only). The reaction mixture was passed through the short path distillation unit twice. The first cut contained 4,4 % ethers while the second cut only contained 1,4 % ethers. The calculated 1-butanol recovery was only 50 %. The remaining reaction mixture should contain < 1,4 % ethers (based on dry organics). The high ether concentration in the first cut can be explained by the fact that 1-butanol+n-butylether and water form a ternary azeotrope. Whether the unsymmetrical ether forms an azeotrope could not be established from the literature.

The processing of the 85 % 1-pentanol + 15 % 2-hexanol mixture (reaction time of 120 minutes, 85 % H_3PO_4 at an acid:alcohol ratio of 2,2:1) gave a product quality of ~ 100 % 1-pentanol (based on alcohol only). The reaction mixture was passed through the unit once. The distillate contained 4,7 % ethers in total. The reaction time allowed was substantially above the required 65 minutes reaction time as found in Experiment 88. The reaction mixture also had to be cooled-off at room temperature to about 50 °C before it was fed to the short path distillation unit. During this cooling-off time the ether formation could also have proceeded.

It was found that the distillates contained no lights for all three systems if short path distillation was used for the recovery of the alcohols. Decomposition of the reaction mixture during the short path distillation thus did not occur. The percentage recoveries of the primary alcohols were very low, but with improved short path distillation conditions on a pilot or commercial plant, they should increase substantially. The conclusion can be made that short path distillation can be employed to recover the organic components from the reaction mixture.

6.3 Purification of the primary alcohols

After the alcohols and byproducts have been recovered from the reaction mixture, the mixture has to be purified to produce > 99,5 % primary alcohol. The byproducts that are formed during the dehydration reaction, namely ethers and reaction water have to be removed. Only the purification of 1-butanol and 1-pentanol will be investigated using conventional distillation. (As mentioned in chapter 5, it is known that Sasol is successfully applying a process for the separation of 2-butanol from 1-propanol. For this reason the system 1-propanol+2-butanol was not investigated further.)

For the process design and for the prediction of the distillation curves, the three parameter NRTL Liquid Activity Coefficient model was used. The interaction parameters were taken from the PRO II database. Missing interaction parameters were estimated by means of the Unifac model.

6.3.1 Purification of 1-butanol

If the alcohol mixture 1-butanol+2-pentanol is subjected to batch dehydration (using H_3PO_4 as catalyst) and subsequent short path distillation the following components will be present in the distillate: 1-butanol, small amounts of 2-pentanol, n-butylether, 3-pentyl butyl ether and water. The ethers and water have to be removed from the alcohols.

A summary of the published and predicted azeotropes that are formed between the components 1-butanol, n-butylether, 3-pentyl butyl ether and water are given in Table 6.5. Azeotropes with slightly different compositions but with substantially lower boiling temperatures are predicted at lower pressures.

No azeotropes are predicted by PRO II at 100 kPa between 1-butanol+3-pentyl butyl ether nor n-butylether+3-pentyl butyl ether. However, at low pressures, namely < 10 kPa a binary azeotrope is predicted between 1-butanol and 3-pentyl ether.

Table 6.5: Azeotropes of 1-butanol, n-butylether, 3-pentyl butyl ether and water

Components	Comp. [mol%]	Pressure / Boiling Temperature	Comp. [mol%]	Pressure / Boiling Temperature	Reference
Water	76,28	101,3 kPa	---	---	Published, [61]
n-Butylether	23,72	95,5 °C			
Water	81,84	100 kPa	81,5	15 kPa	PRO II
n-Butylether	18,16	94,15 °C	18,5	49,8 °C	NRTL02,Unifac
Water	75,8	101,3 kPa	---	---	Published, [61]
1-Butanol	24,2	92,6 °C			
Water	77,6	100 kPa	81,0	15 kPa	PRO II
1-Butanol	22,4	92,6 °C	19,0	51.4 °C	NRTL02,Unifac
1-Butanol	87,5	101,3 kPa	---	---	Published, [61]
n-Butylether	12,5	117,4 °C			
1-Butanol	91,2	100 kPa	76,6	15 kPa	PRO II
n-Butylether	8,8	117,2 °C	23,4	71,0 °C	NRTL02,Unifac
Water	69,8				Published, [61]
1-Butanol	18,2	100 kPa	---	---	
n-Butylether	12,0	90,9 °C			
Water	75,7		77,2		
1-Butanol	15,9	100 kPa	11,8	100 kPa	PRO II
n-Butylether	8,4	91,7 °C	11,0	48,8 °C	NRTL02,Unifac
Water	86,3	100 kPa	88,0	15 kPa	PRO II
3-Pentyl Butyl ether	13,7	95,6 °C	12,0	51,4 °C	NRTL02,Unifac
Water	76,3	100 kPa	80,0		
1-Butanol	15,7	91,5 °C	14,2	15 kPa	PRO II
3-Pentyl Butyl ether	8,0		6,9	49,0 °C	NRTL02,Unifac

The distillation curves of 1-butanol + n-butylether + water at 100 kPa (abs.) as generated with PRO II using NRTL and Unifac parameters are given in Figure 6.3.

One experimental vapour-liquid equilibrium data point at atmospheric pressure was determined. The data point is indicated on Figure 6.3. The experimental and theoretical relative volatilities are given in Table 6.6.

Table 6.6: Relative volatilities for the system 1-butanol, n-butylether and water

Relative volatility	Experimental at atmospheric pressure	PRO II, NRTL & Unifac parameters at atmospheric pressure
α n-butylether, 1-butanol	1.29	1.18
α water, 1-butanol	5.25	6.53

According to the relative volatilities it is very easy to remove water from 1-butanol. The removal of n-butylether will not be that easy, but can be achieved by distillation. The relative volatility as calculated with PRO II for n-pentylether and 1-butanol is also more conservative than the experimentally obtained value. Less transfer stages will probably be needed in practise than predicted with PRO II.

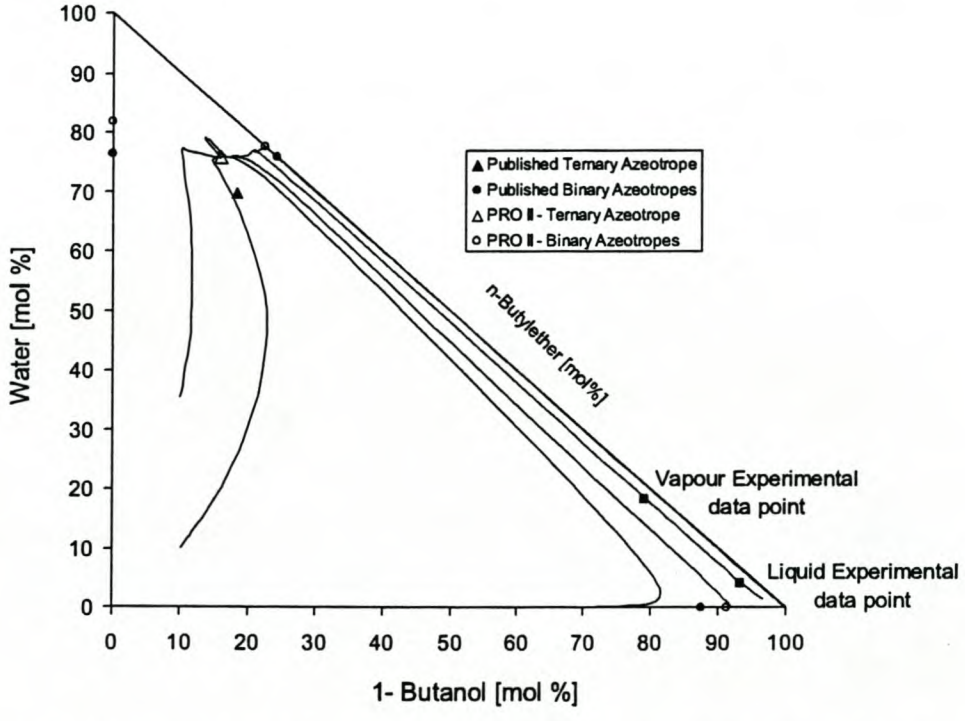


Figure 6.3: Distillation curves for the system 1-butanol + water + n-butylether at 100 kPa(abs.) by PRO II (NRTL02)

According to Figure 6.3 water will be removed predominantly as distillate if 1-butanol+water+n-butylether is fed to a distillation column. If n-butylether is present in a small amount and if enough water is fed to the column all the n-butylether could be removed as part of the distillate.

3-Pentyl butylether is not available commercially. Experimental equilibrium data points thereof could thus not be obtained. The distillation curves of the system 1-butanol + water and 3-pentyl butyl ether as predicted by PRO II using NRTL and UNIFAC parameters are given in Figure 6.4 at 100 kPa(abs.) . If 1-butanol+water+3-pentyl butyl ether are fed to a distillation column, water will be removed predominantly as top product. 3-Pentylether and 1-butanol will be present as part of the azeotrope in the distillate.

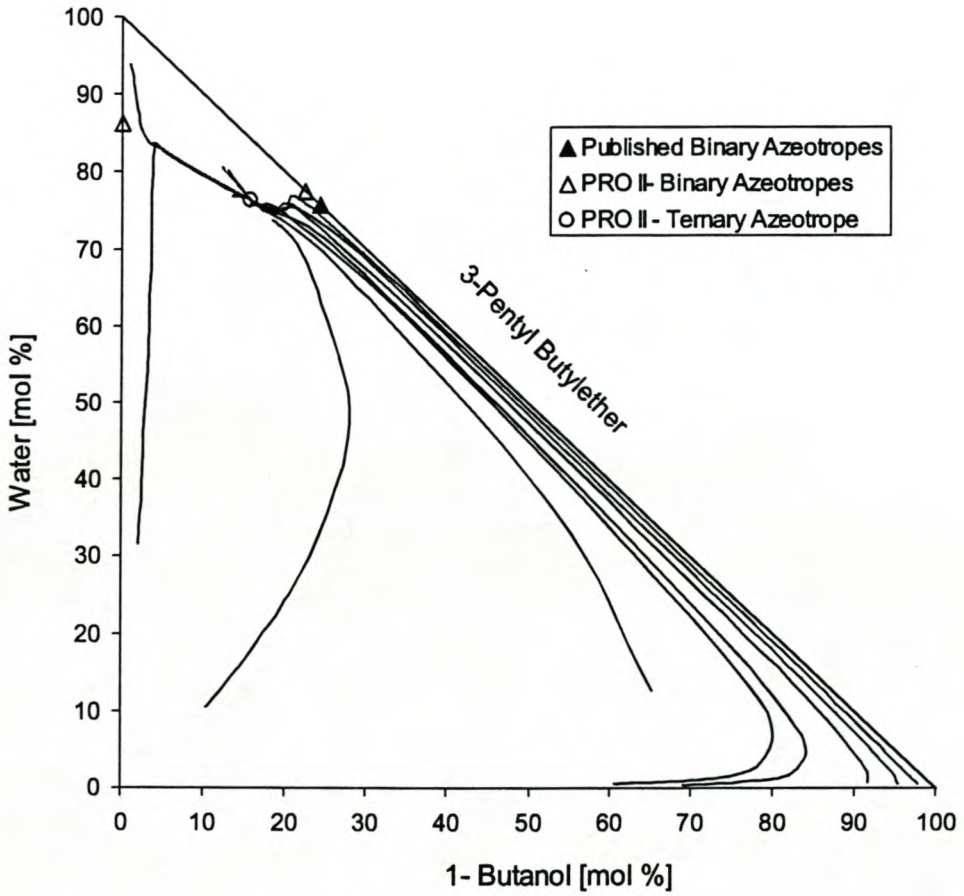


Figure 6.4: Distillation curves for the system 1-butanol + water + 3-pentyl butyl ether at 100 kPa(abs.) as predicted by PRO II (NRTL02)

The distillation curves for the system 1-butanol+n-butylether+3-pentyl butyl ether as predicted by PRO II using NRTL and UNIFAC parameters are given in Figure 6.5 at 100 kPa(abs.) From these curves it is clear that 1-butanol and n-butylether form a low boiling azeotrope. The published azeotrope is also indicated in Figure 6.5. If 1-butanol, n-butylether and 3-pentyl-butyl ether are subjected to distillation, the n-butylether will be removed with the 1-butanol as top product. 3-Pentyl butyl ether will be removed as bottom product. Pure 1-Butanol will thus not be recovered as top product.

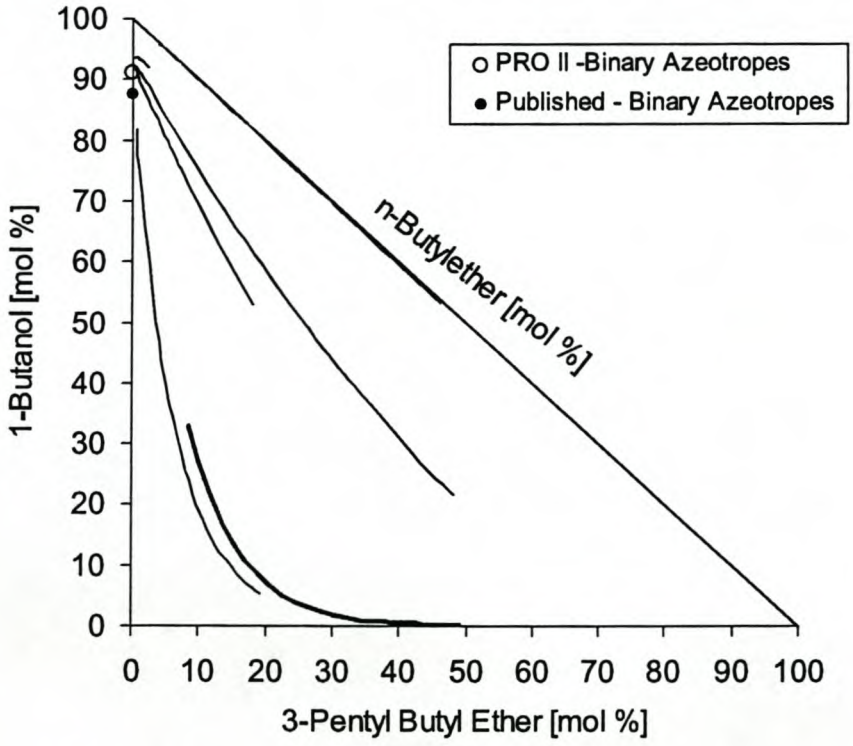


Figure 6.5: Distillation curves for the system 1-butanol + n-butylether and 3-pentyl butyl ether at 100 kPa (abs.) as predicted with PRO II (NRTL02)

From the information above the conclusion can be made that the separation of 1-butanol, n-butylether, 3-pentyl butyl ether and water can be achieved as follows:

- In a first distillation column predominantly water will be removed. 1-butanol, n-butylether and 3-pentyl butyl ether will be present as part of the azeotropes in the distillate. All the n-butylether should be removed as top product as it cannot be separated from the 1-butanol in a second column. The remaining 1-butanol and 3-pentyl butyl ether is removed as bottom product.
- In a second distillation column the purified 1-butanol is removed as distillate and the 3-pentyl butyl ether is removed as bottoms.

A further option would be to allow the dehydration reaction to continue until all the 3-pentyl-butyl ether is dehydrated. Thereafter, only n-butylether and water have to be removed from 1-butanol. This will be achieved by azeotropic distillation in one colum. Low 1-butanol recoveries are expected, because a major part of the 1-butanol will be lost as part of the low boiling ternary azeotrope.

An important advantage if the distillations are performed under vacuum is that the mixtures will not be subjected to high temperatures. From Table 6.5 it can be seen that azeotropes with similar compositions are formed at 15 kPa(abs.) as those that are formed at 100 kPa(abs.). However, their boiling temperatures are considerably lower. In all the predicted azeotropes the mole % 1-butanol is less at 15 kPa(abs.) than at 100 kPa(abs.). Besides the advantage of lower distillation temperatures, a further advantage will be that the amounts of 1-butanol that will be lost with the azeotrope as distillate will be less if the distillation is performed under vacuum. The distillation curves for the 1-butanol+water+n-butylether, 1-butanol+water+3-pentyl butyl ether and 1-butanol+n-butylether+3-pentyl butyl ether at 15 kPa(abs.) are given in Figure 6.6, Figure 6.7 and Figure 6.8. If Figure 6.3 and Figure 6.6 are compared, the conclusion can be made that 1-butanol will be recovered easier as bottoms product at vacuum conditions if 1-butanol+water+n-butylether are fed to a distillation column.

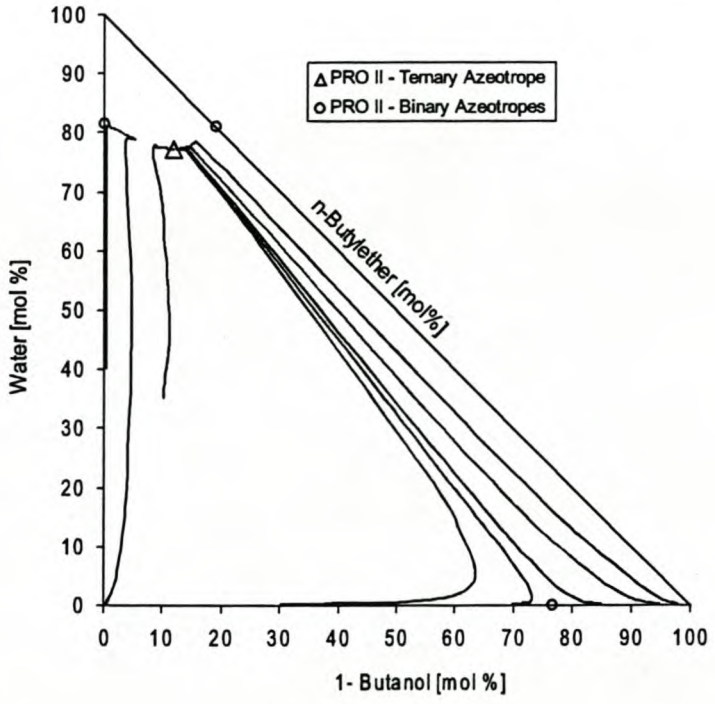


Figure 6.6: Distillation curves for the system 1-butanol + water + n-butylether at 15 kPa (abs.) as predicted with PRO II (NRTL02)

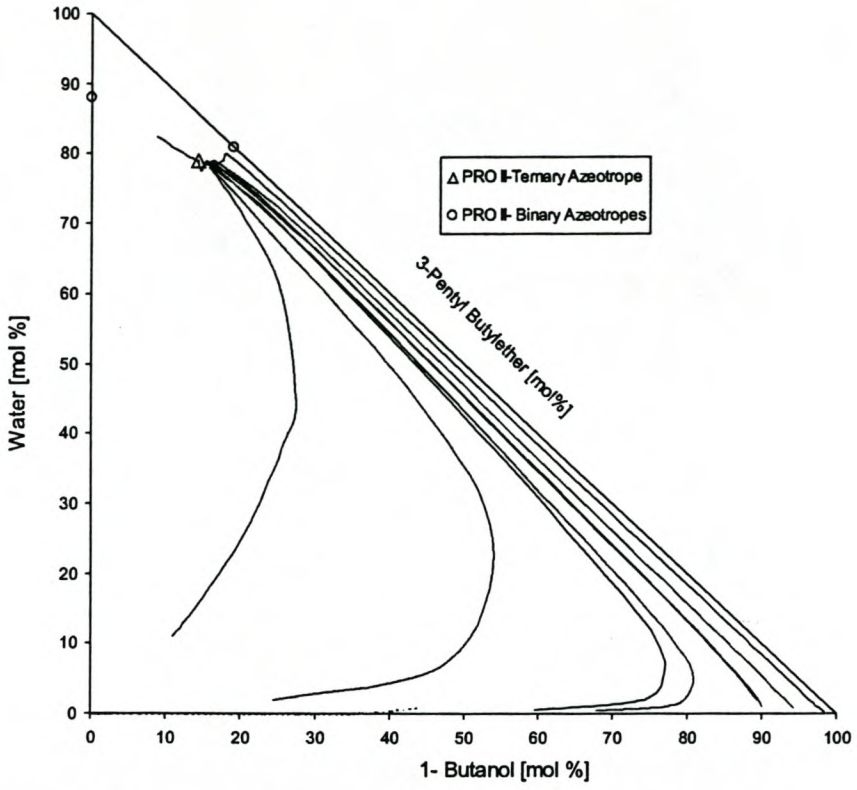


Figure 6.7: Distillation curves for the system 1-butanol + water and 3-pentyl butyl ether at 15 kPa (abs.) as predicted with PRO II (NRTL02)

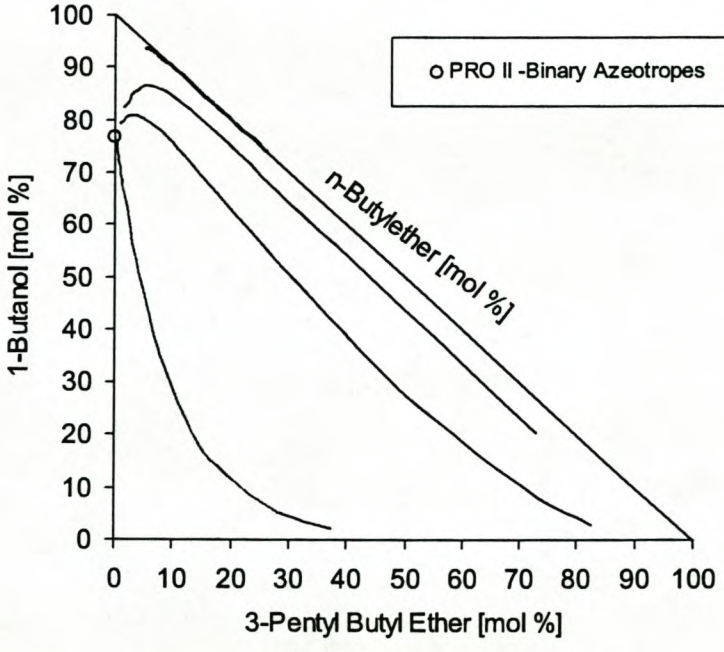


Figure 6.8: Distillation curves for the system 1-butanol + n-butylether and 3-pentyl butyl ether at 15 kPa (abs.) as predicted with PRO II (NRTL02)

6.3.2 Purification of 1-pentanol

The following components will be present in the distillate of the short path distillation unit: 1-pentanol, small amounts of 2-hexanol and 3-hexanol, n-pentylether, 3-hexyl pentyl ether, 2-hexyl pentyl ether and water. The ethers and water have to be removed from the alcohols.

In the simulation of the distillation section a group contribution method will be used for the thermodynamic data of the unsymmetrical ethers. According to the group contribution method 3-hexyl pentyl ether and 2-hexyl pentyl ether are the same. It is thus not important whether 2 or 3 hexyl pentyl ether is formed. They may be treated as one component.

Azeotropes exists between water and the organic compounds. These azeotropes are given in Table 6.7.

Table 6.7: Azeotropes of water, 1-Pentanol, n-Pentylether and 3-Hexyl Pentyl Ether

Components	Comp. [mol%]	Pressure --- Boiling Temperature	Comp. [mol%]	Pressure --- Boiling Temperature	Reference
Water 1-Pentanol	84,8 15,2	101 kPa 95,4 °C	---	---	Published [61]
Water n-Pentanol	86,4 13,6	100 kPa 95,6 °C	90,0 10,0	15 kPa 52,0 °C	PRO II NRTL02,Unifac
Water n-Pentylether	95,2 4,8	100 kPa 98,3 °C	97,1 2,9	15 kPa 53,4 °C	PRO II NRTL02,Unifac
Water 3-Hexyl Pentyl ether	97,1 2,9	100 kPa 98,8 °C	98,3 1,7	15 kPa 53,6 °C	PRO II NRTL02,Unifac
Water 1-Pentanol n-Pentylether	86,6 12,1 1,3	100 kPa 95,6 °C	90,0 10,0 ~ 0,01	15 kPa 52 °C	PRO II NRTL02,Unifac
Water 1-Pentanol 3-Hexyl Pentyl ether	86,4 13,6 ~ 0,01	100 kPa 95,6 °C	90,04 9,96 ~ 0,001	15 kPa 52 °C	PRO II NRTL02,Unifac

Azeotropes with slightly different compositions but with substantially lower boiling temperatures are predicted at lower pressures. At lower pressures the amount of water is also higher in the azeotrope. No azeotropes are predicted between 1-pentanol and n-pentylether or 1-pentanol and 3-hexyl pentyl ether.

The distillation curves of 1-pentanol + n-pentylether + water at 100 kPa (abs.) as generated with PRO II using NRTL and Unifac parameters are given in Figure 6.9. An experimental vapour-liquid equilibrium data point at atmospheric pressure was generated. The data point is indicated on Figure 6.9. The experimental and theoretical relative volatilities are given in Table 6.6.

Table 6.8: Relative volatilities for the system 1-pentanol, n-pentylether and water

Relative volatility	Experimental atmospheric pressure	PRO II NRTL & Unifac parameters atmospheric pressure
α 1-pentanol, n-pentylether	1.99	1.96
α water, 1-pentanol	21.3	14.22

According to the relative volatilities it is very easy to remove water from 1-pentanol. The removal of water is even easier than predicted by PRO II.

From Figure 6.9 it can be seen that if water+1-pentanol+n-pentylether are fed to a distillation column, water will be removed predominantly as top product and pentanol and n-pentylether will be removed as bottom product.

3-Hexyl pentyl ether is not available commercially. An experimental equilibrium data point thereof could thus not be obtained. The distillation curves for the system water+1-pentanol+3-hexyl pentyl ether as predicted by PRO II using NRTL and UNIFAC parameters are given in Figure 6.10 at 100 kPa(abs.). The distillation curves are very similar to those in Figure 6.9. Once again the ether and 1-pentanol will form the bottoms product if they are fed with water to a distillation column.

If a mixture containing water, 1-pentanol and both ethers is fed to a distillation column, all the water should be present in the distillate. The 1-pentanol and ethers will be removed as bottoms product.

A second distillation is needed to remove the ethers from the 1-pentanol.

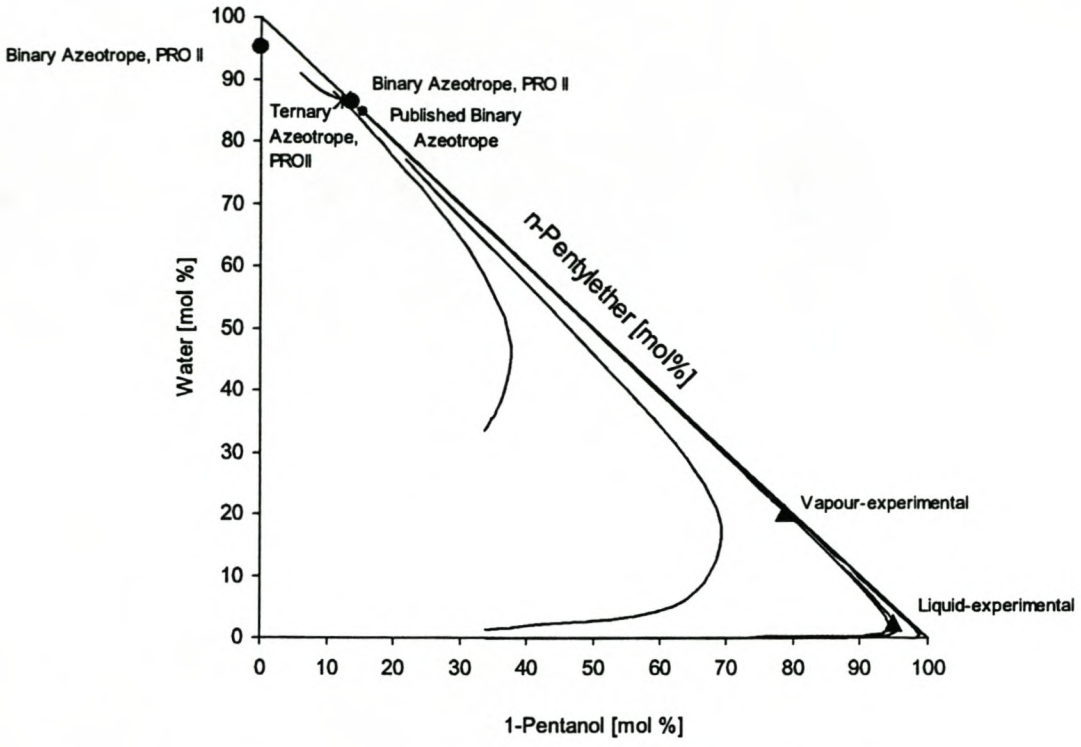


Figure 6.9: Distillation curves for the system 1-pentanol + water + n-pentylether at 100 kPa(abs.) as predicted by PRO II (NRTL02)

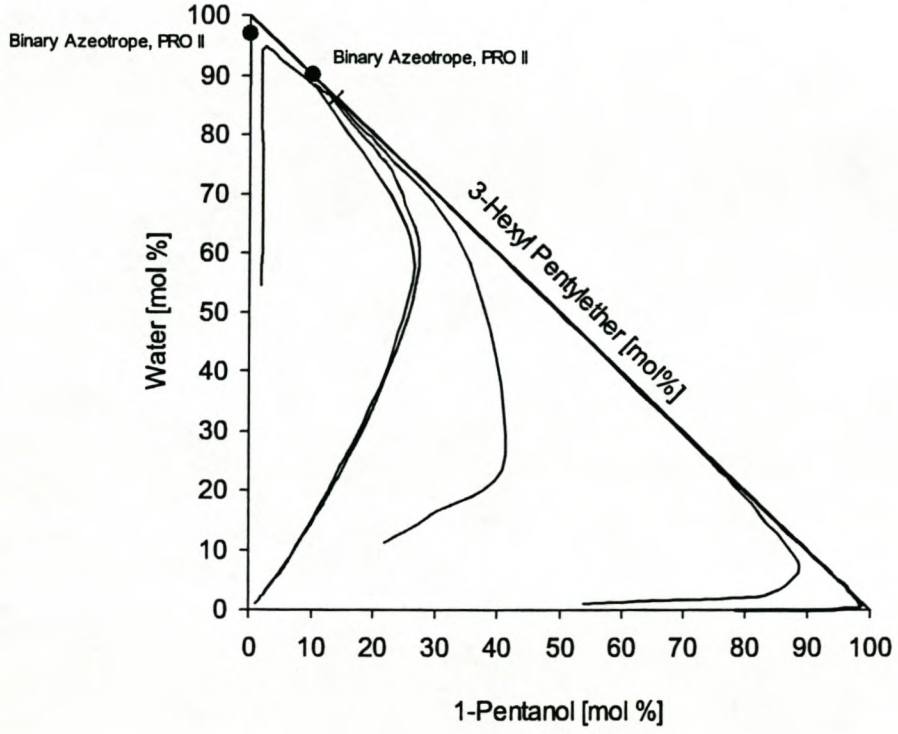


Figure 6.10: Distillation curves for the system 1-pentanol + water + 3-Hexyl Pentyl Ether at 100 kPa(abs.) as predicted by PRO II (NRTL02)

The distillation curves for the system 1-pentanol+n-pentylether+3-hexyl pentyl ether at 100 kPa are given in Figure 6.11. No azeotropes are published nor predicted between any of these three components.

If the mixture 1-pentanol+n-pentylether+3-hexyl pentyl ether is fed to a column, the 1-pentanol will be recovered as distillate and the ethers will be present in the bottoms product according to the distillation curves given in Figure 6.11.

From the information above the conclusion can be made that the separation of 1-pentanol, n-pentylether, 3-hexyl pentyl ether and water can be achieved as follows:

- In a first distillation column mainly the water and some of the n-Pentylether is removed as top product.
- In a second distillation column the purified 1-pentanol is removed as distillate and the ethers are removed as bottom product.

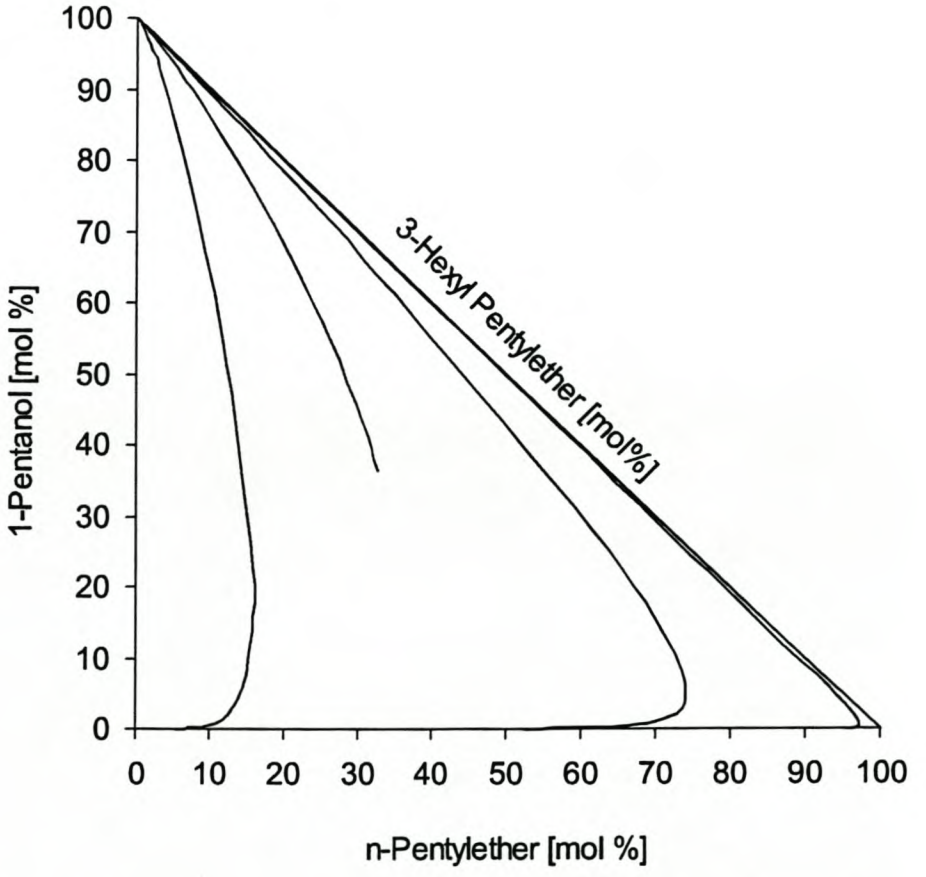


Figure 6.11: Distillation curves for the system 1-pentanol + n-pentylether and 3-hexyl pentyl ether at 100 kPa (abs.) as predicted with PRO II (NRTL02)

Separation at 15 kPa (abs.) will be advantageous because the mixture will not be subjected to very high temperatures. The distillation curves for the systems 1-pentanol+n-pentylether+water, 1-pentanol+3-hexyl-pentyl ether and 1-pentanol+n-pentylether+3-hexylpentyl ether at 15 kPa are given in Figure 6.12, Figure 6.13 and Figure 6.14.

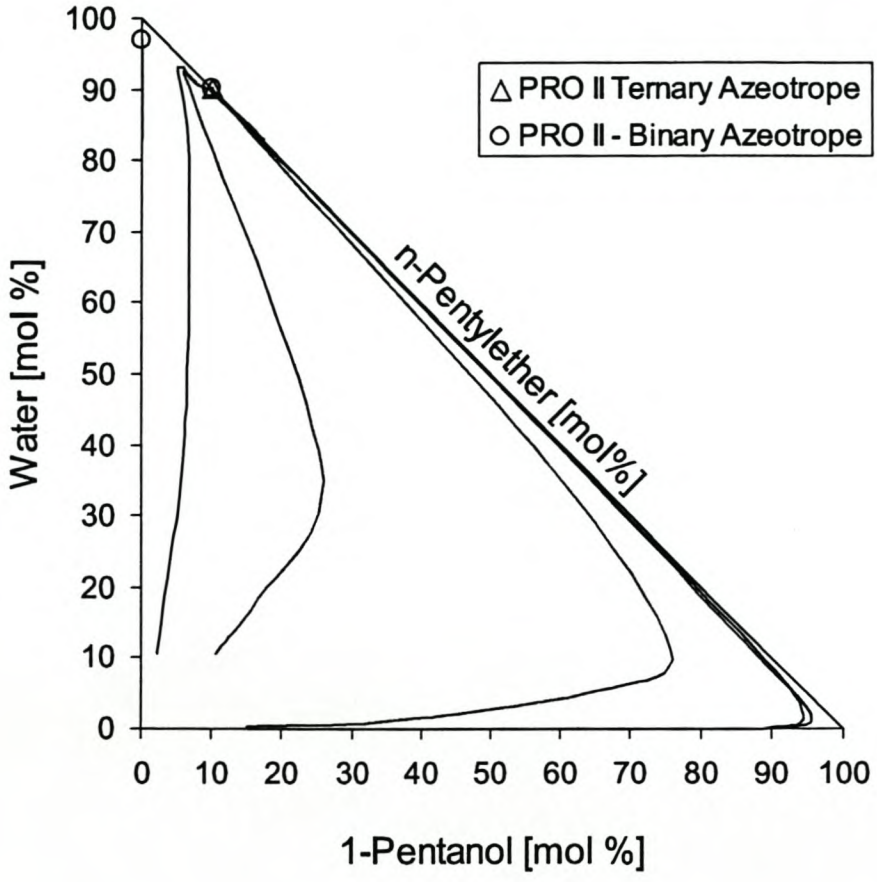


Figure 6.12: Distillation curves for the system 1-pentanol + n-pentylether and water at 15 kPa (abs.) as predicted with PRO II (NRTL02)

From Table 6.7 it can be seen that the ternary azeotropes between water+1-pentanol+ether contain very small amounts, less than 0,01 %, of the respective ether at 15 kPa (abs.). The ethers will thus not be removed as overhead in a first column, if the column is operated at 15 kPa(abs.). Both ethers will be removed as bottoms from the second column.

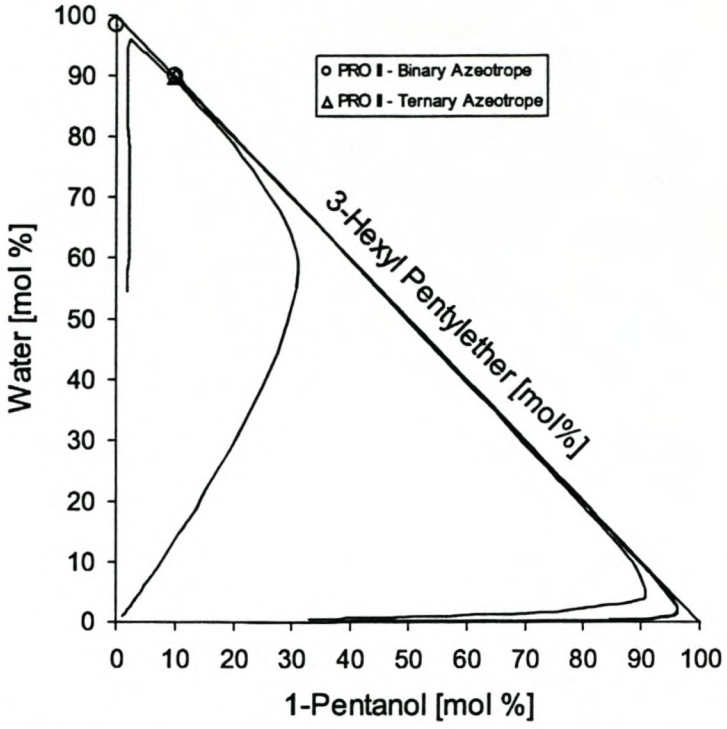


Figure 6.13: Distillation curves for the system 1-pentanol + water and 3-hexyl pentyl ether at 15 kPa (abs.) as predicted with PRO II (NRTL02)

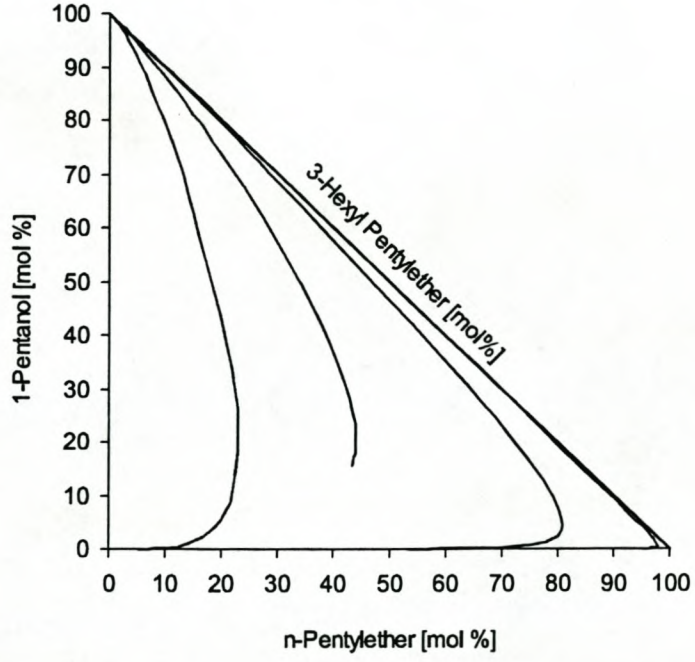


Figure 6.14: Distillation curves for the system 1-pentanol + n-pentylether and 3-hexyl pentyl ether at 15 kPa (abs.) as predicted with PRO II (NRTL02)

6.4 Conclusions and recommendations on the removal and purification of the primary alcohol

Batch distillation at atmospheric pressure cannot be used to recover the alcohol from the reaction mixture. During batch distillation decomposition of the reaction mixture takes place. This causes byproduct formation and substantial losses of the primary alcohol.

Short path distillation can be used to recover the primary alcohol from the reaction mixture. The water and ethers are also present in the distillate.

Further experimental work using short path distillation to separate the alcohols from the reaction mixture should be conducted.

The distillate from the short path distillation unit may be purified by conventional distillation.

For the recovery of 1-butanol from a 1-butanol+n-butylether+water mixture only one azeotropic distillation column is needed. It is essential that the feed does not contain too much n-butylether. The n-butylether will be removed as part of the ternary azeotrope in the distillate. The 1-butanol will be recovered as bottoms product from the column. Predominantly water will be removed as distillate in the first column.

For the recovery of 1-butanol from a 1-butanol+n-butylether+3-pentyl butyl ether +water mixture two distillation columns will be needed. Predominantly water will be removed as distillate from the first column. The 1-butanol will be recovered as distillate from the second column.

For the recovery of 1-pentanol from a 1-pentanol+n-pentylether+3-hexyl pentyl ether + water mixture two distillation columns will be needed. Once again predominantly water will be removed as distillate from the first column. The 1-pentanol will be recovered as distillate from the second column.

In the next chapter the results of a conceptual process design for the alcohol dehydration separation plant will be given.

7 CONCEPTUAL DESIGN OF A CLOSE-BOILING ALCOHOL SEPARATION PLANT

7.1 Introduction

In chapter 5 reaction conditions for the removal of secondary alcohols from a close-boiling primary and secondary alcohol mixture by dehydration of the secondary alcohol has been proposed. In chapter 6 the recovery and purification of the reaction products have been discussed. In this chapter a preliminary process design for the separation of a 85:15 1-butanol:2-Pentanol and a 85:15 1-pentanol:2-hexanol mixture will be discussed. Three conceptual designs will be evaluated. The processes were not optimised. The aim of this part of the study was only to determine whether the primary alcohol product can be purified theoretically and what the overall recoveries will be. The design basis, process description, mass balance and major equipment specification of the proposed processes will be given.

7.2 Conceptual design of a 1-butanol + 2-pentanol reaction separation plant, which produces only n-butylether as byproduct

7.2.1 Introduction

If 1-butanol and 2-pentanol are subjected to dehydration conditions, n-butylether and a mixed ether are formed. It could not be determined by analysis that the mixed ether that is formed is definitely 3-pentyl butyl ether. 3-Pentyl butyl ether is also not available commercially to obtain vapour liquid equilibrium data thereof. To eliminate the mixed ether from the reaction product, the dehydration reaction may be continued until all the mixed ether has also dehydrated. Then n-butylether will be present as the only ether byproduct. This first design will be performed using the experimental results of experiments 66 as design basis. About 4,5 % n-butylether is present as the only byproduct in the reaction product.

7.2.2 Design Basis

The 1-butanol + 2-pentanol separation plant producing only n-butylether as ether byproduct was designed to meet the following criteria:

- An alcohol feed mixture containing 85 % 1-butanol + 15 % 2-pentanol (mass %) was used.
- The catalyst system 90 % H_3PO_4 at an acid:alcohol ratio of 3:1 was used.
- After all the 2-pentanol and formed 3-pentanol is dehydrated the reaction will be allowed to continue until all the 3-pentyl butyl ether is also dehydrated and removed. The reaction time required is about 120 minutes.
- The reaction product composition is as follows:

Component	Amount
1-butanol	determined from mass balance
n-butylether	4,47 kg n-butylether / 100 kg 1-butanol fed in total to the reactor
water	amount in catalyst and reaction water formed
H_3PO_4	90 % H_3PO_4 at an acid:alcohol ratio of 3:1 at the inlet of the reactor

7.2.3 Process Description

A simplified process flow diagram for the removal of 2-pentanol from a 1-butanol+2-pentanol mixture and the purification of the primary alcohol is given in Figure 7.1. A mass balance for the process is given in Table 7.1. The mass balance was generated with PRO II. Details on the input and output files are presented in Appendix H1.

Fresh alcohol (85 % 1-butanol +15 % 2-pentanol) is mixed with the acid and water recycles (14) from the purification system. This mixture is fed to a batch reactor (R). Heat is supplied to the reactor. Steam may be used too as heat supply. Dehydration of the 2-pentanol to pentenes takes place in the reactor. The pentenes are removed continuously (4) from the reaction mixture. The vents are condensed and refluxed. The pentenes are removed by controlling the condenser exit temperature. After all the secondary alcohol and all the mixed ether (3-pentyl butyl ether) is dehydrated the reaction is quenched. The reaction mixture will contain only 1-butanol, n-butylether, water and H_3PO_4.

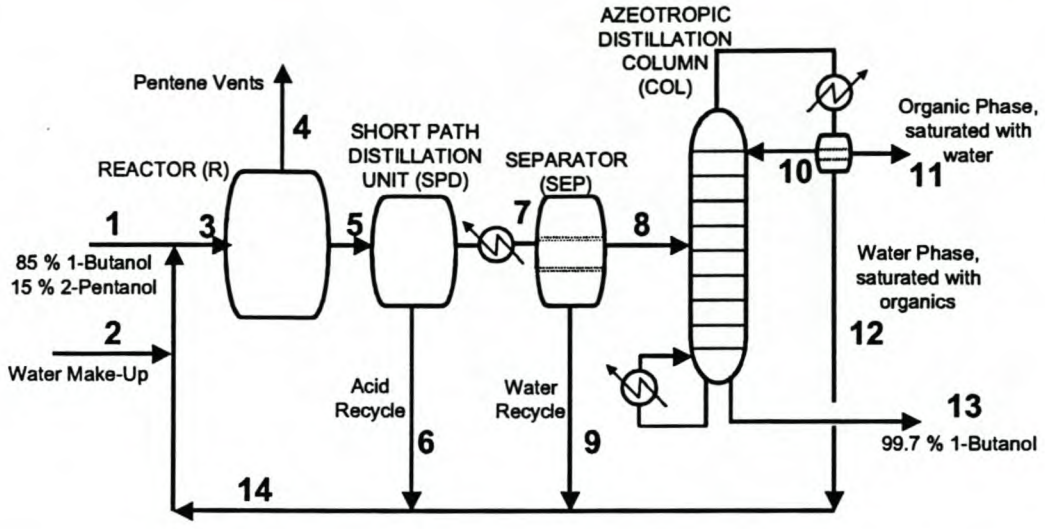


Figure 7.1: Schematic process flow diagram of a 1-butanol+2-pentanol separation plant; only n-butylether is formed as byproduct, 90 % H_3PO_4, acid:alcohol = 3:1, fresh alcohol feed = 85 % 1-butanol + 15 % 2-pentanol

The reaction mixture (5) is then fed to a short path distillation unit (SPD). The distillate (7) of the short path distillation unit contains only 1-butanol, n-butylether and water. The acid recycle stream (6) contains all the H_3PO_4 and some 1-butanol, n-butylether and water.

The distillate from the SPD is cooled and fed to a separator (SEP). In the separator an organic and a water phase are formed. The water phase is saturated with organics. The water phase is recycled (9) to the reactor. The organic phase (8) is fed to a distillation column (COL).

A ternary azeotrope between 1-butanol+n-butylether+water is formed in the top of the distillation column. The overheads of the column is condensed and allowed to separate. Once again an organic and a water phase are formed. Both phases are partly recycled to the top of the column (10). A part of each phase is also withdrawn. The withdrawn water phase (12) is recycled to the reactor. The organic phase contains the n-butylether and the 1-butanol that cannot be recovered (11). The bottoms of the azeotropic distillation column contains 99,7 % (mass) 1-butanol.

The recovery of 1-butanol is only 72 %. A major part of the 1-butanol is lost as part of the low-boiling azeotrope, namely 23 %. A substantial amount of 1-butanol is lost as n-butylether, namely 5 %.

Part of the water lost in the organic stream at the top of the column (11), has to be replaced. Reaction water and water present in the catalyst system is lost in this overhead stream. A water make-up stream at the inlet of the reactor replaces the lost water.

The 1-butanol recovery of the process as described above is very low. The low recoveries are caused by the azeotropes. Extractive distillation could be considered to break the azeotropes. With a suitable extractive agent, the ethers could be forced to the one side and the water+1-butanol to the other side. Extractive distillation would also be used to dry the 1-butanol.

Table 7.1 Mass balance of the 1-butanol+2-pentanol separation process that produces only n-butylether as byproduct

Stream	Mr	1	2	3	4	5	6	7
Description	g/mol	Fresh Alcohol Feed	Water Make-up	Total Reactor Inlet	Pentene Vents	Reactor liquid product	Acid Recycle	SPD Distillate
		mass %	mass %	mass %	mass %	mass %	mass %	mass %
1-Butanol	74	85	0	21.63	0	21.09	3.09	68.77
2-Pentanol	88	15	0	3.36	0	0	0	0
n-Butylether	130	0	0	0.05	0	1.045	0.064	3.64
Water	18	0	100	7.50	0	8.546	1.35	27.6
H3PO4	98	0	0	67.47	0	69.32	95.50	0
Pentene	70	0	0	0	70	0	0	0
Total	kg/h	2301	33	10275	275	10000	7259	2741
Temperature	°C	30	30	30	50	120 to 140	85	85
Pressure	kPa(a)	atm	atm	atm	atm	atm	10	10

Stream	8	9	10a	10b	11	12	13	14
	Column Feed	First Water Recycle	Organic Phase Recycle	Water Phase Recycle	Organic Overhead, Ether rich	Second Water Recycle	1-Butanol Product	Combined acid/water recycle
	mass %	mass %	mass %	mass %	mass %	mass %	mass %	mass %
1-Butanol	76.52	6.52	67.5	5.89	67.5	5.89	99.73	3.35
2-Pentanol	0	0	0	0	0	0	0	0
n-Butylether	4.09	0.036	14.6	0.1	14.6	0.1	0.27	0.06
Water	19.50	93.45	17.9	94.0	17.9	94.0	< 1 ppb	9.3
H3PO4	0	0	0	0	0	0	0	87.3
Total	2441	300	164	254	655	381	1405	7940
Temperature	30	30	30	30	30	30	72	30
Pressure	10	10	15	15	15	15	15	15

7.2.4 Specification of major equipment

The specifications of the major pieces of equipment are given in Table 7.2.

Table 7.2: Specification of major equipment

Batch Reactor	Short Path Distillation Unit	SPD Distillate Separator	Distillation Column	Distillation Column Overhead Separator
atmospheric pressure ~ 120 °C Reaction time ~ 120 minutes Volume = 15 m^3	10 kPa (abs.) 85 °C Heating Duty = 60 kW Condenser Duty = 1 MW	10 kPa (abs.) 30 °C Volume = 4 m^3 Residence time = 30 min	top pressure 15 kPa (abs.) 17 theoretical trays bottom temp. = 72 °C Reboiler Duty = 0,7 MW Condenser Duty = 0,6 MW Tray diameter = 1220 mm	15 kPa (abs.) 30 °C Volume = 4 m^3 Residence time = 30 min

7.3 Conceptual design of a 1-butanol + 2-pentanol reaction separation plant, which produces n-butylether and 2-pentyl ether as byproducts

7.3.1 Introduction

If 1-butanol and 2-pentanol are subjected to dehydration conditions, n-butylether and a mixed ether are formed. It is assumed that this mixed ether is 3-pentyl butyl ether (as discussed in paragraph 5.5). The following design is done assuming that the NRTL and UNIFAC parameters predict the vapour liquid equilibrium data of 3-pentyl butyl ether correctly. This second design will be done using the experimental results of experiment 73 as design basis.

7.3.2 Design Basis

The 1-butanol + 2-pentanol separation plant was designed to meet the following criteria:

- An alcohol feed mixture containing 85 % 1-butanol + 15 % 2-pentanol (mass %) was used.
- The catalyst system 90 % H_3PO_4 at an acid:alcohol ratio of 1,5:1 was used.
- The reaction is quenched after the secondary alcohol content (based on alcohols only) is reduced to < 0,1 mass %. The reaction time required is about 70 minutes.
- The reaction product composition is as follows:

Component	Amount
1-butanol	determined from mass balance
2-pentanol	0,57 % of the 2-pentanol fed to the reactor does not react
3-pentanol	included in the amount of 2-pentanol
n-butylether	0,916 % of the 1-butanol fed to the reactor is converted to n-butylether
3-pentyl butylether	3,83 % of the 2-pentanol fed to the reactor is converted to 3-pentyl butyl ether
water	amount in catalyst and reaction water formed
H_3PO_4	90 % H_3PO_4 at an acid:alcohol ratio of 1,5:1 at the inlet of the reactor

7.3.3 Process description

A schematic flow diagram of the 1-pentanol+2-hexanol separation plant is shown in Figure 7.2. A mass balance is given in Table 7.3.

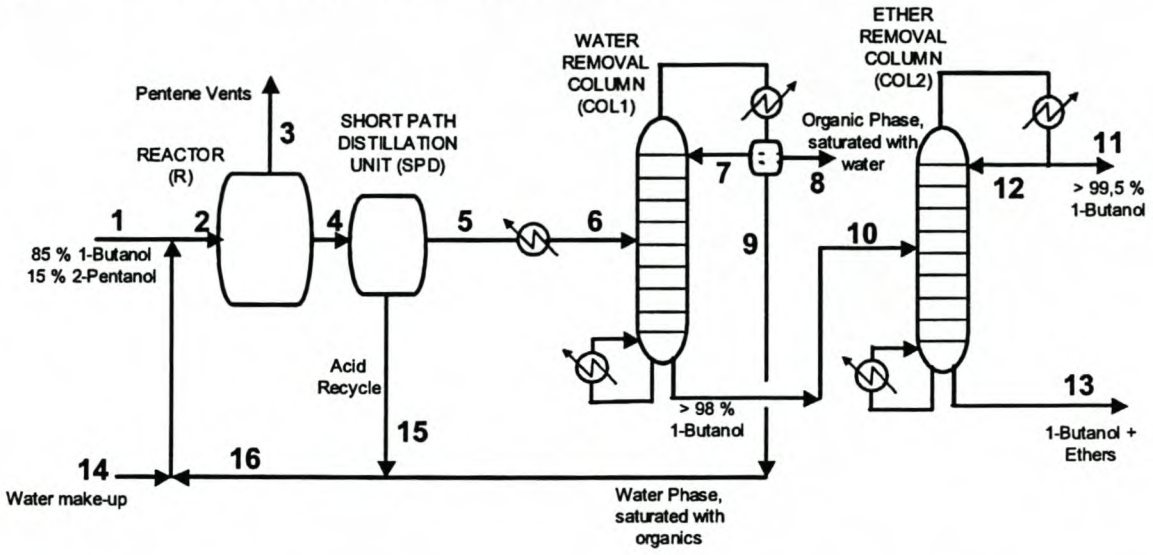


Figure 7.2: 1-Butanol + 2-Pentanol separation plant; ethers to be removed: n-butylether and 3-pentyl-butyl ether are formed as byproducts, 90 % H_3PO_4, acid:alcohol = 1,5:1, fresh alcohol feed = 85 % 1-butanol + 15 % 2-pentanol

The close-boiling alcohol mixture 1-butanol + 2-pentanol is fed (1) to a batch dehydration reactor (R). The H_3PO_4 concentration in the catalyst recycle stream (16) from the separation units is adjusted with water (14) to correct the acid strength. The recycled catalyst is also fed to the batch reactor (R). The reaction mixture is heated. The 2-pentanol is dehydrated to pentene. The reaction vents are cooled off to 580°C in a reflux condenser. The alcohols are refluxed to the reactor and the pentene vent (3) is routed to an external processing unit. After sufficient dehydration of the secondary alcohol the reaction mixture is rapidly cooled off. The reaction mixture (4) is fed to a short path distillation unit (SPD). In this unit all the H_3PO_4 is removed from the reaction product mixture. The acid-rich stream (16) is recycled to the reactor. The distillate (5) of the SPD is condensed and fed to the water and n-butylether removal column.

1-Butanol, water and n-butylether form a low boiling azeotrope. The water and n-butylether are thus removed as top product from the column (COL1). The column is operated under vacuum. The operating pressure is 20 kPa (abs.). The overheads is cooled off and separated. The water phase (9) is recycled to the reactor. The organic phase, which contains mainly 1-butanol, n-butylether and water is fed to a disposal unit.

The bottoms (10) of the first column contains > 98 % 1-Butanol. The main impurity is 3-pentyl-butyl ether, which is removed in a second distillation column (COL2). This second column produces 1-Butanol (11) with a purity of > 99,5 %. The recovery of the 1-butanol is only 72 %. A substantial amount of the 1-butanol (22 %) is lost as part of the low boiling azeotrope in column 1.

The second column is also operated under vacuum, at 15 kPa (abs.). The bottoms (13) of column 2 contains > 20 % 3-pentyl butyl ether.

As discussed in paragraph 7.3.3, extractive distillation should be considered to remove the ethers from the water and alcohol.

Table 7.3 Mass Balance for 1-Butanol+2-Pentanol separation process

Stream	Mr	1	2	3	4	5	6
Description	g/mol	Fresh Alcohol Feed mass %	Total Reactor Inlet mass %	Pentene Vented mass %	Reactor Liquid Product mass %	SPD Distillate mass %	Feed to Column 1 mass %
1-Butanol	74	85	34.44	0	35.44	81.15	81.15
2-Pentanol	88	15	5.55	0	0.033	0.0765	0.0765
n-Butylether	130	0	0.011	0	0.300	0.722	0.722
3-Pentyl-Butyleth	144	0	0.024	0	0.390	0.908	0.908
Water	18	0	6.0	0	7.480	17.14	17.14
H_3PO_4	98	0	54.0	0	56.36	0	0
Pentene	70	0	0	100	0	0	0
Total	kg/h	3859	10440	440	10000	4023	4023
Temperature	°C	30	30	50	about 130	85	30
Pressure	kPa(a)	atm	atm	atm	atm	10	25

Stream	7A	7B	8	9	10	11	12
Description	Organic Recylce to Column 1 mass %	Water Recycle o Column 1 mass %	Organic top product from Column 1 mass %	Water recycle to reactor mass %	Feed to Column 2 mass %	Top product of column 2, 1-Butanol mass %	Recycle to Column 2 mass %
1-Butanol	77.30	6.58	77.30	6.58	98.42	99.54	99.54
2-Pentanol	0.0725	< 50 ppm	0.0725	< 50 ppm	0.093	0.093	0.093
n-Butylether	2.685	0.0242	2.685	0.0242	0.22	0.23	0.23
3-Pentyl-Butylether	0.414	< 1 ppm	0.414	< 1 ppm	1.27	0.138	0.138
Water	19.53	93.4	19.53	93.4	< 50 ppm	< 50 ppm	< 50 ppm
H_3PO_4	0	0	0	0	0	0	0
Pentene	0	0	0	0	0	0	0
Total	866	557	866	557	2600	2470	9880
Temperature	30	30	30	30	78	30	30
Pressure	20	20	20	20	20	15	15

Stream	13	14	15	16
Description	Bottoms of Column 2, ether rich stream mass %	Water make-up mass %	Acid recycle from SPD mass %	Combined recycle before acid conc. correction mass %
1-Butanol	77.17	0	4.67	4.83
2-Pentanol	0.096	0	37 ppm	37 ppm
n-Butylether	<100ppm	0	0.0164	0.171
3-Pentyl-Butylether	22.73	0	0.0417	0.038
Water	< 1 ppb	100	0.979	8.86
H_3PO_4	0	0	94.29	86.25
Pentene	0	0	0	0
Total	130	47	5977	6534
Temperature	30	30	85	30
Pressure	15	100	10	10

7.3.4 Specification of major equipment

The specifications of the major pieces of equipment are given in Table 7.4.

Table 7.4: Specification of major equipment

Batch Reactor	Short Path Distillation Unit	Water and n-butylether removal column (COL1)
Operating pressure: atmospheric, 100 kPa (abs) Operating temperature about 120 °C Reaction time ~70 minutes Volume = 15 m^3	Operating Pressure 10 kPa (abs.) Operating Temperature 85 °C Heating Duty = 1,4 MW Condenser Duty = 1,2 MW	top pressure 20 kPa (abs.) 7 theoretical trays bottom temperature = 78 °C Condenser Duty = 1,3 MW Reboiler Duty = 1,4 MW Tray diameter = 1400 mm

3-Pentyl butyl ether removal column (COL2)	Distillation Column Overhead Separators
top pressure 15 kPa (abs.) 8 theoretical trays bottom temperature = 73 °C Condenser Duty = 2,6 MW Reboilier Duty = 2,5 MW Tray diameter = 2000 mm	same pressure as column; operating temperature 30 °C Column 1, volume = 4 m^3 Residence time = 30 min Column 2, volume = 7 m^3 Residence time = 15 min

7.4 Conceptual design of a 1-pentanol + 2-hexanol reaction separation plant

7.4.1 Introduction

If 1-pentanol and 2-hexanol are subjected to dehydration conditions, n-pentylether and two mixed ethers are formed. It is assumed that these mixed ethers are 3-hexyl pentyl ether and 2-hexyl pentyl ether. The following design is done assuming that the NRTL and UNIFAC parameters predict the vapour liquid equilibrium data of 3-pentyl butyl ether correctly. As mentioned in Chapter 6, 2 and 3 hexyl pentyl ether are the same as predicted by the thermodynamic group contribution method. This third design will be done using the experimental results of experiment 86 as design basis.

7.4.2 Design Basis

The 1-pentanol + 2-hexanol separation plant was designed to meet the following criteria:

- An alcohol feed mixture containing 85 % 1-pentanol + 15 % 2-hexanol was used (mass %).
- Catalyst system 90 % H_3PO_4 at an acid:alcohol ratio of 1.5:1.
- Reaction time > 35 minutes.
- The reaction is quenched after the secondary alcohol content (based on alcohols only) is reduced to < 0,1 mass %.

  96.511 % of the 2-hexanol fed to the reactor is dehydrated to hexene
- The reaction product composition is as follows:

Component	Amount
1-pentanol	determined from mass balance
2-hexanol	0,455 % of 2-hexanol fed to the reactor does not react
3-hexanol	included in the amount of 2-hexanol
n-pentylether	0,974 kg n-pentylether is formed per 100 kg of 1-pentanol fed to the reactor
2-hexyl pentyl ether	3,034 % of the 2-hexanol fed to the reactor is converted to 2-hexyl pentyl ether
3-hexyl pentylether,	included in the amount of 2-hexyl pentyl ether
water	amount in catalyst and reaction water formed
H_3PO_4	90 % H_3PO_4 at an acid:alcohol ratio of 1,5:1 at the inlet of the reactor

7.4.3 Process Description

A schematic flow diagram of the 1-pentanol+2-hexanol separation plant is shown in Figure 7.3. A mass balance is given in Table 7.5

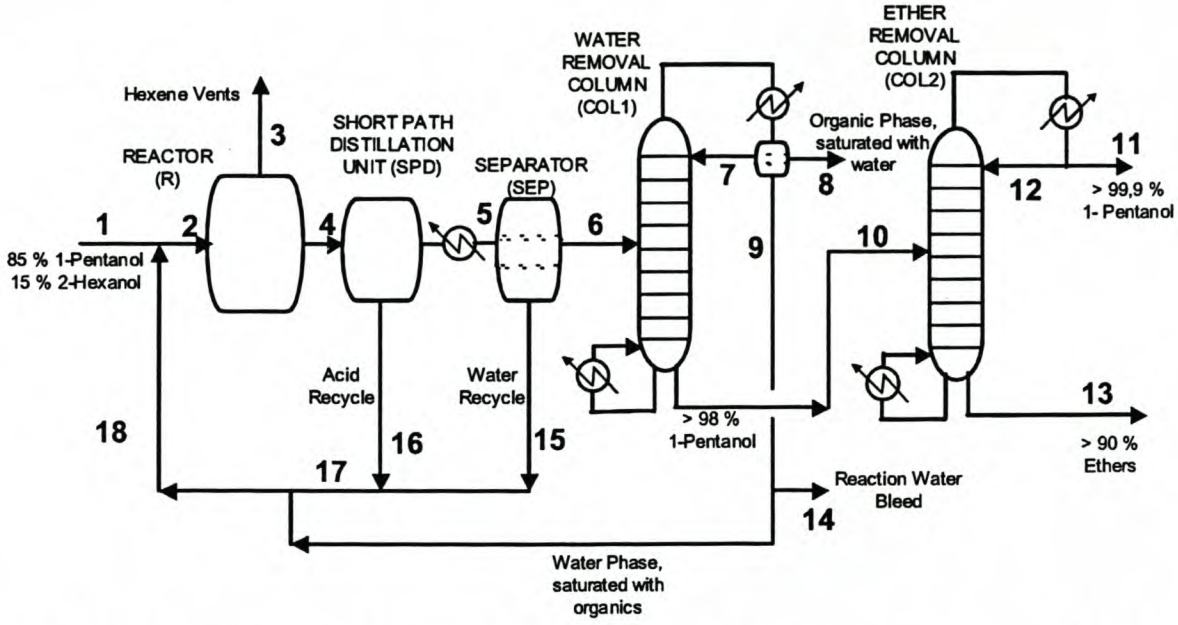


Figure 7.3: 1-Pentanol + 2-Hexanol separation plant, n-pentylether and 3-hexyl pentyl ether are formed as byproducts, 90 % H_3PO_4, acid:alcohol = 1,5:1, fresh alcohol feed = 85 % 1-pentanol + 15 % 2-hexanol

The fresh alcohol (1), organic recycle stream (8) and the catalyst recycle stream (18) is fed to the batch dehydration reactor (R). The reaction mixture is heated. The 2-hexanol is dehydrated to hexene. The reaction vents are cooled off to 80°C in a reflux condenser. The alcohols are refluxed to the reactor and the hexene vent (3) is routed to an external processing unit. After sufficient dehydration of the secondary alcohol the reaction mixture is rapidly cooled off. The reaction mixture (4) is fed to a short path distillation unit (SPD). In this unit all the H_3PO_4 is removed from the reaction product mixture. The acid-rich stream (16) is recycled to the reactor. The distillate (5) of the SPD is condensed and fed to a separator (SEP). In the separator an organic and a water phase are formed. The water phase (15) is recycled to the reactor. The organic phase (6) is fed to the water removal column (COL1).

Water and 1-Pentanol form a low boiling azeotrope. The water is thus removed as top product from the column (COL1). The column is operated under vacuum. The operating pressure is 20 kPa (abs.). The overheads is cooled off and separated. The major part of the water phase (9) is recycled to the reactor. The organic phase (8), which contains mainly 1-Pentanol and only very small amounts of ethers, is also recycled to the reactor.

The bottoms (10) of the first column contains > 97 % 1-Pentanol. The main impurities are ethers, which are removed in a second distillation column (COL2). This second column produces 1-Pentanol (11) with a purity of > 99,9 %. The recovery of the 1-pentanol is > 97 %. This second column is also operated under vacuum, at 15 kPa (abs.). The bottoms (13) of column 2 contains > 80 % ethers.

Table 7.5 Mass Balance for 1-Pentanol+2-Hexanol separation process

Stream	Mr	1	2	3	4	5	6
Description	g/mol	Fresh Alcohol Feed mass %	Total Reactor Inlet mass %	Hexene Vents mass %	Reactor Liquid Product mass %	SPD Distillate Condensed mass %	Separator Organic Phase mass %
1-Pentanol	88	85	34.88	0	35.81	81.64	88.48
2-Hexanol	102	15	5.07	0	0.024	0.055	0.060
n-Pentylether	158	0	0.08	0	0.433	0.994	1.08
2-Hex-Pent-Ether	172	0	0.04	0	0.313	0.712	0.77
Water	18	0	5.99	0	7.2126	16.60	9.61
H_3PO_4	98	0	53.94	0	56.201	0	0
Hexene	84	0	0	100	0	0	0
Total	kg/h	3518	10420	420	10000	4204	3873
Temperature	°C	30	30	80	about 150	110	30
Pressure	kPa (a)	atm	atm	atm	atm	10	25

Stream	7a	7b	8	9	10	11	12
Description	Organic Recylce to Col1 mass %	Water Recycle to Col1 mass %	Organic Top Product Col 1 mass %	Water from Col1- Recycle to Reactor mass %	Col1 Bottoms- Feed to Col2 mass %	1-Pentanol Product Stream mass %	Recycle to Col2 mass %
1-Pentanol	88.62	1.74	88.6	1.74	97.85	99.9	99.9
2-Hexanol	0.061	< 2 ppm	0.061	< 2 ppm	0.066	0.067	0.067
n-Pentylether	1.158	< 1 ppm	1.158	< 1 ppm	1.18	0.019	0.019
2-Hex-Pent-Ether	0.523	< 1 ppm	0.523	< 1 ppm	0.90	10 ppm	10 ppm
Water	9.63	98.3	9.63	98.3	< 5 ppm	5 ppm	5 ppm
H_3PO_4	0	0	0	0	0	0	0
Hexene	0	0	0	0	0	0	0
Total	548	325	548	325	3000	2925	11700
Temperature	30	30	30	30	95	30	30
Pressure	20	20	20	20	20	15	15

Stream	13	14	15	16	17	18
Description	Bottoms Col2 - Ether Rich mass %	Reaction Water Bleed from Col1 mass %	Water Recycle from SPD Separator mass %	Acid Recycle from SPD mass %	Total catalyst Recycle mass %	Catalyst + Organic Recycle mass %
1-Pentanol	17.41	1.74	1.74	2.6	2.50	9.345
2-Hexanol	0.039	< 2 ppm	< 2 ppm	15 ppm	14 ppm	0.0061
n-Pentylether	46.5	< 1 ppm	< 1 ppm	0.026	0.024	0.1141
2-Hex-Pent-Ether	36.0	< 1 ppm	< 1 ppm	0.024	0.022	0.0614
Water	< 1 ppb	98.3	98.3	0.403	9.0	9.048
H_3PO_4	0	0	0	97.0	88.5	81.43
Hexene	0	0	0	0	0	0
Total	75	99	331	5796	6354	6902
Temperature	101	30	30	110	30	30
Pressure	15	20	25	10	100	20

7.4.4 Specification of major equipment

Table 7.6: Specification of major equipment

Batch Reactor	Short Path Distillation Unit	SPD Downstream Separator
Operating pressure: atmospheric, 100 kPa (abs) Operating temperature about 140 °C Reaction time ~35 minutes Volume = 15 m^3	Operating Pressure 10 kPa (abs.) Operating Temperature 110 °C Heating Duty = 1,2 MW Condenser Duty = 1,5 MW	Operating Pressure 25 kPa (abs.) Operating Temperature 30 °C Volume = 3 m^3 Residence time = 30 min

Water removal column (COL1)	Ether removal column (COL2)	Distillation Column Overhead Separators
top pressure 20 kPa (abs.) 8 theoretical trays bottom temperature = 95 °C Reboiler Duty = 0,85 MW Condenser Duty = 0,7 MW Tray diameter = 1220 mm	top pressure 15 kPa (abs.) 17 theoretical trays bottom temperature = 101 °C Reboiler Duty = 2,8 MW Condenser Duty = 3,0 MW Tray diameter = 2300 mm	same pressure as column; operating temperature 30 °C Column 1, volume = 2 m^3 Residence time = 30 min Column 2, volume = 9 m^3 Residence time = 15 min

7.5 Conclusion

Thermal separation processes can be utilized to purify the alcohol product stream of the dehydration reactor.

The ethers are either removed as part of a low boiling azeotrope or as a high boiling component from the alcohol.

For the separation of 1-butanol+2-pentanol recoveries of ~ 70 % of the 1-butanol fed to the processing unit is expected. The 1-butanol product quality is > 99,5 %. A major part of the 1-butanol is lost as part of the low boiling 1-butanol+water+n-butylether azeotrope.

For the separation of 1-pentanol+2-hexanol recoveries of > 98 % of the 1-pentanol fed to the separation plant are expected. The 1-pentanol product quality is > 99,9 %. An even higher purity may be obtained if needed.

8 CONCLUSIONS AND RECOMMENDATIONS

The difference in chemical properties of primary and secondary alcohols may be utilized to separate the alcohols from each other. Specifically the separation of the alcohols in the mixtures 1-butanol+2-pentanol and 1-pentanol+2-hexanol were studied in this work.

Esterification

Primary and secondary alcohols esterify at similar rates. If they are esterified together, only mixed esters are formed. If the esters are separated into different cuts and if the cuts are hydrolysed, alcohol mixtures are formed as products. Esterification of close-boiling alcohols for their removal from each other can thus not be used for their separation.

Dehydration using solid catalysts

Selective dehydration of the secondary alcohols, by using solid resin catalysts in the liquid phase, could not be achieved. The catalysts Amberlyst 131 Wet, Amberlyst 15, Dowex MSC1 and Dowex Macroporous were used. The alcohol mixture 1-propanol+2-butanol and pure 2-pentanol were subjected to dehydration with resin catalyst. Very low dehydration of 2-butanol was achieved with Amberlyst 15 at a low alcohol:catalyst ratio. Very low dehydration of 2-pentanol was achieved with Amberlyst 131 Wet at a alcohol:catalyst ratio of 2,8:1

Further investigations should be conducted on solid catalysts. Gas phase dehydration and subsequent quenching off the organic stream, to achieve the removal of the alkenes, could be investigated.

Further research work is required especially in identifying or developing a solid catalyst that can be used for the liquid phase dehydration of the secondary alcohol. If the secondary alcohol is dehydrated in the liquid phase the temperature may be controlled so that the alkenes are flashed off during the reaction process. A fixed reactor bed could be used in a continuous application.

Dehydration in the liquid phase using liquid catalysts

The most promising results were found using acid catalysts in the liquid phase, i.e.:

- H_3PO_4 – excellent dehydration rates of secondary alcohols and low ether formation,
- H_2SO_4 – the secondary alcohol dehydration rate was low and the ether formation was unacceptably high,
- Oxalic acid – very low dehydration of the secondary alcohol and very high byproduct formation, and
- Potassiumhydrogensulphate – no secondary alcohol dehydration and extremely high byproduct formation.

H_3PO_4 proved to be the only liquid catalyst that could be used to achieve the aim of the dehydration separation process.

When H_3PO_4 is used as liquid catalyst the following reaction variables will influence the dehydration and ether formation rates:

- high acid concentrations – increase ether formation rate and secondary alcohol dehydration rate,
- high acid:alcohol ratio's - increase ether formation rate and secondary alcohol dehydration rate, however the effect is not as strong as the effect of acid concentration,
- amount of secondary alcohol in the feed – the dehydration rate is not very sensitive to the amount of secondary alcohol in the feed, the higher the secondary alcohol concentration, the higher the dehydration rate,
- amount of ether in feed – low amount of symmetrical ethers in the feed do not effect the dehydration and ether formation rate,
- alcohol systems – the secondary alcohol of the higher molecular weight alcohol system is dehydrated faster than the secondary alcohol of lower molecular weight close-boiling alcohol mixtures,
- low reaction pressure/temperature - definitely decreases the secondary alcohol dehydration rate, however no conclusion can be made on the effect of pressure on the ether formation rate, and
- nitrogen stripping – stripping increases the secondary alcohol dehydration rate and decreases the ether formation rate, however stripping will lead to lower primary alcohol recoveries.

A conceptual design for the dehydration separation process of the alcohol mixtures 1-butanol+2-pentanol and 1-pentanol+2-hexanol was done. The plants consisted of the following main units:

Reactor,
short path distillation unit,
separator, and
one or two distillation columns.

The azeotropic nature of the water/n-butylether/1-butanol mixtures influenced the primary alcohol recoveries to a great extent. The following theoretical primary alcohol recoveries were calculated:

Alcohol system	Ether formation	Primary Alcohol Quality mass %	Primary alcohol recovery
1-butanol +2-pentanol	only n-butylether	> 99,5 %	72 %
1-butanol +2-pentanol	n-butylether and 3-pentyl butyl ether	> 99,5 %	72 %
1-pentanol +2-hexanol	n-pentylether, 3-hexyl pentyl ether and 2-hexyl pentyl ether	> 99,9 %	> 98 %

A detail design and economic analysis was not done in this study.

The idea that the secondary alcohol may be removed by dehydration thereof was confirmed. Appropriate reaction conditions were identified and methods for the purification of the reaction products were recommended.

Further development work is recommended to achieve a continuous set-up using H_3PO_4 as catalyst for the selective dehydration of alcohols to enable their separation.

9 REFERENCES

1. Solomons, T.W.G., *Organic Chemistry*. Second ed. Solomons, T.W.G. 1980, New York: John Wiley & Sons. 63, 220&221, 640, 668&669,706.
2. Ericson, K.R.; van Wagenen, H.D., *Alcohols*, in *Kirk-Other, Encyclopedia of Chemical Technlogy, A to Aluminium*, F.M. Herman, Editor. 1963, Interscience Publishers, a division of John Wiley & Sons, Inc.: New York. p. 535-541.
3. Hahn, H.D.; Dämbkes, G.; Rupprich, N., *Butanols*, in *Ullmann's Encyclopedia of Industrial Chemistry*. 2001, Wiley-VCH Verlag GmbH: Weinheim, Germany.
4. Falbe, J.; Bahrmann, H.; Lipps, W., *Introduction to aliphatic alcohols*, in *Ullmann's Encylopedia of Industrial Chemistry*. 2001, Wiley-VCH Verlag GmbH: Weinheim.
5. Ancillotti, F., *Oxygenated fuels: Market expansion and catalytic aspect of synthesis.* Fuel Processing Technology, 1998, October. **57**(3): p. 163-194.
6. Moreira, J.R.; Goldemberg, J., *The alcohol program.* Energy Policy, 1999. Volume 27,(4): p. 229-245.
7. Anon, *Chemical Profile: n-Butanol*, in *Chemical Market Reporter*. 1999, . p. 41.
8. Anon, *Bulk prices of chemicals*, in *Chemical Marketing Reporter*. 2000, : United States of America.
9. De Guzman, D., *US Oxo Alcohols Market Plagued by Oversupply, Feedstock, Energy.* Chemical Market Reporter, 2001. 2001(January 29): p. 28.
10. Lappe, P.; Hofmann, T., *Pentanols*, in *Ullmann's Encyclopedia of Industrial Chemistry*. 2001, Wiley-VCH Verlag GmbH: Weinheim, Germany.
11. Gillette, L.A., *Amyl Alcohols*, in *Aluminium compounds to Azo Dyes*, H.F. Mark, Editor. 1967, John Wiley & Sons: New York. p. 374-379.
12. Anon, *Shell Chem Expands Detergent Aclohols, Builds New US Unit.* Chemical Market Reporter, 2001. January 1: p. 3.
13. Sasol, 2001/05/17, *Sasol Solvents Products, Oxo Alcohols, Tel.011-2800107, http://www.sasol.com.*
14. Cox, P. *SASOL: Aquisition of Condea, 11 December 2000.* http://www.sasol.com, 2000.
15. Anon, *Waarde toevoeging tot die lewe, Sasol Jaarverslag 2000.*
16. Markarian, J., *Chemical Feedstocks Face Downward Pricing.* Chemical Market Reporter, 2001. 259, January 22(4).
17. Bahrmann, H.; Bach, H., *Oxo Synthesis*, in *Ullmann's Encyclopedia of Industrial Chemistry*. 2001, Wiley-VCH Verlag GmbH: Weinheim, Germany.
18. Esterhuizen, F.J., *The separation of alcohols and water*, in *Final year project*, 2000, University of Stellenbosch, Department of Chemical Engineering: Stellenbosch.
19. Armit, J.W., ICI LTD, *Improvements in and relating to the purification of methanol and other alcohols of boiling point below 100 ^{O}C.*, in *www:ep.espacenet.com; European Patent Office*. 1931, GB346658, Great Brittain.
20. IG Farbenindustrie AG, *Process for the purification of alcohols obtained by the catalysed interaction of hydrogen with the oxides of carbon*, in *www:ep.espacenet.com; European Patent Office*. 1929, GB311468, Great Britain.

21. Wainwright, G.E.; Armit, J.W., ICI, *Improvements in and relating to the purification of alcohols*, in *www:ep.espacenet.com; European Patent Office*. 1931, GB350502, Great Britain.
22. IG Farbenindustrie AG, *Improvements in the purification of alcohols*, in *www:ep.espacenet.com; European Patent Office*. 1936, GB446305, Great Britain.
23. Seader, J.D.; Henley, E.J., *Separation Process Principles*. Seader, J.D.e.a. 1998, New York: John Wiley & Sons, Inc.
24. Berg, L., *Separation of n-propanol from 2-butanol by extractive distillation*, in *www:espacenet, European Patent Office*. 1987, US4715933, United States of America.
25. Wankat, P.C., *Introduction to complex distillatio methods*, in *Equilibrium Stages Separations*. 1988, Prentice Hall International (UK) Limited: London.
26. Berg, L., *Separation of 1-propanol from 2-butanol by extractive distillation*, in *www:espacenet.com, European Patent Office*. 1994, US5358608, United States of America.
27. Berg, L., *Separation of 1-butanol from 2-pentanol by extractive distillation*, in *www:espacenet.com, European Patent Office*. 1998, US5709781, United States of America.
28. Berg, L., *Separation of 1-butanol from 2-pentanol by extractive distillation*, in *www:espacenet.com, European Patent Office*. 1995, US5401366, United States of America.
29. Berg, L., *Separation of t-amyl alcohol from n-butanol by extractive distillation*, in *www:espacenet.com; European Patent Office*. 1999, US5961789, United States of America.
30. Berg, L.; Vosburgh, M.G., *Separation of isopropanol from t-butanol by extractive distillation*, in *www:espacenet.com, European Patent Office*. 1987, US4710275, United States of America.
31. Berg, L., *Separation of 2-methyl-1-butanol from 3-methyl-1-butanol by extractive distillation*, in *www:espacenet.com, European Patent Office*. 1997, US5658436, United States of America.
32. Berg, L., *Separation of 2-butanol from t-amyl alcohol by extractive distillation*, in *www:espacenet.com, European Patent Office*. 1994, US5360520, United States of America.
33. Berg, L., *Separation of 2-butanol from t-amyl alcohol by extractive distillation.*, in *www:espacenet.com, European Patent Office*. 1988, US4756803, United States of America.
34. Berg, L., *Separation of ethanol from isopropanol by extractive distillation*, in *www:ep.espacenet.com; European Patent Office*. 1987, US4710274, United States of America.
35. Berg, L., *Separation of ethanol from isopropanol by extractive distillation*, in *www:ep.espacenet.com; European Patent Office*. 1994, US5348625, United States of America.
36. Berg, L., *Separation of ethanol from isopropanol by extractive distillation*, in *www:ep.espacenet.com; European Patent Office*. 1995, US5445716, United States of America.

37. Berg, L.; Vosburgh, M.G., *Separation of ethanol from t-butanol by extractive distillation*, in *www:espacenet.com; European Patent Office*. 1988, US4732653, United States of America.
38. Berg, L., *Separation of 3-methyl-2-butanol from 1-butanol by extractive distillation*, in *www:espacenet.com, European Patent Office*. 1995, US5407540, United States of America.
39. Berg, L., *Separation of 1-propanol from t-amul alcohol by extractive distillation*, in *www:espacenet.com, European Patent Office*. 1998, US5772853, United States of America.
40. Berg, L. et al, *Separation of n-propanol from t-amyl alcohol by extractive distillation*, in *www:espacenet; European Patent Office*. 1990, US4935103, United States of America.
41. Berg, L. et al, *Separation of t-Amyl alcohol from isobutanol by extractive distillation*, in *European Patent Office, www: espacenet.com*. 1987, US4693787, United States of America.
42. Berg, L., *Separation of t-amyl alcohol from 2-methyl-1-propanol by extractive distillation*, in *www:espacenet.com; European Patent Office*. 1998, US5718809, United States of America.
43. Berg, L., *Separation of 3-methyl-2-butanol from 2-pentanol by extractive distillation.*, in *www:espacenet.com; European Patent Office*. 1995, US5417814, United States of America.
44. Berg, L., *Separation of 3-methyl-1-butanol from 1-pentanol by extractive distillation*, in *www:espacenet.com; European Patent Office*. 1998, US5763695, United States of America.
45. Berg, L., *Separation of 2-methyl-1-butanol and 3-methyl-1-butanol from 1-pentanol by extractive separation*, in *www: espacenet.com ; European Patent Office*. 2000, US6024841, United States of America.
46. Berg, L., *Separation of 2-butanol from isobutanol by extractive distillation*, in *www: espacenet.com; European Patent Office*. 1998, US5795447, United States of America.
47. Berg, L., *Separation of 2-methyl1-propanol from 2-butanol by extrative distillation*, in *www: espacenet.com; European Patent Office*. 1998, US5723025, United States of America.
48. Berg, L., *Separation of 2-methyl-butanol-1 from pentanol-1 by extractive distillation*, in *www:espacenet.com; European Patent Office*. 1990, US4969977, United States of America.
49. Berg, L., *Separation of 2-methyl-1-propanol from 1-butanol by extractive distillation*, in *www:espacenet.com; European Patent Office*. 1998, US5723024, United States of America.
50. Berg, L., *Separation of 2-methyl-1-propanol from 2-methyl-1-butanol by extractive distillation*, in *www: espacenet.com; European Patent Office*. 1998, US5738763, United States of America.
51. Berg, L., *Separation of 4-methyl-2-pentanol from 3-methyl-1-butanol by extractive distillation*, in *www: espacenet.com; European Patent Office*. 1998, US5851362, United States of America.

52. Standard Oil Development Company, *Improvements in or relating to the purification of alcohols by extractive distillation*, in *www:ep.espacenet.com; European Patent Office*. 1952, GB672433, Great Britain.
53. Standard Oil Development Company, *Purification of crude aliphatic alcohols by distillation*, in *www:ep.espacenet.com; European Patent Office*. 1951, GB663561, Great Britain.
54. Berg, L.; Yang, Z., *Separation of the propyl alcohols from water by azeotropic or extractive distillation*, in *www:ep.espacenet.com; European Patent Office*. 1992, US5085739, United States of America.
55. Berg, L.; Yang. Z., *Separation of tertiary butyl alcohol from water by azeotropic or extractive distillation*, in *www:ep.espacenet.com*. 1992, US5084142, United States of America.
56. ANON, BASF AG, *Separation of esters and alcohols*, in *www:ep.espacenet.com*. 1959, GB815774, Germany.
57. Berg, L.; Vosburgh, M.G.; *Separation of n-propanol from allyl alcohol by extractive distillation*, in *www:ep.espacenet.com; European Patent Office*. 1986, US4601791, United States of America.
58. Zudkevitch, D., *Extraction and /or extractive distillation of low molecular weight alcohols from aqueous solutions*, in *www:ep.espacenet.com; European Patent Office*. 1984, US4428798, United States of America.
59. Heitmann, W.; Strehlke, G.;Mayer, D., *Aliphatic Ethers*, in *Ullmann's Encyclopedia of Industrial Chemistry*. 2001, Wiley-VCH Verlag GmbH: Weinheim, Germany.
60. Perry R.H., Seader, J.D.; Zdzislaw, M.K., *Section 13: Distillation*, in *Perry's Chemical Engineers' Handbook*, D.W. Green, Editor. 1984, McGraw-Hill: New York.
61. Gmehling, J.,;Menke, J.; Krafczyk, J.; Fischer, K., *Azeotropic Data*. Part I&II. 1994, Weinheim: VCH.
62. Standard Oil Development Company, *Separation of close-boiling alcohols from aqueous liquid mixtures by distillation*, in *www:ep.espacenet.com; European Patent Office*. 1950, GB647903, Great Britain.
63. Berg, L., *Separation of 1-butanol from 2-pentanol by azeotropic distillation*, in *www: esp-espacenet*. 1995, US 5417813, United States of America.
64. Berg, L., *Separation of 1-amyl alcohol from n-butanol by azeotropic distillation*, in www: *ep.espacenet.com;* 1999, US5904815, United States of America.
65. Berg, L., *Separation of 3-methyl-2-butanol from 2-pentanol by azeotropic distillation*, in *www: ep.escapenet.com; European Patent Office*. 1995, US5439561, United States of America.
66. Berg, L., *Separation of 1-propanol from 2-butanol by azeotropic distillation*, in *www:ep.espacenet.com; European Patent Office*. 1994, US5332478, United States of America.
67. Berg, L., *Separation of 2-butanol from tert.amyl alcohol by azeotropic distillation*, in *www:ep.espacenet; European Patent Office*. 1998, US5759359, United States of America.
68. Berg, L., *Separation of 2-butanol from t-amyl alcohol y azeotropic distillation*, in *www:ep.espacenet.com; European Patent Office*. 1994, US5338410, United States of America.

69. Berg, L., *Separation of ethanol from isopropanol by azeotropic distillation*, in *www:ep.espacenet.com; European Patent Office*. 1994, US5338411, United States of America.
70. Berg, L., *Separation of ethanol from isopropanol by azeotropid distillation*, in *www:ep.espacenet.com; European Patent Office*. 1995, US5415741, United States of America.
71. Berg, L., *Separation of ethanol from isopropanol by azeotropic distillation*, in *www:ep.espacenet.com*. 1995, US5437770, United States of America.
72. Berg, L., *Separation of 3-methyl-2-butanol from 1-butanol by azeotropic distillation*, in *www:ep.espacenet.com; European Patent Office*. 1995, US5407542, United States of America.
73. Berg, L., *Separation of t-amyl alcohol from 1-propanol by azeotropic distillation*, in *www:ep.espacenet.com; European Patent Office*. 1998, US5776321, United States of America.
74. Berg, L., *Separation of t-amyl alcohol from 2-methyl-1-propanol by azeotropic distillation*, in *www:ep.espacenet.com; European Patent Office*. 1998, US5738764, United States of America.
75. Berg, L., *Separation of t-amyl alcohol from 2-methyl-1-propanol azeotropic distillation*, in *www:ep.espacenet.com; European Patent Office*. 1999, US5908538, United States of America.
76. Berg, L., *Separation of 3-methyl-2-butanol from 2-pentanol by azeotropic distillation*, in *www:ep.espacenet.com; European Patent Office*. 1995, US5407541, United States of America.
77. Berg, L., *Separation of 2-pentanol, 3-methyl-2-butanol and 1-butanol by azeotropic distillation*, in *www:ep.espacenet.com; European Patent Office*. 1995, US5447608, United States of America.
78. Berg, L., *Separation of 2-methyl-1-butanol and 3-methyl-1-butanol from 1-pentanol by azeotropic distillation*, in *www:ep.espacenet.com; European Patent Office*. 1998, US5779862, United States of America.
79. Berg, L., *Separation of 2-methyl-1-propanol from 2-butanol by azeotropic distillation*, in *www:ep.espacenet.com; European Patent Office*. 1997, US5658435, United States of America.
80. Berg, L., *Separation of 2-methyl-1-propanol from 1-butanol by azeotropic distillation*, in *www:ep.espacenet.com; European Patent Office*. 1998, US5716499, United States of America.
81. Berg, L., *Separation of 2-methyl-1-propanol from 2-methyl-1-butanol by azeotropic distillation*, in *www:ep.espacenet.com; European Patent Office*. 1997, US5645695, United States of America.
82. Berg, L., *Separation of 4-methyl-2-pentanol from 3-methyl-1-butanol by azeotropic distillation*, in *www:ep.espacenet.com; European Patent Office*. 1998, US5776322, United States of America.
83. IG Farbenindustrie AG, *Improvements in the separation of propyl ether from mixtures of the same with propyl alcohol*, in *www:ep.espacenet.com; European Patent Office*. 1936, GB444117, Great Britain.

84. Standard Oil Development Company, *Purification of crude aliphatic alcohols by distillation*, in *www:ep.espacenet.com; European Patent Office*. 1952, GB673768, Great Britain.
85. ESSO, *Purification of Alcohols*, in *www:ep.espacenet.com; European Patent Office*. 1961, GB874583, Great Britain.
86. ICI, *Improvements in and relating to the separation of hydrocarbons from alcohols by azeotropic distillation*, in *www:ep.espacenet.com; European Patent Office*. 1952, GB678166, Great Britain.
87. British Celanese, *Purifying aliphatic alcohols by azeotropic distillation*, in *www:ep.espacenet.com; European Patent Office*. 1952, GB667134, Great Britain.
88. British Celanese, *Purifying propyl alcohols by azeotropic distillation*, in *www:ep.espacenet.com; European Patent Office*. 1951, GB662608, Great Britain.
89. ICI Ltd., *Improvements in and relating to the separation of alcohols*, in *www:ep.espacenet.com; European Patent Office*. 1959, GB815091, Great Britain.
90. ICI Ltd., *Separation of ethers from distillation residues of synthetic alcohols*, in *www:ep.espacenet.com; European Patent Office*. 1965, GB981943, Great Britain.
91. Phillips Petroleum Co., *Separation of hydrocarbon and alcohol azeotropic mixtures by distillation with anhydrous ammonia*, in *www:ep.espacenet.com*. 1984, US4437941, United States of America.
92. Sridhar, S. Huels Chemische Werke AG, *Process for the separation of mixtures of paraffin or respectively paraffins of 6-14 carbon atoms and alcohol or respectively alcohols of 4-8 carbon atoms.*, in *www:ep.espacenet.com; European Patent Office*. 1987, US4652343, United States of America.
93. Leupold, E.I., *Process for the extractive separation of an alcohol-ester mixture*, in *www:ep.espacnet.com; European Patent Office*. 1984, EP0125575, Europe.
94. Hoechst AG, *Process for the separating of enol ethers from reaction mixtures containing alcohols*, in *www:ep.espacenet.com; European Patent Office*. 1991, US50134444, United States of America.
95. Levy, S., *Solvent extraction of alcohols from water solutions with fluorocarbon solvents*, in *www:ep.espacenet.com; European Patent Office*. 1981, US4260836, United States of America.
96. Bright, J.H., *Extraction of alcohols with phospine oxides*, in *www:ep.espacenet.com; European Patent Office*. 1985, US4544779, United States of America.
97. IG Farbenindustrie AG, *Improvements in the purification of alcohols*, in *www:ep.espacenet.com; European Patent Office*. 1938, GB494985, Great Britain.
98. Continental Oil Comapny, *Purification of alcohols*, in *Purification of alcohols*. 1963, GB923464, Great Britain.
99. Ruhrchemie AG, *Process for the separation of aliphatic alcohols from hydrocarbon alcohol mixtures*, in *www:ep.espacenet.com; European Patent Office*. 1953, GB688747, Great Britain.
100. Kaufmann, A.A., *Improved process for the separation of alcohols and phenols from mixtures*, in *www:ep.espacenet.com; European Patent Office*. 1931, GB359953, Great Britain.

101. Ruhrchemie AG, *Process for the separation of alcohols from mixtures with other organic components*, in *www:ep.espacenet.com; European Patent Office*. 1954, GB705601, Great Britain.
102. Boaz, N.W. Eastman Kodak Co., *Method for purification of alcohols*, in *www:ep.espacenet.com; European Patent Office*. 1994, US5312950, United States of America.
103. Standard Oil Development Co., *Improvements in or relating to the purification of alcohols*, in *www:ep.espacenet.com; European Patent Office*. 1954, GB716423, Great Britain.
104. Union Carbide Corp., *Improvements in and relating to the purification of alcohols by distillation*, in *www:ep.espacenet.com; European Patent Office*. 1963, GB919487, Great Britain.
105. Carey, F.A., *Organic Chemistry*. International Edition ed. Carey, F.A. 1996, New York: McGraw-Hill.
106. Continental Oil Company, *Verfahren zur reinigung von hoehermolekularen aliphatischen Alkoholen*, in *www:ep.espacenet; European Patent Office*. 1961, Auslegeschrift: 1 157 208, Germany.
107. Deutsche Erdoel, *Verfahren zur Reinigung synthetisch hergestellter primaerer Monoalkohole*, in *www:ep.espacenet; European Patent Office*. 1970, Offenlegungsschrift 1568415, Germany.
108. Leach, B.; Motz K., Continental Oil, *Purification of Ziegler Alcohols*, in *www:ep.espacenet.com; European Patent Office*. 1974, US3855320, United States of America.
109. Jayadeokar, S.S.; Sharma M.M., *Separation of close boiling alcohols through selective etherification with isobutylene: use of ion exchage resins as catalysts.* Reactive polymers, 1993. **21**: p. 37-43.
110. Kuraray, K.K., *Separation of straight-chain alcohol from oxoalcoholmixture*, in *www:ep.espacenet.com; European Patent Office*. 1983, JP58216133, Japan.
111. Ehime Univ., *Separation of Alcohol*, in *www:ep.espacenet.com; European Patent Office*. 1987, JP62019543, Japan.
112. Standard Oil Development Company, *Purification of alcohols by distillation*, in *www:ep.espacenet.com; European Patent Office*. 1952, GB672635, Great Britain.
113. Hickman, K.C.D., *Vacuum Distillation Apparatus*, in *www:ep.espacenet.com; European Patent Office*. 1939, US2,180,050, United States of America.
114. Fauser, F.; Fischer, W.; Leybold Heaeus GMBH & Co KG, *Method and apparatus for short-path distillation*, in *www:ep.espacenet.com; European Patent Office*. 1985, US4517057, United States of America.
115. Johannisbauer, W.; Jeromin, L.; Nitsche, M.; Henkel KGAA, *Process for the separation of alcohols by distillation*, in *www:ep.espacenet.com; European Patent Office*. 1998, US5710261, United States of America.
116. Matsumoto, H., *Separation of alcohols by adsorption*, in *www:ep.espacenet.com; European Patent Office*. 1983, JP58216132, Japan.
117. Bertram, E.V.B.; Distillers Co Yeast Ltd.; Howlett, J., *Purification of alcohols*, in *www:ep.espacenet.com; European Patent Office*. 1949, GB626279, Great Britain.

118. Bataafsche Petroleum, *Process for the purification of alcohols*, in *www:ep.espacenet.com; European Patent Office*. 1953, GB687380, Great Britain.
119. Idemitsu, P.C.L., *Separation of water/alcohol mixture by supercritical fluid*, in *www:ep.espacenet.com; European Patent Office*. 1987, JP62155908, Japan.
120. Mitsubishi Chem Ind Ltd; Ishii Toshikazu, *Separation of alcohol in organic compound solution*, in *www:ep.espacenet.com; European Patent Office*. 1987, JP62186944, Japan.
121. Union, C.C., *Bulk separation of polyhydric alcohols by selective adsorption on zeolitic molecular sieves.*, in *www:ep.espacenet.com; European Patent Office*. 1984, US4456774, United States of America.
122. Atlantic, R.C., *Separation of isopropyl alcohol from tertiary butyl alcohol by selective adsorption*, in *www:ep.espacenet.com; European Patent Office*. 1985, US4543432, United States of America.
123. Carbone AG, *Process for the separation of C_1-C_3 alcohols from mixtures of these alcohols with other organic liquids*, in *www:ep/espacenet.com; European Patent Office*. 1994, EP0593011, Europe.
124. Agency of Industrial Science&Technology, *Film separation and concentrating method for alcohol aqueous solution*, in *www:ep.espacenet.com; European Patent Office*. 1995, JP7000777, Japan.
125. Exxon Research Engineering Co., *Separation of water/alcohol(s) mixtures*, in *www:ep.espacenet.com; European Patent Office*. 1994, GB2271992, Great Britain.
126. Tsugita Takashi; Takeuchi Shinya; Doi Koichi; Kishimoto Fumito; Tokuyama Soda KK; Katokichi Co Ltd , *Membrane for separation of water-alcohol mixed liquid and process for preparation thereof.*, in *www:ep.espacenet.com; European Patent Office*. 1990, EP0369787, Europe.
127. Osaka City, *Alcohol Separation Method by Pervaporation*, in *www:ep.espacenet.com*. 1997, JP9299764, Japan.
128. Exxon Research Engineering Co., *Separation of alcohol from alcohol/ether/olefin/non-linear hydrocarbon mixtures using polyester or polyester copolymer membranes*, in *www:ep.espacenet.com; European Patent Office*. 1994, US5294344, United States of America.
129. UBE Industries, *Pervaporation process for separating a lower alcohol compound from a mixture of a lower alcohol compound and an ether compound*, in *www:ep.espacenet.com; European Patent Office*. 1991, JP3284334, Japan.
130. UBE Industries Ltd., *Separation of lower alcohol*, in *www:ep.espacenet.com; European Patent Office*. 1992, JP4016213, Japan.
131. Huels Chemische Werke AG, *Process for the separation of low molecular weight alcohols from aqeous solutions*, in *www:ep.espacenet.com; European Patent Office*. 1988, EP0253091, Europe.
132. Rolls Royce, *Process and apparatus for increasing the concentration of alcohol in aqueous solution*, in *www:ep.espacenet,com; European Patent Office*. 1983, GB2088357, Great Britain.
133. Batelle Memorial Institute, *Separation and concentration of lower alcohols from dilute aqueous solutions*, in *www:ep.espacenet.com; European Patent Office*. 1991, US5028240, United States of America.

134. Deutsche Erdoel AG, *Improvements in and relating to the purification of fatty alcohols*, in *www:ep.espacenet.com; European Patent Office*. 1964, GB964649, Great Britain.
135. Henkel &CIE GMBH, *Process for separation of mixtures of high molecular synthetic alcohols into components of different melting point*, in *www:ep.espacenet.com; European Patent Office*. 1953, GB698217, Great Britain.
136. BASF AG, *Improvements in the separation of mixtures of isobutyl and methyl alcohols*, in *www:ep.espacenet.com; European Patent Office*. 1953, GB685904, Great Britain.
137. Brotherton, R.J., *Boron Compounds (Boric Acid Esters)*, in *Blood, Coagulants and anticoagulants to cardiovascular agents*, Mark, H.F. et. al. , Editor. 1978, John Wiley & Sons: New York. p. 111 - 123.
138. Henecka, H., *Säure -Basen-Katalyse*, in *Allgemeine Chemische Methoden*. 1967 (Nachdruck), Georg Thieme Verlag: Stuttgart. p. 14-15.
139. Askani, R., *Abspaltung von Wasser aus Alkoholen in der Dampfphase*, in *Olefine*. 1972, Georg Thieme Verlag: Stuttgart. p. 45-77.
140. Schaumann, E., *Umwandlung durch Elimininierungsreaktionen*, in *Alkohole III*. 1984, Georg Thieme Verlag: Stuttgart. p. 939-940.
141. Hesse, G., *Katalyse über komplexe Kationen und Anionen*, in *Allgemeine Chemische Methoden*. 1967 (Nachdruck), Georg Thieme Verlag: Stuttgart. p. 111-112.
142. Lurie, A.P., *Ethers*, . 1963, John Wiley & Sons. p. 470-498.
143. Stefanidakis, G.; Gwyn, J.E., *Alkylation*, in *Additives to Alpha*, W.A.C. John J. Mcketta, Editor. 1977, Marcel Dekker, Inc.: New York and Basel. p. 403,404.
144. Faber, K., *Alkohole (Allgemein)*, 2001.
145. Ehlers, K.P. *Reinigung von Naβphosphorsäuren* in *Berichte der Bunsen-Gesellschaft für Physikalische Chemie*, 83, 1979, p. 1113-1116, Verlag Chemie, D-6940 Weinheim.

Appendix A - DATA FROM LITERATURE

Table A-1: Physical Properties of Monohydroxy Alcohols at atmospheric pressure

Compound	Name	Melting Point [°C]	Boiling Point [°C]	Specific Gravity [g/cm^3 at 20°C]	Water solubility [g/100g H_2O]
CH_3OH	Methanol	-97	64.7	0.792	∞
CH_3CH_2OH	Ethanol	-114	78.3	0.789	∞
$CH_3CH_2CH_2OH$	1-Propanol	-126	97.2	0.804	∞
$CH_3CH(OH)CH_3$	2-Propanol	-88	82.3	0.786	∞
$CH_3CH_2CH_2CH_2CH_2OH$	1-Butanol	-90	117.7	0.810	7.9
$CH_3CH(CH_3)CH_2OH$	2-Methyl-1-Propanol	-108	108	0.802	10.0
$CH_3CH_2CH(OH)CH_3$	2-Butanol	-114	99.5	0.808	12.5
$(CH_3)_3COH$	ter-Butanol	25	82.5	0.789	∞
$CH_3(CH_2)_3CH_2OH$	1-Pentanol	-78.5	138	0.817	2.4
$CH_3(CH_2)_2CH(OH)CH_3$	2-Pentanol	-	119.9	0.809	
$CH_3CH_2CH(OH)CH_2CH_3$	3-Pentanol		115.3		
$(CH_3)_2C(OH)CH_2CH_3$	ter-amyl alcohol	-8.6	102.4	0.809	
$CH_3CH(CH_3)CH_2CH_2OH$	3-methyl-1-butanol	-117,2	130,6		
$CH_3CH_2CH(CH_3)CH_2OH$	2-methyl-1-butanol		128,7		
$CH_3CH(CH_3)CH(OH)CH_3$	3-methyl-2-butanol		111.5		
$CH_3(CH_2)_4CH_2OH$	1-Hexanol	-52	156.5	0.819	0.6
$CH_3(CH_2)_3CH(OH)CH_3$	2-Hexanol		139.9		
$CH_3(CH_2)_2CH(OH)CH_2CH_3$	3-Hexanol		135.5		
$CH_3CH(CH_3)CH_2CH(OH)CH_3$	4-methyl-2-pentanol		131.7		
$CH_3(CH_2)_5CH_2OH$	1-Heptanol	-34	176	0.822	0.2
$CH_3(CH_2)_4CH(OH)CH_3$	2-Heptanol	-	157	0.817	
$(CH_3CH_2CH_2)_2CHOH$	4-Heptanol	-41.5	155	0.818	

[1], Perry, PRO II

Appendix B - APPENDIX B – LIST OF EXPERIMENTS

Table B1 – List of esterification experiments

Experiment	Feed	Entrainer	Boric Acid
1	1-propanol and boric acid	Cyclohexane	Stoichiometric
2	2-butanol and boric acid.	Cyclohexane	Stoichiometric
3	1-Propanol, 2-butanol and boric acid	Cyclohexane	Stoichiometric
4	1-Propanol, 2-butanol and boric acid	Dipe	15 %
5	1-Propanol, 2-butanol and boric acid	Dipe	50 %

Table B2 – List of dehydration experiments

Experiment Number	Comment	Alcohol Feed	Catalyst	Catalyst: Alcohol
01, 2-Butanol		100 % 2-Butanol	67 % H_2SO_4	1:2
02, 2-Butanol		100 % 2-Butanol	67 % H_2SO_4	1:2
01, 1-Propanol		100 % 1-Propanol	67 % H_2SO_4	1:2
02, 1-Propanol		100 % 1-Propanol	67 % H_2SO_4	1:2
01, Blank		100 % 1-Propanol	None	
03, 2-Butanol		100 % 2-Butanol	67 % H_2SO_4	1:2
04A,B,C,D	Alcohol distilled from acid	85 % 1-Propanol 15 % 2-Butanol	80 % H_2SO_4	Varied
05A,B	Alcohol distilled from acid	85 % 1-Propanol 15 % 2-Butanol	67 % H_2SO_4	Varied
06A,B	Alcohol distilled from acid	85 % 1-Propanol 15 % 2-Butanol	55 % H_2SO_4	Varied
G	Packed Column	85 % 1-Propanol 15 % 2-Butanol	Resin	
R0,R1,R2,R3, R4	Batch, Different Resins	85 % 1-Propanol 15 % 2-Butanol	Resins	
11A,B,D	Alcohol distilled from acid	85 % 1-Propanol 15 % 2-Butanol	Varied % H_3PO_4	Varied
12A,C,D	Alcohol distilled from acid	85 % 1-Propanol 15 % 2-Butanol	88 % H_3PO_4	Varied
13D	Alcohol distilled from acid	85 % 1-Propanol 15 % 2-Butanol	Oxalic Acid	1,1:1
13C	Alcohol distilled from acid	85 % 1-Propanol 15 % 2-Butanol	$NaHSO_4$	1,3:1
14A,B	Alcohol distilled from acid	85 % 1-Propanol 15 % 2-Butanol	85 % H_3PO_4	2,2:1
14C,D	Alcohol distilled from acid	85 % 1-Propanol 15 % 2-Butanol	55 % H_2SO_4	2,2:1
15A,B	Time Varied	85 % 1-Propanol 15 % 2-Butanol	88 % H_3PO_4	2,2:1
16	Ether Production, Alcohol distilled from acid	85 % 1-Propanol 15 % 2-Butanol	87 % H_3PO_4	3,2:1
17	Tridecane added, Alcohol distilled from acid	85 % 1-Propanol 15 % 2-Butanol	88 % H_3PO_4	varied
19B	Alcohol distilled from acid	100 % 2-Butanol	88 % H_3PO_4	
19A,C,D	Time varied	100 % 1-Propanol	88 % H_3PO_4	2,3:1
30A,B,C,D	Alcohol distilled from acid	85 % 1-Butanol 15 % 2-Pentanol	varied % H_3PO_4	2,1:1
31A,B,C,D	Reaction Time varied Alcohol distilled from acid	85 % 1-Butanol 15 % 2-Pentanol	85 % H_3PO_4	2,16:1
32A,B	Alcohol distilled from acid	85 % 1-Butanol 15 % 2-Pentanol	85 % H_3PO_4	varied

33	33A – Na_2CO_3 33B-Alcohol distilled from acid	85 % 1-Butanol 15 % 2-Pentanol	85 % H_3PO_4	2,15:1
36	Short Path Distillation used to recovery the alcohol	85 % 1-Butanol 15 % 2-Pentanol	85 % H_3PO_4	2,15:1
51	Short Path Distillation used to recovery the alcohol	85 % 1-Propanol 15 % 2-Butanol	88 % H_3PO_4	2,15:1
53	Reaction Mix. neutr. $NaHCO_3$	100% 2-Pentanol	90 % H_3PO_4	2,1:1
55	Reaction Mix. neutr. $NaHCO_3$	100% 1-Butanol	90 % H_3PO_4	2,16:1
60	Continuous	85% 1-Propanol 15 % 2-Butanol	88 % H_3PO_4	N.A.
62	Reaction Mix. neutr. $NaHCO_3$	85 % 1-Butanol 15 % 2-Pentanol	85 % H_3PO_4	2,16:1
63	Reaction Mix. neutr. $NaHCO_3$	85 % 1-Butanol 15 % 2-Pentanol	90 % H_3PO_4	2,17:1
64	Reaction Mix. neutr. $NaHCO_3$	85 % 1-Butanol 15 % 2-Pentanol	92.1 % H_3PO_4	2,12:1
65	Reaction Mix. neutr. $NaHCO_3$	85 % 1-Butanol 15 % 2-Pentanol	80 % H_3PO_4	2.16:1
66	Reaction Mix. neutr. $NaHCO_3$	85 % 1-Butanol 15 % 2-Pentanol	90 % H_3PO_4	3:1
67	Reaction Mix. neutr. $NaHCO_3$	85 % 1-Butanol 15 % 2-Pentanol	80 % H_3PO_4	3:1
68	Reaction Mix. neutr. $NaHCO_3$	85 % 1-Butanol 15 % 2-Pentanol	85 % H_3PO_4	3:1
69	Reaction Mix. neutr. $NaHCO_3$	85 % 1-Butanol 15 % 2-Pentanol	85 % H_3PO_4	1.5:1
70	Short Path Distillation used to recovery the alcohol	85 % 1-Pentanol 15 % 2-Hexanol	85 % H_3PO_4	2.15:1
72	Reaction Mix. neutr. $NaHCO_3$	85 % 1-Butanol 15 % 2-Pentanol	80 % H_3PO_4	1.5:1
73	Reaction Mix. neutr. $NaHCO_3$	85 % 1-Butanol 15 % 2-Pentanol	90 % H_3PO_4	1.5:1
75	Reaction Mix. neutr. $NaHCO_3$ Condensor Temperature = 65 °C, too low.	85 % 1-Pentanol 15 % 2-Hexanol	85 % H_3PO_4	2.17:1
76	Reaction Mix. neutr. $NaHCO_3$	85 % 1-Propanol 15 % 2-Butanol	85 % H_3PO_4	2.14:1
77	Reaction Mix. neutr. $NaHCO_3$	85 % 1-Pentanol 15 % 2-Hexanol	85 % H_3PO_4	2.16:1
79	Reaction Mix. neutr. $NaHCO_3$	85 % 1-Pentanol 15 % 2-Hexanol	90 % H_3PO_4	3:1
80	Reaction Mix. neutr. $NaHCO_3$	85 % 1-Pentanol 15 % 2-Hexanol	80 % H_3PO_4	1.5:1
81	Reaction Mix. neutr. $NaHCO_3$	85 % 1-Pentanol 15 % 2-Hexanol	85 % H_3PO_4	1.5:1
82	Reaction Mix. neutr. $NaHCO_3$	85 % 1-Pentanol 15 % 2-Hexanol	85 % H_3PO_4	2:1
83	Reaction Mix. neutr. $NaHCO_3$	85 % 1-Pentanol 15 % 2-Hexanol	90 % H_3PO_4	2.19:1
84	Reaction Mix. neutr. $NaHCO_3$	85 % 1-Pentanol 15 % 2-Hexanol	80 % H_3PO_4	3:1

86	Reaction Mix. neutr. $NaHCO_3$	85 % 1-Pentanol 15 % 2-Hexanol	90 % H_3PO_4	1.5:1
87	Reaction Mix. neutr. $NaHCO_3$	85 % 1-Pentanol 15 % 2-Hexanol	80 % H_3PO_4	2.17:1
88	Reaction Mix. neutr. $NaHCO_3$, N_2 flow low.	85 % 1-Pentanol 15 % 2-Hexanol	85 % H_3PO_4	2.18:1
89	Reaction Mix. Neutr. $NaHCO_3$, Repetition Exp.63.	85 % 1-Butanol 15 % 2-Pentanol	90 % H_3PO_4	2.15:1
90	Reaction Mix. Neutr. $NaHCO_3$	85 % 1-Butanol 15 % 2-Pentanol	55 % H_2SO_4	0.48:1
91	Reaction Mix. Neutr. $NaHCO_3$	85 % 1-Butanol 15 % 2-Pentanol + ether in feed	90 % H_3PO_4	2.16:1
92	Reaction Mix. Neutr. $NaHCO_3$	85 % 1-Butanol 15 % 2-Pentanol	67 % H_2SO_4	0.65:1
93	Reaction Mix. Neutr. $NaHCO_3$, N_2 very low	85 % 1-Butanol 15 % 2-Pentanol	90 % H_3PO_4	2.2:1
94	Reaction Mix. Neutr. $NaHCO_3$,N_2 very high	85 % 1-Butanol 15 % 2-Pentanol	90 % H_3PO_4	2.15:1
95	Reaction Mix. Neutr. $NaHCO_3$ Dipe extraction	85 % 1-Butanol 15 % 2-Pentanol	90 % H_3PO_4	2.16:1
96	Reaction Mix. Neutr. $NaHCO_3$	50 % 1-Butanol 50 % 2-Pentanol	90 % H_3PO_4	2.18:1
97	Reaction Mix. Neutr. $NaHCO_3$	100 % 2-Hexanol	90 % H_3PO_4	2.16:1
98	Reaction Mix. Neutr. $NaHCO_3$	100 % 1-Pentanol	90 % H_3PO_4	2.16:1
99	Reaction Mix. Neutr. $NaHCO_3$, Vacuum	85 % 1-Butanol 15 % 2-Pentanol	90 % H_3PO_4	2.16:1
100	Reaction Mix. neutr. $NaHCO_3$, Vacuum	85 % 1-Pentanol 15 % 2-Hexanol	90 % H_3PO_4	2.16:1

Appendix C - Esterification experiments: Original data and results

Appendix C: Experiment 1 – Esterification of 1-propanol with boric acid.

Reaction Mixture			
Component	Mass [grams]		
Cyclohexane	71.4		
1-Propanol	150.7		
Boric Acid	51.4		
Total Mass	273.5		
Water expected if reaction is completed	44.9 grams		
Time	Total reaction water removed [grams]	Time [min]	Temperature [deg C]
10:21 – On	0		26
10:29 – Starts Boiling	0	0	74.5
10:41	6	12	75.5
10:49	11.2	20	76.5
10:58	16.5	29	77.5
11:17	26.3	48	80
11:36	35.5	67	83
12:12	48.1	103	91.5
12:28	50.1	119	98
12:55	51.7	146	102
13:02	51.7	153	103
13:21 Turn off	No further water removed	172	166
Total Cyclohexane removed		85.6 grams	
Highest Temperature reached		172 °C	
Products	Mass [grams]		
Water	51.7		
Cyclohexane	85.6		
Ester and boric acid	131.1		
Total	268.4		
Losses	273.5-268.4=5.1 grams		
% Losses	2%		

Appendix C: Experiment 2 - Esterification of 2-butanol with boric acid.

Reaction Mixture			
Component	Mass [grams]		
Cyclohexane	73.4		
2-Butanol	185.6		
Boric Acid	51.4		
Total Mass	310.6		
Water expected if reaction is completed	44.9 grams		
Time	Total reaction water removed [grams]	Time [min]	Temperature [deg C]
10:21 – On	0		26
10:31 – Starts Boiling	0	0	78.5
10:39	5	7	79.5
10:47	9.5	15	80.5
10:56	11.6	24	82
11:05	19.3	33	83
11:36	32.8	64	87.5
12:29	45.1	117	99.5
12:50	46.1	148	102.5
Total Cyclohexane removed		86.7 grams	
Highest Temperature reached		185 °C	
Products	Mass [grams]		
Water	46.1		
Cyclohexane	86.7		
Ester and boric acid	176.4		
Total	309.2		
Losses	310.6-309.2=1.2 grams		
% Losses	< 1%		

Appendix C: Experiment 3 - Esterification of 1-propanol+2-butanol with boric acid.

Reaction Mixture Component	Mass [grams]	
Cyclohexane	488.2	
1-Propanol	362.3	
2-Butanol	447.1	
Boric Acid	247.2	
Total Mass	1545.0	
Water expected if reaction is completed		216 grams

Procedure: A batch distillation column with a 6 litre round flask was used as reactor system. The reaction mixture starts boiling t 72 °C. After 8 hours the temperature in the round ball flask was 83 °C and in total 223,6 grams reaction water was removed. Thereafter 479.9 grams of cyclohexane was distilled-off. The liquid temperature was increased to 115 °C. The remaining liquid in the vessel was 774,4 grams, which was mainly esters, however included some of the hexane.

Vacuum Distillation to separate boric acid esters:

Pressure	Temperature	Top Temperature	Reflux Ratio	
mmbar (a)	°C	°C		
500	164	52	10:1	48.5 gram, remaining Hexane, column flooded, not analysed
300-380	153	130	15:1	Cut 1: 238.3 grams
309	155-160	130	15:1	Cut 2: 144.6 grams
304	160	132	15:1	Cut 3: 59.8 grams
320	170	132	15:1	Cut 4: 62.2 grams
330	174	132	15:1	Cut 5: 149.7 grams

Hydrolysis of each cut

Cut	Size [gram]	Water added [grams]	
1	Not weighed	58	The mixtures were heated, cooled, filtered and analysed.
2	144.6	50	
3	59.8	20	
4	62.2	20.2	
5	149.2	53.4	

Cut	2-Butanol [mass %]	1-Propanol [mass %]
1	69.6	30.4
2	40.4	59.6
3	17.7	82.3
4	32.1	67.9
5	81.7	18.3

The amount of reaction water formed > expected. The reaction water formed is saturated with solvent and alcohol, which is included in the mass.

Appendix C: Experiment 4 - Esterification of 1-propanol + 2-butanol with 15 % boric acid according to stoichiometric ratio.

Reaction Mixture	
Component	Mass [grams]
Dipe	101.2
1-Propanol	90.4
2-Butanol	16
Boric Acid	5
Total Mass	212.6
Water expected if reaction is completed: 4.4 grams	
Total reaction water formed: 3.7 grams Temperature increased to 140 °C. 181.7 grams dipe removed. Hydrolysis: 14 grams water added. Reaction mixture heated, cooled, filtered and analysed.	

Experiment 5 - Esterification of 1-propanol + 2-butanol with 50 % boric acid according to stoichiometric ratio.

Reaction Mixture	
Component	Mass [grams]
Dipe	102.5
1-Propanol	90.2
2-Butanol	16.6
Boric Acid	15.7
Total Mass	225.0
Water expected if reaction is completed: 12.6 grams	
Total reaction water formed: 3.7 grams Temperature increased to 160 °C. 165.5 grams dipe removed Hydrolysis: 17 grams water added Reaction mixture heated, cooled, filtered and analysed.	

Appendix D - Original Readings of Dehydration Experiments

Appendix D: Original readings of experiments 01, 02 and 03

Description: Comparison of dehydration rate of 1-propanol and 2-butanol
Feed system: 100 % either 1-Propanol or 2-Butanol; 67 % H_2SO_4
Acid:Alcohol 1:2

Experiment Number	Time [min]	Mass Loss [grams]
01:A,2-Butanol	31	1.6
01:B,2-Butanol	73	5.2
01:F,2-Butanol	43	3.8
01:G,2-Butanol	20	1.5
01:E,2-Butanol	132	15.2
01:H,2-Butanol	303	65.2 (ignored)
01:I ,2-Butanol	192	18.5
01:C,2-Butanol	408	35.3
02:A,2-Butanol	245	18.7
02:B,2-Butanol	352	30.8
03:A,2-Butanol	165	16.4
01:B, 1-Propanol	91	0.6
01:E, 1-Propanol	372	1.2
01:C, 1-Propanol	377	0.4
02:C, 1-Propanol	273	2.3
02:D, 1-Propanol	355	1.9
01:A, Blank, 1-Propanol only heated under reflux , no acid added	423	0,7 grams of 100,2 grams

Appendix D: Original readings of experiments 04,05 and 06

Alcohol Feed: 1-Propanol and 2-Butanol ; Catalyst: Sulpuric Acid, strength varied as indicated
Acid/Aclohol: Varied as indicated
Reaction Pressure: Atmospheric
Reaction Time: 120 minutes to 127 minutes
Comments: After a reaction time of 120 minutes elapsed, the mixture was allowed to cool off to about 80 °C. This was done so that the glassware could be handled. The remaining alcohol was then distilled off. During the distillation the alcohol reacted further, until it was completely removed from the catalyst.

Experiments	Sulphuric Acid Strength	H_2SO_4 mass [grams]	H_2O mass [grams]	1-Propanol mass [grams]	2-Butanol mass [grams]	acid/ alcohol ratio	Reaction Time (minutes)	Distillate mass [gram]
04:A	80 %	12.48	3.12	85	15	0.15:1		78.4
04:B	80 %	36.48	9.1	85.2	15	0.45:1		?
04:C	80 %	40.4	10.1	84.9	15	0.5:1		65
04:D	80 %	82.1	20.5	87.2	15.4	1:1		37
05:A	67 %	68.1	33.6	86.6	15.3	1:1	120	59.8
05:B	67 %	33.7	16.6	85.8	15.1	0.5:1	120	84.3
06:A	55 %	82.8	67.7	84.9	15	1.5:1	127	79.0
06:B	55 %	140.0	114.6	86.7	15.3	2.5:1	127	70.7

Appendix D: Experiments 7 to 10, Resins

Exp. No.	Resin	Alcohol Feed	Alcohol (gram)	Water (gram)	Resin (gram)	Reaction Time (minutes)	Weight loss (gram)	Comments
7	Dowex Macroporous	85 % 1-Propanol 15% 2-Butanol	1000	250	Pack.	Cont.	N/A	
8A	Amberlyst 131 Wet	85 % 1-Propanol 15% 2-Butanol	68	34.1	10.7	120	2.7	
8B	Dowex Macroporous	85 % 1-Propanol 15% 2-Butanol	67.2	33.6	10.2	120	2.4	
8C	Dowex 50wx8-100	85 % 1-Propanol 15% 2-Butanol	67.1	33.6	10.2	120	3.4	
8D	Amberlyst 15	85 % 1-Propanol 15% 2-Butanol	67.1	33.5	10	120	not weighed	Reacts vigorously
8E	Amberlyst 131 Wet	85 % 1-Propanol 15% 2-Butanol	80	4.3	10.7	180	1.1	
8F	Dowex Macroporous	85 % 1-Propanol 15% 2-Butanol	87.1	4.8	10.2	180	1.1	
8G	Dowex 50wx8-100	85 % 1-Propanol 15% 2-Butanol	80	4.4	10.2	180	1	
8H	Amberlyst 15	85 % 1-Propanol 15% 2-Butanol	85.2	5.2	10	180	1.5	
8I	Amberlyst 131 Wet	85 % 1-Propanol 15% 2-Butanol	99.1	5.4	10.7	120	0.9	
8J	Dowex Macroporous	85 % 1-Propanol 15% 2-Butanol	100	6	10.2	120	0.8	
8K	Dowex 50wx8-100	85 % 1-Propanol 15% 2-Butanol	100	5.9	10.2	120	0.6	Starts boiling at 40 °C, reacts vigorously
8L	Amberlyst 15	85 % 1-Propanol 15% 2-Butanol	101.4	6.3	10	120	1.7	Starts boiling at 40 °C, reacts vigorously
9A	Amberlyst 131 Wet	100 % 2-Pentanol	29.7	4.9	10.7	120	3.3	
9B	Dowex Macroporous	100 % 2-Pentanol	29.4	4.6	10.2	120	0.8	
9C	Dowex 50wx8-100	100 % 2-Pentanol	53.5	5.4	10.2	120	0.6	
9D	Amberlyst 15	100 % 2-Pentanol	59.1	11.7	10	120	not weighed	Boil-over. Gas sample only air.
10A	Amberlyst 131 Wet	85 % 1-Propanol 15% 2-Butanol	46.7	5.6	40.7	150	0.8	
10B	Amberlyst 15	85 % 1-Propanol 15% 2-Butanol	80.9	7.4	39.7	90	3.2	Mixture heats slightly. spontaneously

Appendix D: Experiments 11 to 15

Exp. No.	Alcohol Feed	Acid	Feed (gram)		Acid:Alc. Reaction Time (minutes)	Weight Loss Distill. Bottoms Temp. Comments
11A	85 % 1-Propanol 15% 2-Butanol	55 % H_3PO_4	Alcohol Water Acid	100.8 56.8 46.4	1:1 175 min.	0 gram Temperature not logged
11B	85 % 1-Propanol 15% 2-Butanol	72 % H_3PO_4	Alcohol Water Acid	100.4 28.8 73.2	1:1 160 min.	0.1 gram Temperature not logged
11D	85 % 1-Propanol 15% 2-Butanol	88 % H_3PO_4	Alcohol Water Acid	99.6 19.5 142.7	1,6:1 150 min.	28.7 gram 128 °C Acid left: Slightly yellow
12A	85 % 1-Propanol 15% 2-Butanol	88 % H_3PO_4	Alcohol Water Acid	107.7 17.1 125.2	1,3:1 120 min.	2.4 gram 140 °C
12C	85 % 1-Propanol 15% 2-Butanol	88 % H_3PO_4	Alcohol Water Acid	136.4 13.7 100.5	0,84:1 120 min.	0.7 gram Temperature not logged
12D	85 % 1-Propanol 15% 2-Butanol	88 % H_3PO_4	Alcohol Water Acid	79.4 21.2 155.5	2,2:1 120 min.	10.7 gram 120 °C
13D	85 % 1-Propanol 15% 2-Butanol	94,7 % Oxalic Acid	Alcohol Water Acid	101.7 5.9 105.1	1,1:1 60 min.	0.7 gram 105 °C
13C	85 % 1-Propanol 15% 2-Butanol	93,5 % $NaHSO_4$	Alcohol Water Acid	85.6 7.3 103.7	1,3:1 120 min.	3.4 gram 95 °C Mixture discoloured to black, possible coking
14A	85 % 1-Propanol 15% 2-Butanol	85 % H_3PO_4	Alcohol Water Acid	109.9 36.3 205.9	2,2:1 120 min.	7.1 gram 140 °C
14B	85 % 1-Propanol 15% 2-Butanol	85 % H_3PO_4	Alcohol Water Acid	110.3 36.4 206.2	2,2:1 120 min.	8.9 gram 140 °C 14A&B distillate combined for fractionation
14C	85 % 1-Propanol 15% 2-Butanol	55 % H_2SO_4	Alcohol Water Acid	110.1 123.7 151.1	2,5:1 120 min.	12 gram 120 °C
14D	85 % 1-Propanol 15% 2-Butanol	55 % H_2SO_4	Alcohol Water Acid	109.9 124.2 151.8	2,5:1 120 min.	not weighed 120 °C 14C&D distillate combined for fractionation
15A	85 % 1-Propanol 15% 2-Butanol	88 % H_3PO_4	Alcohol Water Acid	110 29.3 207.8	2,16:1 90 min.	10.1 gram 140 °C
15B	85 % 1-Propanol 15% 2-Butanol	88 % H_3PO_4	Alcohol Water Acid	110.4 28.4 208	2,14:1 150 min.	12.9 gram 140 °C

Appendix D: Original readings of experiment 16

Exp. No.	Alcohol Feed	Acid	Feed (gram)		Acid:Alc. Reaction Time (minutes)	Weight Loss Distill. Bottoms Temp. Comments (grams)
16	85 % 1-Propanol 15% 2-Butanol	87 % H_3PO_4	Alcohol Water Acid	1000 417 2800	3,2:1 390 min.	not weighed Top Temp. = 100 °C Distillate fractionated

Fractionation of Distillate of Experiment 16

Exp. No.	Alcohol Feed Mixture	Comments		
16	85 % 1-Propanol 15% 2-Butanol	The lowest steady state top temperature, at total reflux, was 60 °C. A reflux ratio of 200:1 was used. The temperature increased gradually from 60 to 68 °C. Therafter the temperature increased very slowly.		
	Distillate: 870.1 gram	Cut	Temperature oC	Grams
		1	60	8.1
		2	64	10.5
		3	66	9.1
		4	66	16.3
		5	67	17.1
		6	68	14
		7	68	15.7
		8	68	14.9
		9	68	16.21
		10	68	55.6
		11	69.5	55.3
		12	72	29.57
		13	73	31.82
		14	74	38.78
		15	76	33.2
		16	78	13.35
		17	80	10.16
		18	82	29.6
		19A	84	15.25
		19B	85	13.82
		20	86	13.7
		21	86	11.89
		22	86	8.66
		23	86	14
		24	87	16.68
		25	87	13.37
		26	87	12.73
		Remaining Reaction Distillate was separated in a funnel:		
		27A	20	Oily Layer
		27B	not weighed, about 200 gram	Alcohol Layer

Appendix D: Experiments 17 to 19

Exp. No.	Alcohol Feed	Acid	Feed (gram)		Acid:Alc. Reaction Time (minutes)	Weight Loss Distill. Bottoms Temp. Comments (grams)
17A	85 % 1-Propanol 15% 2-Butanol	88 % H_3PO_4	Alcohol Water Acid Tridecane	88.8 22.7 166.6 88.8	2,13:1 120 min.	8.1 195 °C Distillate forms two phases. Top =67 g and Bottom = 31 g.
17B	85 % 1-Propanol 15% 2-Butanol	88 % H_3PO_4	Alcohol Water Acid Tridecane	45.3 22.6 166 88.8	4,2:1 45 min.	4.2 gram 180 °C
19A	100 % 1-Propanol	88 % H_3PO_4	Alcohol Water Acid	30.4 8.3 62.7	2,3:1 120 min.	0 gram 110 °C (not in liquid)
19B	100 % 2-Butanol	88 % H_3PO_4	Alcohol Water Acid	30.6 8.3 62.3	2,3:1 35 min.	22.5 gram Temperature not logged
19C	100 % 1-Propanol	88 % H_3PO_4	Alcohol Water Acid	30.4 8.3 62.7	2,3:1 180 min.	0 gram 110 °C (not in liquid)
19D	100 % 1-Propanol	88 % H_3PO_4	Alcohol Water Acid	30.4 8.3 62.7	2,3:1 60 min.	0 gram 114 °C (not in liquid)

Appendix D: Original readings of Experiment 30A, B, C and D.

Experiment Number	30A	30B	30C	30D
Alcohol Feed	85% 1-Butanol 15% 2-Pentanol	85% 1-Butanol 15% 2-Pentanol	85% 1-Butanol 15% 2-Pentanol	85% 1-Butanol 15% 2-Pentanol
Catalyst	50 % H_3PO_4	85 % H_3PO_4	75 % H_3PO_4	80 % H_3PO_4
Alcohol [gram]	110.1	110.2	110	109.9
Acid [gram]	236.3	236.1	237	236.5
Acid:Alcohol	2,1:1	2,1:1	2,15:1	2,15:1
Condensor Temperature [°C]	50	50	50	50
Reaction Time [minutes]	120	120	120	120
Boiling Temperature	98	118	108	108 to 114
Mass Loss [gram]	0.6	13.3	2.6	8.6
Distillation from acid				
TBottom (not in liquid) [°C]	135	150	140	130
Phases	Two	Two	Two	Two
Organic [gram]	120.6	93.1	112.0	100.2
Water [gram]	78.5	20.4	41.0	25.0
Vent collected in 1-Propanol				
[gram]	0.0	8.6	0.4	not weighed
Distillate, Organic Sample				
Organic Product [gram]	2.228	2.441	2.945	1.963
Methanol for dilution [gram]	1.456	1.089	0.926	1.352

Appendix D: Original readings of Experiment 31A, B, C and D.

Experiment Number	31A	31B	31C	31D
Alcohol Feed	85% 1-Butanol 15% 2-Pentanol	85% 1-Butanol 15% 2-Pentanol	85% 1-Butanol 15% 2-Pentanol	85% 1-Butanol 15% 2-Pentanol
Catalyst	85 % H_3PO_4	85 % H_3PO_4	85 % H_3PO_4	85 % H_3PO_4
Alcohol [gram]	110.1	109.8	110.2	110.1
Acid [gram]	236.5	237.8	239.8	237.4
Acid:Alcohol	2,15:1	2,17:1	2,18:1	2.16:1
Condensor Temperature [°C]	50	50	50	50
Reaction Time [minutes]	90	60	150	30
Boiling Temperature	120	120	not logged	120
Mass Loss [gram]	13.1	10.8	13.8	9.2
Distillation from acid				
TBottom (not in liquid) [°C]	150	150	175	161
Phases	Two	Two	Two	Two
Organic [gram]	94.0	93.4	94.9	94.6
Water [gram]	19.1	20.4	23.1	20.6
Distillate, Organic Sample				
Organic Product [gram]	1.918	1.509	1.841	1.857
Methanol for dilution [gram]	1.698	1.795	1.676	1.724

Appendix D: Original readings of Experiment 32

Experiment Number	32A	32B
Alcohol Feed	85% 1-Butanol 15% 2-Pentanol	85% 1-Butanol 15% 2-Pentanol
Catalyst	85 % H_3PO_4	85 % H_3PO_4
Alcohol [gram]	109.8	109.9
Acid [gram]	440.3	111.9
Acid:Alcohol	4:1	1:1
Condensor Temperature [°C]	50	50
Reaction Time [minutes]	120	120
Boiling Temperature [°C]	123 to 130	97 to 111
Mass Loss [gram]	15.8	2.7
Distillation from acid		
TBottom (not in liquid) [°C]	160	160
Phases	Two	Two
Organic [gram]	82.3	102.8
Water [gram]	23.8	5.0
Distillate, Organic Sample		
Organic Product [gram]	1.865	1.654
Methanol for dilution [gram]	1.599	1.265

Appendix D: Experiment 33 - Original readings

Experiment Number	33	
Alcohol Feed	85% 1-Butanol and 15% 2-Pentanol	
Catalyst	85 % H_3PO_4	
Alcohol [gram]	110	
Acid [gram]	236.1	
Acid:Alcohol	2,15:1	
Condensor Temperature [°C]	50	
Reaction Time [minutes]	120	
Boiling Temperature [°C]	121	
Mass Loss [gram]	13.2	
	A	B
	26 gram Na_2CO_3 added to 166,5 gram reaction mixture before batch distillation	166,5 gram reaction mixture distilled by batch distillation
Distillation from acid		
Tbottom (not in liquid) [°C]	Not logged	180
Phases	Two	Two
Organic [gram]	45.5	44.7
Water [gram]	4.0	10.8
Distillate, Organic Sample		
Organic Product [gram]	2.581	2.356
Methanol for dilution [gram]	1.152	1.510

Appendix D: Experiment 36 - Original readings

Experiment Number	36A	36B
Alcohol Feed	85% 1-Butanol 15% 2-Pentanol	85% 1-Butanol 15% 2-Pentanol
Catalyst	85 % H_3PO_4	85 % H_3PO_4
Alcohol [gram]	110.7	110.7
Acid [gram]	236	236.2
Acid:Alcohol	2,15:1	2,15:1
Condensor Temperature [°C]	50	50
Reaction Time [minutes]	120	120
Boiling Temperature	121	121
Mass Loss [gram]	13.6	13.3
Distillation from acid Add Reaction Mixture together and feed to Short Path Distillation Unit		
	Cut 1	Cut 2
Pressure [bar abs]	0.091	0.11
Heating Temperature [oC]	84	100
Mass [gram]	91.6	49.2
Distillate, Organic Sample		
Organic Product [gram]	1.612	1.955
Methanol for dilution [gram]	1.839	1.165
	Total Distillate	
Phases	Two	
Organic [gram]	109.1	
Water [gram]	21.6	
Remaining Acid and Reaction Mixture after Short Path Distillation =		
	486.8 gram	

Appendix D: Experiment 51 - Original readings

Experiment Number	51A	51B
Alcohol Feed	85% 1-Propanol 15% 2-Butanol	85% 1-Propanol 15% 2-Butanol
Catalyst	88 % H_3PO_4	88 % H_3PO_4
Alcohol [gram]	110.2	110.3
Acid [gram]	236	236.2
Acid:Alcohol	2,14:1	2,16:1
Condensor Temperature [°C]	40	40
Reaction Time [minutes]	125	120
Boiling Temperature [°C]	118	117
Mass Loss [gram]	12.2	12.6
	Distillation from acid	
Add Reaction Mixture together and feed to Short Path Distillation Unit		
Pressure [bar abs]	0,091 to 0,12	
Heating Temperature [°C]	80 to 93	
Mass [gram]	153.6	
Distillate, Organic Sample		
Organic Product [gram]	2.013	
Methanol for dilution [gram]	1.620	
	Distillate	
Phases	One	
Remaining Acid and Reaction Mixture after Short Path Distillation		
	496.6 gram	

Appendix D: Experiment 53 - Original readings and analysis.

Alcohol Feed: 100 % 2-Pentanol; Catalyst: 90 % H_3PO_4
Mass: Alcohol 108.7 grams; 90 % H_3PO_4 ; 223.8 grams
Acid:Alcohol = 2.1:1
Reaction Pressure Atmospheric
Comments: The condenser temperature was maintained at 50.5 °C. The nitrogen flow through sampling system was low. After about 25 minutes the reaction mixture became milky white.

Sample Number	FEED	A	B	C	D	E	F
Time (minutes)	0	2	7.3	15.5	20.5	27.8	1200 Standing, not heated after 28 minutes
Component		Mass %, dry basis					
3-Pentanol	0.000	0.000	0.000	6.266	10.067		0.000
2-Pentanol	100.000	99.612	98.571	89.944	85.443		0.000
Byproduct A (RT=23.14)	0.000	0.287	1.065	2.804	3.327	too diluted, not	70.033
Byproduct B (RT=23.34)	0.000	0.101	0.365	0.986	1.163	detected	29.967
Alcohols Only							
3-Pentanol	0.000	0.000	0.000	6.513	10.540		0.000
2-Pentanol	100.000	100.000	100.000	93.487	89.460		0.000

Appendix D: Experiment 55 - Original readings and analysis.

Alcohol Feed: 100 % 1-Butanol
Catalyst: 90 % H_3PO_4
Mass: Alcohol = 109.4 grams
90 % H_3PO_4 = 236.5 grams
Acid:Alcohol = 2.16:1

Reaction Pressure Atmospheric

Comments: The condenser temperature was maintained at 50.5 °C. The nitrogen flow through sampling system was low.

	Feed	55A	55B	55C	55G	55H	55I
Time (minutes)	0	15	34.5	47.3	219.5	327.4	1311
Component			Mass %, dry basis				
1-Butanol	100	99.577	99.234	98.967	96.079	93.543	80.408
n-Butylether	0	0.423	0.766	1.033	3.921	6.457	19.592

Appendix D: Experiment 62 - Original readings and results.

Alcohol Feed: 85 % 1-Butanol and 15 % 2-Pentanol; Catalyst: 85 % H_3PO_4
Mass: Alcohol Mixture = 157.6 grams; 85 % H_3PO_4 = 341.3 grams
Acid/Alcohol = 2,16:1
Reaction Pressure Atmospheric
Comments: The nitrogen flow through the sample point was low, but could have been altered to flush the sample point. The acid was heated to about 80 °C, before the alcohol was added. The condenser cooling water temperature was maintained at 50,5 °C.

Sample Number	62A	62B	62C	62D	62E	62F	62G
Time (minutes)	15	30	45	60	75	90	120
Component		Mass %, dry basis					
1-Butanol	88.650	91.720	94.650	96.000	97.000	97.780	97.970
2-Pentanol	10.760	7.530	4.330	2.660	1.580	0.840	0.395
n-Butylether	0.240	0.140	0.190	0.290	0.360	0.410	0.640
Mixed Ether 2	0.350	0.610	0.830	1.060	1.060	0.970	1.000
Total Ether	0.590	0.750	1.020	1.350	1.420	1.380	1.640
Alcohols: 1-Butanol	89.176	92.413	95.625	97.304	98.397	99.148	99.598
2-Pentanol	10.824	7.587	4.375	2.696	1.603	0.852	0.402

Sample Number	62H	62I	62J	62K	62L	62M
Time (minutes)	150	195	256	360	480	660
1-Butanol	98.170	98.080	97.870	97.410	96.810	95.900
2-Pentanol	0.100	0.035	0.000	0.000	0.000	0.000
n-Butylether	0.830	1.120	1.530	2.210	2.980	4.000
Mixed Ether 2	0.890	0.770	0.600	0.380	0.210	0.100
Total Ether	1.720	1.890	2.130	2.590	3.190	4.100
Alcohols: 1-Butanol	99.898	99.964	100.000	100.000	100.000	100.000
2-Pentanol	0.102	0.036	0.000	0.000	0.000	0.000

Appendix D: Experiment 63 - Original readings and analysis.

Alcohol Feed: 85 % 1-Butanol and 15 % 2-Pentanol; Catalyst: 90 % H_3PO_4
Mass: Alcohol Mixture = 157.3 grams; 90 % H_3PO_4 = 340.5 grams
Acid/Alcohol = 2,17:1
Reaction Pressure Atmospheric
Comments: The nitrogen flow through the sample point was low, but could have been altered to flush the sample point. The acid was heated to about 80 °C, before the alcohol was added. The condenser cooling water temperature was maintained at 50,5 °C.

Sample Number	Feed	63A	63B	63C	63D	63E
Time (minutes)	0	15	30	45	60	75
Component			Mass %, dry basis			
1-Butanol	85.000	94.630	97.220	97.860	97.920	97.540
2-Pentanol	15.000	3.150	0.530	0.120	0.050	0.060
n-Butylether	0.000	0.620	0.550	0.750	1.090	1.920
Mixed Ether 2	0.000	1.600	1.710	1.270	0.940	0.480
Total Ether	0.000	2.220	2.260	2.020	2.030	2.400
Alcohols :1-Butanol	85.000	96.778	99.458	99.878	99.949	99.939
2-Pentanol	15.000	3.222	0.542	0.122	0.051	0.061

Sample Number	63F	63H	63I	63J	63K
Time (minutes)	90	120	180	270	390
1-Butanol	97.600	97.110	95.840	92.970	90.510
2-Pentanol	0.000	0.000	0.000	0.000	0.000
n-Butylether	1.920	2.640	4.120	7.030	9.490
Mixed Ether 2	0.470	0.250	0.050	0.000	0.000
Total Ether	2.390	2.890	4.170	7.030	9.490
Alcohols: 1-Butanol	100.000	100.000	100.000	100.000	100.000
2-Pentanol	0.000	0.000	0.000	0.000	0.000

Appendix D: Experiment 64 - Original readings and analysis.

Alcohol Feed: 85 % 1-Butanol and 15 % 2-Pentanol; Catalyst: 92.1 % H_3PO_4
Mass: Alcohol Mixture = 157.2 grams; 92.1 % H_3PO_4 = 333.9 grams
Acid:Alcohol = 2,12:1
Reaction Pressure Atmospheric
Comments: The nitrogen flow through the sample point was low, but could have been altered to flush the sample point. The acid was heated to about 80 °C, before the alcohol was added. The condenser temperature was 50.5 °C.

Sample Number	Feed	64A	64B	64D	64G	64I	64J	64K
Time (minutes)	0	15	30	60	120	180	300	420
Component			Mass %, dry basis					
1-Butanol	85	98.830	97.800	97.610	95.440	92.400	90.350	84.470
2-Pentanol	15	1.200	0.130	0.030	0.000	0.000	0.000	0.000
n-Butylether	0	0.620	0.980	2.010	4.520	7.600	9.650	15.530
Mixed Ether 2	0	1.600	1.090	0.350	0.040	0.000	0.000	0.000
Total Ether	0	2.220	2.070	2.360	4.560	7.600	9.650	15.530
Alcohols: 1-Butanol	85	98.80	99.87	99.97	100.00	100.0	100.0	100.0
2-Pentanol	15	1.20	0.13	0.03	0.00	0.0	0.0	0.0

Appendix D: Experiment 65 - Original readings and analysis.

Alcohol Feed: 85 % 1-Butanol and 15 % 2-Pentanol; Catalyst: 80 % H_3PO_4
Mass: Alcohol Mixture = 157.2 grams; 80 % H_3PO_4 = 340 grams
Acid/Alcohol = 2,16:1
Reaction Pressure Atmospheric
Comments: The nitrogen flow through the sample point was low, but could have been altered to flush the sample point. The acid was heated to about 80 °C, before the alcohol was added. The condenser temperature was 50.5 °C. The reaction mixture did not discolour.

Sample Number	Feed	65A	65B	65C	65D	65E
Time (minutes)	0	15	30	60	90	120
Component		Mass %, dry basis				
	Not analysed					
1-Butanol	85	86.180	87.870	88.010	91.050	94.880
2-Pentanol	15	13.440	11.730	11.530	8.260	4.480
n-Butylether	0	0.290	0.200	0.140	0.210	0.200
Mixed Ether 2	0	0.090	0.190	0.320	0.480	0.440
Total Ether	0	0.380	0.390	0.460	0.690	0.640
Alcohols: 1-Butanol	85	86.509	88.223	88.417	91.683	95.491
2-Pentanol	15	13.491	11.777	11.583	8.317	4.509

Sample Number	65F	65G	65H	65I	65J	65K
Time (minutes)	150	180	210	240	270	303
1-Butanol	95.060	96.360	96.670	97.480	97.780	98.410
2-Pentanol	4.070	2.910	2.420	1.680	1.440	0.880
n-Butylether	0.280	0.230	0.280	0.260	0.260	0.250
Mixed Ether 2	0.590	0.500	0.630	0.580	0.520	0.450
Total Ether	0.870	0.730	0.910	0.840	0.780	0.700
Alcohols: 1-Butanol	95.894	97.069	97.558	98.306	98.549	99.114
2-Pentanol	4.106	2.931	2.442	1.694	1.451	0.886

Sample Number	65L	65N	65O	65P	65Q
Time (minutes)	360	483	548	660	780
1-Butanol	98.860	99.550	99.770	99.580	99.840
2-Pentanol	0.480	0.130	0.000	0.090	0.000
n-Butylether	0.230	0.180	0.160	0.320	0.160
Mixed Ether 2	0.340	0.140	0.070	0.010	0.000
Total Ether	0.570	0.320	0.230	0.330	0.160
Alcohols: 1-Butanol	99.517	99.870	100.000	99.910	100.000
2-Pentanol	0.483	0.130	0.000	0.090	0.000

Appendix D: Experiment 66 - Original readings and analysis.

Alcohol Feed: 85 % 1-Butanol and 15 % 2-Pentanol
Catalyst: 90 % H_3PO_4
Mass: Alcohol Mixture = 115.2 grams
90 % H_3PO_4 = 344.7 grams
Acid/Alcohol = 3:1

Reaction Pressure Atmospheric

Comments: The nitrogen flow through the sample point was low, but could have been altered to flush the sample point. The acid was heated to about 80 °C, before the alcohol was added. The condenser temperature was 50.5 °C. The reaction mixture discoloured. The initial boiling temperature of the reaction mixture was 134 °C at atmospheric pressure.

Sample Number	Feed	66A	66B	66C	66D	66E
Time (minutes)	0	0	10	16	30	45
Component			Mass %, dry basis			
	Not analysed					
1-Butanol	85	86.250	94.270	95.740	97.950	97.890
2-Pentanol	15	13.480	1.670	0.630	0.150	0.130
n-Butylether	0	0.060	0.440	0.650	0.890	1.590
Mixed Ether 2	0	0.210	3.630	2.980	1.020	0.390
Total Ether	0	0.27	4.07	3.63	1.91	1.98
Alcohol only						
1-Butanol	85	86.484	98.259	99.346	99.847	99.867
2-Pentanol	15	13.516	1.741	0.654	0.153	0.133
Sample Number	66F	66H	66I	66J	66K	66L
Time (minutes)	62	111	169	238	338	398
Component			Mass %, dry basis			
1-Butanol	97.470	95.510	94.490	88.530	84.720	82.260
2-Pentanol	0.000	0.000	0.000	0.000	0.000	0.000
n-Butylether	2.380	4.490	5.510	11.470	15.280	17.740
Mixed Ether 2	0.150	0.000	0.000	0.000	0.000	0.000
Total Ether	2.530	4.490	5.510	11.470	15.280	17.740
Alcohol only						
1-Butanol	100.000	100.000	100.000	100.000	100.000	100.000
2-Pentanol	0.000	0.000	0.000	0.000	0.000	0.000

Appendix D: Experiment 67 - Original readings and analysis.

Alcohol Feed: 85 % 1-Butanol and 15 % 2-Pentanol
Catalyst: 80 % H_3PO_4
Mass: Alcohol Mixture = 113.3 grams
80 % H_3PO_4 = 339.9 grams
Acid/Alcohol = 3:1
Reaction Pressure Atmospheric
Comments: The nitrogen flow through the sample point was low, but could have been altered to flush the sample point. The acid was heated to about 80 °C, before the alcohol was added. The condenser temperature was 50.5 °C. The reaction mixture did not discolour.

Sample Number	Feed	67A	67B	67C	67D	67E
Time (minutes)	0	5	15	30	45	60
Component		Mass %, dry basis				
	Not analysed					
1-Butanol	85	85.950	88.350	90.790	94.250	96.270
2-Pentanol	15	13.780	11.390	8.730	5.120	3.100
n-Butylether	0	0.220	0.080	0.110	0.140	0.150
Mixed Ether 2	0	0.050	0.180	0.370	0.490	0.480
Total Ether	0	0.270	0.260	0.480	0.630	0.630
Alcohol Only						
1-Butanol	85	86.183	88.580	91.228	94.848	96.880
Secondary Alcohol	15	13.817	11.420	8.772	5.152	3.120

Sample Number	67F	67G	67H	67I	67J
Time (minutes)	90	120	150	180	210
Component		Mass %, dry basis			
1-Butanol	98.030	98.690	98.630	98.710	98.800
2-Pentanol	1.250	0.490	0.280	0.140	0.050
n-Butylether	0.200	0.300	0.450	0.560	0.610
Mixed Ether 2	0.510	0.520	0.630	0.590	0.530
Total Ether	0.710	0.820	1.080	1.150	1.140
Alcohol Only					
1-Butanol	98.741	99.506	99.717	99.858	99.949
Secondary Alcohol	1.259	0.494	0.283	0.142	0.051

Sample Number	67K	67L	67M	67N	67O*
Time (minutes)	270	330	450	553	1680
Component		Mass %, dry basis			
1-Butanol	98.750	98.420	98.190	97.850	97.420
2-Pentanol	0.000	0.000	0.000	0.000	0.000
n-Butylether	0.780	1.200	1.500	1.950	2.480
Mixed Ether 2	0.470	0.380	0.310	0.200	0.090
Total Ether	1.250	1.580	1.810	2.150	2.570
Alcohol Only					
1-Butanol	100.000	100.000	100.000	100.000	100.000
Secondary Alcohol	0.000	0.000	0.000	0.000	0.000

* Sample 67O: The reaction mixture was cooled down after sample 67 N was taken. Thereafter the reaction mixture was kept at room temperature overnight and was boiled the following day for a further 3,5 hours.

Appendix D: Experiment 68 - Original readings and analysis.

Alcohol Feed:	85 % 1-Butanol and 15 % 2-Pentanol
Catalyst:	85 % H_3PO_4
Mass:	Alcohol Mixture = 120.7 grams
	85 % H_3PO_4 = 360 grams
Acid/Alcohol	= 3:1
Reaction Pressure:	Atmospheric
Comments:	The nitrogen flow through the sample point was low, but could have been altered to flush the sample point. The acid was heated to about 80 °C, before the alcohol was added. The condenser temperature was 50.5 °C. The initial boiling temperature of the reaction mixture was 126 °C at atmospheric pressure.

Sample Number	Feed	68A	68B	68C	68D
Time (minutes)	0	5	15	30	45
Component		Mass %, dry basis			
	Not analysed				
1-Butanol	85	85.910	95.210	98.540	98.420
2-Pentanol	15	13.720	4.110	0.650	0.110
n-Butylether	0	0.090	0.160	0.260	0.410
Mixed Ether 2	0	0.200	0.520	0.550	0.540
Total Ether	0.000	0.290	0.680	0.810	0.950
Alcohol Only					
1-Butanol	85	86.229	95.862	99.345	99.888
Secondary Alcohol	15	13.771	4.138	0.655	0.112

Sample Number	68E	68F	68G	68H	68I
Time (minutes)	60	75	90	123	180
Component		Mass %, dry basis			
1-Butanol	99.070	98.920	98.800	98.560	97.760
2-Pentanol	0.000	0.000	0.000	0.000	0.000
n-Butylether	0.520	0.720	0.900	1.220	2.120
Mixed Ether 2	0.410	0.360	0.300	0.210	0.110
Total Ether	0.930	1.080	1.200	1.430	2.230
Alcohol Only					
1-Butanol	100.000	100.000	100.000	100.000	100.000
Secondary Alcohol	0.000	0.000	0.000	0.000	0.000

Sample Number	68J	68K	68L	68M
Time (minutes)	272	390	513	680
Component		Mass %, dry basis		
1-Butanol	97.370	95.450	93.490	91.530
2-Pentanol	0.000	0.000	0.000	0.000
n-Butylether	2.590	4.550	6.510	8.470
Mixed Ether 2	0.030	0.000	0.000	0.000
Total Ether	2.620	4.550	6.510	8.470
Alcohol Only				
1-Butanol	100.000	100.000	100.000	100.000
Secondary Alcohol	0.000	0.000	0.000	0.000

Appendix D: Experiment 69 - Original readings and analysis.

Alcohol Feed: 85 % 1-Butanol and 15 % 2-Pentanol
Catalyst: 85 % H_3PO_4
Mass: Alcohol Mixture = 240.1 grams
85 % H_3PO_4 = 360.1 grams
Acid/Alcohol = 1.5:1

Reaction Pressure: Atmospheric

Comments: The nitrogen flow through the sample point was low, but could have been altered to flush the sample point. The acid was heated to about 80 °C, before the alcohol was added. The condenser temperature was 50.5 °C.

Sample Number	Feed	69A	69B	69C	69D
Time (minutes)	0	1	15	30	60
Component		mass %, dry basis			
1-Butanol	85.000	85.550	86.390	87.670	88.520
2-Pentanol	15.000	14.340	13.290	11.960	10.790
n-Butylether	0.000	0.070	0.160	0.110	0.200
Mixed Ether 2	0.000	0.040	0.170	0.260	0.500
Total Ether	0.000	0.110	0.330	0.370	0.700
Alcohol only					
1-Butanol	85.000	85.644	86.667	87.996	89.135
2-Pentanol	15.000	14.356	13.333	12.004	10.865
Sample Number	69E	69F	69K	69G	69L
Time (minutes)	90	120	150	180	208
Component		mass %, dry basis			
1-Butanol	89.890	90.982	91.984	94.425	95.415
2-Pentanol	9.220	7.903	6.583	4.151	2.859
n-Butylether	0.250	0.328	0.440	0.454	0.590
Mixed Ether 2	0.650	0.788	0.993	0.970	1.136
Total Ether	0.900	1.116	1.433	1.423	1.726
Alcohol only					
1-Butanol	90.697	92.008	95.789	93.321	97.090
2-Pentanol	9.303	7.992	4.211	6.679	2.910
Sample Number	69H	69M	69I	69J	
Time (minutes)	270	335	390	510	
Component		mass %, dry basis			
1-Butanol	96.299	96.486	96.770	97.147	
2-Pentanol	1.662	1.215	0.861	0.169	
n-Butylether	0.796	1.001	1.092	1.547	
Mixed Ether 2	1.243	1.298	1.277	1.136	
Total Ether	2.039	2.299	2.369	2.683	
Alcohol only					
1-Butanol	98.304	98.756	99.118	99.826	
2-Pentanol	1.696	1.244	0.882	0.174	

Appendix D: Experiment 70 - Original readings and analysis

Experiment Number	70A	70B
Alcohol Feed	85% 1-Pentanol 15% 2-Hexanol	85% 1-Pentanol 15% 2-Hexanol
Catalyst	85 % H_3PO_4	85 % H_3PO_4
1-Pentanol [gram]	93.5	93.8
2-Hexanol [gram]	16.6	16.7
Acid [gram]	235.7	237.1
Acid:Alcohol	2,14:1	2,15:1
Condensor Temperature [oC]	65	65
Reaction Time [minutes]	about 120	about 120
Boiling Temperature	127	not logged
Mass Loss [gram]	14.5	15.5
	Distillation from acid	
Add Reaction Mixture together and feed to Short Path Distillation Unit		
Pressure [bar abs]	0.095	
Heating Temperature [oC]	108	Glikol/Water mixture
Distillate, Organic Sample		
Organic Product [gram]	2.121	
Methanol for dilution [gram]	1.226	
	Total Distillate	
Phases	Two	
Organic [gram]	102.1	
Water [gram]	38.0	
Remaining Acid and Reaction mixture after Short Path Distillation		
	475.9 gram	

Experiment 72: Original readings and analysis.

Alcohol Feed: 85 % 1-Butanol and 15 % 2-Pentanol
Catalyst: 80 % H_3PO_4
Mass: Alcohol Mixture = 141.0 grams
80 % H_3PO_4 = 210.1 grams
Acid/Alcohol = 1.49:1
Reaction Pressure Atmospheric
Comments: The condenser temperature was maintained at 51 °C. The nitrogen flow through sampling system was low, but not necessarily constant. The acid was heated to about 80 °C before the alcohol mixture was added.

Sample Number	Feed	72A	72B	72C	72E	72F	72G	72H
Time (minutes)	0	0	18	42	140	221	350	441
Component	Mass %							
1-Butanol	85	86.367	85.641	86.712	87.370	88.773	90.909	91.294
2-Pentanol	15	13.572	14.246	13.107	12.143	10.530	8.026	7.397
n-Butylether	0	0.053	0.062	0.076	0.157	0.217	0.339	0.442
Mixed Ether 2	0	0.009	0.051	0.105	0.330	0.481	0.726	0.867
Total Ether	0	0.062	0.113	0.181	0.346	0.698	1.065	1.309
Alcohol only								
1-Butanol	85	86.420	85.738	86.869	87.797	89.396	91.887	92.504
2-Pentanol	15	13.580	14.262	13.131	12.203	10.604	8.113	7.496

Appendix D: Experiment 73 - Original readings and analysis.

Alcohol Feed: 85 % 1-Butanol and 15 % 2-Pentanol
Catalyst: 90 % H_3PO_4
Mass: Alcohol Mixture = 240.2 grams
90 % H_3PO_4 = 360.3 grams
Acid/Alcohol = 1.5:1

Reaction Pressure Atmospheric

Comments: The condenser temperature was maintained at 51 °C. The nitrogen flow through sampling system was low, but not necessarily constant. Sample A was taken 5 minutes after the alcohol was added to the acid. The mixture was about 40 °C and was only heated further after sample A was taken.

Sample Number	Feed	73A	B	C	D
Time (minutes)	0	0	0	12	29
Component		Mass %, dry basis			
1-Butanol	85.000	85.347	84.527	90.247	96.092
2-Pentanol	15.000	14.653	15.280	8.822	2.387
n-Butylether	0.000	0.000	0.054	0.167	0.327
Mixed Ether 2	0.000	0.000	0.138	0.764	1.194
Total Ether	0.000	0.000	0.192	0.931	1.521
Alcohol Only					
1-Butanol	85.000	85.347	84.690	91.095	97.576
2-Pentanol	15.000	14.653	15.310	8.905	2.424
Sample Number	E	F	G	H	I
Time (minutes)	41	65	90	156	213
Component		Mass %, dry basis			
1-Butanol	97.396	97.939	97.947	97.553	96.811
2-Pentanol	0.922	0.198	0.027	0.054	0.000
n-Butylether	0.456	0.738	1.085	1.847	2.817
Mixed Ether 2	1.226	1.126	0.941	0.546	0.372
Total Ether	1.682	1.863	2.026	2.392	3.189
Alcohol Only					
1-Butanol	99.062	99.799	99.972	99.945	100.000
2-Pentanol	0.938	0.201	0.028	0.055	0.000
Sample Number	J	K	L	M	
Time (minutes)	289	382	504	608	
Component		Mass %, dry basis			
1-Butanol	95.913	94.580	92.592	90.578	
2-Pentanol	0.000	0.000	0.000	0.000	
n-Butylether	3.855	5.311	7.408	9.422	
Mixed Ether 2	0.232	0.110	0.000	0.000	
Total Ether	4.087	5.420	7.408	9.422	
Alcohol Only					
1-Butanol	100.000	100.000	100.000	100.000	
2-Pentanol	0.000	0.000	0.000	0.000	

Appendix D: Experiment 75 - Original readings and analysis.

Alcohol Feed: 85 % 1-Pentanol and 15 % 2-Hexanol
Catalyst: 85 % H_3PO_4
Mass: Alcohol Mixture = 137.2 grams
85 % H_3PO_4 = 298.4 grams
Acid:Alcohol = 2.17:1

Reaction Pressure: Atmospheric

Comments: The nitrogen flow through the sample point was low and constant. The acid was heated to about 80 °C, before the alcohol was added. The condenser temperature was 65 °C. This temperature is too low for sufficient hexene removal. The boiling points of the hexene isomers vary between 63,3 and 68,8 °C (at atmospheric pressure). The sample at 5 minutes was analysed twice.

Sample Number	Feed	TN75B01	TN75B02	TN75C01	TN75D01	TN75F01
Time (minutes)	0	5	5*	17	25	47
Components			Mass %, dry basis			
1-Pentanol	85.000	88.524	88.408	94.531	96.565	97.912
3-Hexanol	0.000	0.273	0.265	0.342	0.210	0.048
2-Hexanol	15.000	10.761	10.763	4.121	1.826	0.268
Mixed Ether 3&6	not determined					
n-Pentylether	0.000	0.108	0.246	0.184	0.314	0.660
Mixed Ether 4	0.000	0.067	0.065	0.185	0.239	0.240
Mixed Ether 5	.	0.267	0.254	0.638	0.846	0.871
Total Ether	0.000	0.441	0.565	1.006	1.399	1.772
Alcohols Only						
1-Pentanol	85.000	88.916	88.910	95.492	97.935	99.678
Total Secondary Alcohol	15.000	11.084	11.090	4.508	2.065	0.322

Sample Number	TN75H01	TN75I01	TN75K01	TN75L01	TN75M01
Time (minutes)	90	120	180	297	512
Components			Mass %, dry basis		
1-Pentanol	97.710	97.326	96.643	94.186	89.179
3-Hexanol	0.033	0.032	0.019	0.005	0.000
2-Hexanol	0.105	0.094	0.068	0.059	0.000
Mixed Ether 3&6	not determined				
n-Pentylether	1.329	1.794	2.749	5.468	10.771
Mixed Ether 4	0.162	0.144	0.098	0.038	0.004
Mixed Ether 5	0.662	0.610	0.423	0.244	0.046
Total Ether	2.153	2.548	3.270	5.749	10.821
Alcohols Only					
1-Pentanol	99.860	99.871	99.910	99.931	100.000
Total Secondary Alcohol	0.140	0.129	0.090	0.069	0.000

* not plotted on graph in Appendix E

Appendix D: Experiment 76 - Original readings and analysis.

Alcohol Feed: 85 % 1-Propanol and 15 % 2-Butanol; Catalyst: 85 % H_3PO_4
Mass: Alcohol Mixture = 141.5 grams
85 % H_3PO_4 = 303.1 grams
Acid:Alcohol = 2.14:1
Reaction Pressure: Atmospheric
Comments: The nitrogen flow through the sample point was low and constant. The acid was heated before the alcohol was added. The condenser temperature was 40 °C. The reaction mixture started to boil at 110 °C. The reaction mixture temperature varied between 110 and 114 °C.

Sample Number	76A01	76B05	76D02	76E02	76F02	76G01	76H02	76I01
Time (minutes)	1	38	93	144	265	375	521	581
Component	mass %							
1-Propanol	84.566	88.381	95.652	97.538	98.769	99.428	99.345	99.395
2-Butanol	15.434	11.450	3.749	2.108	0.456	0.244	0.116	0.000
n-Propylether	0.000	0.000	0.080	0.038	0.224	0.075	0.238	0.334
2-butyl-propylether	0.000	0.168	0.519	0.317	0.551	0.253	0.300	0.271
Total Ether	0.000	0.168	0.599	0.354	0.775	0.327	0.538	0.605
Alcohols:								
1-Propanol	84.566	88.531	96.228	97.885	99.540	99.755	99.883	100.000
2-Butanol	15.434	11.469	3.772	2.115	0.460	0.245	0.117	0.000

Appendix D: Experiment 77 - Original readings and analysis.

Alcohol Feed: 85 % 1-Pentanol and 15 % 2-Hexanol; Catalyst: 85 % H_3PO_4
Mass: Alcohol Mixture = 208.5 grams; 85 % H_3PO_4 = 166.7 grams
Acid:Alcohol = 2.16:1
Reaction Pressure: Atmospheric
Comments: The nitrogen flow through the sample point was low and constant. The acid was heated to about 80 °C, before the alcohol was added. The condenser temperature was maintained at 72 °C. The reaction mixture started to boil at 134 °C. Mixed Ether 3&6 not detected.

Sample Number	TN77Fe01	TN77A03	TN77C01	TN77E01	TN77F02	TN77G01
Time (minutes)	0	1	14	43	56	74
Component		Mass %, dry basis				
1-Pentanol	84.719	86.489	95.250	98.249	98.456	98.305
3-Hexanol	0.000	0.166	0.254	0.024	0.000	0.000
2-Hexanol	15.261	13.154	3.509	0.308	0.064	0.020
n-Pentylether	0.020	0.041	0.206	0.633	0.832	1.127
Mixed Ether 4	0.000	0.041	0.151	0.131	0.094	0.075
Mixed Ether 5	0.000	0.109	0.630	0.656	0.554	0.473
Total Ether	0.020	0.191	0.987	1.420	1.480	1.676
Alcohols: 1-Pentanol	84.736	86.654	96.200	99.664	99.936	99.980
3-Hexanol	0.000	0.166	0.256	0.024	0.000	0.000
2-Hexanol	15.264	13.180	3.544	0.312	0.064	0.020
Secondary Alcohols	15.264	13.346	3.800	0.336	0.064	0.020

Sample Number	TN77I01	TN77J01	TN77K01	TN77L01	TN77M01
Component		Mass %, dry basis			
1-Pentanol	97.640	97.137	96.769	95.921	94.186
3-Hexanol	0.000	0.000	0.000	0.000	0.000
2-Hexanol	0.080	0.058	0.012	0.007	0.012
n-Pentylether	1.959	2.554	3.074	3.971	5.741
Mixed Ether 4	0.028	0.020	0.000	0.000	0.000
Mixed Ether 5	0.293	0.230	0.144	0.101	0.062
Total Ether	2.280	2.805	3.219	4.072	5.803
Alcohols: 1-Pentanol	99.918	99.940	99.988	99.993	99.988
3-Hexanol	0.000	0.000	0.000	0.000	0.000
2-Hexanol	0.082	0.060	0.012	0.007	0.012
Secondary Alcohols	0.082	0.060	0.012	0.007	0.012

Appendix D: Experiment 79 - Original readings and analysis.

Alcohol Feed: 85 % 1-Pentanol and 15 % 2-Hexanol
Catalyst: 90 % H_3PO_4
Mass: Alcohol Mixture = 67.3 grams
90 % H_3PO_4 = 200 grams
Acid:Alcohol = 2.97:1

Reaction Pressure: Atmospheric

Comments: The nitrogen flow through the sample point was normal. The acid was heated to about 80 °C, before the alcohol was added. The condenser temperature was maintained at 72 °C. The temperature of the vapour reaction mixture after 12 minutes was 136 °C (measured close to the liquid/vapour interface). Mixed Ether 3 & 6 not detected.

Sample Number	TN79Fe01	TN79C10	TN79D01	TN79E01	TN79G01
Time (minutes)	0	4	9.5	20	34.5
Component		Mass %, dry basis			
1-Pentanol	83.580	89.788	96.611	97.535	96.045
3-Hexanol	0.000	0.322	0.150	0.038	0.000
2-Hexanol	16.403	9.131	1.173	0.235	0.043
n-Pentylether	0.016	0.222	0.427	1.565	3.804
Mixed Ether 4	0.000	0.159	0.490	0.135	0.020
Mixed Ether 5	0.000	0.378	1.150	0.492	0.088
Total Ethers	0.016	0.759	2.066	2.192	3.912
Alcohols only					
1-Pentanol	83.594	90.475	98.650	99.722	99.956
3-Hexanol	0.000	0.322	0.150	0.038	0.000
2-Hexanol	16.403	9.131	1.173	0.235	0.043
Total Secondary Alcohols	16.406	9.525	1.350	0.278	0.044

Sample Number	TN79H01	TN79I01	TN79I02	TN79J01
Time (minutes)	40.5	85	85	165
Component		Mass %, dry basis		
1-Pentanol	95.263	93.976	93.739	87.829
3-Hexanol	0.000	0.000	0.000	0.000
2-Hexanol	0.005	0.059	0.040	0.110
n-Pentylether	4.731	5.965	6.220	12.060
Mixed Ether 4	0.000	0.000	0.000	0.000
Mixed Ether 5	0.000	0.000	0.000	0.000
Total Ethers	4.731	5.965	6.220	12.060
Alcohols only				
1-Pentanol	99.994	99.938	99.957	99.875
3-Hexanol	0.000	0.000	0.000	0.000
2-Hexanol	0.005	0.059	0.040	0.110
Total Secondary Alcohols	0.006	0.062	0.043	0.125

Appendix D: Experiment 80 - Original readings and analysis.

Alcohol Feed: 85 % 1-Pentanol and 15 % 2-Hexanol
Catalyst: 80 % H_3PO_4
Mass: Alcohol Mixture = 72.7 grams
90 % H_3PO_4 = 109.3 grams
Acid:Alcohol = 1.5:1

Reaction Pressure: Atmospheric

Comments: The nitrogen flow through the sample point was low but not necessarily constant. The acid was heated to about 80 °C, before the alcohol was added. The condenser temperature was maintained at 72.5 °C. The temperature of the vapour of the reaction mixture after 90 minutes was 120 °C (measured close to the liquid/vapour interface).

Sample Number	TN80A01	TN80B01	TN80C01	TN80D01	TN80E01	TN80F01
Time (minutes)	0	3	20	42	60	90
Component		Mass %, dry basis				
1-Pentanol	85.064	85.489	86.665	87.763	89.655	91.394
3-Hexanol	0.000	0.027	0.115	0.196	0.260	0.278
2-Hexanol	14.900	14.421	13.037	11.656	9.546	7.587
Mixed Ether 3 & 6		not determined				
n-Pentylether	0.036	0.040	0.061	0.112	0.151	0.214
Mixed Ether 4	0.000	0.003	0.010	0.028	0.043	0.065
Mixed Ether 5	0.000	0.021	0.112	0.246	0.345	0.462
Total Ether	0.036	0.064	0.183	0.385	0.540	0.741
Alcohols only						
1-Pentanol	85.095	85.543	86.824	88.102	90.141	92.076
3-Hexanol	0.000	0.027	0.115	0.196	0.261	0.281
2-Hexanol	14.905	14.430	13.061	11.701	9.598	7.643
Total Secondary Alcohols	14.905	14.457	13.176	11.898	9.859	7.924

Sample Number	TN80G01	TN80H01	TN80I01	TN80J01	TN80K01
Time (minutes)	120	154	182	240	307
Component		Mass %, dry basis			
1-Pentanol	93.169	95.001	95.835	97.051	97.853
3-Hexanol	0.267	0.224	0.178	0.103	0.029
2-Hexanol	5.569	3.660	2.649	1.334	0.356
Mixed Ether 3 & 6		not determined			
n-Pentylether	0.305	0.366	0.469	0.610	0.853
Mixed Ether 4	0.089	0.103	0.121	0.129	0.129
Mixed Ether 5	0.601	0.646	0.748	0.772	0.781
Total Ether	0.995	1.115	1.338	1.512	1.762
Alcohols only					
1-Pentanol	94.105	96.073	97.134	98.541	99.609
3-Hexanol	0.269	0.226	0.181	0.105	0.029
2-Hexanol	5.625	3.701	2.685	1.354	0.362
Total Secondary Alcohols	5.895	3.927	2.866	1.459	0.391

Appendix D: Experiment 81 - Original readings and analysis.

Alcohol Feed: 85 % 1-Pentanol and 15 % 2-Hexanol
Catalyst: 85 % H_3PO_4
Mass: Alcohol Mixture = 80.1 grams
85 % H_3PO_4 = 120 grams
Acid:Alcohol = 1.5:1

Reaction Pressure: Atmospheric

Comments: The nitrogen flow through the sample point was low but not necessarily constant. The acid was heated to about 80 °C, before the alcohol was added. The condenser temperature was maintained at 73 °C. After 120 minutes the reaction mixture started to discolour.

Sample Number	TN81Fe01	TN81A01	TN81B01	TN81C01	TN81D01
Time (minutes)	0	0	12	30	60
Component		Mass %, dry basis			
1-Pentanol	85.358	85.707	88.226	91.749	95.489
3-Hexanol	0.000	0.044	0.196	0.279	0.186
2-Hexanol	14.619	14.190	11.219	7.159	3.004
Mixed Ether 3		not determined			
n-Pentylether	0.023	0.023	0.081	0.211	0.415
Mixed Ether 4	0.000	0.000	0.031	0.068	0.110
Mixed Ether 5	0.000	0.036	0.247	0.535	0.783
Mixed Ether 6	0.000	0.000	0.000	0.000	0.012
Total Ethers	0.023	0.059	0.359	0.813	1.320
1-Pentanol	85.377	85.758	88.544	92.501	96.767
3-Hexanol	0.000	0.044	0.196	0.282	0.189
2-Hexanol	14.623	14.198	11.260	7.217	3.044
Total Secondary Alcohol	14.623	14.242	11.456	7.499	3.233
Sample Number	TN81E01	TN81F01	TN81G01	TN81H01	TN81I01
Time (minutes)	90	120	143	216	293
Component					not used
1-Pentanol	97.025	97.534	97.657	97.502	96.407
3-Hexanol	0.099	0.046	0.027	0.000	0.000
2-Hexanol	1.173	0.463	0.232	0.038	0.460
Mixed Ether 3		not determined			
n-Pentylether	0.673	0.908	1.065	1.579	2.339
Mixed Ether 4	0.128	0.126	0.122	0.095	0.072
Mixed Ether 5	0.881	0.895	0.858	0.743	0.659
Mixed Ether 6	0.020	0.027	0.038	0.042	0.062
Total Ethers	1.702	1.956	2.084	2.460	3.132
1-Pentanol	98.705	99.481	99.736	99.961	99.525
3-Hexanol	0.101	0.047	0.028	0.000	0.000
2-Hexanol	1.193	0.473	0.237	0.039	0.475
Total Secondary Alcohol	1.295	0.519	0.264	0.039	0.475

Appendix D: Experiment 82 - Original readings and analysis.

Alcohol Feed: 85 % 1-Pentanol and 15 % 2-Hexanol
Catalyst: 85 % H_3PO_4
Mass: Alcohol Mixture = 67.1 grams
85 % H_3PO_4 = 200 grams
Acid:Alcohol = 3:1

Reaction Pressure: Atmospheric

Comments: The nitrogen flow through the sample point was low but not necessarily constant. The acid was heated to about 80 °C, before the alcohol was added. The condenser temperature was maintained at 72 °C.

Sample Number	82Fe01	82A01	82B01	82C01	82D01	82E01
Time (minutes)	0	0.1	5	15	32	45.5
Component		Mass %, dry basis				
1-Pentanol	84.760	85.570	91.627	97.924	98.609	98.565
3-Hexanol	0.000	0.076	0.510	0.128	0.029	0.020
2-Hexanol	15.221	14.287	7.324	0.901	0.115	0.079
Mixed Ether 3		not determined				
n-Pentylether	0.018	0.018	0.073	0.219	0.549	0.791
Mixed Ether 4	0.000	0.017	0.127	0.224	0.154	0.107
Mixed Ether 5	0.000	0.031	0.339	0.605	0.545	0.433
Mixed Ether 6	0.000	0.000	0.000	0.000	0.000	0.005
Total Ethers	0.018	0.066	0.539	1.048	1.247	1.336
Alcohols Only						
1-Pentanol	84.776	85.627	92.123	98.961	99.854	99.899
3-Hexanol	0.000	0.076	0.513	0.129	0.029	0.020
2-Hexanol	15.224	14.297	7.364	0.910	0.116	0.080
Secondary Alcohols	15.224	14.373	7.877	1.039	0.146	0.101

Sample Number	82F01	82G02	82H01	82I01	82J01	82K01
Time (minutes)	60	75	91	151	210	410
Component		Mass %, dry basis				
1-Pentanol	98.536	98.242	98.115	97.151	95.935	91.147
3-Hexanol	0.008	0.004	0.010	0.000	0.000	0.000
2-Hexanol	0.040	0.044	0.013	0.056	0.066	0.097
Mixed Ether 3		not determined				
n-Pentylether	1.013	1.372	1.612	2.696	3.963	8.756
Mixed Ether 4	0.070	0.048	0.032	0.006	0.000	0.000
Mixed Ether 5	0.331	0.283	0.211	0.085	0.036	0.000
Mixed Ether 6	0.002	0.006	0.007	0.006	0.000	0.000
Total Ethers	1.416	1.709	1.862	2.793	3.999	8.756
Alcohols Only						
1-Pentanol	99.952	99.951	99.976	99.942	99.931	99.894
3-Hexanol	0.008	0.004	0.010	0.000	0.000	0.000
2-Hexanol	0.040	0.045	0.014	0.058	0.069	0.106
Secondary Alcohols	0.048	0.049	0.024	0.058	0.069	0.106

Appendix D: Experiment 83 - Original readings and analysis.

Alcohol Feed: 85 % 1-Pentanol and 15 % 2-Hexanol
Catalyst: 90 % H_3PO_4
Mass: Alcohol Mixture = 67.8 grams
90 % H_3PO_4 = 148.3 grams
Acid:Alcohol = 2.19:1
Reaction Pressure: Atmospheric
Comments: The starting time was not logged correctly. It was adjusted by taking the average in rate decrease of 2-Hexanol of Experiments 79 and 86. In experiments 79 and 86 the same acid strength was used as in experiment 83, but a 3:1 and 1.5:1 acid: alcohol ratio was used respectively. 10.25 minutes were added to the starting time. The nitrogen flow through sampling system was low, but not necessarily constant. After about 60 minutes the reaction mixture started to discolour. The acid was heated to about 80 °C, before the alcohol was added. The condenser temperature was maintained at 72 °C.

Sample Number	83Fe01	83A01	83B02	83C01	83D01	83E01
	Time added: 10 minutes					
Original time (minutes)	0.0	0.0	12.0	18.0	27.0	34.5
Adjusted time (minutes)	0.0	10.3	22.3	28.3	37.3	44.8
Component			Mass %, dry basis.			
1-Pentanol	84.943	95.831	97.719	97.991	97.915	97.702
3-Hexanol	0.000	0.355	0.065	0.030	0.022	0.016
2-Hexanol	15.057	2.480	0.204	0.079	0.048	0.040
Mixed Ether 3			not determined			
n-Pentylether	0.000	0.192	0.782	0.921	1.348	1.743
Mixed Ether 4	0.000	0.329	0.331	0.226	0.132	0.090
Mixed Ether 5	0.000	0.812	0.899	0.752	0.525	0.398
Mixed Ether 6	0.000	0.000	0.000	0.000	0.010	0.010
Total Ethers	0.000	1.334	2.012	1.899	2.014	2.241
Alcohols Only: 1-Pentanol	84.943	95.831	97.719	97.991	97.915	97.702
3-Hexanol	0.000	0.355	0.065	0.030	0.022	0.016
2-Hexanol	15.057	2.480	0.204	0.079	0.048	0.040
Secondary Alcohols	15.057	2.835	0.269	0.110	0.071	0.056

Sample Number	83F01	83G01	83H01	83I01	83J01	83K01
	Time added: 10.25 min			Time [minutes]		
Original time (minutes)	46.0	61.0	78.0	111.0	152.0	240.0
Adjusted time (minutes)	56.3	71.3	88.3	121.3	162.3	250.3
Component			Mass %, dry basis.			
1-Pentanol	97.145	96.496	95.358	93.255	90.849	82.441
3-Hexanol	0.008	0.004	0.000	0.000	0.000	0.000
2-Hexanol	0.025	0.010	0.007	0.000	0.000	0.000
Mixed Ether 3			not determined			
n-Pentylether	2.496	3.302	4.547	6.707	9.140	17.540
Mixed Ether 4	0.054	0.026	0.010	0.000	0.000	0.000
Mixed Ether 5	0.263	0.149	0.064	0.016	0.000	0.000
Mixed Ether 6	0.009	0.013	0.015	0.023	0.011	0.019
Total Ethers	2.822	3.490	4.635	6.745	9.151	17.559
Alcohols Only: 1-Pentanol	97.145	96.496	95.358	93.255	90.849	82.441
3-Hexanol	0.008	0.004	0.000	0.000	0.000	0.000
2-Hexanol	0.025	0.010	0.007	0.000	0.000	0.000
Secondary Alcohols	0.032	0.013	0.007	0.000	0.000	0.000

Appendix D: Experiment 84 - Original readings and analysis.

Alcohol Feed: 85 % 1-Pentanol and 15 % 2-Hexanol

Catalyst: 80 % H_3PO_4

Mass: Alcohol Mixture = 66.7 grams
80 % H_3PO_4 = 200 grams

Acid:Alcohol = 3:1

Reaction Pressure: Atmospheric

Comments: The nitrogen flow through sampling system was low, but not necessarily constant. The acid was heated to about 80 °C, before the alcohol was added. The condenser temperature was maintained at 72 °C.

Sample Number	84Fe01	84A01	84B01	84C01	84D01
Time (minutes)	0	4	13	40	47
Component		Mass %, dry basis			
1-Pentanol	85.030	86.827	89.999	95.815	97.395
3-Hexanol	0.000	0.166	0.371	0.202	0.132
2-Hexanol	14.952	12.876	9.318	3.285	1.663
Mixed Ether 3		Not determined			
n-Pentylether	0.018	0.059	0.077	0.196	0.249
Mixed Ether 4	0.000	0.013	0.037	0.080	0.088
Mixed Ether 5	0.000	0.059	0.198	0.422	0.474
Mixed Ether 6	0.000	0.000	0.000	0.000	0.000
Total Ethers	0.018	0.131	0.312	0.698	0.811
Alcohols Only					
1-Pentanol	85.045	86.941	90.281	96.489	98.191
3-Hexanol	0.000	0.166	0.372	0.204	0.133
2-Hexanol	14.955	12.893	9.348	3.308	1.676
Secondary Alcohols	14.955	13.059	9.719	3.511	1.809

Sample Number	84E01	84F01	84G01	84H01	84I01
Time (minutes)	80.5	120	167	333	586
Component					
1-Pentanol	98.505	98.679	98.456	97.610	96.143
3-Hexanol	0.046	0.014	0.000	0.000	0.000
2-Hexanol	0.415	0.092	0.068	0.012	0.000
Mixed Ether 3		Not determined			
n-Pentylether	0.441	0.684	0.989	2.098	3.736
Mixed Ether 4	0.098	0.082	0.070	0.027	0.000
Mixed Ether 5	0.496	0.450	0.417	0.252	0.121
Mixed Ether 6	0.000	0.000	0.006	0.008	0.013
Total Ethers	1.034	1.216	1.482	2.385	3.870
Alcohols Only					
1-Pentanol	99.534	99.893	99.931	99.988	100.000
3-Hexanol	0.047	0.014	0.000	0.000	0.000
2-Hexanol	0.419	0.093	0.069	0.012	0.000
Secondary Alcohols	0.466	0.107	0.069	0.012	0.000

Appendix D: Experiment 86 - Original readings and analysis.

Alcohol Feed: 85 % 1-Pentanol and 15 % 2-Hexanol

Catalyst: 90 % H_3PO_4

Mass: Alcohol Mixture = 66.7 grams
90 % H_3PO_4 = 99.9 grams

Acid:Alcohol = 1.5:1

Reaction Pressure: Atmospheric

Comments: The nitrogen flow through sampling system was low, but not necessarily constant. The acid was heated to about 80 °C, before the alcohol was added. The condenser temperature was maintained at 72 °C. The reaction mixture discoloured after 50 minutes.

Sample Number	86Fe01	86A01	86B01	86C01	86D01	86E01
Time (minutes)	0	1	5	8	16	26.5
Component		Mass %, dry basis				
1-Pentanol	84.560	87.603	90.513	93.571	97.173	97.971
3-Hexanol	0.000	0.159	0.296	0.279	0.110	0.033
2-Hexanol	15.423	11.729	8.518	5.183	1.254	0.247
Mixed Ether 3		not determined				
n-Pentylether	0.017	0.301	0.160	0.198	0.406	0.723
Mixed Ether 4	0.000	0.050	0.102	0.152	0.203	0.187
Mixed Ether 5	0.000	0.159	0.410	0.616	0.854	0.825
Mixed Ether 6	0.000	0.000	0.000	0.000	0.000	0.014
Total Ethers	0.017	0.510	0.673	0.967	1.463	1.749
Alcohol Only						
1-Pentanol	84.575	88.052	91.126	94.485	98.616	99.715
3-Hexanol	0.000	0.160	0.298	0.282	0.112	0.033
2-Hexanol	15.425	11.789	8.576	5.233	1.273	0.251
Secondary Alcohol	15.425	11.948	8.874	5.515	1.384	0.285
Sample Number	86F01	86G01	86H01	86I01	86J01	86K01
Time (minutes)	33.5	52.5	80.5	105	153	187
Component		Mass %, dry basis				
1-Pentanol	98.027	97.793	97.183	96.403	94.803	93.030
3-Hexanol	0.012	0.000	0.000	0.000	0.000	0.000
2-Hexanol	0.089	0.019	0.008	0.000	0.000	0.000
Mixed Ether 3		not determined				
n-Pentylether	0.935	1.502	2.348	3.249	5.012	6.839
Mixed Ether 4	0.157	0.092	0.042	0.021	0.000	0.000
Mixed Ether 5	0.760	0.565	0.377	0.271	0.119	0.061
Mixed Ether 6	0.019	0.030	0.041	0.057	0.066	0.070
Total Ethers	1.871	2.189	2.808	3.597	5.197	6.970
Alcohol Only						
1-Pentanol	99.897	99.981	99.991	100.000	100.000	100.000
3-Hexanol	0.013	0.000	0.000	0.000	0.000	0.000
2-Hexanol	0.091	0.019	0.009	0.000	0.000	0.000
Secondary Alcohol	0.103	0.019	0.009	0.000	0.000	0.000

Appendix D: Experiment 87 - Original readings and analysis.

Alcohol Feed: 85 % 1-Pentanol and 15 % 2-Hexanol

Catalyst: 80 % H_3PO_4

Mass: Alcohol Mixture = 75.9 grams
80 % H_3PO_4 = 165 grams

Acid:Alcohol = 2.17:1

Reaction Pressure: Atmospheric

Comments: The nitrogen flow through sampling system was low, but not necessarily constant. The acid was heated to about 80 °C, before the alcohol was added. The condenser temperature was maintained at 72 °C. The reaction mixture discoloured after 50 minutes. In the period between 131 and 183 minutes, the sample point was open to atmosphere. There was thus no nitrogen flow through the system during this period.

Sample Number	87Fe01	87A01	87B01	87C01	87D01	87E01
Time (minutes)	0	0	16.4	30.5	67	107.5
Component		Mass %, dry basis				
1-Pentanol	84.939	85.228	88.291	91.186	95.304	96.895
3-Hexanol	0.000	0.012	0.246	0.297	0.213	0.102
2-Hexanol	15.061	14.736	11.188	8.012	3.573	1.820
Mixed Ether 3		not determined				
n-Pentylether	0.000	0.024	0.073	0.127	0.279	0.448
Mixed Ether 4	0.000	0.000	0.020	0.039	0.071	0.082
Mixed Ether 5	0.000	0.000	0.183	0.340	0.560	0.647
Mixed Ether 6	0.000	0.000	0.000	0.000	0.000	0.007
Total Ethers	0.000	0.024	0.276	0.505	0.909	1.184
Alcohols Only						
1-Pentanol	84.939	85.249	88.535	91.649	96.179	98.055
3-Hexanol	0.000	0.012	0.247	0.298	0.215	0.103
2-Hexanol	15.061	14.739	11.219	8.053	3.605	1.841
Secondary Alcohols	15.061	14.751	11.465	8.351	3.821	1.945
Sample Number	87F01	87G02	87H01	87I01	87J01	87K01
Time (minutes)	131	183.5	217	248	381.5	560.5
Component		Mass %, dry basis				
1-Pentanol	97.924	98.285	98.204	98.115	97.676	96.846
3-Hexanol	0.052	0.015	0.006	0.002	0.000	0.000
2-Hexanol	0.702	0.180	0.077	0.036	0.012	0.034
Mixed Ether 3		not determined				
n-Pentylether	0.566	0.811	0.997	1.156	1.753	2.681
Mixed Ether 4	0.082	0.073	0.073	0.068	0.047	0.032
Mixed Ether 5	0.665	0.617	0.625	0.605	0.487	0.384
Mixed Ether 6	0.008	0.020	0.017	0.019	0.025	0.023
Total Ethers	1.321	1.520	1.712	1.848	2.313	3.121
Alcohols Only						
1-Pentanol	99.235	99.802	99.915	99.962	99.988	99.965
3-Hexanol	0.053	0.015	0.006	0.002	0.000	0.000
2-Hexanol	0.712	0.183	0.079	0.037	0.012	0.035
Secondary Alcohols	0.765	0.198	0.085	0.038	0.012	0.035

Appendix D: Experiment 88 - Original readings and analysis.

Experiment 77 was repeated, to test whether the results are repeatable.

Alcohol Feed: 85 % 1-Pentanol and 15 % 2-Hexanol

Catalyst: 85 % H_3PO_4

Mass: Alcohol Mixture = 63.3 grams
85 % H_3PO_4 = 138.1 grams

Acid:Alcohol = 2.18:1

Reaction Pressure: Atmospheric

Comments: The nitrogen flow through sampling system was low and constant. The acid was heated to about 80 °C, before the alcohol was added. The condenser temperature was maintained at 72 °C. The reaction mixture discoloured after 45 minutes. After 70 minutes the mixture discoloured to golden yellow and after 90 minutes the mixture was dark yellow. There were no visual traces of coking or any dark particles present.

Every second sample was washed with dichloromethane on the following day. These samples (second set) were also analysed a day after the first set of samples. This was done to determine whether the preparation of the sample influences the analytical results.

Experiment 88 - First set of samples

Sample Number	88Fe01	88C01	88E01	88G01	88I01
Time (minutes)	0.0	2.3	6.0	14.0	25.1
Component			Mass %, dry basis		
1-Pentanol	83.124	87.253	89.450	93.122	96.592
3-Hexanol	0.000	0.157	0.276	0.324	0.176
2-Hexanol	16.859	12.410	9.895	5.826	2.142
Mixed Ether 3		not determined			
n-Pentylether	0.017	0.038	0.076	0.152	0.284
Mixed Ether 4	0.000	0.032	0.054	0.101	0.144
Mixed Ether 5	0.000	0.111	0.249	0.472	0.654
Mixed Ether 6	0.000	0.000	0.000	0.002	0.008
Total Ethers	0.017	0.180	0.379	0.728	1.090
Alcohols only					
1-Pentanol	83.138	87.411	89.791	93.805	97.657
3-Hexanol	0.000	0.157	0.277	0.327	0.178
2-Hexanol	16.862	12.432	9.933	5.869	2.166
Secondary Alcohols	16.86	12.59	10.21	6.20	2.34

Appendix D: Experiment 88 -First set of sample continued.

Sample Number	88K01	88M01	88O01	88Q01	88S01
Time (minutes)	38.0	50.3	60.0	73.7	120.0
Component			Mass %, dry basis		
1-Pentanol	98.021	98.324	98.413	98.306	97.974
3-Hexanol	0.065	0.034	0.016	0.004	0.000
2-Hexanol	0.621	0.221	0.090	0.026	0.011
Mixed Ether 3		not determined			
n-Pentylether	0.445	0.600	0.725	0.921	1.413
Mixed Ether 4	0.149	0.139	0.123	0.112	0.076
Mixed Ether 5	0.686	0.666	0.612	0.601	0.489
Mixed Ether 6	0.013	0.015	0.021	0.030	0.037
Total Ethers	1.293	1.421	1.480	1.665	2.015
Alcohols only					
1-Pentanol	99.304	99.741	99.892	99.970	99.989
3-Hexanol	0.066	0.035	0.016	0.004	0.000
2-Hexanol	0.630	0.224	0.092	0.026	0.011
Secondary Alcohols	0.696	0.259	0.108	0.030	0.011

Experiment 88 Second set of samples

Sample Number	88D01	88F01	88H01	88J01	88L01
Time (minutes)	4.1	9.0	20.1	30.7	45.4
Component			Mass %, dry basis		
1-Pentanol	88.271	91.046	95.501	97.479	98.265
3-Hexanol	0.236	0.337	0.245	0.112	0.039
2-Hexanol	11.226	8.085	3.287	1.203	0.297
Mixed Ether 3		not determined			
n-Pentylether	0.051	0.105	0.228	0.362	0.556
Mixed Ether 4	0.042	0.076	0.132	0.150	0.144
Mixed Ether 5	0.174	0.352	0.603	0.686	0.684
Mixed Ether 6	0.000	0.000	0.005	0.010	0.016
Total Ethers	0.267	0.532	0.967	1.207	1.400
Alcohols only					
1-Pentanol	88.507	91.533	96.434	98.669	99.660
3-Hexanol	0.237	0.339	0.247	0.113	0.039
2-Hexanol	11.256	8.128	3.319	1.217	0.301
Secondary Alcohols	11.493	8.467	3.566	1.331	0.340
Sample Number	88N01	88P01	88R01	88T01	88U01
Time (minutes)	60.0	60.0	90.0	133.6	180.0
Component			Mass %, dry basis		
1-Pentanol	98.409	98.307	98.128	97.796	97.355
3-Hexanol	0.013	0.016	0.000	0.000	0.000
2-Hexanol	0.071	0.095	0.012	0.016	0.008
Mixed Ether 3		not determined			
n-Pentylether	0.729	0.760	1.148	1.574	2.169
Mixed Ether 4	0.128	0.136	0.101	0.073	0.046
Mixed Ether 5	0.627	0.656	0.576	0.494	0.372
Mixed Ether 6	0.024	0.031	0.035	0.047	0.049
Total Ethers	1.507	1.583	1.860	2.188	2.636
Alcohols only					
1-Pentanol	99.915	99.888	99.988	99.983	99.991
3-Hexanol	0.013	0.016	0.000	0.000	0.000
2-Hexanol	0.073	0.096	0.012	0.017	0.009
Secondary Alcohols	0.085	0.112	0.012	0.017	0.009

Appendix D: Experiment 89 - Original readings and analysis.

Alcohol Feed: 85 % 1-Butanol and 15 % 2-Pentanol, Catalyst: 90 % H_3PO_4
Mass: Alcohol Mixture = 158.6 grams
90 % H_3PO_4 = 340.6 grams
Acid/Alcohol = 2.15:1
Reaction Pressure: Atmospheric
Comments: The nitrogen flow through the sample point was kept constant. The acid was heated to about 80 °C, before the alcohol was added. The condenser temperature was 50.5 °C. The mixture discoloured after 10 minutes to light yellow. The boiling temperature of the liquid was initially 112 °C and after 65 minutes 132 °C.

Sample Number	89Fe01	89B01	89C01	89D01	89E01	89F01	89G01
Time (minutes)	0	0	8.2	13.1	19.1	23.4	29.4
Component		Mass %, dry basis					
1-Butanol	84.903	85.053	90.583	93.551	95.876	96.988	97.546
3-Pentanol	0.000	0.050	0.370	0.453	0.256	0.140	0.095
2-Pentanol	15.003	14.789	8.286	4.838	2.365	1.212	0.614
Mixed Ether 1	0.000	0.000	0.000	0.000	0.000	0.000	0.000
n-Butylether	0.051	0.051	0.124	0.181	0.271	0.343	0.444
Mixed Ether 2	0.042	0.058	0.637	0.977	1.232	1.317	1.301
Total Ethers	0.093	0.109	0.761	1.158	1.503	1.659	1.745
Alcohols Only :1-Butanol	84.983	85.146	91.277	94.647	97.339	98.625	99.279
3-Pentanol	0.000	0.050	0.373	0.458	0.260	0.142	0.096
2-Pentanol	15.017	14.805	8.350	4.895	2.401	1.233	0.625
Total Secondary Alcohol	15.017	14.854	8.723	5.353	2.661	1.375	0.721
Sample Number	89H01	89I01	89J01	89K01	89L01	89M01	89N01
Time (minutes)	36.5	44.7	55.5	65	75	86.8	120
Component		Mass %, dry basis					
1-Butanol	98.005	98.042	98.211	98.154	97.986	97.980	97.497
3-Pentanol	0.046	0.029	0.017	0.010	0.008	0.005	0.003
2-Pentanol	0.233	0.123	0.065	0.041	0.031	0.026	0.010
Mixed Ether 1	0.000	0.000	0.000	0.000	0.000	0.000	0.000
n-Butylether	0.560	0.724	0.853	1.069	1.334	1.478	2.206
Mixed Ether 2	1.157	1.083	0.853	0.726	0.640	0.510	0.285
Total Ethers	1.717	1.806	1.707	1.795	1.975	1.989	2.491
Alcohols Only: 1-Butanol	99.717	99.845	99.917	99.948	99.960	99.968	99.987
3-Pentanol	0.047	0.029	0.017	0.011	0.008	0.005	0.003
2-Pentanol	0.237	0.126	0.066	0.042	0.032	0.026	0.010
Total Secondary Alcohol	0.283	0.155	0.083	0.052	0.040	0.032	0.013
Sample Number	89O01	89P01	89Q01	89R01	89S01	89T01	89U01
Time (minutes)	135.5	157	210	240	270	300	360
Component		Mass %, dry basis					
1-Butanol	97.190	96.846	95.670	95.167	94.744	93.651	92.646
3-Pentanol	0.002	0.000	0.000	0.000	0.000	0.000	0.000
2-Pentanol	0.011	0.010	0.000	0.003	0.000	0.000	0.000
Mixed Ether 1	0.000	0.000	0.000	0.000	0.000	0.000	0.000
n-Butylether	2.582	2.996	4.268	4.791	5.230	6.331	7.346
Mixed Ether 2	0.215	0.148	0.062	0.039	0.026	0.018	0.008
Total Ethers	2.798	3.145	4.330	4.830	5.256	6.349	7.354
Alcohols Only: 1-Butanol	99.987	99.990	100.000	99.996	100.000	100.000	100.000
3-Pentanol	0.002	0.000	0.000	0.000	0.000	0.000	0.000
2-Pentanol	0.011	0.010	0.000	0.004	0.000	0.000	0.000
Total Secondary Alcohol	0.013	0.010	0.000	0.004	0.000	0.000	0.000

Appendix D: Experiment 90 - Original readings and analysis.

Alcohol Feed: 85 % 1-Butanol and 15 % 2-Pentanol
Catalyst: 55 % H_2SO_4
Mass: Alcohol Mixture = 157.3 grams
55 % H_2SO_4 = 75.5 grams
Acid/Alcohol = 0.48:1

Reaction Pressure: Atmospheric

Comments: The nitrogen flow through the sample point was kept constant. The acid was heated to about 80 °C, before the alcohol was added. The condenser temperature was 50.5 °C. The mixture did not discolour at any time. The boiling temperature of the liquid was initially 103 °C.

Sample Number	90A01	90B01	90D01	90F01	90H01
Time (minutes)	0	5.33	20	48.5	85
Component		Mass %, dry basis			
1-Butanol	84.383	83.932	83.824	83.910	83.962
3-Pentanol	0.000	0.000	0.000	0.000	0.026
2-Pentanol	15.553	15.937	15.876	15.515	15.102
Mixed Ether 1	0.000	0.007	0.022	0.026	0.013
n-Butylether	0.056	0.075	0.129	0.232	0.371
Mixed Ether 2	0.007	0.032	0.111	0.264	0.455
Total Ether	0.063	0.113	0.263	0.521	0.839
Alcohols Only					
1-Butanol	84.437	84.042	84.076	84.395	84.733
3-Pentanol	0.000	0.000	0.000	0.000	0.026
2-Pentanol	15.563	15.958	15.924	15.605	15.241
Total Secondary Alcohol	15.563	15.958	15.924	15.605	15.267
Sample Number	90J01	90L01	90M01	90N01	90O01
Time (minutes)	125.33	196.2	240	282.4	824
Component		Mass %, dry basis			
1-Butanol	84.033	84.222	84.526	84.581	84.885
3-Pentanol	0.043	0.071	0.078	0.093	0.161
2-Pentanol	14.689	13.898	13.250	12.790	8.370
Mixed Ether 1	0.000	0.000	0.037	0.003	0.021
n-Butylether	0.506	0.738	0.860	1.045	3.041
Mixed Ether 2	0.645	0.960	1.125	1.349	3.297
Total Ether	1.151	1.697	2.022	2.397	6.359
Alcohols Only					
1-Butanol	85.084	85.773	86.379	86.782	90.868
3-Pentanol	0.044	0.072	0.080	0.095	0.172
2-Pentanol	14.873	14.154	13.541	13.123	8.960
Total Secondary Alcohol	14.916	14.227	13.621	13.218	9.132

Appendix D: Experiment 91 - Original readings and analysis.

Alcohol Feed: 85 % 1-Butanol and 15 % 2-Pentanol
Ether Feed: n-Butylether was added to the feed
Catalyst: 90 % H_3PO_4
Mass: Alcohol Mixture = 157.1 grams
90 % H_3PO_4 = 340.0 grams
n-Butylether = 5.0 grams

Acid/Alcohol = 2.16:1

Reaction Pressure: Atmospheric

Comments: The nitrogen flow through the sample point was kept constant. The acid was heated to about 80 °C, before the alcohol and ether was added. The condenser temperature was 50.5 °C. The boiling temperature of the liquid was initially 128 °C. The reaction mixture discolours after 5 minutes to yellow. After 40 minutes the reaction mixture was golden-yellow.

Sample Number	91A01	91B01	91C01	91D01	91E01	91F01
Time (minutes)	0.5	5	15	39.5	45	51.5
Component		Mass %, dry basis				
1-Butanol	83.181	85.428	90.658	94.157	94.745	94.188
3-Pentanol	0.079	0.273	0.446	0.081	0.066	0.051
2-Pentanol	13.512	11.006	4.380	0.372	0.246	0.183
Mixed Ether 1	0.000	0.000	0.000	0.000	0.000	0.000
n-Butylether	3.092	2.893	3.166	3.702	3.473	4.078
Mixed Ether 2	0.137	0.400	1.350	1.689	1.471	1.500
Total Ether	3.228	3.293	4.516	5.391	4.943	5.578
Alcohols Only						
1-Butanol	85.956	88.337	94.946	99.522	99.672	99.752
3-Pentanol	0.081	0.283	0.467	0.085	0.069	0.054
2-Pentanol	13.963	11.381	4.587	0.393	0.258	0.194
Total Secondary Alcohol	14.044	11.663	5.054	0.478	0.328	0.248

Sample Number	91G01	91I01	91M01	91O01	91P01
Time (minutes)	60	86	150	228	300
Component		Mass %, dry basis			
1-Butanol	94.593	94.292	93.732	92.268	89.214
3-Pentanol	0.043	0.032	0.014	0.007	0.000
2-Pentanol	0.135	0.094	0.046	0.024	0.015
Mixed Ether 1	0.000	0.000	0.000	0.000	0.000
n-Butylether	3.978	4.676	5.825	7.548	10.693
Mixed Ether 2	1.251	0.906	0.382	0.152	0.078
Total Ether	5.229	5.582	6.207	7.700	10.771
Alcohols Only					
1-Butanol	99.812	99.866	99.935	99.966	99.983
3-Pentanol	0.045	0.034	0.015	0.008	0.000
2-Pentanol	0.143	0.100	0.049	0.026	0.017
Total Secondary Alcohol	0.188	0.134	0.065	0.034	0.017

Appendix D: Experiment 92 - Original readings and analysis.

Alcohol Feed: 85 % 1-Butanol and 15 % 2-Pentanol
Catalyst: 67 % H_2SO_4
Mass: Alcohol Mixture = 157.3 grams
67 % H_2SO_4 = 103.0 grams
Acid/Alcohol = 0.65:1

Reaction Pressure: Atmospheric

Comments: The nitrogen flow through the sample point was kept constant. The acid was heated to about 80 °C, before the alcohol was added. The condenser temperature was 50.5 °C. The mixture did not discolour at any time. The boiling temperature of the liquid was initially 109 °C.

Sample Number	92A01	92B01	92C01	92D01	92E01	92F01
Time (minutes)	0.1	3.5	10	17.3	29.8	44.9
Component		Mass %, dry basis				
1-Butanol	82.357	83.403	83.617	85.045	86.210	85.845
3-Pentanol	0.000	0.043	0.092	0.130	0.173	0.221
2-Pentanol	17.472	16.103	15.326	13.548	11.620	10.821
Mixed Ether 1		not determined				
n-Butylether	0.095	0.189	0.353	0.461	0.720	1.145
Mixed Ether 2	0.075	0.262	0.613	0.815	1.277	1.969
Total Ether	0.171	0.451	0.965	1.277	1.997	3.114
Alcohols Only						
Total	99.829	99.549	99.035	98.723	98.003	96.886
1-Butanol	82.498	83.781	84.432	86.145	87.966	88.603
3-Pentanol	0.000	0.043	0.093	0.132	0.177	0.228
2-Pentanol	17.502	16.176	15.475	13.724	11.857	11.169
Total Secondary Alcohol	17.502	16.219	15.568	13.855	12.034	11.397

Sample Number	92H01	92I01	92J01	92K01	92L01	92M01
Time (minutes)	81.7	107	128.6	166	182.2	303.5
Component		Mass %, dry basis				
1-Butanol	88.462	87.444	86.445	87.242	89.322	85.647
3-Pentanol	0.210	0.195	0.185	0.133	0.103	0.040
2-Pentanol	6.960	5.920	4.723	3.189	2.422	0.548
Mixed Ether 1	not determined					
n-Butylether	1.810	2.844	4.123	4.887	4.423	9.293
Mixed Ether 2	2.558	3.597	4.523	4.549	3.729	4.472
Total Ether	4.368	6.441	8.646	9.436	8.152	13.765
Alcohols Only						
Total	95.632	93.559	91.354	90.564	91.848	86.235
1-Butanol	92.502	93.464	94.627	96.332	97.250	99.318
3-Pentanol	0.220	0.208	0.203	0.147	0.112	0.047
2-Pentanol	7.278	6.328	5.170	3.521	2.637	0.635
Total Secondary Alcohol	7.498	6.536	5.373	3.668	2.750	0.682

Appendix D: Experiment 93 - Original readings and analysis.

Alcohol Feed: 85 % 1-Butanol and 15 % 2-Pentanol
Catalyst: 90 % H_3PO_4
Mass: Alcohol Mixture = 146 grams
90 % H_3PO_4 = 315.7 grams
Acid/Alcohol = 2.2:1

Reaction Pressure: Atmospheric

Comments: **The nitrogen flow through the sample point was kept constant and low.** The acid was heated to about 80 °C, before the alcohol was added. The condenser temperature was 50.5 °C.

Sample Number	93A01	93B01	93C01	93E01	93F01	93G01
Time (minutes)	0.5	5	11.2	26.2	39	56.8
Component		Mass %, dry basis				
1-Butanol	86.059	89.146	92.127	97.055	97.598	97.588
3-Pentanol	0.118	0.337	0.410	0.150	0.074	0.045
2-Pentanol	13.499	9.854	6.043	0.729	0.256	0.137
n-Butylether	0.151	0.117	0.221	0.426	0.676	1.168
Mixed Ether 2	0.172	0.546	1.199	1.640	1.396	1.062
Total Ether	0.323	100.000	100.000	100.000	100.000	100.000
Alcohols Only						
1-Butanol	86.338	89.741	93.454	99.102	99.663	99.813
3-Pentanol	0.119	0.339	0.416	0.153	0.075	0.046
2-Pentanol	13.543	9.920	6.130	0.744	0.262	0.140
Total Secondary Alcohols	13.662	10.259	6.546	0.898	0.337	0.187

Sample Number	93H01	93I01	93J01	93K01	93L01
Time (minutes)	71	92.5	120.0	168.0	394.0
Component		Mass %, dry basis			
1-Butanol	97.269	97.110	96.503	94.718	85.126
3-Pentanol	0.040	0.026	0.017	0.012	0.000
2-Pentanol	0.123	0.090	0.062	0.025	0.039
n-Butylether	1.666	2.202	3.089	5.099	14.835
Mixed Ether 2	0.902	0.571	0.329	0.146	0.000
Total Ethers	100.000	2.773	3.418	5.245	14.835
Alcohols Only					
1-Butanol	99.833	99.880	99.918	99.961	99.954
3-Pentanol	0.041	0.027	0.017	0.012	0.000
2-Pentanol	0.126	0.093	0.064	0.027	0.046
Total Secondary Alcohols	0.167	0.120	0.082	0.039	0.046

Appendix D: Experiment 94 - Original readings and analysis.

Alcohol Feed: 85 % 1-Butanol and 15 % 2-Pentanol
Catalyst: 90 % H_3PO_4
Mass: Alcohol Mixture = 109.4 grams
90 % H_3PO_4 = 235.1 grams
Acid:Alcohol = 2.15:1
Reaction Pressure: Atmospheric

Comments: **The nitrogen flow through the sample point was kept constant but very high.** The acid was heated to about 80 °C, before the alcohol was added. The condenser temperature was 50.5 °C.

Sample Number	94A	94B	94C	94D	94E
Time (minutes)	0.75	6.5	15.1	21.5	31.2
Component		Mass %, dry basis			
1-Butanol	84.974	86.580	94.002	96.916	98.464
3-Pentanol	0.012	0.138	0.394	0.186	0.040
2-Pentanol	14.942	12.982	4.251	1.296	0.217
n-Butylether	0.051	0.068	0.157	0.240	0.364
Mixed Ether 2	0.022	0.232	1.197	1.361	0.915
Total Ether	0.073	0.300	1.354	1.601	1.279
Alcohols only: 1-Butanol	85.036	86.841	95.292	98.493	99.739
3-Pentanol	0.012	0.138	0.399	0.189	0.041
2-Pentanol	14.953	13.021	4.309	1.317	0.220
Total Secondary Alcohol	14.964	13.159	4.708	1.507	0.261

Sample Number	94F	94G	94H	94I
Time (minutes)	37.7	46.7	54.2	60
Component				
1-Butanol	98.846	99.008	99.149	99.243
3-Pentanol	0.020	0.007	0.005	0.000
2-Pentanol	0.058	0.034	0.014	0.000
n-Butylether	0.460	0.611	0.652	0.657
Mixed Ether 2	0.615	0.340	0.181	0.100
Total Ether	1.076	0.951	0.833	0.757
Alcohols only: 1-Butanol	99.921	99.958	99.981	100.000
3-Pentanol	0.020	0.007	0.005	0.000
2-Pentanol	0.059	0.035	0.014	0.000
Total Secondary Alcohol	0.079	0.042	0.019	0.000

Sample Number	94J	94K	94L	94M
Time (minutes)	70.3	81	100	122
Component				
1-Butanol	99.182	99.058	98.809	98.757
3-Pentanol	0.000	0.000	0.000	0.000
2-Pentanol	0.000	0.000	0.000	0.000
n-Butylether	0.778	0.928	1.191	1.243
Mixed Ether 2	0.040	0.014	0.000	0.000
Total Ether	0.818	0.942	1.191	1.243
Alcohols only: 1-Butanol	100.000	100.000	100.000	100.000
3-Pentanol	0.000	0.000	0.000	0.000
2-Pentanol	0.000	0.000	0.000	0.000
Total Secondary Alcohol	0.000	0.000	0.000	0.000

Appendix D: Experiment 95 - Original readings and analysis.

Alcohol Feed: 85 % 1-Butanol and 15 % 2-Pentanol
Catalyst: 90 % H_3PO_4
Mass: Alcohol Mixture = 149.9 grams
90 % H_3PO_4 = 324.0 grams
Acid:Alcohol = 2.16:1
Reaction Pressure: Atmospheric
Comments: The nitrogen flow through the sample point was low and constant. The acid was heated to about 80 °C, before the alcohol was added. The condenser temperature was 50.5 °C. The reaction boiling temperature was 139 °C after 10 minutes. After 70 minutes the reaction flask was removed from the heat and mixture was treated as described in the table below, see samples G, H and I.

Sample Number	Feed	A	B	C	D	E	F
Time (minutes)	0	3	8.3	19	38	48.5	69.8
Component		Mass %, dry basis					
1-Butanol	84.676	85.421	91.011	95.963	97.934	98.108	98.101
3-Pentanol	0.000	0.078	0.403	0.224	0.032	0.013	0.005
2-Pentanol	15.253	14.344	7.737	2.189	0.213	0.055	0.029
n-Butylether	0.071	0.069	0.140	0.300	0.669	0.895	1.301
Mixed Ether 2	0.000	0.088	0.710	1.325	1.152	0.929	0.565
Total Ether	0.071	0.157	0.850	1.624	1.821	1.824	1.865
Alcohols Only							
1-Butanol	84.736	85.555	91.791	97.547	99.750	99.931	99.965
3-Pentanol	0.000	0.078	0.406	0.227	0.033	0.013	0.005
2-Pentanol	15.264	14.367	7.803	2.225	0.217	0.056	0.030
Total Secondary Alcohol	15.264	14.445	8.209	2.453	0.250	0.069	0.035

Sample Number	G	H	I
	The mixture was allowed to cool off to 70 °C and then it was sampled. The remaining 174.1 gram of the reaction mixture was added to 150 g DIPE.	The DIPE/Reaction mixture was kept at room temperature in a separating flask. After 4,5 hours the top phase was analysed. The analyses is shown below.	The bottom phase (acid/water/organics) was neutralised and analysed. The analysis is shown below.
Component	Mass %, dry basis		
1-Butanol	97.560	15.941	99.089
3-Pentanol	0.010	0.000	0.011
2-Pentanol	0.034	0.000	0.032
n-Butylether	1.727	58.999	0.666
Mixed Ether 2	0.669	25.060	0.201
Total Ether	2.396	84.059	0.868
Alcohols Only			
1-Butanol	99.955	100.000	99.956
3-Pentanol	0.010	0.000	0.011
2-Pentanol	0.035	0.000	0.033
Total Secondary Alcohol	0.045	0.000	0.044

Appendix D: Experiment 96 - Original readings and analysis.

Alcohol Feed: 50 % 1-Butanol and 50 % 2-Pentanol
Catalyst: 90 % H_3PO_4
Mass: Alcohol Mixture = 78.9 grams
90 % H_3PO_4 = 172.0 grams
Acid:Alcohol = 2.18:1

Reaction Pressure: Atmospheric

Comments: The nitrogen flow through the sample point was low and constant. The acid was heated to about 80 °C, before the alcohol was added. The condenser temperature was 50.5 °C. Losses of the reaction mixture vapour phase occurred between samples H and I. The sampling system was open.

Sample Number	Feed	A	B	C	D	E
Time (minutes)	0	3.3	9.1	15.3	23.1	33
Component		Mass %, dry basis				
1-Butanol	50.777	57.042	72.760	89.162	94.541	97.750
3-Pentanol	0.000	0.850	1.650	0.958	0.323	0.084
2-Pentanol	49.182	41.592	23.851	7.129	1.586	0.272
n-Butylether	0.042	0.051	0.080	0.113	0.264	0.382
Mixed Ether 2	0.000	0.465	1.660	2.637	3.285	1.513
Total Ethers	0.042	0.516	1.739	2.751	3.549	1.895
Alcohols Only						
1-Butanol	50.798	57.338	74.048	91.684	98.020	99.638
3-Pentanol	0.000	0.854	1.679	0.985	0.335	0.085
2-Pentanol	49.202	41.808	24.273	7.331	1.644	0.277
Total Secondary Alcohols	49.202	42.662	25.952	8.316	1.980	0.362

Sample Number	F	G	H	I	J
Time (minutes)	52.7	73.3	82.6	113	139
Component	Mass %, dry basis				
1-Butanol	98.093	98.426	98.214	98.096	97.507
3-Pentanol	0.045	0.025	0.012	0.000	0.000
2-Pentanol	0.144	0.065	0.043	0.000	0.000
n-Butylether	0.784	1.119	1.458	1.833	2.464
Mixed Ether 2	0.933	0.366	0.273	0.072	0.029
Total Ethers	1.717	1.484	1.731	1.904	2.493
Alcohols Only					
1-Butanol	99.807	99.909	99.944	100.000	100.000
3-Pentanol	0.046	0.025	0.012	0.000	0.000
2-Pentanol	0.147	0.066	0.043	0.000	0.000
Total Secondary Alcohols	0.193	0.091	0.056	0.000	0.000

Appendix D: Experiment 97 - Original readings and analysis.

Alcohol Feed: 100 % 2-Hexanol
Catalyst: 90 % H_3PO_4
Mass: Alcohol = 32.8 grams
90 % H_3PO_4 = 70.9 grams
Acid/Alcohol = 2,16:1
Reaction Pressure: Atmospheric
Comments: The condenser temperature was maintained at 70 °C. The nitrogen flow through sampling system was low. The reaction was extremely vigorous. Almost all the alcohol was dehydrated after about 10 minutes. Samples A and B were taken during the heating process. Sample A was taken before the reaction mixture reached 70 °C and B was taken at 70 °C.

Sample Number	A	B	C	D	E	F	G
Time (minutes)	0.0	0.0	0.3	1.2	2.5	4.0	6.5
Component		Mass %, dry basis					
3-Hexanol	0.000	0.105	0.359	0.852	2.517	5.471	7.421
2-Hexanol	100.000	99.895	99.529	98.907	96.826	90.486	57.982
Byproduct C	0.000	0.000	0.013	0.027	0.080	0.489	4.257
Byproduct D	0.000	0.000	0.045	0.095	0.262	1.514	13.062
Byproduct E	0.000	0.000	0.010	0.022	0.059	0.476	4.077
Byproduct F	0.000	0.000	0.046	0.098	0.256	1.564	13.201
Total Byproducts	0.000	0.000	0.113	0.241	0.658	4.043	34.597
Total Alcohol	100.000	100.000	99.887	99.759	99.342	95.957	65.403
3-Hexanol	0.000	0.105	0.359	0.854	2.533	5.702	11.347
2-Hexanol	100.000	99.895	99.641	99.146	97.467	94.298	88.653

Appendix D: Experiment 98 - Original readings and analysis.

Alcohol Feed: 100 % 1-Pentanol
Catalyst: 90 % H_3PO_4
Mass: Alcohol = 147.6 grams; 90 % H_3PO_4 = 318.5 grams
Acid/Alcohol = 2.16:1
Reaction Pressure Atmospheric
Comments: The condenser temperature was maintained at 70 °C. The nitrogen flow through sampling system was low.

Sample Number	A	B	C	E	G	I
Time (minutes)	0.0	0.7	3.0	8.6	22.5	37.0
Component			Mass %, dry basis			
1-Pentanol	99.611	99.513	99.399	99.142	98.424	97.556
Byproduct G	0.000	0.045	0.058	0.071	0.086	0.105
Byproduct H	0.334	0.307	0.309	0.290	0.292	0.321
Byproduct I	0.022	0.022	0.022	0.023	0.022	0.030
n-Pentylether	0.033	0.113	0.211	0.474	1.176	1.988
Total Ether + Byp.	0.389	0.487	0.601	0.858	1.576	2.444

Sample Number	K	M	O	P	Q
Time (minutes)	64.0	89.7	145.2	736.0	805.0
Component			Mass %, dry basis		
1-Pentanol	96.201	94.793	92.202	73.523	67.028
Byproduct G	0.112	0.121	0.121	0.099	0.103
Byproduct H	0.339	0.357	0.389	0.443	0.498
Byproduct I	0.042	0.046	0.061	0.151	0.178
n-Pentylether	3.307	4.683	7.228	25.784	32.192
Total Ether + Byp.	3.799	5.207	7.798	26.477	32.972

Appendix D: Experiment 99 - Original readings and analysis.

Alcohol Feed: 85 % 1-Butanol and 15 % 2-Pentanol
Catalyst: 90 % H_3PO_4
Mass: Alcohol Mixture = 157.3 grams
90 % H_3PO_4 = 339.8 grams
Acid:Alcohol = 2.16:1

Reaction Pressure: **Vacuum,** varied between 540 and 660 mbar(a).

Comments: Initially (first 15 minutes) a nitrogen purge flow was maintained through the sample point. The reaction mixture started to discolour almost immediately after the vacuum was drawn. After 30 about minutes the mixtures discoloured to deep red. The condenser temperature was maintained at 41 °C. The heat was switched off and the vacuum was broken so that a sample could be taken. Initially the system was not very stable, the vacuum, nitrogen purge and temperature changed. 28 grams were collected as vents. The vent condensate separated into two phases, an organic phase (26 g) and a water phase (2 g).

Sample Number	FEED	A*	B	C	D
Time (minutes)	0	0	13.5	33.5	47
Component		Mass %, dry basis			
1-Butanol	84.087	83.993	86.042	91.554	95.309
3-Pentanol	0.000	0.000	0.088	0.410	0.294
2-Pentanol	15.789	14.918	13.450	7.048	2.935
Mixed Ether 1	0.000	1.020	0.189	0.046	0.225
n-Butylether	0.124	0.068	0.078	0.119	0.141
Mixed Ether 2	0.000	0.000	0.153	0.823	1.096
Total ether	0.124	1.089	0.420	0.988	1.461
Alcohol only					
1-Butanol	84.192	84.917	86.405	92.467	96.722
3-Pentanol	0.000	0.000	0.088	0.414	0.299
2-Pentanol	15.808	15.083	13.507	7.119	2.979
Total Secondary Alcohols	15.808	15.083	13.595	7.533	3.278

Sample Number	E	F	G	H	Vent
Time (minutes)	69.5	104	144	240	Top phase
Component		Mass %, dry basis			Organic
1-Butanol	97.701	99.308	99.578	98.572	92.
3-Pentanol	0.148	0.022	0.000	0.000	0.1
2-Pentanol	0.980	0.085	0.009	0.000	1.3
Mixed Ether 1	0.142	0.000	0.014	0.174	0.0
n-Butylether	0.129	0.195	0.340	1.230	2.9
Mixed Ether 2	0.900	0.391	0.059	0.024	2.9
Total ether	1.170	0.586	0.413	1.428	5.8
Alcohol only					
1-Butanol	98.858	99.893	99.991	100.000	98.440
3-Pentanol	0.150	0.022	0.000	0.000	0.129
2-Pentanol	0.992	0.085	0.009	0.000	1.431
Total Secondary Alcohols	1.142	0.107	0.009	0.000	1.560

* sample ignored in graphs plotted in Appendix E

Appendix D: Experiment 100 - Original readings and analysis.

Alcohol Feed: 85 % 1-Pentanol and 15 % 2-Hexanol

Catalyst: 90 % H_3PO_4

Mass: Alcohol Mixture = 67.23 grams
85 % H_3PO_4 = 146.5 grams

Acid:Alcohol = 2.18:1

Reaction Pressure: **Vacuum, varied between 590 and 650 mbar(abs.)**

Comments: The nitrogen purge flow through the sample point was kept closed. The condenser temperature was maintained at 61,5 °C. Every time a sample was taken, the heat was switched off and the vacuum was broken. The vents were collected in a trap which was placed in an ice bucket. After the ice has molten and 24 hours later about 2 grams were collected as vents. The reaction temperature was about 118 °C.

Sample Number	Feed	A	B	C	D	E
Time (minutes)	0.0	2.0	12.0	22.0	36.5	51.5
Component		Mass %, dry basis				
1-Pentanol	84.232	88.414	95.545	97.719	97.691	96.497
3-Hexanol	0.000	0.292	0.307	0.074	0.024	0.009
2-Hexanol	15.749	10.975	2.754	0.260	0.055	0.026
Mixed Ether 3	0.000	0.000	0.010	0.051	0.139	0.322
n-Pentylether	0.019	0.046	0.199	0.555	1.231	2.640
Mixed Ether 4	0.000	0.070	0.350	0.368	0.180	0.083
Mixed Ether 5	0.000	0.202	0.836	0.972	0.680	0.422
Mixed Ether 6		not detected				
Total Ether	0.019	0.319	1.394	1.947	2.229	3.468
1-Pentanol	84.248	88.697	96.895	99.659	99.919	99.964
3-Hexanol	0.000	0.293	0.311	0.076	0.025	0.009
2-Hexanol	15.752	11.010	2.793	0.265	0.056	0.027
Total Secondary Alcohol	15.752	11.303	3.105	0.341	0.081	0.036

Sample Number	F	G	H	I	VENT
Time (minutes)	66.5	84.0	99.0	140.0	
Component		Mass %, dry basis			
1-Pentanol	95.089	92.552	91.151	89.691	99.895
3-Hexanol	0.006	0.000	0.007	0.000	0.002
2-Hexanol	0.016	0.000	0.012	0.000	0.032
Mixed Ether 3	0.476	0.728	0.796	0.715	0.007
n-Pentylether	4.112	6.594	7.972	9.594	0.056
Mixed Ether 4	0.045	0.017	0.009	0.000	0.003
Mixed Ether 5	0.256	0.110	0.053	0.000	0.006
Mixed Ether 6		not detected			
Total Ether	4.890	7.448	8.830	10.309	0.072
1-Pentanol	99.977	100.000	99.979	100.000	99.966
3-Hexanol	0.006	0.000	0.008	0.000	0.002
2-Hexanol	0.017	0.000	0.013	0.000	0.032
Total Secondary Alcohol	0.023	0.000	0.021	0.000	0.034

Appendix E - Results of dehydration experiments

Appendix E - Results of Experiments 04,05,06.

No.	Reaction Mixture		Reaction Time	Mass Loss	Distillate		Comments
		%	[min]	[gram]		[mass] %	
04: A	Acid Strength	80	563	0,2	1-Propanol	88.1	Based on alcohol only.
	H_2SO_4	10.8			2-Butanol	11.9	
	H_2O	2.7			1-Propanol recovery	74	
	1-Propanol	73.5			Heavy Byproducts	9	No cracking
	2-Butanol	13					
04: B	Acid Strength	80	689	6.3	1-Propanol	96.3	Based on alcohol only.
	H_2SO_4	25.0			2-Butanol	3.7	
	H_2O	6.2			1-Propanol recovery	?	
	1-Propanol	58.4			Heavy Byproducts	55.7	No cracking
	2-Butanol	10.3					
04: C	Acid Strength	80	359	6.2	1-Propanol	96.4	Based on alcohol only.
	H_2SO_4	26.9			2-Butanol	3.6	
	H_2O	6.7			1-Propanol recovery	34	
	1-Propanol	56.4			Heavy Byproducts	51.8	Cracking, bottoms black
	2-Butanol	10.0					
04: D	Acid Strength	80	294	13.7	1-Propanol	99.8	Based on alcohol only.
	H_2SO_4	40.0			2-Butanol	0.2	
	H_2O	10			1-Propanol recovery	14	Cracking during reaction & Distillation
	1-Propanol	42.5			Heavy Byproducts	65.2	
	2-Butanol	7.5					
05: A	Acid Strength	67	127	9.8	1-Propanol	99.0	Based on alcohol only.
	H_2SO_4	33.4			2-Butanol	1.0	
	H_2O	16.5			1-Propanol recovery	55	
	1-Propanol	42.3			Heavy Byproducts	18.4	No cracking
	2-Butanol	7.5					
05: B	Acid Strength	67	127	0.6	1-Propanol	90.5	Based on alcohol only.
	H_2SO_4	22.3			2-Butanol	9.5	
	H_2O	11.0			1-Propanol recovery	72	
	1-Propanol	56.7			Heavy Byproducts	16.1	Cracking, bottoms black
	2-Butanol	10					
06: A	Acid Strength	55	120	5.4	1-Propanol	94.2	Based on alcohol only.
	H_2SO_4	33.1			2-Butanol	5.8	
	H_2O	27.0			1-Propanol recovery	88	
	1-Propanol	33.9			Heavy Byproducts	6.6	No cracking
	2-Butanol	6					
06: B	Acid Strength	55	120	12.2	1-Propanol	99.9	Not detected
	H_2SO_4	39.3			2-Butanol		
	H_2O	32.1			1-Propanol recovery	75	
	1-Propanol	24.3			Heavy Byproducts	8.1	No cracking
	2-Butanol	4.3					

Appendix E: Results of solid catalysts, Resins, experiments 7 to 10

Exp. No.	Resin	Alcohol Feed	Reaction System	Reaction Time (min.)	Mass loss (gram)	Analysis of Distillate: Primay Alcohol (mass %)	Analysis of Distillate: Sec. Alcohol (mass %)	Ratio Dry Alcohol: Resin	water [mass%]
7-G01	Dowex Macroporous	85 % 1-Propanol 15% 2-Butanol	Column	after 60	N/A	85.1	14.9	N/A	20
7-GO 2	Dowex Macroporous	85 % 1-Propanol 15% 2-Butanol	Column	after 120	N/A	85.2	14.8		
7-G03	Dowex Macroporous	85 % 1-Propanol 15% 2-Butanol	Column	last droplets	N/A	85.2	14.8		
8A	Amberlyst 131 Wet	85 % 1-Propanol 15% 2-Butanol	Total Reflux Reactor	120	2.7	85.3	14.7	6.4:1	33
8B	Dowex Macroporous	85 % 1-Propanol 15% 2-Butanol	Total Reflux Reactor	120	2.4	85.3	14.7	4.6:1	33
8C	Dowex 50wx8-100	85 % 1-Propanol 15% 2-Butanol	Total Reflux Reactor	120	3.4	85.0	15.0	6.6:1	33
8D	Amberlyst 15	85 % 1-Propanol 15% 2-Butanol	Total Reflux Reactor	120	not weigh.	85.1	14.9	6.7:1	33
8E	Amberlyst 131 Wet	85 % 1-Propanol 15% 2-Butanol	Total Reflux Reactor	180	1.1	85.4	14.6	7.5:1	5
8F	Dowex Macroporous	85 % 1-Propanol 15% 2-Butanol	Total Reflux Reactor	180	1.1	85.6	14.4	8.5:1	5
8G	Dowex 50wx8-100	85 % 1-Propanol 15% 2-Butanol	Total Reflux Reactor	180	1	85.5	14.5	8:1	5
8H	Amberlyst 15	85 % 1-Propanol 15% 2-Butanol	Total Reflux Reactor	180	1.5	85.3	14.7	8.5:1	5.8
8I	Amberlyst 131 Wet	85 % 1-Propanol 15% 2-Butanol	Total Reflux Reactor	120	0.9	84.9	15.1	10:1	5.2
8J	Dowex Macroporous	85 % 1-Propanol 15% 2-Butanol	Total Reflux Reactor	120	0.8	85.2	14.8	10:1	5.7
8K	Dowex 50wx8-100	85 % 1-Propanol 15% 2-Butanol	Total Reflux Reactor	120	0.6	84.8	15.2	10:1	5.6
8L	Amberlyst 15	85 % 1-Propanol 15% 2-Butanol	Total Reflux Reactor	120	1.7	85.0	15.0	10:1	5.8
9A	Amberlyst 131 Wet	100 % 2-Pentanol	Total Reflux Reactor	120	3.3	n/a		3:1	14
9B	Dowex Macroporous	100 % 2-Pentanol	Total Reflux Reactor	120	0.8	n/a		3:1	14
9C	Dowex 50wx8-100	100 % 2-Pentanol	Total Reflux Reactor	120	0.6	n/a		5:1	9
9D	Amberlyst 15	100 % 2-Pentanol	Total Reflux Reactor	120	not weighed	n/a		6:1	17
10A	Amberlyst 131 Wet	85 % 1-Propanol 15% 2-Butanol	Total Reflux Reactor	150	0.8	83.2	16.8	1.1:1	10
10B	Amberlyst 15	85 % 1-Propanol 15% 2-Butanol	Total Reflux Reactor	90	3.2	86.6	13.4	2:1	8

Appendix E: Results of experiments 11 to 13

Exp. No.	Alcohol Feed	Acid	Acid:Alc. - Reaction Time - Distillation Temp.	Recovery 1-Propanol / Quality 1-Propanol (alcohols only) (mass %)	Water (mass %)	Product Composition (mass %, dry basis)	
11A	85 % 1-Propanol 15% 2-Butanol	55 % H_3PO_4	1:1 175 min.	N/A / 85 %	Not Analysed	Lights 1-Propanol 2-Butanol Heavies	0 84.6 15.4 None
11B	85 % 1-Propanol 15% 2-Butanol	72 % H_3PO_4	1:1 160 min.	N/A / 86 %	Not Analysed	Lights 1-Propanol 2-Butanol Heavies	1.4 84.6 13.8 0.2
11D	85 % 1-Propanol 15% 2-Butanol	88 % H_3PO_4	1,6:1 150 min. 128 °C	61 % / 99.5 %	18.3	Lights 1-Propanol 2-Butanol Heavies	0.9 93.0 0.5 5.7
12A	85 % 1-Propanol 15% 2-Butanol	88 % H_3PO_4	1,3:1 120 min. 140 °C	N/A / 93.0 %	Not Analysed	Lights 1-Propanol 2-Butanol Heavies	4.4 84.6 6.4 4.6
12C	85 % 1-Propanol 15% 2-Butanol	88 % H_3PO_4	0,84:1 120 min.	N/A / 87.7 %	Not Analysed	Lights 1-Propanol 2-Butanol Heavies	3.2 83.0 11.7 2.2
12D	85 % 1-Propanol 15% 2-Butanol	88 % H_3PO_4	2,2:1 120 min. 120 °C	71 % / 99.4 %	20	Lights 1-Propanol 2-Butanol Heavies	1.7 92.7 0.6 5.0
13D	85 % 1-Propanol 15% 2-Butanol	94,7 % Oxalic Acid	1,1:1 60 min. 105 °C	80 gram wet Alcohol / 88.7 %	Not Analysed	Many byproducts were formed	
13C	85 % 1-Propanol 15% 2-Butanol	93,5 % $NaHSO_4$	1,3:1 120 min. 95 °C	41 gram wet Alcohol / 82 %	Not Analysed	Many byproducts were formed	

Appendix E – Results of Experiments 14 A, B, C, D

Exp. No.	Alcohol Feed	Acid	Acid:Alc. - Reaction Time - Distillation Temp.	Recovery 1-Propanol / Quality 1-Propanol (alcohols only) (mass %)			Product Composition (mass %, dry basis)
14A	85 % 1-Propanol 15% 2-Butanol	85 % H_3PO_4	2,2:1 120 min. 140 °C	57 % 96.6 %		Before Fractionation Lights	Distilled till Bot. 140 °C
14B	85 % 1-Propanol 15% 2-Butanol	85 % H_3PO_4	2,2:1 120 min. 140 °C	Water %	20.1	1-Propanol 2-Butanol Heavies Total	2.07 88.31 3.08 6.54 145.8 gram
14 A&B	Cut 1 T_{top}=74-86 °C Lights 1-Propanol 2-Butanol Heavies Total	Mass %, dry basis 7.4 39.0 1.4 52.2 15.7 gram	Cut 2 T_{top}=86 °C Lights 1-Propanol 2-Butanol Heavies Total	Mass %, dry basis 0.0 96.2 3.6 0.3 82.4 gram		Rest T_{bottom}=140 °C Lights 1-Propanol 2-Butanol Heavies Total	Mass %, dry basis 0.0 96.8 3.2 0.0 37 gram
	Water % % of original sample	Two phases 10	Water % % of original sample	28 55		Water % % of original sample	4.6 25

Exp. No.	Alcohol Feed	Acid	Acid:Alc. - Reaction Time - Distillation Temp.	Recovery 1-Propanol / Quality 1-Propanol (alcohols only) (mass %)			Product Composition (mass %, dry basis)
14C	85 % 1-Propanol 15% 2-Butanol	55 % H_2SO_4	2,5:1 120 min. 120 °C	52 98.6		Before Fractionation Lights	Distilled Bot. 120 °C
14D	85 % 1-Propanol 15% 2-Butanol	55 % H_2SO_4	2,5:1 120 min. 120 °C	Water %	32.1	1-Propanol 2-Butanol Heavies Total	0.3 92.1 1.3 6.2 145.8 gram
14 C&D	Cut 1 T_{top}=84-85 °C Lights 1-Propanol 2-Butanol Heavies Total	Mass %, dry basis 52.8 43.3 0.0 3.8 13.7 gram	Cut 2 T_{top}= 86 °C Lights 1-Propanol 2-Butanol Heavies Total	Mass %, dry basis 0.0 97.9 1.6 0.5 90.3 gram		Cut 3 T_{top}=86-87 °C Lights 1-Propanol 2-Butanol Heavies Total	Mass %, dry basis 0.0 98.5 1.4 0.1 4.1 gram
	Water % % of original sample	Two phases 9	Water % % of original sample	27.8 58		Water % % of original sample	28.4 3
14 C&D	Rest T_{bottom}=178 °C Lights 1-Propanol 2-Butanol Heavies Total	Mass %, dry basis 0 100.0 0.0 0.0 41 gram	Rest Water % % of original sample	48 26			

Appendix E: Results of Experiments 15&19

Exp. No.	Alcohol Feed	Acid	Acid:Alc. - Reaction Time - Distillation Temp.	Recovery 1-Propanol / Quality 1-Propanol (alcohols only) (mass %)	Water (mass %)	Product Composition (mass %, dry basis)	
15A	85 % 1-Propanol 15% 2-Butanol	88 % H_3PO_4	2,16:1 90 min. 140 °C	81 / 98.7	21.4	Lights 1-Propanol 2-Butanol Heavies	0.00 91.49 1.19 7.32
15B	85 % 1-Propanol 15% 2-Butanol	88 % H_3PO_4	2,14:1 150 min. 140 °C	80 / 100	22	Lights 1-Propanol 2-Butanol Heavies	0.00 93.10 0.00 6.81

Exp. No.	Alcohol Feed	Acid	Acid:Alc. - Reaction Time - Distillation Temp.	Product Composition (mass %, dry basis)	
19A	100 % 1-Propanol	88 % H_3PO_4	2,3:1 120 min. 110 °C (not in liquid)	1-Propanol 1-(1-methylethoxy)-propane 1,1'-oxybis-propane	95.5 2 2.5
19B	100 % 2-Butanol	88 % H_3PO_4	2,3:1 35 min.		
19C	100 % 1-Propanol	88 % H_3PO_4	2,3:1 180 min. 110 °C (not in liquid)	1-Propanol 1-(1-methylethoxy)-propane 1,1'-oxybis-propane	93.5 3.1 3.4
19D	100 % 1-Propanol	88 % H_3PO_4	2,3:1 60 min. 114 °C (not in liquid)	1-Propanol 1-(1-methylethoxy)-propane 1,1'-oxybis-propane	94.3 3.1 2.6

Appendix E: Results of Experiment 30 A, B, C and D

Experiment Number	30A	30B	30C	30D
Alcohol Feed	85% 1-Butanol 15% 2-Pentanol	85% 1-Butanol 15% 2-Pentanol	85% 1-Butanol 15% 2-Pentanol	85% 1-Butanol 15% 2-Pentanol
Catalyst	50 % H_3PO_4	85 % H_3PO_4	75 % H_3PO_4	80 % H_3PO_4
Acid:Alcohol	2,1:1	2,1:1	2,15:1	2,15:1
Reaction Time [minutes]	120	120	120	120
Distillation from acid				
T_{Bottom} [°C]	135	150	140	130
Recovery of 1-Butanol	94%	72%	81.3%	80.8%
Alcohol Composition				
[mass %, alcohols only]				
1-Butanol	85.3	100	92	96.9
2-Pentanol	14.7	0	8	3.1
Composition of Organic Phase				
[mass %, dry basis]				
Lights	0	5.7	7.4	7.2
1-Butanol	85.3	87.6	82.6	86.4
2-Pentanol	14.7	0	7.2	2.6
Heavies	0	6.7	2.8	3.8
Water, calculated [mass %]	15	17.4	17.8	12.8
Composition of Organic Phase				
[mass %, excluding lights]				
1-Butanol	85.3	92.9	89.2	93.1
2-Pentanol	14.7	0.0	7.8	2.8
Heavies (mainly ethers)	0.0	7.1	3.0	4.1

Appendix E: Results of Experiment 31 A, B, C and D.

Experiment Number	31A	31B	31C	31D
Alcohol Feed	85% 1-Butanol 15% 2-Pentanol	85% 1-Butanol 15% 2-Pentanol	85% 1-Butanol 15% 2-Pentanol	85% 1-Butanol 15% 2-Pentanol
Catalyst	85 % H_3PO_4	85 % H_3PO_4	85 % H_3PO_4	85 % H_3PO_4
Acid:Alcohol	2,15:1	2,17:1	2,18:1	2.16:1
Reaction Time [minutes]	90	60	150	30
Distillation from acid				
T_{Bottom} [°C]	150	150	175	161
Recovery of 1-Butanol	71%	70%	69.5%	71.5%
Alcohol Composition				
[mass %, alcohols only]				
1-Butanol	100	100	100	98.5
2-Pentanol	0	0	0	1.5
Composition of Organic Phase				
[mass %, dry basis]				
Lights	5.65	6	5.7	10.3
1-Butanol	88.75	86.4	87.5	81.6
2-Pentanol	0	0	0	1.3
Heavies	5.6	7.6	6.8	6.8
Water, calculated [mass %]	18.9	18.9	21.6	13.3
Composition of Organic Phase				
[mass %, excluding lights]				
1-Butanol	94.1	91.9	92.8	91.0
2-Pentanol	0.0	0.0	0.0	1.4
Heavies (mainly ethers)	5.9	8.1	7.2	7.6

Appendix E: Results of Experiment 32

Experiment Number	32A	32B
Alcohol Feed	85% 1-Butanol 15% 2-Pentanol	85% 1-Butanol 15% 2-Pentanol
Catalyst	85 % H_3PO_4	85 % H_3PO_4
Acid:Alcohol	4:1	1:1
Reaction Time [minutes]	120	120
Distillation from acid		
T_{bottom} [oC]	150	161
Recovery of 1-Butanol	66%	87%
Alcohol Composition		
[mass %, alcohols only]		
1-Butanol	100	92
2-Pentanol	0	8
Composition of Organic Phase	[mass %, dry basis]	
Lights	6.2	13.1
2-Butanol	2.3	0
1-Butanol	82.1	76.4
2-Pentanol	0	6.2
Heavies	9.4	4.2
Composition of Organic Phase		
[mass %, excluding lights]		
1-Butanol	89.7	88.0
2-Pentanol	0.0	7.1
Heavies (mainly ethers)	10.3	4.8

Appendix E: Results of Experiment 33

Experiment Number	33A	33B
Alcohol Feed	85% 1-Butanol 15% 2-Pentanol	85% 1-Butanol 15% 2-Pentanol
Catalyst	85 % H_3PO_4	85 % H_3PO_4
Acid:Alcohol	2,15:1	2,15:1
Reaction Time [minutes]	120	120
	Neutralized with 26 gram Na_2CO_3	
Distillation from acid		
T_{bottom} [oC]	Not logged	180
Recovery of 1-Butanol	91%	71%
Alcohol Composition		
[mass %, alcohols only]		
1-Butanol	100	100
2-Pentanol	0	0
Composition of Organic Phase		
[mass %, dry basis]		
Lights	0	5
1-Butanol	98.1	88.9
2-Pentanol	0	0
Heavies	1.9	6.1
Water, calculated [mass %]	10.5	20.9
Composition of Organic Phase		
[mass %, excluding lights]		
1-Butanol	98.1	93.6
2-Pentanol	0.0	0.0
Heavies (mainly ethers)	1.9	6.4

Appendix E: Results of Experiment 36

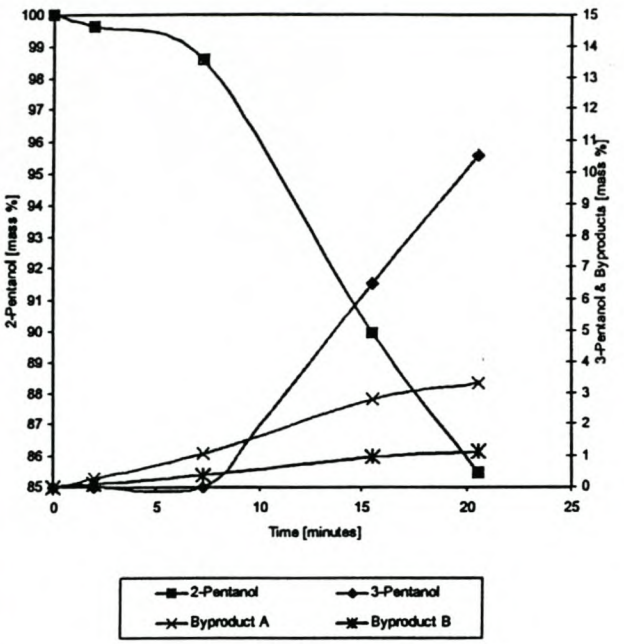
Experiment Number	36A	36B
Alcohol Feed	85% 1-Butanol 15% 2-Pentanol	85% 1-Butanol 15% 2-Pentanol
Catalyst	85 % H_3PO_4	85 % H_3PO_4
Acid:Alcohol	2,15:1	2,15:1
Reaction Time [minutes]	120	120
	Distillation from acid	
Add Reaction Mixture together and feed to Short Path Distillation Unit		
Composition of Organic Phase [mass %, dry basis]	Cut 1	Cut 2
1-Butanol	95.6	98.6
2-Pentanol	0	0
n-Butylether	2.2	0.7
Mixed Ether 2	2.2	0.7
Alcohol Composition [mass %, alcohols only]		
1-Butanol	100	100
2-Pentanol	0	0
Theoretical Alcohol left in remaining Acid&Alcohol Mixture (if all the water is assumed to be in Cuts 1 and 2)		= 85 gram

Appendix E: Results of Experiment 51

Experiment Number	51A	51B
Alcohol Feed	85% 1-Propanol 15% 2-Butanol	85% 1-Propanol 15% 2-Butanol
Catalyst	88 % H_3PO_4	88 % H_3PO_4
Acid:Alcohol	2,14:1	2,16:1
Reaction Time [minutes]	125	120
	Distillation from acid	
Add Reaction Mixture together and feed to Short Path Distillation Unit		
	Composition of Organic Phase [mass %, dry basis]	
1-Propanol	96.3	
2-Butanol	1.0	
n-Propylether	0.7	
2-Butyl Propyl Ether	2.0	
Alcohol Composition [mass %, alcohols only]		
1-Butanol	99.0	
2-Pentanol	1.0	

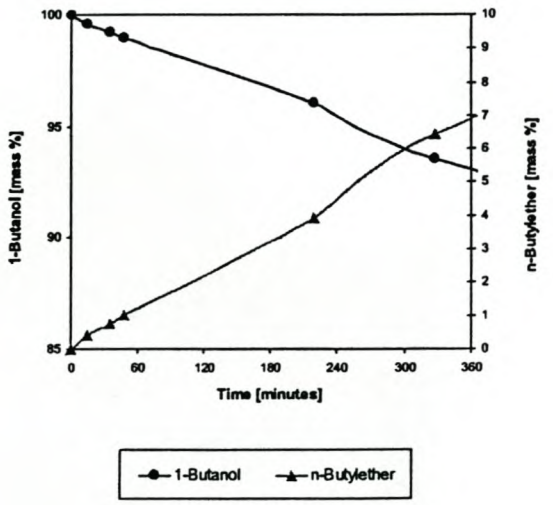
Appendix E: Experiment 53

Feed Composition	Reaction Conditions:
Alcohol Mixture: (mass %) 100 % 2-Pentanol	Atmospheric Pressure Nitrogen Flow: Normal Mixed Ether 2, which is present in all the 1-Butanol/2-Pentanol reaction systems, was not present in experiment 53 at all. Mixed Ether 2 can thus not be an ether which consists of two Pentanol groups.
Catalyst: 85 % H_3PO_4	
Acid:2-Pentanol = 2,1:1	



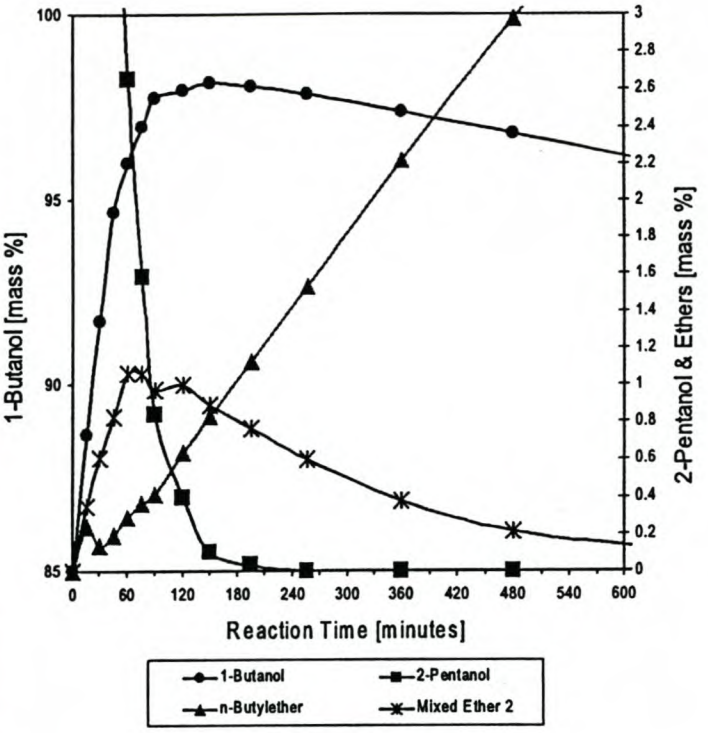
Appendix E: Experiment 55

Feed Composition	Reaction Conditions:
Alcohol Mixture: (mass %) 100 % 1-Butanol	Atmospheric Pressure Nitrogen Flow: Normal Mixed Ether 2, which is present in all the 1-Butanol/2-Pentanol reaction systems, was not present in experiment 55 at all. Mixed Ether 2 can thus not be an ether which consists of two Butanol groups. Rate of increase of n-Butylether ~ 0,015 g/g organics.min
Catalyst: 85 % H_3PO_4	
Acid:1-Butanol = 2,16:1	



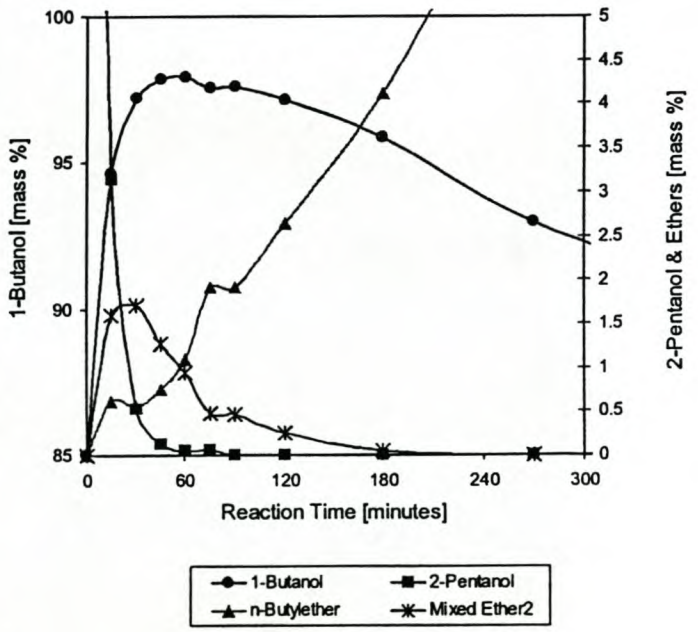
Appendix E: Experiment 62

Feed Composition	
Alcohol Mixture: (mass %) 85 % 1-Butanol + 15 % 2-Pentanol Catalyst: 85 % H_3PO_4 Acid:Alcohol = 2,16:1	
Reaction Conditions:	
Atmospheric Pressure Nitrogen Flow: Normal	
Reaction time required to reduce the secondary alcohol content (based on alcohol only) to less than 0,1 mass % = > 150 minutes	
Reaction Time = 150 minutes	
Product Composition	(mass %) dry basis
1-Butanol 3-Pentanol 2-Pentanol Mixed Ether 1 n-Butylether Mixed Ether 2	98.17 not determined 0.1 not determined 0.83 0.89
Total Secondary Alcohol Total Ether	0.1 1.72
Rate of increase of n-Butylether ~ 0.006 g/g organics.min	



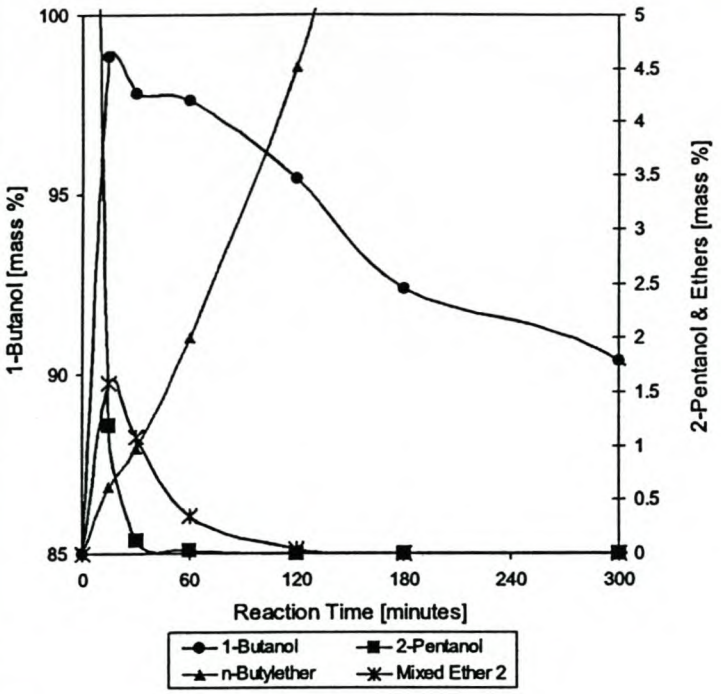
Appendix E: Experiment 63.

Feed Composition	
Alcohol Mixture: (mass %) 85 % 1-Butanol + 15 % 2-Pentanol Catalyst: 90 % H_3PO_4 Acid:Alcohol =2,16:1	
Reaction Conditions:	
Atmospheric Pressure; Nitrogen Flow: Norma	
Reaction time required to reduce the secondary alcohol content (based on alcohol only) to less than 0,1 mass % = > 55 minutes.77	
Reaction Time = 55 minutes	
Product Composition	(mass %) dry basis
1-Butanol 3-Pentanol 2-Pentanol Mixed Ether 1 n-Butylether Mixed Ether 2	97.95 not determined 0.05 not determined 0.95 1.05
Total Secondary Alcohol	0.05
Total Ether	2.0
Rate of increase of n-Butylether ~ 0.024 g/g organics.min	



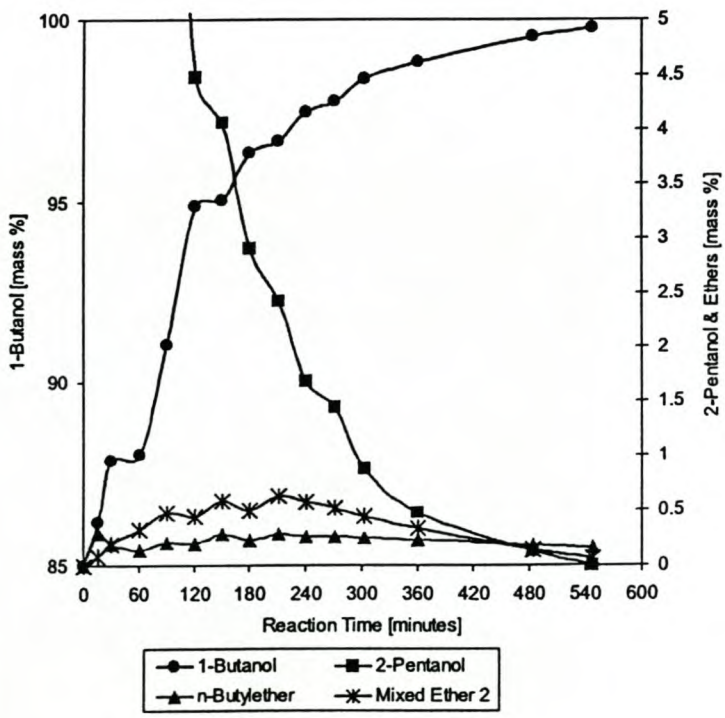
Appendix E: Experiment 64.

Feed Composition	
Alcohol Mixture: (mass %) 85 % 1-Butanol +15 % 2-Pentanol Catalyst: 92.1 % H_3PO_4 Acid:Alcohol = 2.16:1	
Reaction Conditions:	
Atmospheric Pressure Nitrogen Flow: Normal	
Reaction time required to reduce the secondary alcohol content (based on alcohol only) to less than 0.1 mass % = > 40 minutes.	
Reaction Time	= 40 minutes
Product Composition	(mass %) dry basis
1-Butanol 3-Pentanol 2-Pentanol Mixed Ether 1 n-Butylether Mixed Ether 2	97.6 not determined 0.05 not determined 1.3 0.95
Total Secondary Alcohol	0.05
Total Ether	2.25
Rate of increase of n-Butylether ~ 0.036 g/g organics.min	



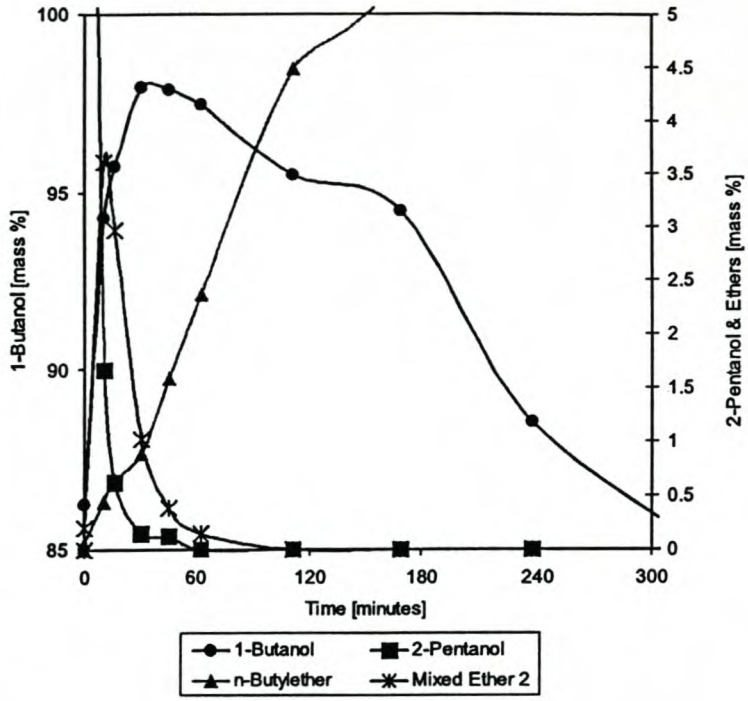
Appendix E: Experiment 65.

Feed Composition	
Alcohol Mixture: (mass %) 85 % 1-Butanol+ 15 % 2-Pentanol Catalyst: 80 % H_3PO_4 Acid:Alcohol =2,16:1	
Reaction Conditions	
Atmospheric Pressure Nitrogen Flow: Normal	
Reaction time required to reduce the secondary alcohol content (based on alcohol only) to less than 0,1 mass % = > 500 minutes.	
Reaction Time	= 500 minutes
Product Composition	(mass %) dry basis
1-Butanol 3-Pentanol 2-Pentanol Mixed Ether 1 n-Butylether Mixed Ether 2	99.61 not determined 0.1 not determined 0.17 0.12
Total Secondary Alcohol	0.1
Total Ether	0.29
Rate of increase of n-Butylether ~ decrease or constant	



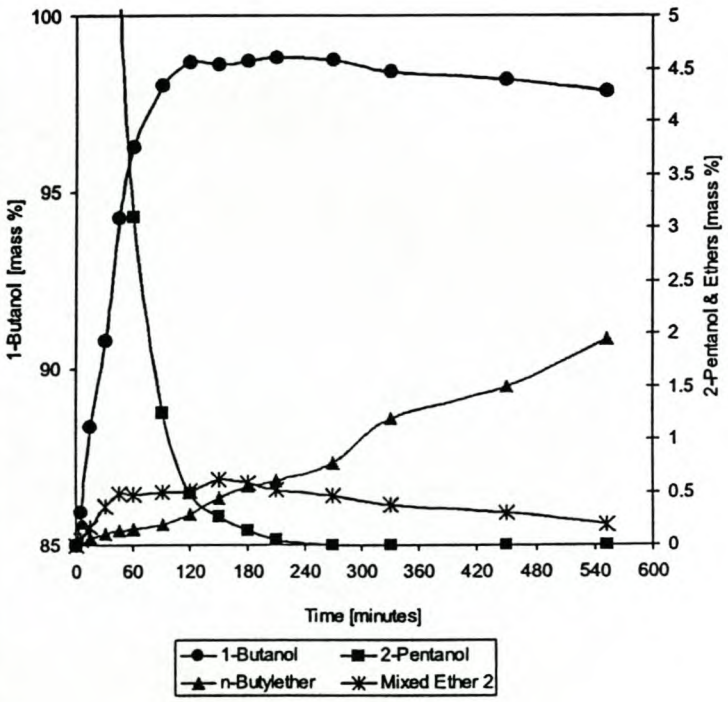
Appendix E: Experiment 66.

Feed Composition	
Alcohol Mixture: (mass %) 85 % 1-Butanol+ 15 % 2-Pentanol Catalyst: 90 % H_3PO_4 Acid:Alcohol = 3:1	
Reaction Conditions	
Atmospheric Pressure Nitrogen Flow: Normal	
Reaction time required to reduce the secondary alcohol content (based on alcohol only) to less than 0,1 mass % = > 50 minutes.	
Reaction Time	= 50 minutes
Product Composition	(mass %) dry basis
1-Butanol	97.83
3-Pentanol	not determined
2-Pentanol	0.05
Mixed Ether 1	not determined
n-Butylether	1.85
Mixed Ether 2	0.27
Total Secondary Alcohol	0.05
Total Ether	2.12
Rate of increase of n-Butylether ~ 0.045 g/g organics.min	



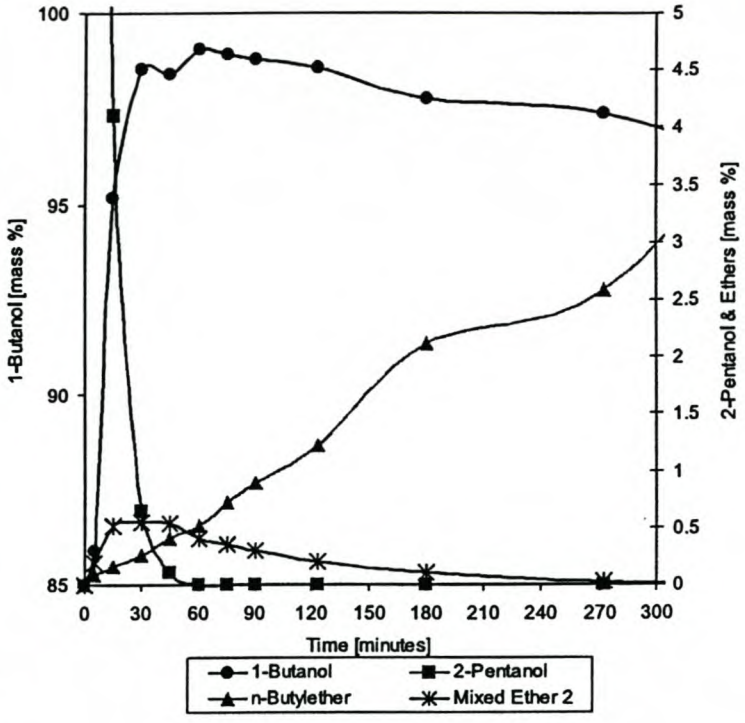
Appendix E: Experiment 67.

Feed Composition	
Alcohol Mixture: (mass %) 85 % 1-Butanol+ 15 % 2-Pentanol Catalyst: 80 % H_3PO_4 Acid:Alcohol = 3:1	
Reaction Conditions	
Atmospheric Pressure Nitrogen Flow: Normal	
Reaction time required to reduce the secondary alcohol content (based on alcohol only) to less than 0,1 mass % = > 190 minutes.	
Reaction Time	= 190 minutes
Product Composition	(mass %) dry basis
1-Butanol	98.76
3-Pentanol	not determined
2-Pentanol	0.1
Mixed Ether 1	not determined
n-Butylether	0.57
Mixed Ether 2	0.57
Total Secondary Alcohol	0.1
Total Ether	1.14
Rate of increase of n-Butylether ~ 0.003 g/g organics.min	



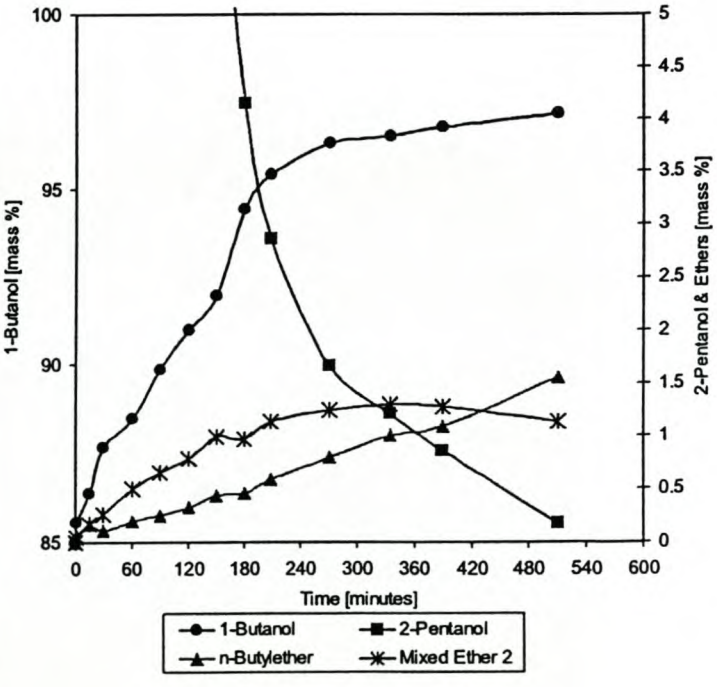
Appendix E: Experiment 68.

Feed Composition	
Alcohol Mixture: (mass %) 85 % 1-Butanol+ 15 % 2-Pentanol Catalyst: 85 % H_3PO_4 Acid:Alcohol = 3:1	
Reaction Conditions	
Atmospheric Pressure Nitrogen Flow: Normal	
Reaction time required to reduce the secondary alcohol content (based on alcohol only) to less than 0,1 mass % = > 47 minutes.	
Reaction Time	= 47 minutes
Product Composition	(mass %) dry basis
1-Butanol	98.95
3-Pentanol	not determined
2-Pentanol	0.07
Mixed Ether 1	not determined
n-Butylether	0.44
Mixed Ether 2	0.54
Total Secondary Alcohol	0.07
Total Ether	0.98
Rate of increase of n-Butylether ~ 0.013 g/g organics.min	



Appendix E: Experiment 69.

Feed Composition	
Alcohol Mixture: (mass %) 85 % 1-Butanol+ 15 % 2-Pentanol Catalyst: 85 % H_3PO_4 Acid:Alcohol = :1.5:1	
Reaction Conditions	
Atmospheric Pressure Nitrogen Flow: Normal	
Reaction time required to reduce the secondary alcohol content (based on alcohol only) to less than 0,1 mass % = > 550 minutes.	
Reaction Time	= 550 minutes
Product Composition	(mass %) dry basis
1-Butanol	97.15
3-Pentanol	not determined
2-Pentanol	0.05
Mixed Ether 1	not determined
n-Butylether	1.75
Mixed Ether 2	1.05
Total Secondary Alcohol	0.05
Total Ether	2.8
Rate of increase of n-Butylether ~ 0.003 g/g organics.min	

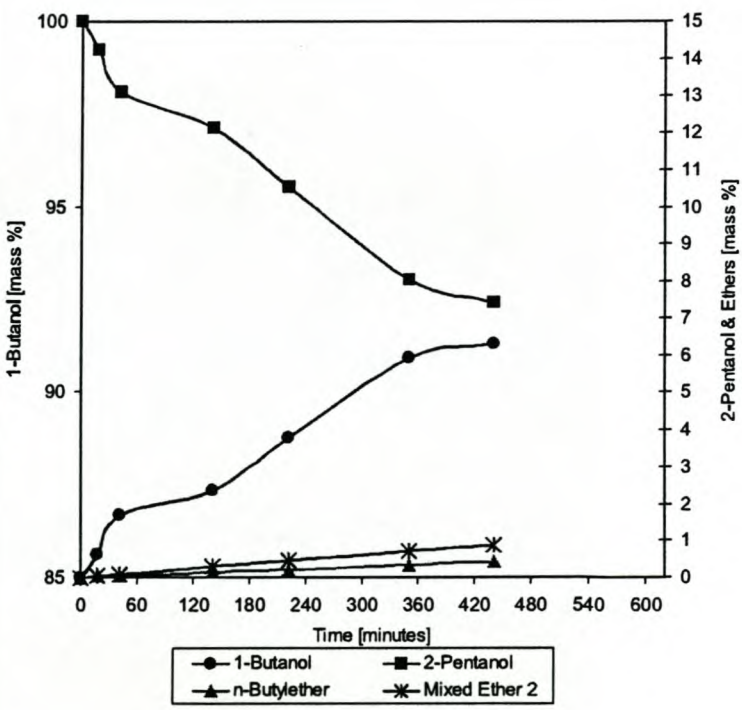


Appendix E: Results of Experiment 70

Experiment Number	70A	70B
Alcohol Feed	85% 1-Pentanol 15% 2-Hexanol	85% 1-Pentanol 15% 2-Hexanol
Catalyst	85 % H3PO4	85 % H3PO4
Acid:Alcohol	2,14:1	2,15:1
Reaction Time [minutes]	about 120	about 120
	Distillation from acid	
Add Reaction Mixture together and feed to Short Path Distillation Unit		
Composition of Organic Phase [mass %, dry basis]		
1-Pentanol	95.3	
2-Hexanol	0	
n-Pentylether	3.3	
Mixed Ethers	1.4	
Alcohol Composition [mass %, alcohols only]		
1-Pentanol	100	
2-Hexanol	0	
	Water [mass %]	
Organic phase	9.9	
Water phase	99.9	
Theoretical Alcohol left in remaining Acid/Alcohol Mixture (if all the water is assumed to be in Distillate)		74 gram

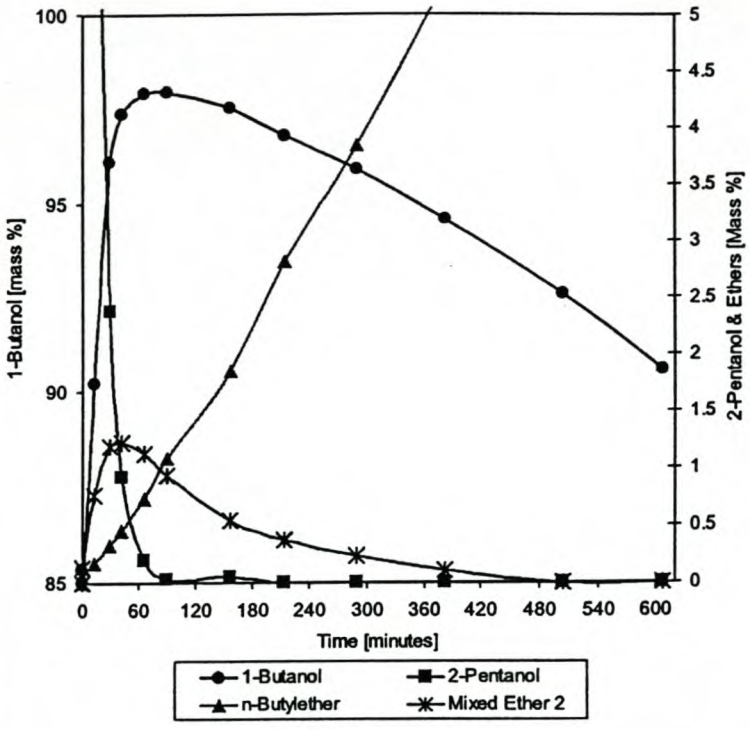
Appendix E: Experiment 72.

Feed Composition	
Alcohol Mixture: (mass %) 85 % 1-Butanol+ 15 % 2-Pentanol Catalyst: 80 % H_3PO_4 Acid:Alcohol = 1.5:1	
Reaction Conditions	
Atmospheric Pressure Nitrogen Flow: Normal	
Reaction time required to reduce the secondary alcohol content (based on alcohol only) to less than 0,1 mass % = > 20 hours	
Reaction Time	> 20 hours
Product Composition	(mass %) dry basis
1-Butanol	91.3
3-Pentanol	not determined
2-Pentanol	7.4
Mixed Ether 1	not determined
n-Butylether	0.4
Mixed Ether 2	0.9
Total Secondary Alcohol	7.4
Total Ether	1.3
Rate of increase of n-Butylether ~ 0.0009 g/g organics.min	



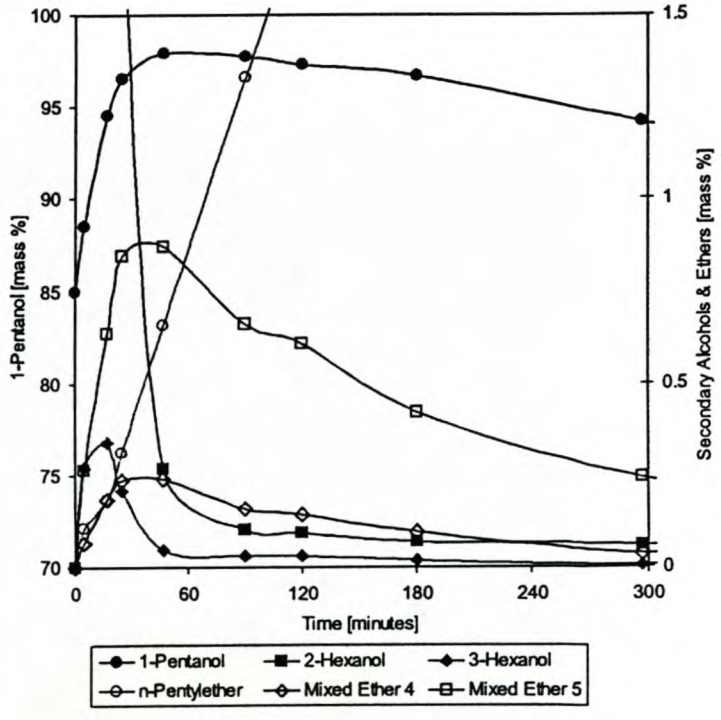
Appendix E: Experiment 73.

Feed Composition	
Alcohol Mixture: (mass %) 85 % 1-Butanol+ 15 % 2-Pentanol Catalyst: 90 % H_3PO_4 Acid:Alcohol = 1.5:1	
Reaction Conditions	
Atmospheric Pressure Nitrogen Flow:	
Reaction time required to reduce the secondary alcohol content (based on alcohol only) to less than 0,1 mass % = > 70 minutes.	
Reaction Time	= 70 minutes
Product Composition	(mass %) dry basis
1-Butanol	98.0
3-Pentanol	not determined
2-Pentanol	0.1
Mixed Ether 1	not determined
n-Butylether	0.8
Mixed Ether 2	1.1
Total Secondary Alcohol	0.1
Total Ether	1.9
Rate of increase of n-Butylether ~ 0.0115 g/g organics.min	

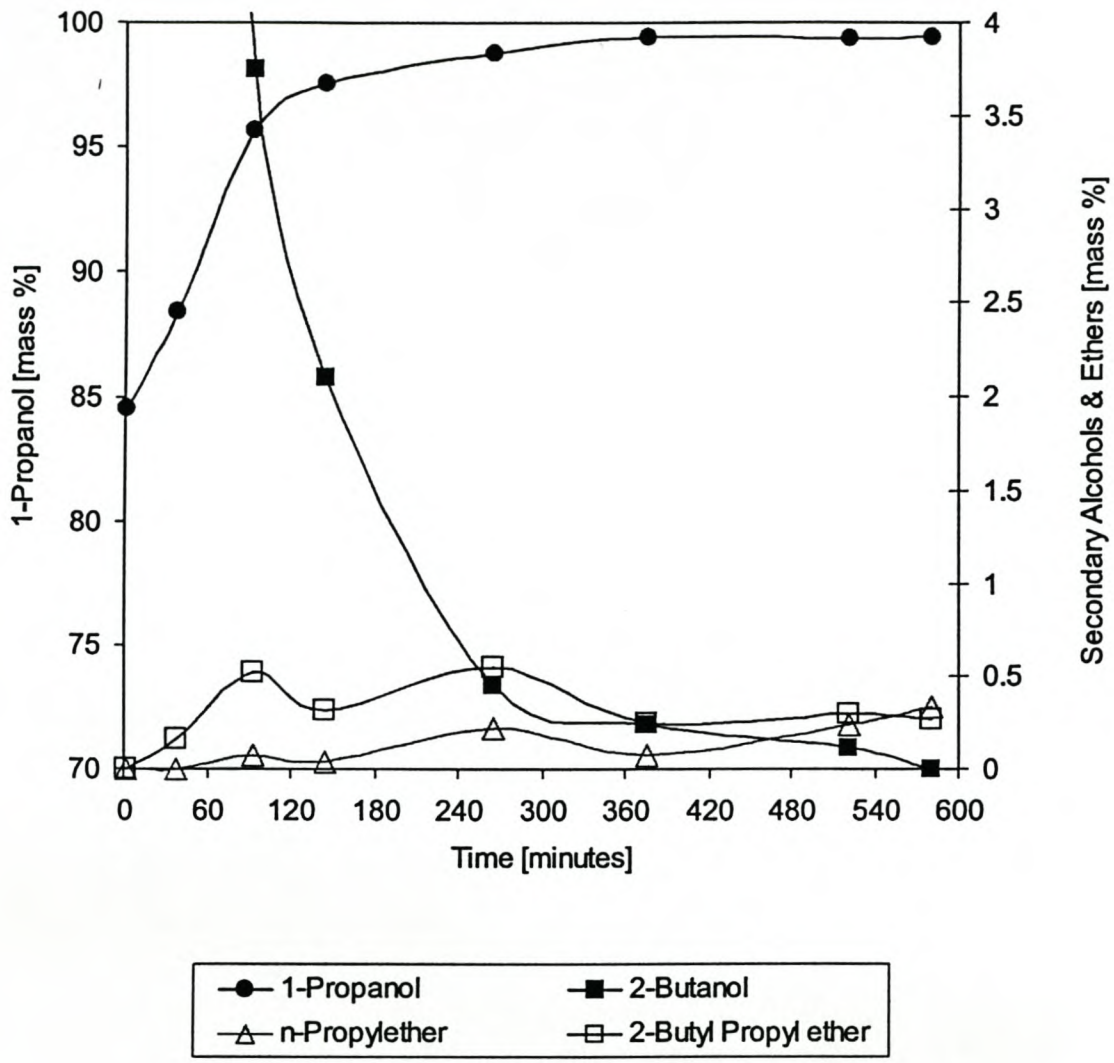


Appendix E: Experiment 75.

Feed Composition.	
Alcohol Mixture: (mass %) 85 % 1-Pentanol +15 % 2-Hexanol Catalyst: 85 % H_3PO_4 Acid:Alcohol = 2.17:1	
Reaction Conditions:	
Atmospheric Pressure Nitrogen Flow: normal Condenser Temperature too low, 65 °C alkene removal inadequate	
Reaction time required to reduce the secondary alcohol content (based on alc.only) to < 0.1 mass % ~ > 180 min.	
Reaction Time	180 minutes
Product Composition	(mass %) dry basis
1-Pentanol	96.643
3-Hexanol	0.019
2-Hexanol	0.068
Mixed Ether 3&6	not determined
n-Pentylether	2.749
Mixed Ether 4	0.098
Mixed Ether 5	0.423
Tot. Sec. Alcohol	0.087
Total Ether	3.270
Rate of increase of n-Pentylether ~ 0.017 g/g organics.min	



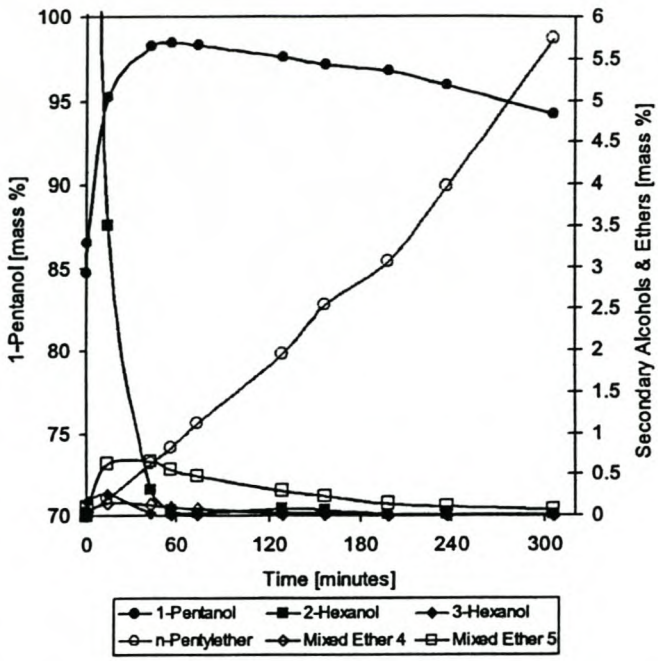
Appendix E: Experiment 76.

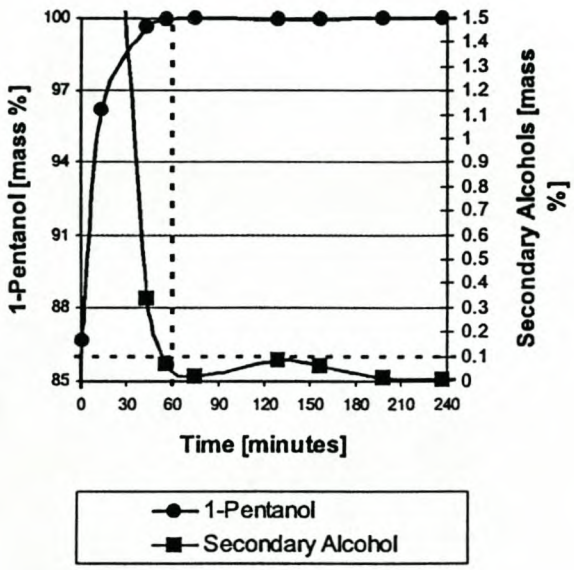


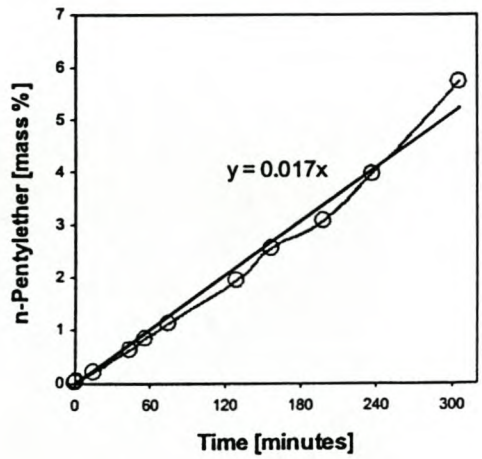
Feed Composition	Reaction Conditions:	Reaction Time	600 minutes
Alcohol Mixture: (mass %) 85 % 1-Propanol 15 % 2-Butanol	Atmospheric Pressure Nitrogen Flow: normal	**Product Composition**	(mass %) dry basis
		1-Propanol	99.30
		2-Butanol	0.05
	Reaction time required to reduce the secondary alcohol content (based on alcohol only) to less than 0.1 mass % ~ > 580 min.	n-Propylether	0.40
		2 Butyl Propyl Ether	0.25
Catalyst: 85 % H_3PO_4		*Total Secondary Alcohol*	*0.05*
		Total Ether	*0.65*
Acid:Alcohol = 2.14:1			
	Rate of increase of n-Propylether ~ 0.0007 g/g organics.min		

Appendix E: Experiment 77.

Feed Composition.	
Alcohol Mixture: (mass %) 85 % 1-Pentanol +15 % 2-Hexanol Catalyst: 85 % H_3PO_4 Acid:Alcohol = 2.17:1	
Reaction Conditions:	
Atmospheric Pressure Nitrogen Flow: normal	
Reaction time required to reduce the secondary alcohol content (based on alc. only) to < 0.1 mass % ~ > 60 min.	
Reaction Time	minutes
Product Composition	(mass %) dry basis
1-Pentanol	98.42
3-Hexanol	0
2-Hexanol	0.05
Mixed Ethers 3&6	not determined
n-Pentylether	0.9
Mixed Ether 4	0.09
Mixed Ether 5	0.54
Tot, Sec. Alc.	0.05
Total Ether	1.53
Rate of increase of n-Pentylether ~ 0.017 g/g organics.min	

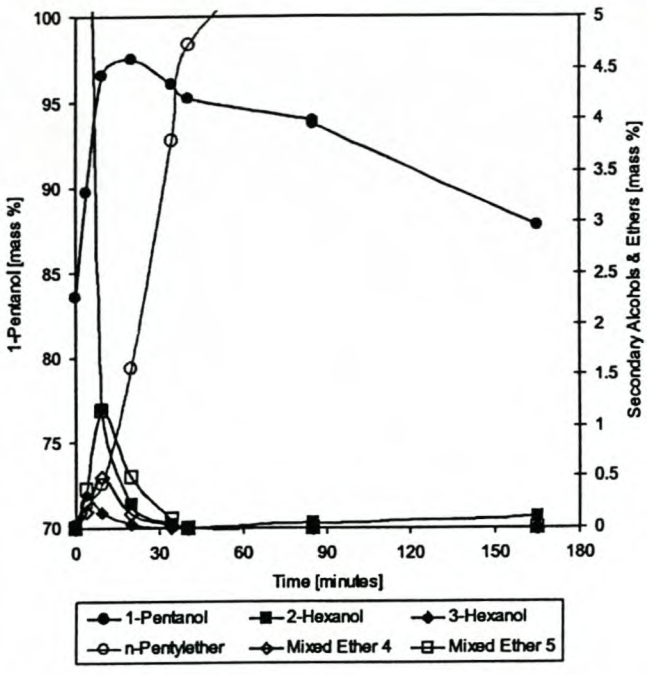






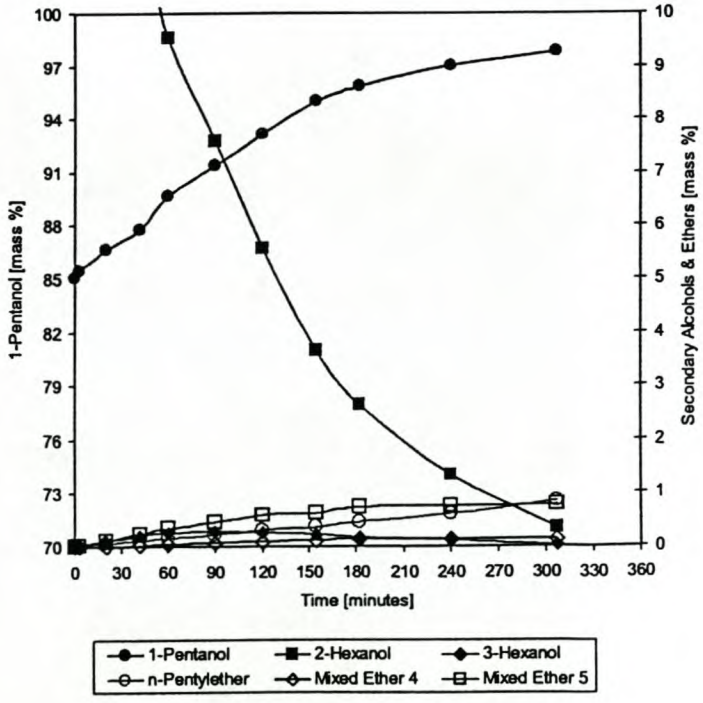
Appendix E: Experiment 79.

Feed Composition.		
Alcohol Mixture: (mass %) 85 % 1-Pentanol +15 % 2-Hexanol Catalyst: 90 % H_3PO_4 Acid:Alcohol = 3:1		
Reaction Conditions:		
Atmospheric Pressure Nitrogen Flow: normal		
Reaction time required to reduce the secondary alcohol content (based on alc. only) to < 0.1 mass % ~> 30 min.		
Reaction Time	30 min.	40 min (datapoint)
Product Composition	dry basis [mass%]	
1-Pentanol	96.37	95.263
3-Hexanol	0.08	0
2-Hexanol	0.01	0.005
Mixed Ethers 3&6	not determined	
n-Pentylether	3.29	4.73
Mixed Ether 4	0.05	0
Mixed Ether 5	0.2	0
Tot.Sec. Alcohol	0.09	0.05
Total Ether	3.54	4.73
Rate of increase of n-Pentylether ~ 0.12 g/g organics.min		



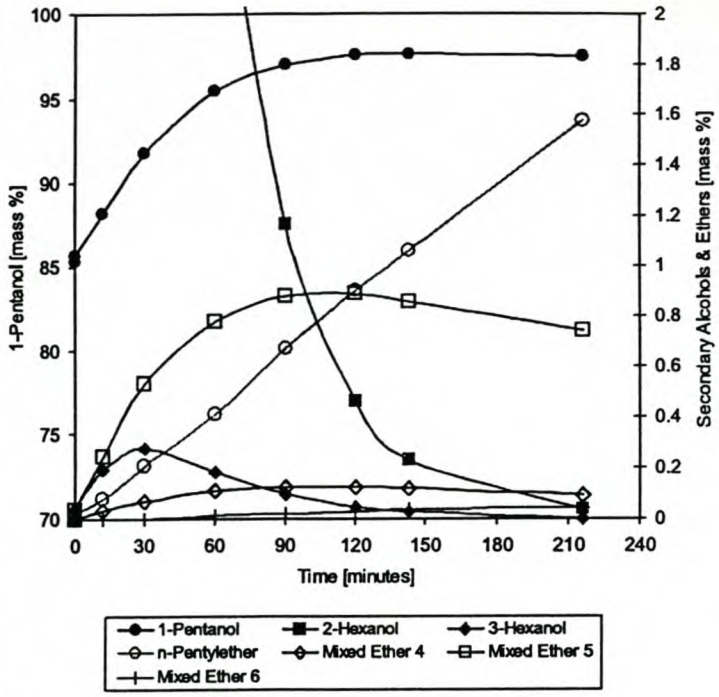
Appendix E: Experiment 80.

Feed Composition.	
Alcohol Mixture: (mass %) 85 % 1-Pentanol +15 % 2-Hexanol Catalyst: 80 % H_3PO_4 Acid:Alcohol = 1.5:1	
Reaction Conditions:	
Atmospheric Pressure Nitrogen Flow: normal	
Reaction time required to reduce the secondary alcohol content (based on alc. only) to < 0.1 mass % ~> 360 min.	
Reaction Time	360 minutes (extrapolated)
Product Composition	(mass %) dry basis
1-Pentanol	97.98
3-Hexanol	0.01
2-Hexanol	0.05
Mixed Ethers 3&6	not determined
n-Pentylether	1.05
Mixed Ether 4	0.14
Mixed Ether 5	0.77
Tot.Sec. Alcohol	0.06
Total Ether	1.96
Rate of increase of n-Pentylether ~ 0.0026 g/g organics.min	



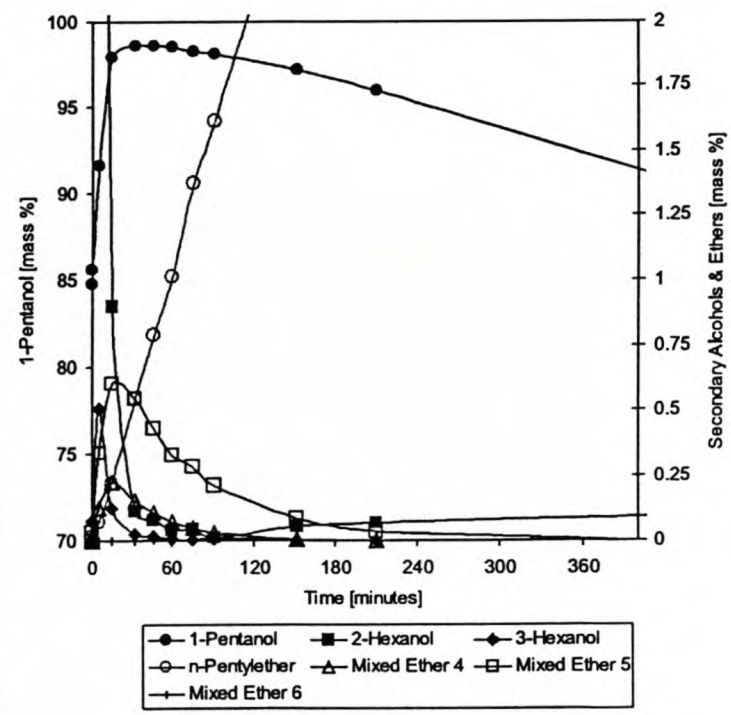
Appendix E: Experiment 81.

Feed Composition.	
Alcohol Mixture: (mass %) 85 % 1-Pentanol +15 % 2-Hexanol Catalyst: 85 % H_3PO_4 Acid:Alcohol = 1.5:1	
Reaction Conditions:	
Atmospheric Pressure Nitrogen Flow: normal	
Reaction time required to reduce the secondary alcohol content (based on alc. only) to < 0.1 mass % ~> 200 min.	
Reaction Time	200 minutes
Product Composition	(mass %) dry basis
1-Pentanol	97.46
3-Hexanol	0.01
2-Hexanol	0.08
Mixed Ethers 3	not determined
n-Pentylether	1.54
Mixed Ether 4	0.1
Mixed Ether 5	0.77
Mixed Ether 6	0.04
Tot.Sec. Alcohol	0.09
Total Ether	2.45
Rate of increase of n-Pentylether ~ 0.0077 g/g organics.min	



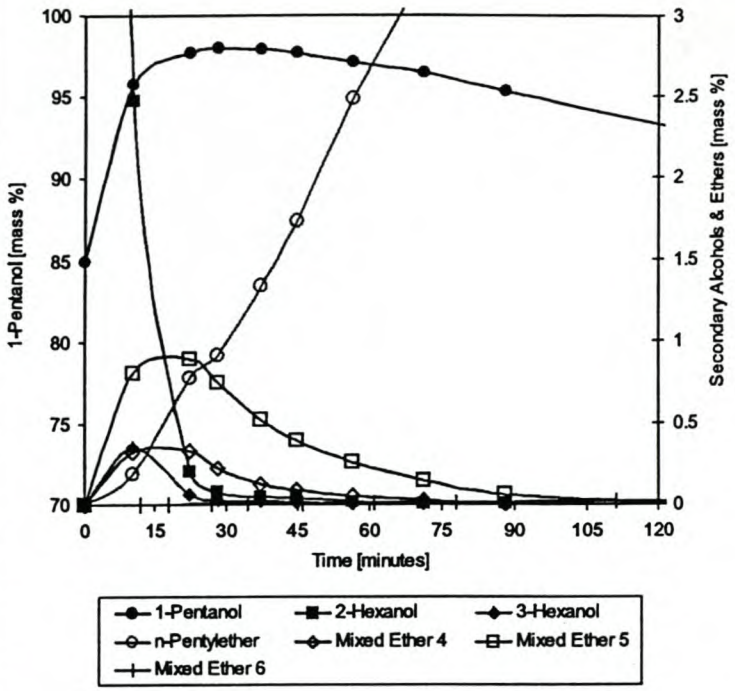
Appendix E: Experiment 82.

Feed Composition.	
Alcohol Mixture: (mass %) 85 % 1-Pentanol +15 % 2-Hexanol Catalyst: 85 % H_3PO_4 Acid:Alcohol = 3:1	
Reaction Conditions:	
Atmospheric Pressure Nitrogen Flow: normal	
Reaction time required to reduce the secondary alcohol content (based on alc. only) to < 0.1 mass % ~> 45 min.	
Reaction Time	45.5 minutes (datapoint)
Product Composition	(mass %) dry basis
1-Pentanol	98.565
3-Hexanol	0.02
2-Hexanol	0.079
Mixed Ethers 3	not determined
n-Pentylether	0.791
Mixed Ether 4	0.107
Mixed Ether 5	0.433
Mixed Ether 6	0.005
Tot.Sec. Alcohol	0.099
Total Ether	1.336
Rate of increase of n-Pentylether ~ 0.020 g/g organics.min	



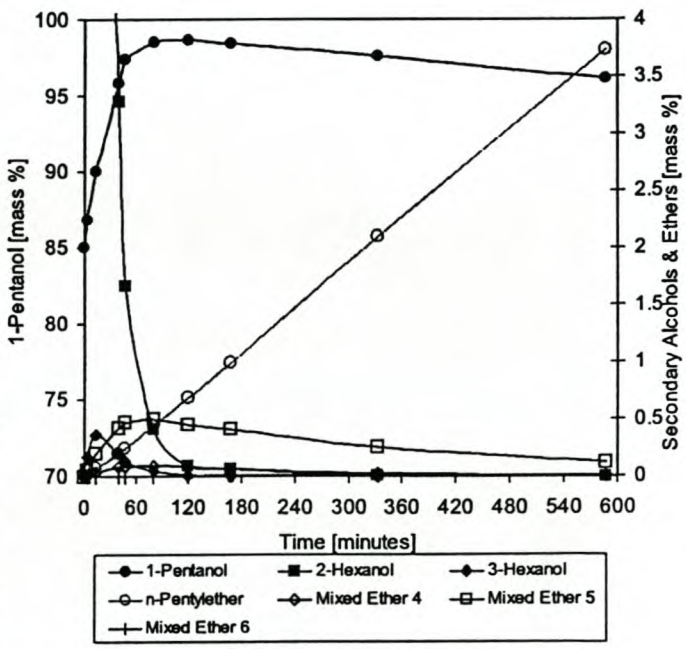
Appendix E: Experiment 83.

Feed Composition.	
Alcohol Mixture: (mass %) 85 % 1-Pentanol +15 % 2-Hexanol Catalyst: 90 % H_3PO_4 Acid:Alcohol = 2.19:1	
Reaction Conditions:	
Atmospheric Pressure Nitrogen Flow: normal	
Reaction time required to reduce the secondary alcohol content (based on alc. only) to < 0.1 mass % ~> 30 min.	
Reaction Time	30 minutes
Product Composition	(mass %) dry basis
1-Pentanol	97.976
3-Hexanol	0.029
2-Hexanol	0.073
Mixed Ethers 3	not determined
n-Pentylether	1.004
Mixed Ether 4	0.208
Mixed Ether 5	0.708
Mixed Ether 6	0.002
Tot.Sec. Alcohol	0.102
Total Ether	1.922
Rate of increase of n-Pentylether ~ 0.057 g/g organics.min	



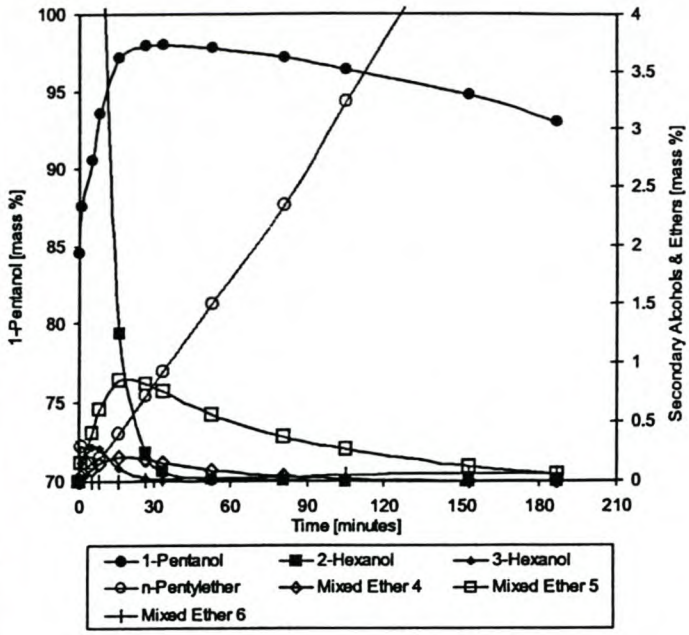
Appendix E: Experiment 84.

Feed Composition.	
Alcohol Mixture: (mass %) 85 % 1-Pentanol +15 % 2-Hexanol Catalyst: 80 % H_3PO_4 Acid:Alcohol = 3:1	
Reaction Conditions:	
Atmospheric Pressure Nitrogen Flow: normal	
Reaction time required to reduce the secondary alcohol content (based on alc. only) to < 0.1 mass % ~> 130 min.	
Reaction Time	minutes
Product Composition	(mass %) dry basis
1-Pentanol	98.63
3-Hexanol	0.01
2-Hexanol	0.08
Mixed Ethers 3	not determined
n-Pentylether	0.75
Mixed Ether 4	0.09
Mixed Ether 5	0.44
Mixed Ether 6	0.002
Tot.Sec. Alcohol	0.09
Total Ether	1.28
Rate of increase of n-Pentylether ~ 0.0064 g/g organics.min	



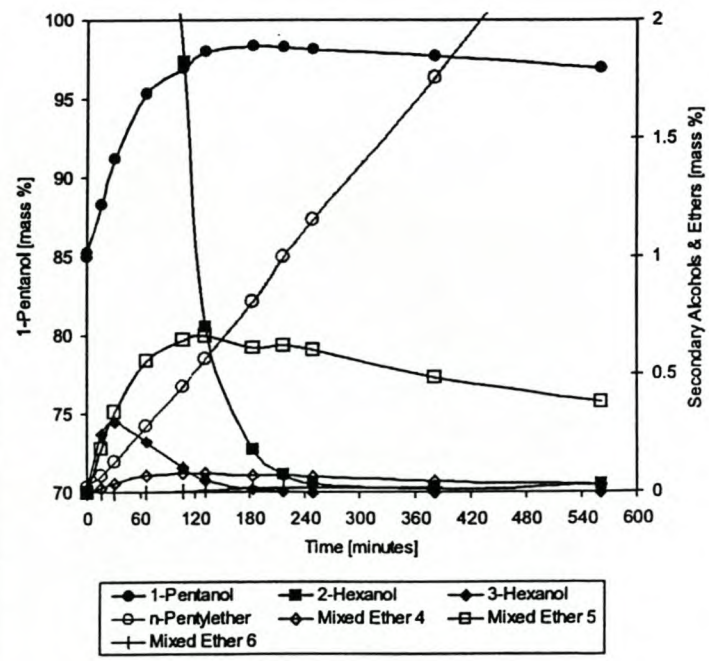
Appendix E: Experiment 86.

Feed Composition.	
Alcohol Mixture: (mass %) 85 % 1-Pentanol +15 % 2-Hexanol Catalyst: 90 % H_3PO_4 Acid:Alcohol = 1.5:1	
Reaction Conditions:	
Atmospheric Pressure Nitrogen Flow: normal	
Reaction time required to reduce the secondary alcohol content (based on alc. only) to < 0.1 mass % ~> 35 min.	
Reaction Time	35 minutes
Product Composition	(mass %) dry basis
1-Pentanol	98.03
3-Hexanol	0.01
2-Hexanol	0.07
Mixed Ethers 3	not determined
n-Pentylether	0.97
Mixed Ether 4	0.15
Mixed Ether 5	0.75
Mixed Ether 6	0.02
Tot.Sec. Alcohol	0.08
Total Ether	1.89
Rate of increase of n-Pentylether ~ 0.028 g/g organics.min	



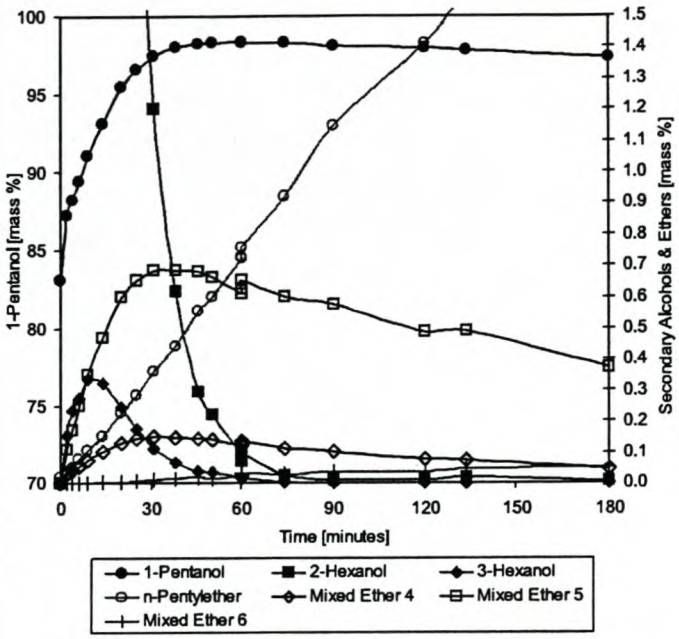
Appendix E Experiment 87.

Feed Composition.	
Alcohol Mixture: (mass %) 85 % 1-Pentanol +15 % 2-Hexanol Catalyst: 80 % H_3PO_4 Acid:Alcohol = 2.16:1	
Reaction Conditions:	
Atmospheric Pressure Nitrogen Flow: normal	
Reaction time required to reduce the secondary alcohol content (based on alc. only) to < 0.1 mass % ~> 210 min.	
Reaction Time	210 minutes
Product Composition	(mass %) dry basis
1-Pentanol	98.22
3-Hexanol	0.01
2-Hexanol	0.09
Mixed Ethers 3	not determined
n-Pentylether	0.96
Mixee Ether 4	0.07
Mixed Ether 5	0.63
Mixed Ether 6	0.02
Tot.Sec. Alcohol	0.10
Total Ether	1.68
Rate of increase of n-Pentylether ~ 0.0047 g/g organics.min	



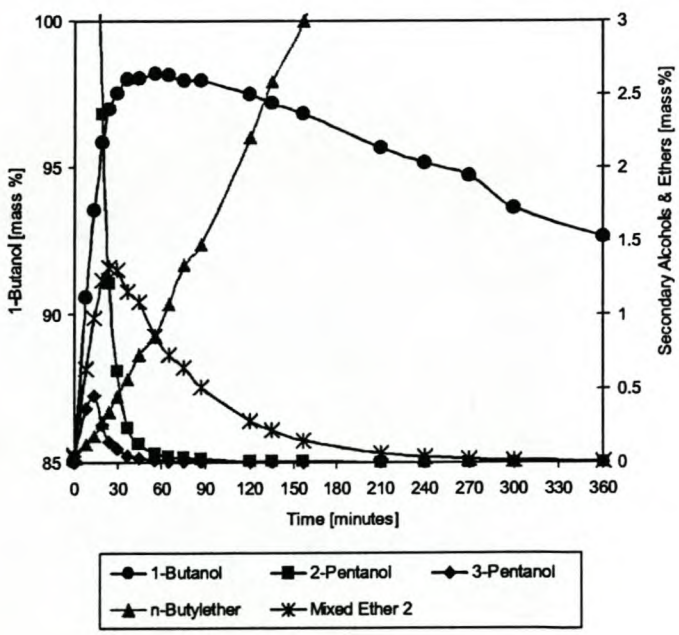
Appendix E: Experiment 88.

Feed Composition.	
Alcohol Mixture: (mass %) 85 % 1-Pentanol +15 % 2-Hexanol Catalyst: 85 % H_3PO_4 Acid:Alcohol = 2.18:1	
Reaction Conditions:	
Atmospheric Pressure Nitrogen Flow: normal	
Reaction time required to reduce the secondary alcohol content (based on alc. only) to < 0.1 mass % ~> 65 min.	
Reaction Time	65 minutes
Product Composition	(mass %) dry basis
1-Pentanol	98.351
3-Hexanol	0.011
2-Hexanol	0.064
Mixed Ethers 3	not determined
n-Pentylether	0.805
Mixed Ether 4	0.123
Mixed Ether 5	0.621
Mixed Ether 6	0.027
Tot.Sec. Alcohol	0.076
Total Ether	1.575
Rate of increase of n-Pentylether ~ 0.013 g/g organics.min	



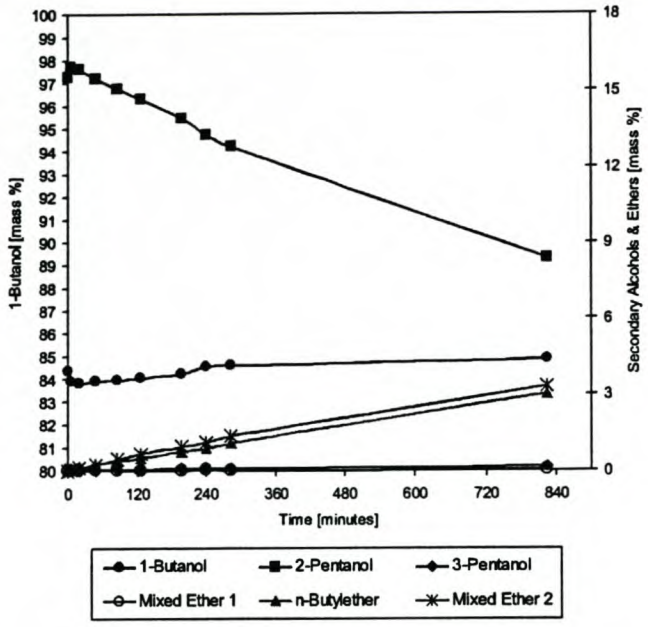
Appendix E: Experiment 89.

Feed Composition	
Alcohol Mixture: (mass %) 85 % 1-Butanol+ 15 % 2-Pentanol Catalyst: 90 % H_3PO_4 Acid:Alcohol = 2.15:1	
Reaction Conditions	
Atmospheric Pressure Nitrogen Flow: Normal	
Reaction time required to reduce the secondary alcohol content (based on alcohol only) to less than 0,1 mass % = > 55 minutes.	
Reaction Time	= 55 minutes
Product Composition	(mass %) dry basis
1-Butanol	98.211
3-Pentanol	0.017
2-Pentanol	0.065
Mixed Ether 1	not determined
n-Butylether	0.853
Mixed Ether 2	0.853
Total Secondary Alcohol	0.082
Total Ether	1.706
Rate of increase of n-Butylether ~ 0.0207 g/g organics.min	



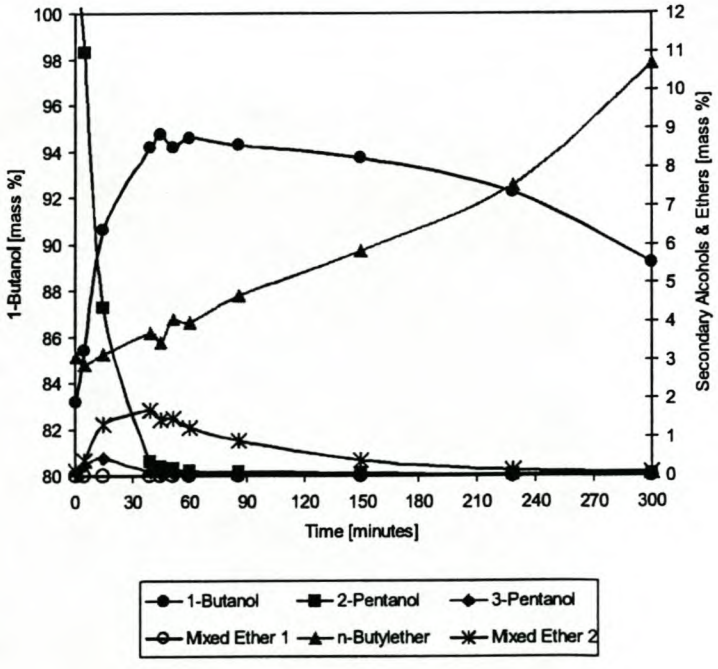
Appendix E: Experiment 90.

Feed Composition	
Alcohol Mixture: (mass %) 85 % 1-Butanol+ 15 % 2-Pentanol Catalyst: 55 % H_2SO_4 Acid:Alcohol = 0.48:1	
Reaction Conditions	
Atmospheric Pressure Nitrogen Flow: Normal	
Reaction time required to reduce the secondary alcohol content (based on alcohol only) to less than 0,1 mass % = > 30 hours.	
Reaction Time	= 824 minutes
Product Composition	(mass %) dry basis
1-Butanol	84.89
3-Pentanol	0.16
2-Pentanol	8.37
Mixed Ether 1	0.02
n-Butylether	3.04
Mixed Ether 2	3.30
Total Secondary Alcohol	9.13
Total Ether	6.36
Rate of increase of n-Butylether ~ 0.0036 g/g organics.min	



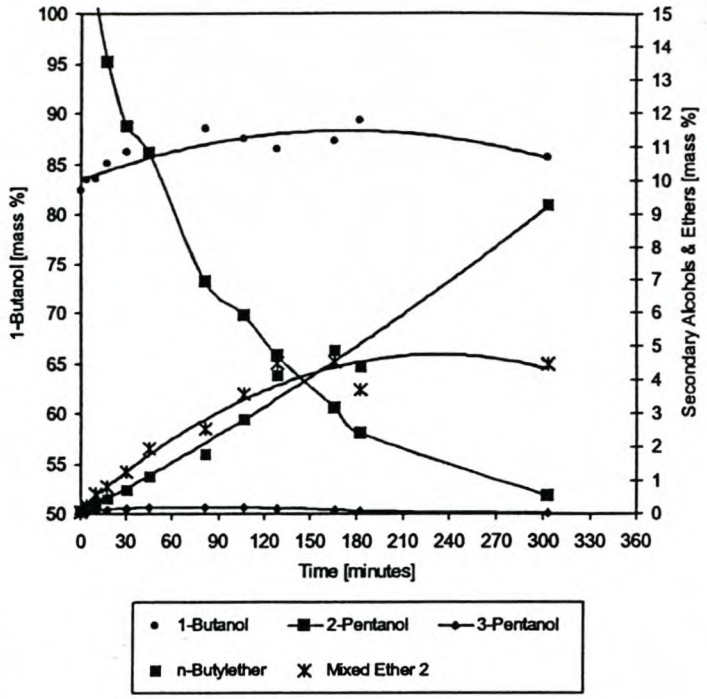
Appendix E Experiment 91.

Feed Composition	
Alcohol Mixture: (mass %) 82.4 % 1-Butanol+ 14.5 % 2-Pentanol + 3.1 % n-Butylether Catalyst: 90 % H_3PO_4 Acid:Alcohol = 2.16:1	
Reaction Conditions	
Atmospheric Pressure Nitrogen Flow: Normal	
Reaction time required to reduce the secondary alcohol content (based on alcohol only) to less than 0,1 mass % = > 120 minutes.	
Reaction Time	= 120 minutes
Product Composition	(mass %) dry basis
1-Butanol	94.1
3-Pentanol	0.02
2-Pentanol	0.07
Mixed Ether 1	not determined
n-Butylether	5.4
Mixed Ether 2	0.6
Total Secondary Alcohol	0.09
Total Ether	6.0
Rate of increase of n-Butylether ~ 0.0224 g/g organics.min	



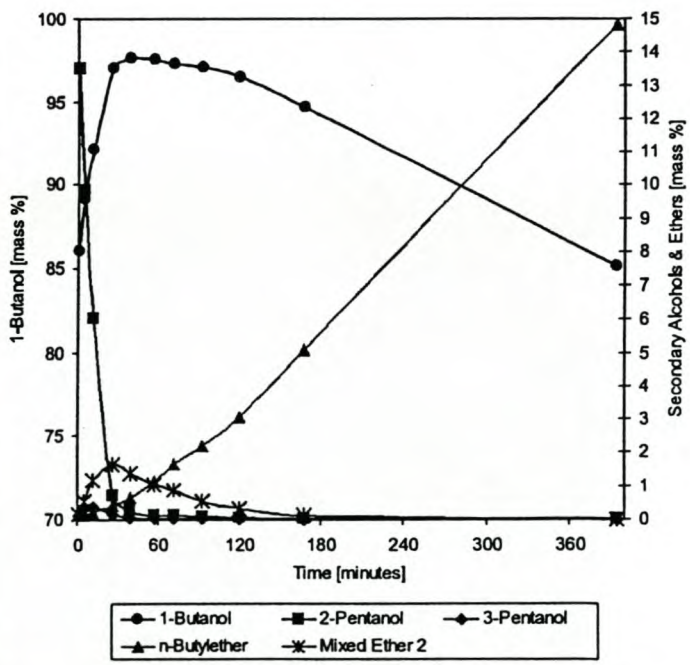
Appendix E: Experiment 92.

Feed Composition	
Alcohol Mixture: (mass %) 85 % 1-Butanol+ 15 % 2-Pentanol Catalyst: 67 % H_2SO_4 Acid:Alcohol = 0.65:1	
Reaction Conditions	
Atmospheric Pressure Nitrogen Flow: Normal	
Reaction time required to reduce the secondary alcohol content (based on alcohol only) to less than 0,1 mass % = > 360 minutes.	
Reaction Time	= 360 minutes
Product Composition	(mass %) dry basis
1-Butanol 3-Pentanol 2-Pentanol Mixed Ether 1 n-Butylether Mixed Ether 2	85.0 0 0.1 not determined 11 4
Total Secondary Alcohol	0.1
Total Ether	15
Rate of increase of n-Butylether ~ 0.030 g/g organis.min	



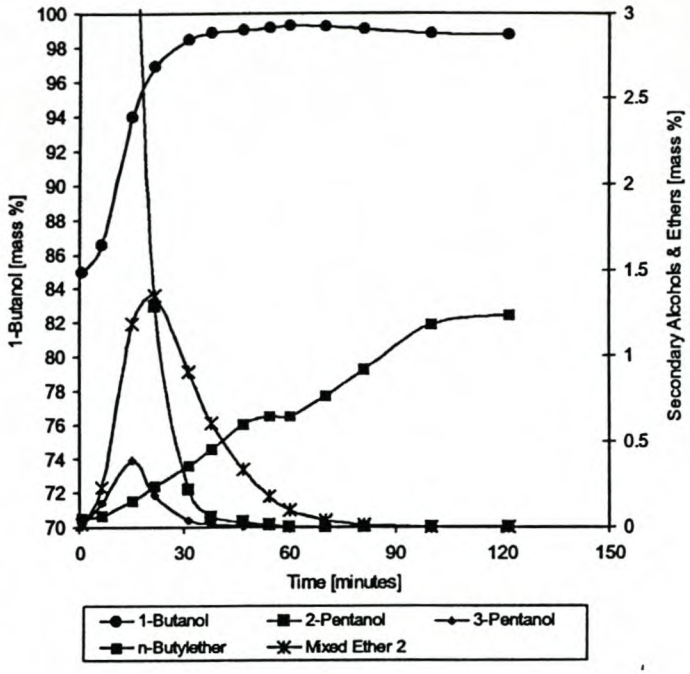
Appendix E: Experiment 93.

Feed Composition	
Alcohol Mixture: (mass %) 85 % 1-Butanol+ 15 % 2-Pentanol Catalyst: 90 % H_3PO_4 Acid:Alcohol = 2.16:1	
Reaction Conditions	
Atmospheric Pressure Nitrogen Flow: low	
Reaction time required to reduce the secondary alcohol content (based on alcohol only) to less than 0,1 mass % = > 105 minutes.	
Reaction Time	= 105 minutes
Product Composition	(mass %) dry basis
1-Butanol 3-Pentanol 2-Pentanol Mixed Ether 1 n-Butylether Mixed Ether 2	96.834 0.022 0.077 not determined 2.605 0.461
Tot. Sec. Alcohol	0.1
Total Ether	3.07
Rate of increase of n-Butylether ~ 0.032 g/g organis.min	



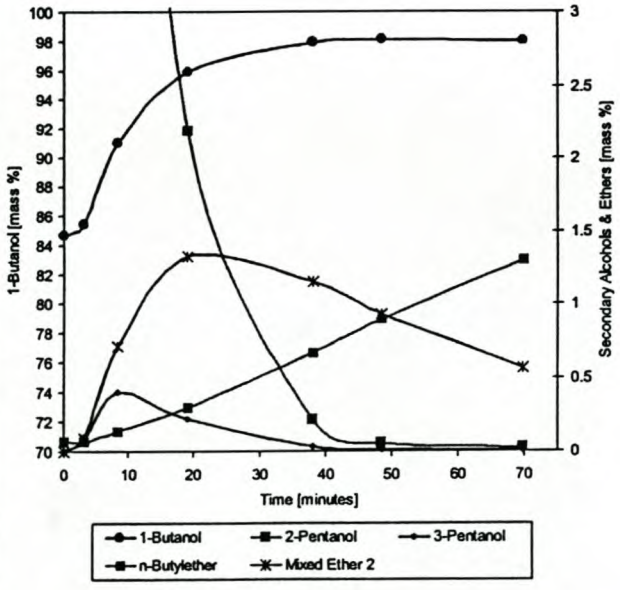
Appendix E: Experiment 94.

Feed Composition		
Alcohol Mixture: (mass %) 85 % 1-Butanol+ 15 % 2-Pentanol Catalyst: 90 % H_3PO_4 Acid:Alcohol = 2.16:1		
Reaction Conditions		
Atmospheric Pressure Nitrogen Flow: very high		
Reaction time required to reduce the secondary alcohol content (based on alcohol only) to less than 0,1 mass % = > 38 minutes.		
Reaction Time [min]	38	60
Product Composition	(mass %) dry basis	
1-Butanol	96.84	99.24
3-Pentanol	0.020	0
2-Pentanol	0.058	0
Mixed Ether 1	not determined	
n-Butylether	0.460	0.657
Mixed Ether 2	0.615	0.1
Total Secondary Alcohol	0.08	0
Total Ether	1.1	0.76
Rate of increase of n-Butylether ~ 0.012 g/g organis.min		



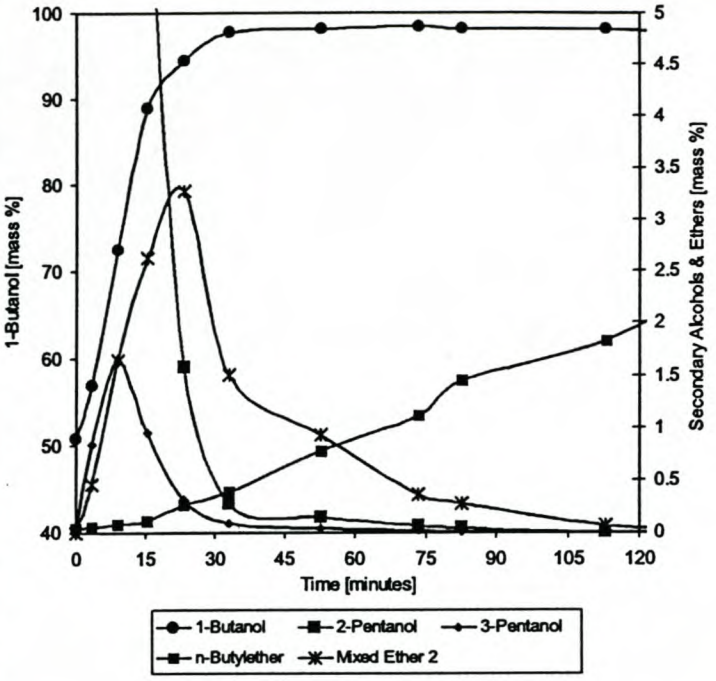
Appendix E: Experiment 95.

Feed Composition		
Alcohol Mixture: (mass %) 85 % 1-Butanol+ 15 % 2-Pentanol Catalyst: 90 % H_3PO_4 Acid:Alcohol = 2.16:1		
Reaction Conditions		
Atmospheric Pressure Nitrogen Flow: normal		
Reaction time required to reduce the secondary alcohol content (based on alcohol only) to less than 0,1 mass % > 45 minutes.		
Reaction Time	48.5min	60 min.
Product Composition	(mass %) dry basis	
1-Butanol	98.108	98.104
3-Pentanol	0.013	0.009
2-Pentanol	0.055	0.041
Mixed Ether 1	not determined	
n-Butylether	0.895	1.114
Mixed Ether 2	0.929	0.732
Total Sec.lcohol	0.07	0.05
Total Ether	1.824	1.846
Rate of increase of n-Butylether ~ 0.0204 g/g organis.min		



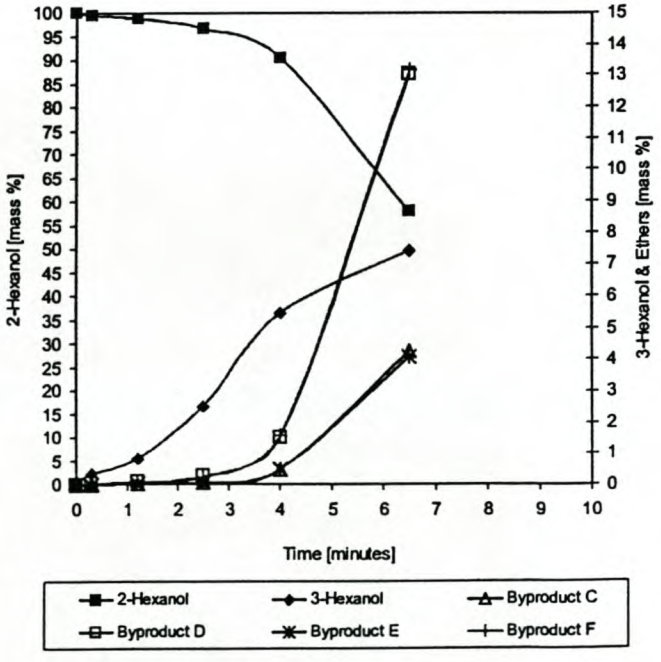
Appendix E: Experiment 96.

Feed Composition	
Alcohol Mixture: (mass %) 50 % 1-Butanol+ 50 % 2-Pentanol Catalyst: 90 % H_3PO_4 Acid:Alcohol = 2.18:1	
Reaction Conditions	
Atmospheric Pressure Nitrogen Flow: normal	
Reaction time required to reduce the secondary alcohol content (based on alcohol only) to less than 0,1 mass % = > 75 minutes.	
Reaction Time	= 75 minutes
Product Composition	(mass %) dry basis
1-Butanol	98.26
3-Pentanol	0.025
2-Pentanol	0.065
Mixed Ether 1	not determined
n-Butylether	1.25
Mixed Ether 2	0.4
To.l Sec. Alcohol	0.09
Total Ether	1.65
Rate of increase of n-Butylether ~ 0.018 g/g organis.min	



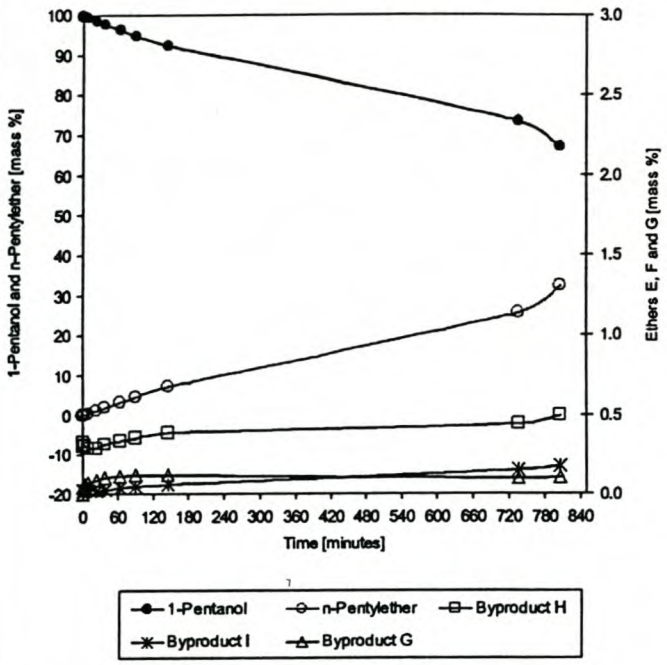
Appendix E: Experiment 97.

Feed Composition
Alcohol Mixture: (mass %) 100 % 2-Hexanol Catalyst: 85% H_3PO_4 ; Acid:Alcohol = 2.16:1
Reaction Conditions:
Atmospheric Pressure Nitrogen Flow: normal
Results: After 7 minutes almost all the alcohol was dehydrated. Mixed Ether 4 and Mixed Ether 5, which were present in all reaction mixtures where 1-Pentanol and 2-Hexanol were reacted, were not traced in any of the samples of experiment 97. It can thus be concluded that Ether 2 and 3 are not combinations of secondary alcohols only. Four further byproducts (C,D,E and F) were detected, however, they were not present in any experiments where the alcohol mixture was reacted.



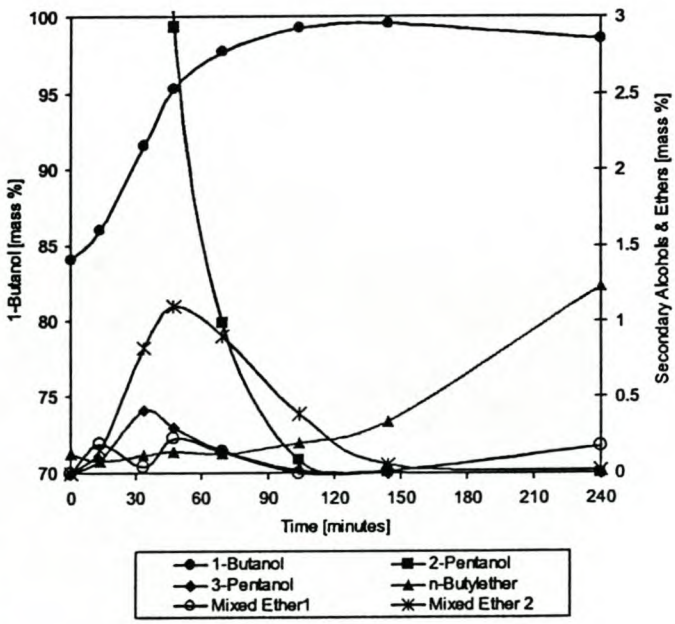
Appendix E: Experiment 98.

Feed Composition
Alcohol Mixture: (mass %) 100 % 1-Pentanol Catalyst: 90% H_3PO_4.; Acid:Alcohol = 2.16:1
Reaction Conditions:
Atmospheric Pressure; Nitrogen Flow: normal
Results: Mixed Ether 4 and Mixed Ether 5, which were present in all reaction mixtures were 1-Pentanol and 2-Hexanol were reacted, were not traced in any of the samples of experiment 98. It can thus be concluded that Mixed Ethers 4 and 5 are not combinations of 1-Pentanol only. Three further byproducts (G, H and I) were detected, however, they were not present in any experiments where the alcohol mixture was reacted. These byproducts were present in very low quantities (<0,5 mass %).



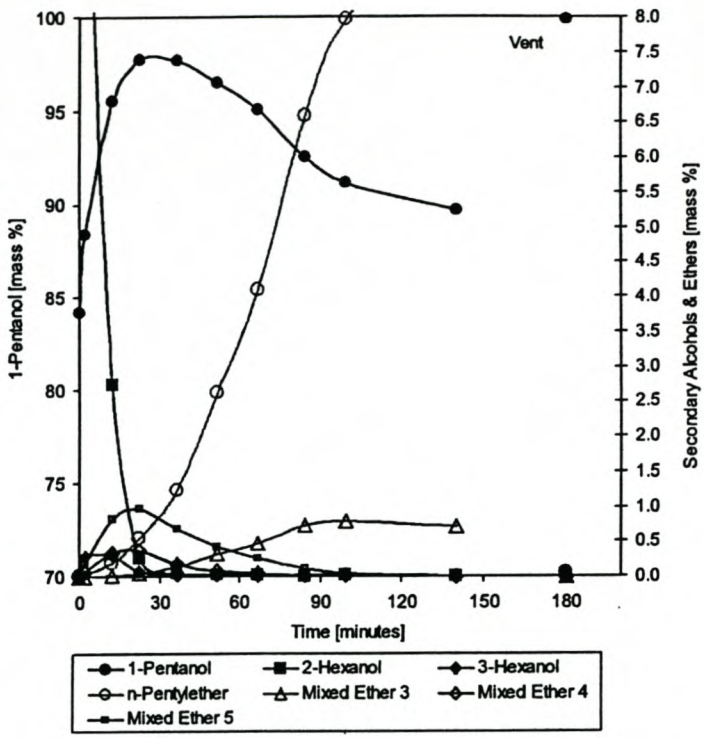
Appendix E: Experiment 99.

Feed Composition		
Alcohol Mixture: (mass %) 85 % 1-Butanol+ 15 % 2-Pentanol Catalyst: 90 % H_3PO_4 Acid:Alcohol = 2.16:1		
Reaction Conditions		
VACUUM Nitrogen Flow: normal		
Reaction time required to reduce the secondary alcohol content (based on alcohol only) to less than 0,1 mass % > 105minutes.		
Reaction Time [min]	105	120
Product Composition	(mass %) dry basis	
1-Butanol	99.31	99.55
3-Pentanol	0.02	0
2-Pentanol	0.08	0.02
Mixed Ether 1	0.01	0.01
n-Butylether	0.20	0.20
Mixed Ether 2	0.39	0.23
Total Secondary Alcohol	0.1	0.02
Total Ether	0.60	0.44
Rate of increase of n-Butylether ~ 0.023 g/g organis.min		



Appendix E: Experiment 100.

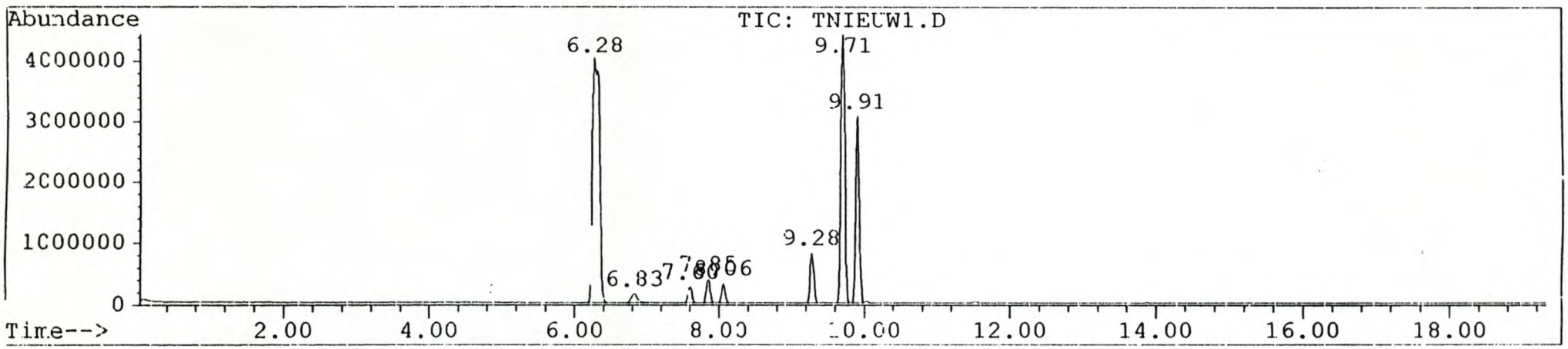
Feed Composition.	
Alcohol Mixture: (mass %) 85 % 1-Pentanol +15 % 2-Hexanol Catalyst: 90 % H_3PO_4 Acid:Alcohol = 2.18:1	
Reaction Conditions:	
VACUUM Nitrogen Flow: none	
Reaction time required to reduce the secondary alcohol content (based on alcohol only) to less than 0.1 mass % ~ > 35 min.	
Reaction Time	36.5 minutes (datapoint)
Product Composition	(mass %) dry basis
1-Pentanol	97.691
3-Hexanol	0.024
2-Hexanol	0.055
Mixed Ether 3	0.139
n-Pentylether	1.231
Mixed Ether 4	0.180
Mixed Ether 5	0.680
Mixed Ether 6	not determined
Total Secondary Alcohol	0.081
Total Ether	2.229
Rate of increase of n-Pentylether at 35 min.~ 0.074 g/g organics.min Rate of increase of n-Pentylether at 20 min.~ 0.03 g/g organics.min	



Information from Data File:
File : C:\HPCHEM\1\DATA\TNIEUW1.D
Operator :
Acquired :
Sample Name: Gasmonster
Misc Info :
Vial Number: 1

Search Libraries: c:\DATABASE\GCDEVAL.L Minimum Quality: 1
c:\DATABASE\wiley138.l Minimum Quality: 0

Unknown Spectrum: Apex minus start of peak
Integration Params: current RTEINT parameters



Pk#	RT	Area%	Library/ID	Ref#	CAS#	Qual
1	6.28	44.18	C:\DATABASE\WILEY138.L			
			Oxygen	115881	007782-44-7	2
			Nitrogen	115851	007727-37-9	1
			Carbon monoxide	115839	000630-08-0	1

APPENDIX F1: Analyses of vent stream for the system 1-butanol+2-pentanol

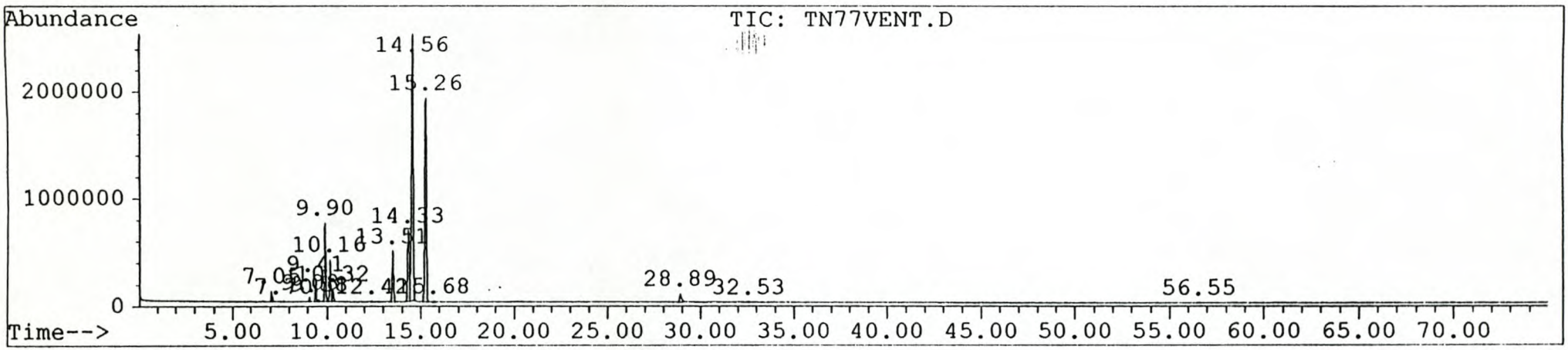
2	6.83	1.49	C:\DATABASE\GCDEVAL.L			
			Water	37	000000-00-0	1

3	7.60	1.43	C:\DATABASE\WILEY138.L			
			1-Butene	116017	000106-98-9	90
			2-Butene, (E)-	116021	000624-64-6	87
			2-Butene, (Z)-	116019	000590-18-1	83
4	7.85	2.11	C:\DATABASE\WILEY138.L			
			1-Butene	116017	000106-98-9	87
			1-Propene, 2-methyl-	116024	000115-11-7	87
			2-Butene, (Z)-	116019	000590-18-1	87
5	8.06	1.75	C:\DATABASE\WILEY138.L			
			2-Butene, (Z)-	116019	000590-18-1	87
			Cyclobutane	116025	000287-23-0	87
			1-Propene, 2-methyl-	116024	000115-11-7	83
6	9.28	4.47	C:\DATABASE\WILEY138.L			
			1-Pentene	116332	000109-67-1	86
			Cyclopentane	116347	000287-92-3	80
			Cyclobutanone	116322	001191-95-3	64
7	9.71	26.86	C:\DATABASE\WILEY138.L			
			Cyclopropane, 1,2-dimethyl-, trans	116344	002402-06-4	94
			2-Pentene	116333	000109-68-2	91
			2-Pentene, (E)-	116337	000646-04-8	90
8	9.91	17.71	C:\DATABASE\WILEY138.L			
			2-Pentene, (Z)-	116334	000627-20-3	91
			2-Pentene	116336	000109-68-2	91
			2-Pentene, (E)-	116338	000646-04-8	87

Information from Data File:
File : C:\HPCHEM\1\DATA\TN77VENT.D
Operator : Traute
Acquired : 30 Jan 80 9:33 am using AcqMethod IZAK1
Sample Name: Vents
Misc Info : Total Vents
Vial Number: 1

Search Libraries: c:\DATABASE\GCDEVAL.L Minimum Quality: 1
c:\DATABASE\wiley138.l Minimum Quality: 0

Unknown Spectrum: Apex minus start of peak
Integration Params: current RTEINT parameters



Pk#	RT	Area%	Library/ID	Ref#	CAS#	Qual
1	7.05	1.33	C:\DATABASE\GCDEVAL.L			
			Water	37	000000-00-0	1
2	7.70	0.09	C:\DATABASE\WILEY138.L			
			1-Propene, 2-methyl-	116022	000115-11-7	80
			1-Butene	116017	000106-98-9	47
			2-Butene	116020	000107-01-7	9

3	9.08	0.45	C:\DATABASE\WILEY138.L			
			Butane, 2-methyl-	116461	000078-78-4	91
			Butane, 2,3-dimethyl-	116	000079-29-8	64
			Pentane	116454	000109-66-0	50
4	9.41	1.98	C:\DATABASE\WILEY138.L			
			1-Pentene	116332	000109-67-1	91
			Cyclopentane	116347	000287-92-3	80
			Cyclobutane, methyl-	116346	000598-61-8	43
5	9.58	0.27	C:\DATABASE\WILEY138.L			
			2-Pentene, (Z)-	116334	000627-20-3	91
			Cyclopropane, 1,2-dimethyl-, trans	116344	002402-06-4	90
			2-Pentene	116333	000109-68-2	87
6	9.90	7.30	C:\DATABASE\WILEY138.L			
			2-Pentene	116333	000109-68-2	91
			Cyclopropane, 1,2-dimethyl-, trans	116344	002402-06-4	90
			2-Pentene, (E)-	116338	000646-04-8	87
7	10.16	3.99	C:\DATABASE\WILEY138.L			
			Cyclopropane, 1,2-dimethyl-, trans	116344	002402-06-4	87
			2-Pentene, (Z)-	116334	000627-20-3	87
			2-Pentene, (E)-	116337	000646-04-8	87
8	10.32	1.25	C:\DATABASE\WILEY138.L			
			Cyclopropane, 1,2-dimethyl-, cis-	116343	000930-18-7	91
			2-Pentene	116333	000109-68-2	91
			2-Pentene, (Z)-	116335	000627-20-3	91
9	12.42	0.14	C:\DATABASE\WILEY138.L			
			Pentane, 2-methyl-	106	000107-83-5	47
			1-Butene, 3,3-dimethyl-	116920	000558-37-2	35
			5-HYDROXYPENTAN-2-ONE	118243	001071-73-4	25
10	13.51	6.08	C:\DATABASE\WILEY138.L			
			1-Hexene	116884	000592-41-6	87
			2H-Pyran-2-one, tetrahydro-3,6-dim	5862	003720-22-7	64
			Cyclohexane	116929	000110-82-7	52

11	14.33	9.91	C:\DATABASE\WILEY138.L			
			3-Hexene, (E)-	116893	013269-52-8	90
			2-Hexene	116887	000592-43-8	87
			2-Hexene, (Z)-	116886	007688-21-3	83
12	14.56	37.70	C:\DATABASE\WILEY138.L			
			2-Hexene	116885	000592-43-8	94
			2-Hexene, (Z)-	116886	007688-21-3	91
			Cyclopentanone	116859	000120-92-3	59
13	15.26	27.61	C:\DATABASE\WILEY138.L			
			2-Hexene, (Z)-	116886	007688-21-3	91
			2-Hexene	116887	000592-43-8	91
			3-Hexene, (E)-	116893	013269-52-8	91
14	15.68	0.18	C:\DATABASE\WILEY138.L			
			2-Pentene, 3-methyl-, (E)-	116907	000616-12-6	87
			Pentane, 3-methylene-	116914	000760-21-4	80
			2-Butene, 2,3-dimethyl-	116921	000563-79-1	80
15	28.89	1.50	C:\DATABASE\WILEY138.L			
			1-Pentanol	256	000071-41-0	90
			1-Pentene	116332	000109-67-1	59
			1-Butanol, 3-methyl- (impure)	117287	000123-51-3	53
16	32.53	0.15	C:\DATABASE\WILEY138.L			
			2-Hexanol	118287	000626-93-7	83
			2-Pentanol, 4-methyl-	118331	000108-11-2	78
			4-Penten-2-ol	117074	000625-31-0	36
17	56.55	0.06	C:\DATABASE\WILEY138.L			
			Ethene, 1,1'-oxybis-	116317	000109-93-3	25
			Azetidine, 2-methyl-	116361	019812-49-8	4
			Heptane, 3,3,4-trimethyl-	10267	020278-87-9	4

Appendix G - Sampling and analytical procedures

Appendix G1-Neutralisation of reaction liquid with sodiumbicarbonate.

Samples were withdrawn at varying time intervals from the reaction mixture. The sample point was purged continuously with 99,9 % nitrogen. This was done to ensure that no dead legs were formed in the sample point. The sample point was also flushed with a little reaction mixture before taking each sample.Sample sizes varied between 1 and 3 ml. They were neutralized with an excess amount of $NaHCO_3$ The neutralization reaction is as follows:

$$3NaHCO_3 + H_3PO_4 \rightarrow Na_3PO_4 + 3H_2O + 3CO_2$$

The organic sample was washed out of the solid with dicloromethane. It was mostly homogeneous. The water in the reaction mixture (including the reaction water) and the water formed during neutralisation was partly hold in the solid sodiumphosphate as cristalwater and the rest was dissolved in the organic liquid product. Very few samples (less than 2%) consisted of two phases. For these samples only the top organic phase was analysed – however in some cases these samples were milky. Too high levels of water must have been in the organic phase, and this would make the GC analysis unreliable.

While the organic sample was washed out with dichloromethane, the salt was filtered out with a laboratory vacuum filter. Thereafter only the organic fluid (this contained the alcohol product) diluted with dicloromethane, was anlysed. For the most samples the solid that was filtered out was a loose cristal-like powder. In a few instances, very few, the solid was cloggy.

Samples could be taken at different reaction time increments, thus separate experiments did not have to be performed to determine the influence of reaction time on dehydration.

Appendix G2 - Analytical Procedures

Analysis of the organic phases were done with a Gas Chromatograph (GC). The GC had a flame ionization detector. For all the analysis of the 1-propanol+ 2-butanol system mainly a non-polar capillary column (50m) was used. This column was used for about half of the 1-butanol+2-pentanol analysis and one 1-pentanol+2-hexanol analysis (Experiment 70). In order to achieve better separation of the secondary alcohols and byproducts of the system 1-pentanol+2-hexanol, the column was changed to a slightly polar capillary column (50 m). Details on GC time programs are given in the tables below.

	Alcohol System	
Temperature programs	1-propanol + 2-butanol	1-butanol + 2-pentanol
Column, capillary column, 50 metre	non-polar	non-polar
Experiments	1 to 19; 51; 60; 76	30-33; 36; 62-69; 72; 73
Initial Column Temperature [°C]	60	
Column hold time [min]	20	
First final column Temperature [oC]	220	
Temperature increase rate [°C/min]	30	
Column hold time [min.]	6	
Second final Column Temperature [°C]	-	
Temperature increase rate [°C/min.]	-	
Column hold time	-	
Injector temperature [°C]	240	
Detector temperature [°C]	300	

	Alcohol System	
Temperature programs	1-butanol + 2-pentanol	1-pentanol+ 2-hexanol
Column, capillary column, 50 metre	slightly polar	slightly polar
Experiments	53;55; 89 to 96; 99	75; 77; 79 to 84; 86 to 88; 97; 98; 100
Initial Column Temperature [°C]	40	45
Column hold time [min]	17	15
First final column Temperature [oC]	225	104
Temperature increase rate [°C/min]	16	2
Column hold time [min.]	6	1
Second final Column Temperature [oC]	-	225
Temperature increase rate [°C/min.]	-	30
Column hold time	-	5
Injector temperature [°C]	240	240
Detector temperature [°C]	300	300

A megabore column was also used for some of the analyses of the 1-propanol+2-butanol system, however it did not give a good separation. No analyses obtained from this column are reported.

Unknown components were identified with a Mass Spectrometer. The water contents in the organic phases and water phases were determined with a Karl Fischer apparatus.

Some experiments were repeated to ensure that the experimental data is repeatable (see par. 5.9).

Appendix H - Conceptual design calculations

Appendix H1- Design calculations of a 1-butanol + 2-pentanol reaction separation plant, which produces only n-butylether as byproduct.

Appendix H1 - Reactor calculations:

Determination of design basis:

Results of Experiment 66 were used as design basis. Catalyst system: 90 % H_3PO_4 with acid:alcohol = 3:1; Reaction time ~ 110 minutes.

Composition of organics after removal of all the secondary alcohol and dehydration of mixed ether 2:

1-Butanol = 95,5 mass % and n-Butylether = 4,5 mass %

Reactions:

1) Dehydration of 2-pentanol:

$CH_3CH_2CH_2CHOHCH_3 \rightarrow CH_3CH_2CH{=}CHCH_3 + H_2O$

2) Formation of n-butylether:

$2CH_3CH_2CH_2CH_2OH \rightarrow CH_3CH_2CH_2CHOCHCH_2CH_2CH_3 + H_2O$

Mass Balance on Reactor:

0 = In – Out + Formed – Reacted

Basis= 100 kg dry organics in reactor outlet

95,5 kg 1-Butanol + 4,5 kg n-Butylether

1-Butanol	In	=	Out	+	Reacted to form ether
		=	95,5	+	$(4{,}5/Mr_{n\text{-butylether}})*2*Mr_{1\text{-Butanol}}$
		=	100,623 kg		
Yield of n-Butylether		=	4,5 kg n-butylether / 100,623 kg 1-butanol fed		
		=	4,472 kg n-butylether / 100 kg 1-butanol fed		

All the 2-Pentanol dehydrated to pentene and flashed off.

Basis= 10 000 kg reactor feed to short path distillation (SPD) unit

From ProII simulation of the thermal separation processes, the combined acid recycle stream is as below (convergence was reached after several simulation runs).

A pseudo component was used in the place of H3PO4 because thermodinamic data of H3PO4 was not available in PRO II.

Stream	Mr	14
Description	[kg/kmol]	Combined acid/water recycle
		mass %
1-Butanol	74	3.3516
2-Pentanol	88	0
n-Butylether	130	0.0647
Water	18	9.2858
H3PO4	98	87.298
Pentene	70	0
Total		7940.49 kg/h

See Figure 7.1 in Chapter 7

Water Make-up:

H_3PO_4 recycled = $x_{14,\,H3PO4}$*Stream 14 = 6931.9 kg

Water required = (0,1/0,9) * 6931.9 = 770.2 kg

Water present in recycle stream = $x_{14,water}$*Stream 14 = 737.34 kg

Water make-up thus required = 32.87 kg

Fresh Alcohol required:

Acid / 3 = (6931.9+770.2)/3 = 2567.37 kg

Alcohol in recycle stream = $(x_{14,1\text{-butanol}} + x_{14,2\text{-pentanol}})$*stream 14 = 266.13 kg

Fresh alcohol to be fed = 2301.24 kg

Reactions: as above

Pentene vents, all the 2-pentanol dehydrated to pentene:

kmol pentanol dehydrated = $(x_{1,2\text{-pentanol}}$*Stream 1)$Mr_{2\text{-pentanol}}$ = 3,9226 kmol

kg pentene vented = kmol pentanol dehydrated * $Mr_{pentene}$ = 274.6 kg

n-Butylether formed:

0,0447 kg n-Butylether / kg 1-butanol in total reactor feed
n-Butylether formed = 0,04472 [266.13 + 0,85*2301.24] = 99.38 kg = 0,7644 kmol
1-Butanol converted:
1-Butanol reacted = 2 * moles of n-Butylether formed = 1,529 kmol = 113.14 kg
Water formed:
Total water formed = water from pentene reaction + water from ether reaction
= 3,9226 * 18 + 0,7644* 18 = 84.37 kg water
Mass Balance over Reactor:

0	=	In – Out + Formed – Reacted
Out	=	In + Formed - Reacted
1-Butanol Out	=	In – Reacted
	=	$x_{14,1\text{-butanol}}$*stream 14 + 0,85*2301.24 – 113.14 = 2109.0 kg
2-Pentanol Out	=	0
n-Butylether Out		= In + Formed
		= $x_{14,n\text{-butylether}}$*stream 14 + 99.38 = 104.52 kg
Water Out		= In + Formed
		= 737.34 + 32.87 + 84.37 = 854.58 kg
H_3PO_4 Out		= In = 6931.9 kg
% 1-Butanol recovery		= Product/Fresh Feed * 100
		= {[0.997*1405]/[0.85*2301.24]} * 100 = 72 %

Appendix H1 - PROII Input file

```
$ Generated by PRO/II Keyword Generation System <version 5.55>
$ Generated on: Fri Nov 23 08:57:45 2001
TITLE DATE=12/29/00
 PRINT INPUT=ALL, STREAM=ALL, RATE=M,WT, FRACTION=M,WT, PERCENT=M,WT, &
      MBALANCE, ION=NONE
 TOLERANCE FLASH=3E-6, STREAM=1E-5,-5.5556E-5,1E-7,1E-6
 DIMENSION SI, TEMP=C, STDTEMP=0, STDPRES=101.325
 SEQUENCE DEFINED=SPD,HE,SPD-SEP,E1,P2,P1,F1,SP2,SP1,T1,M1
 CALCULATION TRIALS=80, RVPBASIS=APIN, TVP=37.778, RECYCLE=ALL
COMPONENT DATA
 LIBID 1,BUTANOL/2,DBE/3,WATER
 NONLIB 4,Acid-Catalyst, FILL=SIMSCI
 STRUCTURE 4,211(2),601(4),901(2)
THERMODYNAMIC DATA
 METHOD SYSTEM=NRTL, SET=NRTL01, DEFAULT
  KVAL(VLE) FILL=UFT1, AZEOTROPE=SIMSCI
 METHOD SYSTEM(VLLE)=NRTL, SET=NRTL02
  KVAL(VLE) FILL=UFT1, AZEOTROPE=SIMSCI
  KVAL(LLE) FILL=UFT1, AZEOTROPE=SIMSCI
STREAM DATA
 PROPERTY STREAM=5-REAC-PROD, TEMPERATURE=80, PRESSURE=10, PHASE=M,
&
      RATE(WT)=10000, COMPOSITION(WT)=1,2109.14/2,104.511/3,854.62/ &
     4,6932.24, NORMALIZE, SET=NRTL02
 PROPERTY STREAM=10B-H2O-REC, TEMPERATURE=30, PRESSURE=101, PHASE=M,
&
      RATE(WT)=200, COMPOSITION(M)=1,50/3,50
 PROPERTY STREAM=10A-ORG-COL, TEMPERATURE=30, PRESSURE=101,
PHASE=M, &
      RATE(WT)=200, COMPOSITION(M)=3,50/1,50
UNIT OPERATIONS
 FLASH UID=SPD
    FEED 5-REAC-PROD
    PRODUCT  V=7-SPD-DIST, W=6-SPD-ACID
    ISO  TEMPERATURE=85
 HX  UID=HE
    HOT  FEED=7-SPD-DIST, M=EXIT-HE
    OPER HTEMP=30
```

```
 FLASH UID=SPD-SEP
    FEED EXIT-HE
    PRODUCT  L=8-COL-FEED, W=9-H2O-REC
    ISO  TEMPERATURE=30
    METHOD SET=NRTL02
 HX  UID=E1
    HOT  FEED=9-H2O-REC,6-SPD-ACID, M=CAT-REC-COLD
    OPER HTEMP=30
 PUMP UID=P2
    FEED CAT-REC-COLD
    PRODUCT  M=CAT-REC-POUT
    OPERATION PRESSURE=15
 PUMP UID=P1
    FEED 8-COL-FEED
    PRODUCT  M=FEED-COL-HP
    OPERATION PRESSURE=102
 FLASH UID=F1
    FEED OVERHEADS-C1
    PRODUCT  L=S5, W=S4
    ISO  TEMPERATURE=30
    METHOD SET=NRTL02
 SPLITTER UID=SP2
    FEED S5
    PRODUCT  M=10A-ORG-COL, M=11-WET-ORG
    OPERATION OPTION=NORM
    SPEC STREAM=10A-ORG-COL, RATE(WT,KG/H),TOTAL,WET, DIVIDE, &
          STREAM=S5, RATE(WT,KG/H),TOTAL,WET, VALUE=0.2
    SPEC STREAM=11-WET-ORG, RATE(WT,KG/H),TOTAL,WET, DIVIDE, &
          STREAM=S5, RATE(WT,KG/H),TOTAL,WET, VALUE=0.8
 SPLITTER UID=SP1
    FEED S4
    PRODUCT  M=10B-H2O-REC, M=12-H20-REAC
    OPERATION OPTION=NORM
    SPEC STREAM=10B-H2O-REC, RATE(WT,KG/H),TOTAL,WET, DIVIDE, &
          STREAM=S4, RATE(WT,KG/H),TOTAL,WET, VALUE=0.4
    SPEC STREAM=12-H20-REAC, RATE(WT,KG/H),TOTAL,WET, DIVIDE, &
          STREAM=S4, RATE(WT,KG/H),TOTAL,WET, VALUE=0.6
 COLUMN UID=T1
    PARAMETER TRAY=17,CHEMDIST=30
    FEED 10B-H2O-REC,1/10A-ORG-COL,1/FEED-COL-HP,4
    PRODUCT  OVHD(M)=OVERHEADS-C1, BTMS(WT)=13-BUTANOL,1405, &
          SUPERSEDE=ON
    DUTY 1,17
    PSPEC PTOP=15
    PRINT PROPTABLE=PART
    ESTIMATE MODEL=CHEM, RRATIO(L)=3
    SPEC STREAM=13-BUTANOL, RATE(WT,KG/H),TOTAL,WET, VALUE=1405
    VARY DUTY=1
    VLLECHECK CHECK=OFF
    QCOLUMN QCONDENSER=0, QREBOILER=0, QCOLUMN=0, QTRAY=0
    REBOILER TYPE=KETTLE
    METHOD SET=NRTL01
 MIXER UID=M1
    FEED 12-H20-REAC,CAT-REC-POUT
    PRODUCT  M=14-CAT-REC
END
```

Appendix H1 - Summarized PROII Output file

See Figure 7.1, Chapter 7

STREAM ID	CAT-REC-COLD	CAT-REC-POUT	EXIT-HE	FEED-COL-HP
NAME				
PHASE	LIQUID	LIQUID	LIQUID	LIQUID
FLUID WEIGHT PERCENTS				
1 BUTANOL	3.2235	3.2235	68.765	76.4191
2 DBE	0.0628	0.0628	3.6432	4.0867
3 WATER	5.0103	5.0103	27.5918	19.4942
4 Acid-Catalyst	91.7034	91.7034	4.22E-06	4.60E-06
TOTAL RATE, KG/HR	7559.0342	7559.0342	2741.1293	2440.974
TEMPERATURE, C	30	30.0008	30	30.04
PRESSURE, KPA	10	15	10	102
ENTHALPY, M*KJ/HR	0.7401	0.7401	0.2331	0.1967
MOLECULAR WEIGHT	141.454	141.454	40.2046	46.632
WEIGHT FRAC VAPOR	0	0	0	0
WEIGHT FRAC LIQUID	1	1	1	1

STREAM ID	OVERHEADS-C1	S4	S5	5-REAC-PROD
NAME				
PHASE	VAPOR	LIQUID	LIQUID	MIXED
FLUID WEIGHT PERCENTS				
1 BUTANOL	40.5493	5.8892	67.4831	21.0903
2 DBE	8.2624	0.1009	14.6046	1.0451
3 WATER	51.1882	94.0098	17.9123	8.5458
4 Acid-Catalyst	8.23E-17	3.40E-17	1.20E-16	69.3188
TOTAL RATE, KG/HR	1453.9087	635.765	818.1436	10000.0082
TEMPERATURE, C	49.1192	30	30	80
PRESSURE, KPA	15	15	15	10
ENTHALPY, M*KJ/HR	2.4484	0.0777	0.0648	5.1731
MOLECULAR WEIGHT	28.9694	18.8727	49.5823	94.5327
WEIGHT FRAC VAPOR	1	0	0	0.265
WEIGHT FRAC LIQUID	0	1	1	0.735

STREAM ID	6-SPD-ACID	7-SPD-DIST	8-COL-FEED	9-H2O-REC
NAME				
PHASE	LIQUID	VAPOR	LIQUID	LIQUID
FLUID WEIGHT PERCENTS				
1 BUTANOL	3.0872	68.765	76.4191	6.5189
2 DBE	0.0639	3.6432	4.0867	0.036
3 WATER	1.3535	27.5918	19.4942	93.4451
4 Acid-Catalyst	95.4953	4.22E-06	4.60E-06	1.18E-06

TOTAL RATE, KG/HR	7258.8789	2741.1293	2440.974	300.1554
TEMPERATURE, C	85	85	30	30
PRESSURE, KPA	10	10	10	10
ENTHALPY, M*KJ/HR	1.7382	3.6497	0.1965	0.0366
MOLECULAR WEIGHT	193.0345	40.2046	46.632	18.9563
WEIGHT FRAC VAPOR	0	1	0	0
WEIGHT FRAC LIQUID	1	0	1	1

STREAM ID	10A-ORG-COL	10B-H2O-REC	11-WET-ORG	12-H20-REAC
NAME			2nd Column Feed	
PHASE	LIQUID	LIQUID	LIQUID	LIQUID
FLUID WEIGHT PERCENTS				
1 BUTANOL	67.4831	5.8892	67.4831	5.8892
2 DBE	14.6046	0.1009	14.6046	0.1009
3 WATER	17.9123	94.0098	17.9123	94.0098
4 Acid-Catalyst	1.20E-16	3.40E-17	1.20E-16	3.40E-17
TOTAL RATE, KG/HR	163.6287	254.306	654.5149	381.459
TEMPERATURE, C	30	30	30	30
PRESSURE, KPA	15	15	15	15
ENTHALPY, M*KJ/HR	0.013	0.0311	0.0519	0.0466
MOLECULAR WEIGHT	49.5823	18.8727	49.5823	18.8727
WEIGHT FRAC VAPOR	0	0	0	0
WEIGHT FRAC LIQUID	1	1	1	1

STREAM ID	13-BUTANOL	14-CAT-REC
NAME		
PHASE	LIQUID	LIQUID
FLUID WEIGHT PERCENTS		
1 BUTANOL	99.7309	3.3516
2 DBE	0.2691	0.0647
3 WATER	6.21E-10	9.2858
4 Acid-Catalyst	7.99E-06	87.298
TOTAL RATE, KG/HR	1405	7940.4933
TEMPERATURE, C	72.1267	30.0007
PRESSURE, KPA	15	15
ENTHALPY, M*KJ/HR	0.2491	0.7868
MOLECULAR WEIGHT	74.21	107.8135
WEIGHT FRAC VAPOR	0	0
WEIGHT FRAC LIQUID	1	1

Appendix H2- Design calculations of a 1-butanol + 2-pentanol reaction separation plant, which produces n-butylether and 3-pentyl-butyl ether as byproduct.

Appendix H2-Reactor calculations

Determination of design basis:

Results of Experiment 73 were used as design basis. Catalyst system: 90 % H_3PO_4 with acid:aclcohol = 1,5:1; Reaction time ~ 70 minutes.

Composition of organics after the amount of 2-pentanol was reduced to < 0,1 % based on alcohols only.

		mass %
1-Butanol	=	98,0
2-Pentanol	=	0,1
n-Butylether	=	0,8
3-Pentyl butyl ether	=	1,1

Reactions:

1) Dehydration of 2-pentanol:

$CH_3CH_2CH_2CHOHCH_3 \rightarrow CH_3CH_2CH{=}CHCH_3 + H_2O$

2) Formation of n-butylether:

$2CH_3CH_2CH_2CH_2OH \rightarrow CH_3CH_2CH_2CHOCHCH_2CH_2CH_3 + H_2O$

3) Formation of 3-pentyl butyl ether

$$\underset{\text{2-Pentene}}{CH_3CH_2CH{=}CHCH_3} + \underset{\text{1-Butanol}}{CH_3CH_2CH_2CH_2OH} \xrightarrow{H_3PO_4} \underset{\substack{\text{Mixed Ether 2}\\ \text{3 Pentyl Butyl Ether}}}{(CH_3CH_2)_2CHOC_4H_9} + H_2O$$

Mass Balance on Reactor:

0 = In – Out + Formed – Reacted

Basis= 100 kg dry organics in reactor outlet

98,0 kg 1-Butanol + 0,1 kg 2-Pentanol + 0,8 kg n-Butylether +1,1 kg 3-Pentyl-butyl ether

1-Butanol In = Out + Reacted to form ether

IN = 98,0 + $[(0,8/Mr_{n\text{-butylether}})*2 + (1,1/Mr_{n\text{-3-P-B-ether}})]*Mr_{1\text{-Butanol}}$

= 99,476 kg

2-Pentanol In = $(0,15/0,85)*IN_{1\text{-butanol}}$ = 17,5546 kg

2-Pentanol reacted as follows:

fraction that did not react = (0,1)/17,5546 = 0,0056965

fraction converted to ether = $[(1,1/Mr_{n\text{-3-P-B-ether}})]*Mr_{1\text{-pentanol}}]/17,5546$

= 0,038293

fraction dehydrated = [1 – 0,0056965 – 0,038293] = 0.95601

Fraction of 1-butanol converted to n-butylether

= $[(0,8/Mr_{n\text{-butylether}})*Mr_{1\text{-butanol}}*2]/$ 99,476

= 0.0091557

Basis= 10 000 kg reactor feed to short path distillation (SPD) unit

From ProII simulation of the thermal separation processes, the combined acid recycle stream is as below (convergence was reached after several simulation runs).

Stream	Mr	16
Description	[kg/kmol]	Combined recycle before acid conc. correction mass %
1-Butanol	74	4.833
2-Pentanol	88	0.00374
n-Butylether	130	0.0171
3-Pentyl-Butyleth	144	0.0381
Water	18	8.86
H_3PO_4	98	86.248
Pentene	70	0
Total		6534.43 kg/h

See Figure 7.2 in Chapter 7

Water Make-up:

H_3PO_4 recycled = $x_{16,\ H3PO4}$ *Stream 16 = 5635,82 kg
Water required = (0,1/0,9) * 5635,8 = 626,2 kg
Water present in recycle stream = $x_{16,water}$*Stream 16 = 579,0 kg
Water make-up thus required = 47,25 kg
Fresh Alcohol required:
Acid / 1,5 = (5635,8+626,2)/1,5 = 4174,7 kg
Alcohol in recycle stream = ($x_{16,1\text{-butanol}}$ + $x_{16,2\text{-pentanol}}$)*stream 16 = 316,05 kg
Fresh alcohol to be fed = 3858,65 kg
1-Butanol in total fed to reactor=0,85*3858,65 + $x_{16,1\text{-butanol}}$*stream16=3595,66 kg
2-Pentanol in total fed to reactor=0,15*3858,65+$x_{16,2\text{-pentanol}}$*stream16=579,0 kg
Reactions: equations as above
Conversion of 2-Pentanol
Pentene vents: fraction of 2-pentanol dehydrated to pentene = 0.95601
pentene vent stream = [(0,95601*579,0)/$Mr_{2\text{-pentanol}}$]*$Mr_{pentene}$ = 440,34 kg
2-Pentanol that did not react = 0,0056965*579,0 = 3,3 kg
3-Pentyl Butyl ether formed=[0,038293*579,0/$Mr_{2\text{-pentanol}}$]*$Mr_{3\text{-P-B-ether}}$= 36,28 kg
Assumption: The n-Pentyl Butyl ether that enters the reactor remains unchanged. In a real reactor system the amount would decrease. The n-Pentyl Butyl ether used in this design is thus higher than the actual expected amount.
Conversion of 1-Butanol
Conversion of 1-Butanol to 3-Pentyl butyl ether =(36,28/ $Mr_{3\text{-P-B-ether}}$)*$Mr_{1\text{-butanol}}$]
= 18,65 kg
Conversion of 1-butanol to n-butylether:
= 0.0091557*3595,66= 32,92 kg
n-butylether formed = [32,92/(2*$Mr_{1\text{-butanol}}$)]*$Mr_{n\text{-butylether}}$= 28,92 kg
1-Butanol converted:
1-Butanol reacted = 18,65 + 32,92 = 51,57 kg
Water formed:
Total water formed =water from pentene reaction + water from ether reactions
= [440,34/$Mr_{Pentene}$ + 36,28/$Mr_{3\text{-P-B-ether}}$ + 28,92/$Mr_{n\text{-butylether}}$]*18 = 121,77 kg
Mass Balance over Reactor:
0 = In – Out + Formed – Reacted
Out = In + Formed - Reacted
1-Butanol Out = In – Reacted
= 3595,66 – 51,57 = 3544,1 kg
2-Pentanol Out = 3,3 kg
n-Butylether Out = In + Formed
= $x_{16,nbutylether}$*stream 16 + 28,92 = 30,0 kg
3-Pentyl butyl ether Out = In + Formed
= $x_{16,3\text{-P-B-ether}}$*stream 16 + 36,28 = 38,77 kg
Water Out = In + Formed
= 626,2 + 121,77 = 748,0 kg
H_3PO_4 Out = In = 5635,8 kg

% 1-Butanol recovery = Product/Fresh Feed * 100
= {[0.9953*2470]/[0.85*3858,65]} * 100 = 75 %

Appendix H2- Proll Input File

```
$ Generated by PRO/II Keyword Generation System <version 5.55>
$ Generated on: Fri Nov 23 10:52:19 2001
TITLE DATE=12/29/00
 PRINT INPUT=ALL, STREAM=ALL, RATE=M,WT, FRACTION=M,WT, PERCENT=M,WT, &
       MBALANCE, ION=NONE
 TOLERANCE FLASH=3E-6, STREAM=1E-5,-5.5556E-5,1E-7,1E-6
 DIMENSION SI, TEMP=C, STDTEMP=0, STDPRES=101.325
 SEQUENCE DEFINED=1SPD,2HE-S-SPD,P1,T1,F1,SP2,SP1,T2,F2,SP4,E1, &
      REC--H2O-MIX
 CALCULATION TRIALS=80, RVPBASIS=APIN, TVP=37.778, RECYCLE=ALL
COMPONENT DATA
 LIBID 1,BUTANOL/2,2PENTNOL/3,DBE/5,WATER
 NONLIB 4,ME2/6,Acid-Catalyst, FILL=SIMSCI
 STRUCTURE 4,601(1),900(3),901(5),902(1)/6,211(2),601(4),901(2)
THERMODYNAMIC DATA
 METHOD SYSTEM=NRTL, SET=NRTL01, DEFAULT
  KVAL(VLE) FILL=UFT1, AZEOTROPE=SIMSCI
 METHOD SYSTEM(VLLE)=NRTL, SET=NRTL02
  KVAL(VLE) FILL=UFT1, AZEOTROPE=SIMSCI
  KVAL(LLE) FILL=UFT1, AZEOTROPE=SIMSCI
STREAM DATA
 PROPERTY STREAM=7B-C1-H2OREC, TEMPERATURE=20, PRESSURE=101,
PHASE=M, &
      RATE(WT)=200, COMPOSITION(M)=5,50, NORMALIZE
 PROPERTY STREAM=7A-ORG-REC, TEMPERATURE=20, PRESSURE=101, PHASE=M,
&
      RATE(WT)=200, COMPOSITION(M)=5,50, NORMALIZE
 PROPERTY STREAM=12-COL2-REC, TEMPERATURE=20, PRESSURE=101, PHASE=M,
&
      RATE(WT)=100, COMPOSITION(M)=5,50, NORMALIZE
 PROPERTY STREAM=4-FEED, TEMPERATURE=40, PRESSURE=10, PHASE=M,  &
     RATE(WT)=10000, COMPOSITION(WT)=1,3542.64/2,3.299/3,30.0154/ &
     4,39.009/5,747.784/6,5633.99, NORMALIZE, SET=DEFAULT
 NAME 8-COL1-ORG,lost organics/ &
     16-SPD-ACID,Acid Recycle from SPD to reactor
UNIT OPERATIONS
 FLASH UID=1SPD
    FEED 4-FEED
    PRODUCT  W=15-SPD-ACID, V=5-SPD-DIST
    ISO  TEMPERATURE=85
    METHOD SET=NRTL01
 HX   UID=2HE-S-SPD
    HOT  FEED=5-SPD-DIST, M=5SPD-DIST
    OPER HTEMP=30
 PUMP UID=P1
    FEED 5SPD-DIST
    PRODUCT  M=6-COL1-FEED
    OPERATION PRESSURE=25
 COLUMN UID=T1
    PARAMETER TRAY=7,CHEMDIST=30
    FEED 7B-C1-H2OREC,1/7A-ORG-REC,1/6-COL1-FEED,3
    PRODUCT  OVHD(M)=OVERHEADS-C1, BTMS(WT)=10-COL2-FEED,2600, &
          SUPERSEDE=ON
    DUTY 1,7
    PSPEC PTOP=20
    PRINT PROPTABLE=PART
    ESTIMATE MODEL=CHEM, RRATIO(L)=3
    SPEC STREAM=10-COL2-FEED, RATE(WT,KG/H),TOTAL,WET, VALUE=2600
    VARY DUTY=1
```

```
    VLLECHECK CHECK=OFF
    QCOLUMN QCONDENSER=0, QREBOILER=0, QCOLUMN=0, QTRAY=0
    REBOILER TYPE=KETTLE
    METHOD SET=NRTL01
  FLASH UID=F1
    FEED OVERHEADS-C1
    PRODUCT  L=COL1-ORG, W=COL1-H2O
    ISO  TEMPERATURE=30
    METHOD SET=NRTL02
  SPLITTER UID=SP2
    FEED COL1-ORG
    PRODUCT  M=7A-ORG-REC, M=8-COL1-ORG
    OPERATION OPTION=NORM
    SPEC STREAM=7A-ORG-REC, RATE(WT,KG/H),TOTAL,WET, DIVIDE, &
          STREAM=COL1-ORG, RATE(WT,KG/H),TOTAL,WET, VALUE=0.5
    SPEC STREAM=8-COL1-ORG, RATE(WT,KG/H),TOTAL,WET, DIVIDE, &
          STREAM=COL1-ORG, RATE(WT,KG/H),TOTAL,WET, VALUE=0.5
  SPLITTER UID=SP1
    FEED COL1-H2O
    PRODUCT  M=7B-C1-H2OREC, M=9-COL1-H2O
    OPERATION OPTION=NORM
    SPEC STREAM=7B-C1-H2OREC, RATE(WT,KG/H),TOTAL,WET, DIVIDE, &
          STREAM=COL1-H2O, RATE(WT,KG/H),TOTAL,WET, VALUE=0.5
    SPEC STREAM=9-COL1-H2O, RATE(WT,KG/H),TOTAL,WET, DIVIDE, &
          STREAM=COL1-H2O, RATE(WT,KG/H),TOTAL,WET, VALUE=0.5
  COLUMN UID=T2
    PARAMETER TRAY=8,CHEMDIST=34 DAMPING=0.6
    FEED 12-COL2-REC,1/10-COL2-FEED,3
    PRODUCT  OVHD(M)=COL2-OVERHEA, BTMS(WT)=13-COL2-BOT,150, &
          SUPERSEDE=ON
    DUTY 1,8
    PSPEC PTOP=15
    PRINT PROPTABLE=PART
    ESTIMATE MODEL=CHEM, RRATIO(L)=10
    SPEC STREAM=13-COL2-BOT, RATE(WT,KG/H),TOTAL,WET, VALUE=130
    VARY DUTY=1
    VLLECHECK CHECK=OFF
    QCOLUMN QCONDENSER=0, QREBOILER=0, QCOLUMN=0, QTRAY=0
    REBOILER TYPE=KETTLE
    METHOD SET=NRTL01
  FLASH UID=F2
    FEED COL2-OVERHEA
    PRODUCT  W=COL2-COND-EX
    ISO  TEMPERATURE=30
    METHOD SET=NRTL02
  SPLITTER UID=SP4
    FEED COL2-COND-EX
    PRODUCT  M=12-COL2-REC, M=11-1-BUTANOL
    OPERATION OPTION=NORM
    SPEC STREAM=12-COL2-REC, RATE(WT,KG/H),TOTAL,WET, DIVIDE, &
          STREAM=COL2-COND-EX, RATE(WT,KG/H),TOTAL,WET, &
          VALUE=0.8
    SPEC STREAM=11-1-BUTANOL, RATE(WT,KG/H),TOTAL,WET, DIVIDE, &
          STREAM=COL2-COND-EX, RATE(WT,KG/H),TOTAL,WET, &
          VALUE=0.2
  HX  UID=E1
    HOT  FEED=16-SPD-ACID, M=S1
    OPER HTEMP=30
  MIXER UID=REC--H2O-MIX
    FEED 9-COL1-H2O,S1
```

PRODUCT M=16-TOT-REC
END

Appendix H2- Summarized PRO II Output File

See Figure 7.2 Chapter 7

STREAM ID	COL1-H2O	COL1-ORG	COL2-COND-EX	COL2-OVERHEA
PHASE	LIQUID	LIQUID	LIQUID	VAPOR
FLUID WEIGHT PERCENTS				
1 BUTANOL	6.5822	77.3026	99.5372	99.5372
2 2PENTNOL	3.91E-03	0.0725	0.0932	0.0932
3 DBE	0.0242	2.6846	0.2292	0.2292
4 ME2	4.36E-05	0.4136	0.138	0.138
5 WATER	93.3897	19.5267	2.40E-03	2.40E-03
6 Acid-Catalyst	2.90E-17	1.13E-16	0	0
TOTAL RATE, KG/HR	1114.5131	1731.1503	12349.999	12349.999
TEMPERATURE, C	30	30	30	72.1482
PRESSURE, KPA	20	20	15	15
ENTHALPY, M*KJ/HR	0.1358	0.1394	0.8613	10.1684
MOLECULAR WEIGHT	18.9644	46.4933	74.2572	74.2572
WEIGHT FRAC VAPOR	0	0	0	1
WEIGHT FRAC LIQUID	1	1	1	0

STREAM ID	OVERHEADS-C1	S1	4-FEED	5SPD-DIST
PHASE	VAPOR	LIQUID	LIQUID	LIQUID
FLUID WEIGHT PERCENTS				
1 BUTANOL	49.6047	4.6697	35.438	81.1538
2 2PENTNOL	0.0456	3.73E-03	0.033	0.0765
3 DBE	1.6426	0.0164	0.3003	0.722
4 ME2	0.2517	0.0417	0.3902	0.9081
5 WATER	48.4554	0.9792	7.4803	17.1396
6 Acid-Catalyst	8.04E-17	94.2892	56.3583	3.50E-06
TOTAL RATE, KG/HR	2845.6634	5977.1765	10000.0082	4022.8317
TEMPERATURE, C	55.8578	30	40	30
PRESSURE, KPA	20	10	10	10
ENTHALPY, M*KJ/HR	4.7459	0.5761	1.1595	0.3188
MOLECULAR WEIGHT	29.6414	194.7438	88.1071	48.5815
WEIGHT FRAC VAPOR	1	0	0	0
WEIGHT FRAC LIQUID	0	1	1	1

STREAM ID	5-SPD-DIST	6-COL1-FEED	7A-ORG-REC	7B-C1-H2OREC
PHASE	VAPOR	LIQUID	LIQUID	LIQUID
FLUID WEIGHT PERCENTS				
1 BUTANOL	81.1538	81.1538	77.3026	6.5822
2 2PENTNOL	0.0765	0.0765	0.0725	3.91E-03
3 DBE	0.722	0.722	2.6846	0.0242
4 ME2	0.9081	0.9081	0.4136	4.36E-05
5 WATER	17.1396	17.1396	19.5267	93.3897
6 Acid-Catalyst	3.50E-06	3.50E-06	1.13E-16	2.90E-17

TOTAL RATE, KG/HR	4022.8317	4022.8317	865.5752	557.2565
TEMPERATURE, C	85	30.0066	30	30
PRESSURE, KPA	10	25	20	20
ENTHALPY, M*KJ/HR	4.6213	0.3188	0.0697	0.0679
MOLECULAR WEIGHT	48.5815	48.5815	46.4933	18.9644
WEIGHT FRAC VAPOR	1	0	0	0
WEIGHT FRAC LIQUID	0	1	1	1

STREAM ID	8-COL1-ORG	9-COL1-H2O	10-COL2-FEED	11-1-BUTANOL
PHASE	LIQUID	LIQUID	LIQUID	LIQUID
FLUID WEIGHT PERCENTS				
1 BUTANOL	77.3026	6.5822	98.4188	99.5372
2 2PENTNOL	0.0725	3.91E-03	0.0934	0.0932
3 DBE	2.6846	0.0242	0.2182	0.2292
4 ME2	0.4136	4.36E-05	1.2673	0.138
5 WATER	19.5267	93.3897	2.28E-03	2.40E-03
6 Acid-Catalyst	1.13E-16	2.90E-17	5.41E-06	0
TOTAL RATE, KG/HR	865.5752	557.2565	2600	2469.9998
TEMPERATURE, C	30	30	78.1502	30
PRESSURE, KPA	20	20	20	15
ENTHALPY, M*KJ/HR	0.0697	0.0679	0.5026	0.1723
MOLECULAR WEIGHT	46.4933	18.9644	74.7032	74.2572
WEIGHT FRAC VAPOR	0	0	0	0
WEIGHT FRAC LIQUID	1	1	1	1

STREAM ID	12-COL2-REC	13-COL2-BOT	15-SPD-ACID	16-TOT-REC
NAME				
PHASE	LIQUID	LIQUID	LIQUID	LIQUID
FLUID WEIGHT PERCENTS				
1 BUTANOL	99.5372	77.1697	4.6697	4.8328
2 2PENTNOL	0.0932	0.0964	3.73E-03	3.74E-03
3 DBE	0.2292	8.60E-03	0.0164	0.0171
4 ME2	0.138	22.7253	0.0417	0.0381
5 WATER	2.40E-03	5.60E-10	0.9792	8.86
6 Acid-Catalyst	0	1.08E-04	94.2892	86.2483
TOTAL RATE, KG/HR	9879.9992	130	5977.1765	6534.433
TEMPERATURE, C	30	73.3742	85	30
PRESSURE, KPA	15	15	10	10
ENTHALPY, M*KJ/HR	0.689	0.0229	1.4262	0.644
MOLECULAR WEIGHT	74.2572	84.3263	194.7438	108.768
WEIGHT FRAC VAPOR	0	0	0	0
WEIGHT FRAC LIQUID	1	1	1	1

Appendix H3 - Design calculations of a 1-pentanol + 2-hexanol reaction separation plant, which produces n-pentylether and 3-hexyl pentyl ether as byproduct.

Appendix H3-Reactor calculations

Determination of design basis:

Results of Experiment 86 were used as design basis. Catalyst system: 90 % H_3PO_4 with acid:aclcohol = 1,5:1; Reaction time ~ 35 minutes. The amount of Mixed Ether 6 is ignored. Composition of organics after the amount of secondary alcohol was reduced to < 0,1 % based on alcohols only.

		mass %
1-Pentanol	=	98,05
3-Hexanol	=	0,01
2-Hexanol	=	0.07
n-Pentylether	=	0,97
2-Hexyl-Pentyl ether	=	0,15
3-Hexyl-Pentyl ether	=	0,75

The following assumptions were made (same components according to group contribution method):

- 3-Hexanol and 2-Hexanol may be treated as 0,08 % 2-Hexanol
- 2-Hexyl-Pentyl ether and 3-Hexyl-Pentyl ether may be treated as 0,9 % 3-Hexyl-Pentyl ether
- The 3-Hexyl-Pentyl ether in the recycle stream does not react and leave the reactor unchanged. In reality the 3-Hexyl-Pentyl ether will dehydrate in the reactor. The amounts of 3-Hexyl-Pentyl ether are thus higher in these calculations than expected.

The organic product composition was simplified to the following:

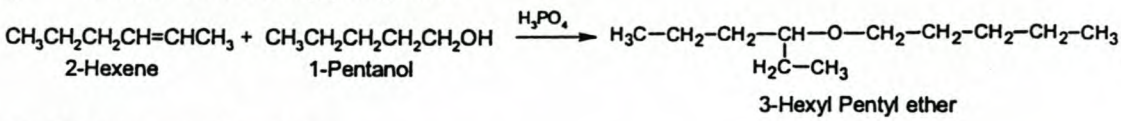
		mass %
1-Pentanol	=	98,05
2-Hexanol	=	0.08
n-Pentylether	=	0,97
3-Hexyl-Pentyl ether	=	0,9

Reactions:

1) Dehydration of 2-hexanol:
$CH_3CH_2CH_2CH_2CHOHCH_3 \rightarrow CH_3CH_2CH_2CH{=}CHCH_3 + H_2O$

2) Formation of n-pentylether:
$2CH_3CH_2CH_2CH_2CH_2OH \rightarrow CH_3CH_2CH_2CH_2CH_2OCH_2CH_2CH_2CH_2CH_3 + H_2O$

3) Formation of 3-hexyl pentyl ether



2-Hexene 1-Pentanol 3-Hexyl Pentyl ether

Mass Balance over Reactor:

0 = In – Out + Formed – Reacted

Basis = 100 kg dry organics in reactor outlet
98,05 kg 1-Pentanol + 0,08 kg 2-Hexanol +
0,97 kg n-Pentylether +0,9 kg 3-Hexyl Pentyl ether

1-Pentanol In = Out + Reacted to form ether

In = 98,05 + $[(0{,}97/Mr_{\text{n-pentylether}})*2 + (0{,}9/Mr_{\text{n-3-H-P-ether}})]*Mr_{\text{1-Pentanol}}$

= 99,591 kg

2-Hexanol In = $(0{,}15/0{,}85)*In_{\text{1-butanol}}$ = 17,575 kg

2-Hexanol reacted as follows:

fraction that did not react = (0,08)/17,571 = 0,004552

fraction converted to ether = $[(0{,}9/Mr_{\text{n-3-H-P-ether}})]*Mr_{\text{2-Hexanol}}]/17{,}575$
= 0,030368

fraction dehydrated = [1 – 0,004552 – 0,030368] = 0.96508

Fraction of 1-pentanol converted to n-pentylether
= $[(0{,}97/Mr_{\text{n-pentylether}})*Mr_{\text{1-pentanol}}*2]/ 99{,}575$
= 0,0108512

or 0,97 kg n-pentylether formed/99,575 kg 1-pentanol fed
0,0097414 kg n-pentylether formed/ kg 1-pentanol fed

Basis= 10 000 kg reactor feed to short path distillation (SPD) unit
From ProII simulation of the thermal separation processes, the combined acid recycle stream is as below (convergence was reached after several simulation runs).
See Figure 7.3 Chapter 7.

Stream	Mr	18
Description	[kg/kmol]	Tot. catalyst Recycle mass %
1-Pentanol	88	9,3371
2-Hexanol	102	0,0061
n-Pentylether	158	0,1141
3-Hex-Pent-Ether	172	0,0614
Water	18	9,0482
H_3PO_4	98	81,4331
Hexene	84	0
Total		6901,5 kg/h

Water Make-up:
H_3PO_4 recycled = $x_{18,\ H3PO4}$ *Stream 18 = 5620,11 kg
Water required = (0,1/0,9) * 5620.11 = 624,46 kg
Water present in recycle stream = $x_{18,water}$*Stream 18 = 624,46 kg
Water make-up thus required = 0 kg
Fresh Alcohol required:
Acid / 1.5 = (5620,11 + 624,46)/1,5 = 4163,05 kg
Alcohol in recycle stream = ($x_{18,1\text{-pentanol}}$ + $x_{18,2\text{-hexanol}}$)*stream 18 = 644,82 kg
Fresh alcohol to be fed = 3518,23 kg
1-Pentanol in total fed to reactor = 0,85*3518,23+$x_{18,1\text{-pentanol}}$*stream18 = 3634,90 kg
2-Hexanol in total fed to reactor = 0,15*3518,23+$x_{18,2\text{-hexanol}}$*stream18 = 528,16 kg
Reactions: equations as above
Conversion of 2-Hexanol:
Hexene vents: fraction of 2-hexanol dehydrated to hexene = 0.96508
hexene vent stream = [(0,96508*528,16)/$Mr_{2\text{-hexanol}}$]*Mr_{hexene} = 419,77 kg
2-Hexanol that did not react = 0,004552*528,16 = 2,40 kg
3-Hexyl Pentyl ether formed = [0,030368*528,16/$Mr_{2\text{-hexanol}}$]*$Mr_{3\text{-H-P-ether}}$ = 27,05 kg
Conversion of 1-Pentanol:
Conversion of 1-Pentanol to 3-Hexyl-pentyl ether =
= (27,05/ $Mr_{3\text{-H-P-ether}}$)*$Mr_{1\text{-pentanol}}$] = 13,84 kg
Conversion of 1-Pentanol to n-Pentylether:
= 0,0108512*3634,9= 39,44 kg 1-Pentanol converted
n-pentylether formed = [39,44/(2*$Mr_{1\text{-pentanol}}$)]*$Mr_{n\text{-pentylether}}$= 35,41 kg
1-Pentanol converted:
1-Pentanol reacted = 13,84 + 39,44 = 53,28 kg
Water formed:
Total water formed =water from hexene reaction + water from ether reactions
= [419,77/Mr_{hexene} + 27,05/$Mr_{3\text{-H-P-ether}}$ + 35,41/$Mr_{n\text{-Pentylether}}$]*18 = 96,82 kg
Mass Balance over Reactor:
0 = In – Out + Formed – Reacted
Out = In + Formed - Reacted
1-Pentanol Out = In – Reacted = 3634,90 – 53,28 = 3581,62 kg
2-Hexanol Out = 2,4 kg
n-Pentylether Out = In + Formed
= $x_{18,npentylether}$*stream 18 + 35,41 = 43,28 kg
3-Hexyl pentyl ether Out = In + Formed = $x_{18,3\text{-H-P-ether}}$*stream 18 + 27,05 = 31,29 kg
Water Out = In + Formed = 624,46 + 96,82 = 721,28 kg
H_3PO_4 Out = In = 5620,1 kg
% 1-Pentanol recovery = Product/Fresh Feed * 100
= {[0.999135*2925]/[0.85*3218,23]} * 100 = 97,7 %

Appendix H3-Pro II Input file

```
$ Generated by PRO/II Keyword Generation System <version 5.55>
$ Generated on: Thu Nov 22 09:21:26 2001
TITLE DATE=12/29/00
 PRINT INPUT=ALL, STREAM=ALL, RATE=M,WT, FRACTION=M,WT, PERCENT=M,WT, &
      MBALANCE, ION=NONE
 TOLERANCE FLASH=3E-6, STREAM=1E-5,-5.5556E-5,1E-7,1E-6
 DIMENSION SI, TEMP=C, STDTEMP=0, STDPRES=101.325
 SEQUENCE DEFINED=1SPD,2HE-S-SPD,P1,F3,T1,F1,SP2,SP1,T2,F2,SP4,SP3, &
     E1,P2,REC--H2O-MIX,M1
 CALCULATION TRIALS=80, RVPBASIS=APIN, TVP=37.778, RECYCLE=ALL
COMPONENT DATA
 LIBID 1,PENTANOL/2,2HEXANOL/3,DPNE/5,WATER
 NONLIB 4,3-HexylPentyl E/6,PEGllikol, FILL=SIMSCI
 STRUCTURE 4,601(1),900(3),901(6),902(1)/6,211(2),601(4),901(2)
THERMODYNAMIC DATA
 METHOD SYSTEM=NRTL, SET=NRTL01, DEFAULT
  KVAL(VLE) FILL=UFT1, AZEOTROPE=SIMSCI
 METHOD SYSTEM(VLLE)=NRTL, SET=NRTL02
  KVAL(VLE) FILL=UFT1, AZEOTROPE=SIMSCI
  KVAL(LLE) FILL=UFT1, AZEOTROPE=SIMSCI
STREAM DATA
 PROPERTY STREAM=7B-H2OR1, TEMPERATURE=30, PRESSURE=101, PHASE=M, &
      RATE(WT)=200, COMPOSITION(M)=5,50, NORMALIZE
 PROPERTY STREAM=7A-ORG-REC1, TEMPERATURE=30, PRESSURE=101,
PHASE=M, &
      RATE(WT)=200, COMPOSITION(M)=5,50, NORMALIZE
 PROPERTY STREAM=12-COL2-REC, TEMPERATURE=30, PRESSURE=101, PHASE=M,
&
      RATE(WT)=100, COMPOSITION(M)=5,50, NORMALIZE
 PROPERTY STREAM=4-FEED, TEMPERATURE=40, PRESSURE=10, PHASE=M,  &
     RATE(WT)=10000, COMPOSITION(WT)=1,3581.52/2,2.4044/3,43.2982/ &
     4,31.2933/5,721.237/6,5619.9, NORMALIZE, SET=NRTL01
 NAME 8-COL1-ORG,recycled organics
UNIT OPERATIONS
 FLASH UID=1SPD
    FEED 4-FEED
    PRODUCT  W=16-SPD-A-REC, V=SPD-VAP
    ISO  TEMPERATURE=110
    METHOD SET=NRTL01
 HX  UID=2HE-S-SPD
    HOT  FEED=SPD-VAP, M=5-SPD-DIST
    OPER HTEMP=30
 PUMP UID=P1
    FEED 5-SPD-DIST
    PRODUCT  M=SEP-INLET
    OPERATION PRESSURE=25
 FLASH UID=F3
    FEED SEP-INLET
    PRODUCT  W=15-WATER-SEP, L=6-COL1-FEED
    ISO  TEMPERATURE=30
    METHOD SET=NRTL02
 COLUMN UID=T1
    PARAMETER TRAY=8,CHEMDIST=30
    FEED 7B-H2OR1,1/7A-ORG-REC1,1/6-COL1-FEED,3
    PRODUCT  OVHD(M)=OVERHEADS-C1, BTMS(WT)=10-COL2-FEED,3000, &
          SUPERSEDE=ON
    DUTY 1,8
    PSPEC PTOP=20
    PRINT PROPTABLE=PART
```

```
   ESTIMATE MODEL=CHEM, RRATIO(L)=3
   SPEC STREAM=10-COL2-FEED, RATE(WT,KG/H),TOTAL,WET, VALUE=3000
   VARY DUTY=1
   VLLECHECK CHECK=OFF
   QCOLUMN QCONDENSER=0, QREBOILER=0, QCOLUMN=0, QTRAY=0
   REBOILER TYPE=KETTLE
   METHOD SET=NRTL01
FLASH UID=F1
   FEED OVERHEADS-C1
   PRODUCT  L=COL1-ORG, W=COL1-H2O
   ISO  TEMPERATURE=30
   METHOD SET=NRTL02
SPLITTER UID=SP2
   FEED COL1-ORG
   PRODUCT  M=7A-ORG-REC1, M=8-COL1-ORG
   OPERATION OPTION=NORM
   SPEC STREAM=7A-ORG-REC1, RATE(WT,KG/H),TOTAL,WET, DIVIDE, &
        STREAM=COL1-ORG, RATE(WT,KG/H),TOTAL,WET, VALUE=0.5
   SPEC STREAM=8-COL1-ORG, RATE(WT,KG/H),TOTAL,WET, DIVIDE, &
        STREAM=COL1-ORG, RATE(WT,KG/H),TOTAL,WET, VALUE=0.5
SPLITTER UID=SP1
   FEED COL1-H2O
   PRODUCT  M=7B-H2OR1, M=9-COL1-H2O-R
   OPERATION OPTION=NORM
   SPEC STREAM=7B-H2OR1, RATE(WT,KG/H),TOTAL,WET, DIVIDE, &
        STREAM=COL1-H2O, RATE(WT,KG/H),TOTAL,WET, VALUE=0.5
   SPEC STREAM=9-COL1-H2O-R, RATE(WT,KG/H),TOTAL,WET, DIVIDE, &
        STREAM=COL1-H2O, RATE(WT,KG/H),TOTAL,WET, VALUE=0.5
COLUMN UID=T2
   PARAMETER TRAY=17,CHEMDIST=34 DAMPING=0.6
   FEED 12-COL2-REC,1/10-COL2-FEED,6
   PRODUCT  OVHD(M)=COL2-OVERHEA, BTMS(WT)=13-ETHERS,74.9999, &
        SUPERSEDE=ON
   DUTY 1,17
   PSPEC PTOP=15
   PRINT PROPTABLE=PART
   ESTIMATE MODEL=CHEM, RRATIO(L)=10
   SPEC STREAM=13-ETHERS, RATE(WT,KG/H),TOTAL,WET, VALUE=75
   VARY DUTY=1
   VLLECHECK CHECK=OFF
   QCOLUMN QCONDENSER=0, QREBOILER=0, QCOLUMN=0, QTRAY=0
   REBOILER TYPE=KETTLE
   METHOD SET=NRTL01
FLASH UID=F2
   FEED COL2-OVERHEA
   PRODUCT  W=COL2-OVH-CON
   ISO  TEMPERATURE=30
   METHOD SET=NRTL02
SPLITTER UID=SP4
   FEED COL2-OVH-CON
   PRODUCT  M=12-COL2-REC, M=11-PENTANOL
   OPERATION OPTION=NORM
   SPEC STREAM=12-COL2-REC, RATE(WT,KG/H),TOTAL,WET, DIVIDE, &
        STREAM=COL2-OVH-CON, RATE(WT,KG/H),TOTAL,WET, &
        VALUE=0.8
   SPEC STREAM=11-PENTANOL, RATE(WT,KG/H),TOTAL,WET, DIVIDE, &
        STREAM=COL2-OVH-CON, RATE(WT,KG/H),TOTAL,WET, &
        VALUE=0.2
SPLITTER UID=SP3
   FEED 9-COL1-H2O-R
```

```
    PRODUCT  M=H2O-COL-REAC, M=14-H2O-BLEED
    OPERATION OPTION=FILL
    SPEC STREAM=H2O-COL-REAC, RATE(WT,KG/H),TOTAL,WET, DIVIDE, &
          STREAM=9-COL1-H2O-R, RATE(WT,KG/H),TOTAL,WET, &
          VALUE=0.69696
  HX  UID=E1
    HOT  FEED=15-WATER-SEP,16-SPD-A-REC, M=S1
    OPER HTEMP=30
  PUMP UID=P2
    FEED S1
    PRODUCT  M=S2
    OPERATION PRESSURE=20
  MIXER UID=REC--H2O-MIX
    FEED H2O-COL-REAC,S2
    PRODUCT  M=17-CAT-REC
    METHOD SET=NRTL01
  MIXER UID=M1
    FEED 17-CAT-REC,8-COL1-ORG
    PRODUCT  M=18-TOT-REC
END
```

See Figure 7.3, Chapter 7

Appendix H3 - Pro II Output file

PROJECT PRO/II VERSION 5.55 ELEC V6.0 386/EM

SIMULATION SCIENCES INC. PAGE P-36

STREAM ID	COL1-H2O	COL1-ORG	COL2-OVERHEA	COL2-OVH-CON
PHASE	LIQUID	LIQUID	VAPOR	LIQUID
FLUID WEIGHT PERCENTS				
1 PENTANOL	1.7389	88.6234	99.9135	99.9135
2 2HEXANOL	1.18E-04	6.05E-02	0.0668	0.0668
3 DPNE	1.99E-05	1.16E+00	0.0188	0.0188
4 3-HexylPentyl E	2.88E-06	5.23E-01	6.93E-04	6.93E-04
5 WATER	9.83E+01	9.6347	2.01E-04	2.01E-04
6 ACID	1.64E-17	1.05E-16	2.70E-17	2.70E-17
TOTAL RATE, KG/HR	650.15	1095.57	14625.00	14625.00
TEMPERATURE, C	30	30	88.3122	30
PRESSURE, KPA	20	20	15	15
ENTHALPY, M*KJ/HR	0.081	0.0813	11.7123	1.0073
MOLECULAR WEIGHT	18.2678	64.4689	88.165	88.165
WEIGHT FRAC VAPOR	0	0	1	0
WEIGHT FRAC LIQUID	1	1	0	1

STREAM ID	H2O-COL-REAC	OVERHEADS-C1	SEP-INLET	SPD-VAP
PHASE	LIQUID	VAPOR	LIQUID	VAPOR
FLUID WEIGHT PERCENTS				
1 PENTANOL	1.7389	56.2654	81.6404	81.6404
2 2HEXANOL	1.18E-04	3.80E-02	0.0551	0.0551
3 DPNE	1.99E-05	7.27E-01	0.9935	0.9935
4 3-HexylPentyl E	2.88E-06	3.28E-01	7.12E-01	0.7116
5 WATER	9.83E+01	4.26E+01	16.5993	16.5993
6 ACID	1.64E-17	7.18E-17	9.47E-05	9.47E-05
TOTAL RATE, KG/HR	226.56	1745.72	4204.29	4204.29
TEMPERATURE, C	30	55.0346	30.0067	110
PRESSURE, KPA	20	20	25	10
ENTHALPY, M*KJ/HR	0.0282	2.6853	0.3288	4.7959
MOLECULAR WEIGHT	18.2678	33.1988	53.8064	53.8064
WEIGHT FRAC VAPOR	0	1	0	1
WEIGHT FRAC LIQUID	1	0	1	0

STREAM ID	S1	S2	4-FEED	5-SPD-DIST
PHASE	LIQUID	LIQUID	LIQUID	LIQUID
FLUID WEIGHT PERCENTS				
1 PENTANOL	2.5297	2.5297	35.8164	81.6404
2 2HEXANOL	1.46E-03	1.46E-03	0.024	0.0551
3 DPNE	0.025	0.025	0.433	0.9935
4 3-HexylPentyl E	0.0225	0.0225	0.3129	0.7116
5 WATER	5.6969	5.6969	7.2126	16.5993
6 ACID	91.7246	91.7246	56.201	9.47E-05
TOTAL RATE, KG/HR	6127.15	6127.15	10000.01	4204.29
TEMPERATURE, C	30	30.0015	40	30
PRESSURE, KPA	10	20	10	10
ENTHALPY, M*KJ/HR	0.6022	0.6022	1.1536	0.3288
MOLECULAR WEIGHT	136.9536	136.9536	95.4811	53.8064
WEIGHT FRAC VAPOR	0	0	0	0
WEIGHT FRAC LIQUID	1	1	1	1

STREAM ID	6-COL1-FEED	7A-ORG-REC1	7B-H2OR1	8-COL1-ORG
NAME				recycled organics
PHASE	LIQUID	LIQUID	LIQUID	LIQUID
FLUID WEIGHT PERCENTS				
1 PENTANOL	88.4785	88.6234	1.7389	88.6234
2 2HEXANOL	0.0598	0.0605	1.18E-04	0.0605
3 DPNE	1.0785	1.1584	1.99E-05	1.1584
4 3-HexylPentyl E	0.7725	0.523	2.88E-06	0.523
5 WATER	9.6106	9.6347	98.261	9.6347
6 ACID	1.01E-04	1.05E-16	1.64E-17	1.05E-16
TOTAL RATE, KG/HR	3872.86	547.79	325.08	547.79
TEMPERATURE, C	30	30	30	30
PRESSURE, KPA	25	20	20	20
ENTHALPY, M*KJ/HR	0.2875	0.0407	0.0405	0.0407
MOLECULAR WEIGHT	64.5541	64.4689	18.2678	64.4689
WEIGHT FRAC VAPOR	0	0	0	0
WEIGHT FRAC LIQUID	1	1	1	1

STREAM ID	9-COL1-H2O-R	10-COL2-FEED	11-PENTANOL	12-COL2-REC
NAME				
PHASE	LIQUID	LIQUID	LIQUID	LIQUID
FLUID WEIGHT PERCENTS				
1 PENTANOL	1.7389	97.8509	99.9135	99.9135
2 2HEXANOL	1.18E-04	0.0661	0.0668	0.0668
3 DPNE	1.99E-05	1.1808	0.0188	0.0188
4 3-HexylPentyl E	2.88E-06	0.9018	6.93E-04	6.93E-04
5 WATER	98.261	1.96E-04	2.01E-04	2.01E-04
6 ACID	1.64E-17	1.31E-04	2.70E-17	2.70E-17
TOTAL RATE, KG/HR	325.08	3000.00	2925.00	11700.00
TEMPERATURE, C	30	94.8576	30	30
PRESSURE, KPA	20	20	15	15
ENTHALPY, M*KJ/HR	0.0405	0.7329	0.2015	0.8058
MOLECULAR WEIGHT	18.2678	89.0152	88.165	88.165
WEIGHT FRAC VAPOR	0.00E+00	0.00E+00	0.00E+00	0.00E+00
WEIGHT FRAC LIQUID	1.00E+00	1.00E+00	1.00E+00	1.00E+00

STREAM ID	13-ETHERS	14-H2O-BLEED	15-WATER-SEP	16-SPD-A-REC
PHASE	LIQUID	LIQUID	LIQUID	LIQUID

FLUID WEIGHT PERCENTS				
1 PENTANOL	17.4098	1.7389	1.7371	2.575
2 2HEXANOL	0.0393	1.18E-04	1.17E-04	1.54E-03
3 DPNE	46.5013	1.99E-05	1.85E-05	0.0264
4 3-HexylPentyl E	36.0442	2.88E-06	4.24E-06	0.0237
5 WATER	1.26E-18	98.261	98.2627	0.4034
6 ACID	5.24E-03	1.64E-17	1.59E-05	96.9699
TOTAL RATE, KG/HR	75.00	98.51	331.43	5795.71
TEMPERATURE, C	101.3176	30	30	110
PRESSURE, KPA	15	20	25	10
ENTHALPY, M*KJ/HR	0.0175	0.0123	0.0413	1.7578
MOLECULAR WEIGHT	142.666	18.2678	18.2675	217.9212
WEIGHT FRAC VAPOR	0.00E+00	0.00E+00	0	0
WEIGHT FRAC LIQUID	1.00E+00	1.00E+00	1	1

STREAM ID	17-CAT-REC	18-TOT-REC
NAME		
PHASE	LIQUID	LIQUID
FLUID WEIGHT PERCENTS		
1 PENTANOL	2.5015	9.3371
2 2HEXANOL	1.41E-03	6.10E-03
3 DPNE	0.0241	0.1141
4 3-HexylPentyl E	0.0217	0.0614
5 WATER	8.9976	9.0482
6 ACID	88.4538	81.4331
TOTAL RATE, KG/HR	6353.71	6901.50
TEMPERATURE, C	30.0014	30.0013
PRESSURE, KPA	20	20
ENTHALPY, M*KJ/HR	0.6304	0.6711
MOLECULAR WEIGHT	111.1931	105.1446
WEIGHT FRAC VAPOR	0	0
WEIGHT FRAC LIQUID	1	1