# Possible Applications for Vacuum Pyrolysis in the Processing of Waste Materials

By

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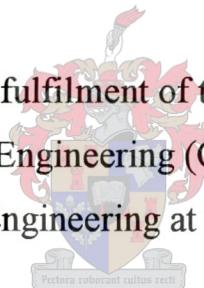
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Stellenbosch
March 2001

Declaration

I, the undersigned, hereby declare that the work contained in this thesis is my own original work and that I have not previously in its entirety or in part submitted it at any university for a degree.

Willem Adriaan de Jongh   9 February 2001

Abstract

Current global trends in government, industry and popular opinion indicate that recycling will become essential in the future. Vacuum pyrolysis is a new technology with many recycling applications that have not yet been investigated. This study is a contribution towards the better understanding of the vacuum pyrolysis process and also towards finding possible economically favourable recycling applications.

A batch operated tube furnace, which allowed the controlled heating of different materials in a vacuum, was designed and built. The gases and vapours passed though a series of progressively colder vacuum traps, condensing the vapours for further study. The products from the process are charcoal, oil, an aqueous phase and non-condensable gases. The charcoal and oils' possible economic values (R2500-R5000/ton of charcoal, while the plant product oil can be sold as a low sulphur fuel, with a retail value of approximately R1.42 per litre) were determined along with the oils' chemical composition.

Several possible feedstocks were studied, including intruder plant species, leather wastes, sewage sludge and a simplified representation of municipal solid waste. The three intruder plants studied were Kraalbos (*Galenia africane*), Scholtzbos (*Pteronia pallens*) and Asbos (*Psilocaolon absimile*). These plants yielded 40%, 42% and 48% (charcoal per kilogram dry feedstock) respectively at their maximum oil yield temperatures of 380°C, 480°C and 450°C respectively. The maximum oil yields were 36%, 32% and 20% respectively (also on a dry feedstock basis). It was found that the plants with ash contents below 10% yielded commercially competitive charcoal, and that all of the plants yielded oils with heating values in the range of 24MJ/kg, containing several high value compounds. Asbos was the only plant that did not produce usable charcoal, as its ash content of 40% was double that of commercial charcoals.

The leather wastes represent a previously unrecognised application of the technology that could bring huge financial rewards to the tanning industry and could provide a more environmentally friendly alternative to lined landfilling. The cost of landfilling

for a medium sized tannery can be as high as R1000 000 a year. Apart from the volume reductions achieved (up to a factor 8) it was found that landfilling might be totally avoided if the chrome contained in the charcoal product could be extracted and reused.

Sewage sludge was studied, as it is a hazardous waste that requires costly disposal in a lined landfill. It was revealed that volume reductions of up to a factor 3.5 were possible with corresponding charcoal and oil yields of 40% and 38% respectively at 500°C. It was also found that the charcoal product could be used as compost, which would then turn a costly waste into a commodity product. The oil from both the leather and sewage sludge had high energy values (26.7MJ/kg and 30.9MJ/kg respectively) and might either be sold as a bunker fuel or used in the process as a make-up heat source. The value of the oil depends on the problems posed by the oils' high nitrogen content (±5%-6%).

A further study was also made of the co-pyrolysis of PVC and wood to determine the interaction between the feedstocks and as a simplified representation of municipal solid wastes. It was found that the HCl released from the PVC caused acid hydrolysis of the wood and led to lower charcoal (reduced from 32.6% to 29.7% on dry feedstock basis, at the maximum co-pyrolysis oil yield temperature of 460°C) and much higher oil yields (42.4% for the co-pyrolysis compared to 23.6% for the plant material at 460°C). An existing computer program (CEA by Gordan and McBride) was also employed in order to find explanations for some of the vacuum pyrolysis results.

Although large specialist vacuum pyrolysis plants have been designed in the past (mostly to dispose of used tyre waste) it will be necessary to determine the process economics for small-scale applications if the technology is to be applied at the source of the problem. Overall vacuum pyrolysis appears to be a very promising technology that could solve many waste problems in an environmentally friendly and economically beneficial manner.

Opsomming

Hedendaagse neigings in regering, industrie en populêre opinie toon dat hergebruikstegnologieë al hoe meer noodsaaklik sal word in die toekoms. Vakuum pirolise is 'n nuwe tegnologie met vele moonlike hergebruik toepassings wat nog nie bestudeer is nie. Hierdie studie is 'n bydrae tot 'n dieper begrip van vakuum pirolise en ook tot die verdere soeke na nuwe toepassings vir die tegnologie.

'n Enkellading buis-oond, wat die beheerde verhitting van verskillende materiale in vakuum toegelaat het, is ontwerp en gebou. Die gevormde gasse en dampe het deur 'n progressief kouer reeks van vakuum valle beweeg waar dit vir verdere studie gekondenseer en opgevang is. Die produkte van die proses is houtskool, olie, 'n waterryke fase en nie-kondenseerbare gasse. Die houtskool en olie se moontlike waarde (R2500-R5000/ton houtskool, terwyl die plant produk olie verkoop kan word as 'n lae swael verhittings olie met 'n kleinmaat kommersieële verkoopswaarde van R1.42/l), saam met die chemiese samestelling van die olie fase, is bepaal.

Die vakuum pirolise van verskeie moontlike voerstowwe is bestudeer, insluitende indringerplante, leerafval, rioolslyk en 'n vereenvoudigde voorstelling van munisipale afval. Die drie plant spesies wat bestudeer is, is: Kraalbos (*Galenia africane*), Scholtzbos (*Pteronia pallens*) en Asbos (*Psilocaolon absimile*). Die plante het opbrengste van 40%, 42% en 48% (houtskool per kilogram droë voerstof) onderskeidelik gelewer by elk van die plante se maksimum olie opbrengs temperature van 380°C, 480°C en 450°C onderskeidelik. Die maksimum olie opbrengste was 36%, 32%, 20% (olie per kilogram droë voerstof) vir die onderskeie plante. Daar is bevind dat die plante met as-inhoude van minder as 10% kommersieel kompeterende houtskool gelewer het. Dit is ook gevind dat die olie van al die plante verbrandingswaardes in die orde van 24MJ/kg lewer en dat die olies ook verskeie waardevolle chemikalieë bevat. Asbos was die enigste van die bestudeerde plante wat nie maklik bruikbare houtskool gelewer het nie. Die Asbos houtskool was minder bruikbaar as gevolg van die uiters hoë as-inhoude van tot 40% met gevolglike lae energie waarde.

Die vakuum pirolise van leerafval is 'n toepassing wat nog nie voorheen ondersoek is nie. Dit kan moontlik lei tot groot finansiële voordele vir die leerlooi industrie en kan ook 'n meer omgewingsvriendelike alternatief tot belynde afval storting bied. Die koste verbonde aan die storting van leer afval van 'n medium grootte looiery kan tot R1000 000 per jaar beloop. Behalwe vir die volume verkleining behaal (tot 'n faktor 8), is daar ook gevind dat afvalstorting totaal vermy kan word as die hoë hoeveelheid chroom (12% van die houtskool) uit die houtskool verwyder en hergebruik kan word.

Rioolslyk is ook bestudeer, siende dat dit ook 'n probleem afvalstof is wat teen groot koste gestort moet word. Die studie het getoon dat volume verkleinings van tot 'n faktor 3.5 en houtskool en olie opbrengste van onderskeidelik 40% en 38% by 500°C behaal kan word. 'n Ondersoek van die houtskool het getoon dat dit gebruik kan word as 'n kompos, wat dan sal beteken dat 'n probleem afvalstof verander word na 'n omgewingsvriendelike en ekonomies waardevolle produk. Die olie van beide die rioolslyk en leer het hoë energiewaardes (26.7MJ/kg en 30.9MJ/kg onderskeidelik) en kan verkoop word as verbrandingsolie of gebruik word in die vakuum pirolise proses as 'n hulp-hitte bron. Die gebruikswaarde van die olie sal baie afhang van die probleme wat deur die uiters hoë stikstof-inhoud (±5%-6%) veroorsaak gaan word.

'n Verdere studie van die ko-pirolise van PVC en hout is ook gedoen om die interaksie tussen die afvalstowwe te bestudeer en ook om as 'n vereenvoudigde voorstelling van munisipale afval te dien. Daar is gevind dat die HCl wat afkom as PVC verhit word, suur hidrolise van die houtstrukture veroorsaak en lei tot laer houtskool (verminder van 32.6% na 29.7% droë voerstof basis, by die maksimum olie opbrengs temperatuur van 460°C) en veel hoër olie opbrengste (42.4% vir die ko-pirolise in vergelyking met 23.6% vir die plant materiaal by 460°C). 'n Studie van die energie wat verkry kan word uit die olie en houtskool het getoon dat 16% tot 28% meer energie verteenwoordig word deur die produkte per kilogram droë voerstof vir die ko-pirolise proses bo normale vakuum pirolise.

Alhoewel groot spesialis vakuum pirolise aanlegte in die verlede ontwerp is (meestal vir die verwerking van gebruikte motor buitebande) sal dit nogstans noodsaaklik wees om die winsgewindheid van kleinermaat prosesse te bestudeer sodat vakuum pirolise

by die oorsprong van die afvalstof toegepas kan word. Dit blyk dat vakuum pirolise 'n baie belowende tegnologie is wat verskeie afval probleme op 'n omgewingsvriendelike en ekonomies winsgewinde wyse kan oplos.

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Table of Contents

List of Tables

List of figures

Chapter 1: Introduction

1.1 The need for new recycling technologies

The excess of waste that our society generates and the lack of new viable dumping sites have generated a need for new recycling and waste processing technologies. In the past landfilling or incineration have been the most economic options, but with new legislation and increased public awareness, it has become necessary to overcome the inherent problems of these waste handling systems, such as the air polluting gases and heavy metal content of the fly ash produced by incineration. Landfilling will soon become too expensive as new dumping sites become harder to find and old sites fill up at an alarming rate. There are also the contamination of the ground water and the unsightliness of these sites to consider. Other less obvious waste sources could also benefit from new recycling technologies. These waste producers such as the leather tanning industry and producers of municipal sewage sludge pay large amounts of money to have their waste landfilled and would welcome any technology that will reduce the disposal costs involved.

1.2 Vacuum pyrolysis as possible solution

Vacuum pyrolysis is a technology that has been studied in the laboratory for many years, but it is only recently that vacuum pyrolysis plants have been erected for industrial scale usage. This technology offers many advantages over standard pyrolysis techniques, such as the reduction of gas emissions, the creation of valuable chemicals and significant waste volume reduction. Charcoal, oils and pyrolytic liquors are produced, and these products can be upgraded in some instances to create high value chemicals that make the process economically more viable.

1

1.3 What is vacuum pyrolysis?

Vacuum pyrolysis is a thermochemical conversion technology that involves the rapid cracking of complex polymeric structures at low pressures and moderately high temperatures. Materials such as lignocellulosics produce high yields of complex primary oil rich in oxygen, together with a good quality wood charcoal as by-product. Other waste materials such as leather and dry sewage sludge can also be processed to achieve economically advantageous, environmentally favourable alternatives to landfilling. Non-condensable gases and a large percentage of water, depending on the raw material, are also produced as by-products.

1.4 Previous progress in the field

Previous research done by Pakdel, Roy, Darmstadt, Miranda and Chaala has paved the way for the industrial application of vacuum pyrolysis. Several waste materials have been studied and many new innovative and economically favourable applications have been found. Such applications include the cleaning of contaminated soils, turning wood mill wastes into valuable chemicals and charcoal, and the recycling of used tyre rubber and automobile shredder wastes, to name but a few.

1.5 The aim of this study

The relatively short history of research in the field of vacuum pyrolysis means that there are many possible applications of the technology that have not yet been investigated. This study in part focused on finding new economically attractive waste and other feedstock sources that have not previously been studied. It also investigates some of the factors influencing the charcoal and oil yields.

The aims of the study were:
- To design and build a laboratory vacuum pyrolysis set-up to study the basic principles of vacuum pyrolysis.

- To investigate the variables influencing the charcoal and oil yield and its characteristics, using the vacuum pyrolysis set-up.

- To investigate the possibility of using vacuum pyrolysis as a means of making intruder plant clearing projects profitable.

- To find new economically viable applications of vacuum pyrolysis as a recycling technology e.g. tannery waste and municipal sludge.

- To study the interaction between PVC and plant material during vacuum pyrolysis, as this would be a possible simplified representation for the vacuum pyrolysis of municipal solid waste **[Mcgee et al. (1995)]**.

Chapter 2: An Overview of Waste Processing by Vacuum Pyrolysis

2.1. Wood derived wastes

Pyrolysis of wood under reduced pressure was first performed in 1914 by Klason **[Pakdel H. and C. Roy (1988)]**. The objectives of his work were to find the cause of the exothermic reaction and to identify the primary and secondary pyrolysis products.

In 1980 the federal government of Canada embraced an "off-oil" policy under the National Energy Program. The substitution of light and heavy oil with technologies such as gas, electricity and biomass (via combustion) was encouraged through funding for individual homeowners and industry. The bio-oil, oil derived from biomass, was not yet ready for the general market, and although there was an environmental policy towards alternative energy sources, record oil prices and imported and domestic shortfalls of oil meant that bio-oil became a long-term goal.

In 1984 the Canadian government decided to focus on short-term results, and there were serious budgets cuts to the bio-oil R&D project. Several of the laboratories stopped working on bio-oil. The research project was brought back on track by fundamental strategic changes, new industrial partners and the collaboration between four countries (Canada, USA, Finland and Sweden) as members of the International Energy Agency's Bio-energy Agreement. The countries pooled resources and achieved great advances in this field. An approach of diversification, which tries to consider a whole range of products and reactants, has also evolved. Products include oils of varying quality, fine chemicals, gasoline and higher value carbon products.

Lynd L.R., C.E. Wyman and Tillman U. Gerngross (1999) emphasised the importance of a biologically based industry as the only sustainable source of commodity products (fuels, chemicals and materials). The world's oil production is expected to start falling by 2010, while a British National Research Council study projects that 50% of organic chemicals will be produced from plant material by 2020. Shell LTD's preferred scenario for world energy supply and economic development

4

entails utilisation of plant biomass on a scale exceeding that of oil by 2060. **[Lynd et al. (1999)]**

Biocommodity engineering is defined as the production of commodity products from biomass using recent biotechnological advances. A diversity of potential feedstocks is available in the form of residues from the forestry, agricultural, and other established industries, as well as from dedicated crops for the purpose of providing feedstocks for biocommodity processes. In biocommodity engineering the price of the feedstock has a significant influence on the process economics. This differs from the biopharmaceutical industry where feedstock prices and equipment plays a small role in the cost effectiveness of the process. For a biocommodity process in North America to be cost competitive with the oil industry, the oil price must be above $12.70 a barrel if the feedstock costs $40/ton. The feedstock price of $40/delivered dry ton was calculated as the price at which farmers would be fully compensated for producing cellulosic crops as opposed to more traditional crops.

With an oil price hovering at over $30 a barrel, and every indication that it will rise even further in the future as supply starts to decrease, the future of biomass based technologies seems assured.

Biocommodity engineering as an emerging industry will rely heavily on advances in biotechnology and related fields. Even though vacuum pyrolysis still falls under the auspices of chemical engineering, it is a move in the direction of a biologically based sustainable technology. Vacuum pyrolysis would have all the advantages of the biochemical route: sustainability, political and environmental benefits. As vacuum pyrolysis starts to mature as an industrial technology it should expand in the same way as the biochemical technologies.

Professor H. Pakdel, C. Roy, and others from the University Laval in Canada, have extensively researched the specific bio-oil process of vacuum pyrolysis. Before the specific process of wood vacuum pyrolysis can be investigated, however, one must first look at the preceding process of pyrolysis.

Pyrolysis, or the thermal degradation of a material at atmospheric pressure, usually in an inert atmosphere, has been extensively used in the past for the making of charcoal from wood and for waste incineration. The AUTOCHEM plant located in Premery, France, is based on the principle of external gas circulation and is a completely continuous process which produces 20 000t of charcoal per year. Brazilian beehive kilns are used for charcoal production and are run as a batch process. The charcoal produced is mainly destined for the iron, cement and barbecue industries.

The parallels between pyrolysis and vacuum pyrolysis enable one to predict the general behaviour of vacuum pyrolysis that corresponds with wood pyrolysis. It also gives insight into the mechanisms involved in char and pyrolysis oil formation.

Bilboa R., J. Arauzo and M.L. Salvador (1994) investigated the effect of the heating rate on solid conversion, and Bilboa et al. found that for atmospheric pyrolysis the heating rate did have a pronounced influence. Bilboa et al. also studied the pyrolysis kinetics of powdery cellulose and pine sawdust and derived a model for the gas formation at atmospheric pressure in an inert atmosphere. The model also predicts the conversion of the wood to charcoal. Factors such as heating rate, final pyrolysis temperature and variation of the temperature through the bed were investigated. The variation of the temperature through the bed gave rise to concern about using average bed temperatures in the model. It was also shown that CO_2 and CO are the most abundant gases formed during atmospheric pyrolysis.

Milosavjec I., E.M. Suuberg (1995) also studied the global mass loss kinetics of wood during pyrolysis. The aim of the study was to examine the problem of the different kinetics reported in literature for cellulose decomposition. It was found that the kinetics are sensitive to the heating rate employed in the experiments, and that there was also a previously unrecognised shift in the mechanism near 600K.

The effect of ash and moisture content in atmospheric pyrolysis was investigated by **Gray M.R. , W.H.Corcan and G.R. Gavalas (1985)** and several interesting trends were revealed. The samples were heated at 300°C/min in a helium atmosphere to ensure that the drying and pyrolysis were simultaneous.

The presence of moisture increased the yield of char by as much as 5% compared with the dry samples. Moisture suppressed tar formation from demineralised samples at 470°C, but enhanced the formation of tar for samples containing ash above and below 390°C. Ash and added calcium catalysed the conversion of tar into aqueous products, while moisture interacted with tar formation or trapping reactions to increase the yield of char. The surface area of the wet samples was less than half that of the dry samples. Moisture also decreased the activity of the ash components for the conversion of tar into aqueous products. The ash components usually found in wood suppressed the formation of tar and boosted the formation of aqueous products. Calcium also enhanced fragmentation reactions.

Intensive study of vacuum pyrolysis as a method of bio-oil production truly got underway with the design and testing of a semi-continuous multiple-hearth vacuum pyrolysis reactor **[Roy C, R. Lemieux, B. de Caumia and D. Blanchette (1988)]**.
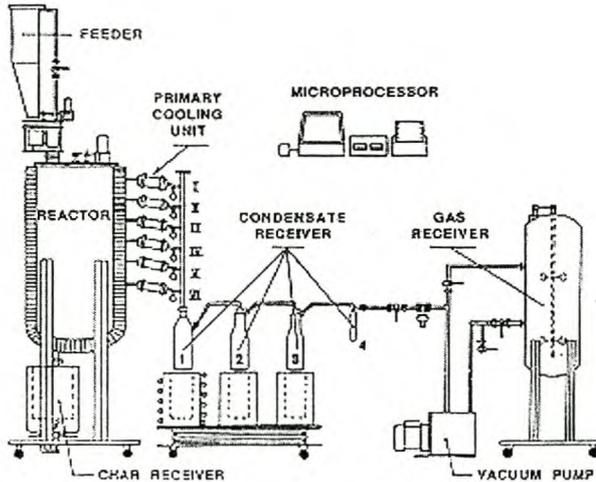
Figure 2. 1 Process development unit (P.D.U) [Roy et al., 1988]

The objectives of the process development unit (P.D.U.) were threefold. Firstly, the unit was used to obtain engineering data such as the overall thermal efficiency and the heat requirements for the reactions. Secondly, the configuration and mechanical operation of the reactor set-up had to be tested before its scale-up for the pilot plant phase of the project.

Another aim of the project was to develop a process that would reduce the organics lost in the aqueous phase. This was achieved by using multiple stages (multiple-hearth reactor), where the biomass passes over consecutive plates at different temperatures; the gas was then led off from each plate under vacuum conditions. The gases from the consecutive plates were passed through a separate condenser for each plate, which ensured that most of the water was trapped from the different heating sections of the reactor before mixing with the rest of the oil occurred. Bio-oil yields are reported to be as high as 50%. The pyrolysis oil and the charcoal both have higher calorific values than the feedstock. It was determined that the reaction is slightly endothermic for wood particles, with 733 kJ/kg of air-dry wood heat required. The standard heat of reaction at 323K and 1.6 kPa is approximately 92kJ/kg of air-dry wood. The energy efficiency of the experimental set-up was empirically determined to be 82%.

There are several parameters that influence the production of the charcoal and the pyrolytic liquor during vacuum pyrolysis of wood. **Roy C., H. Pakdel (1990)** investigated the role of extractives. There was a dispute as to whether the components of the pyrolysed feedstock interact during pyrolysis or whether they decompose individually. This paper shows that there are interactions between the different components, as was seen during atmospheric pressure pyrolysis. **[McGhee B., F. Norton, C.E. Snape and P.J. Hall (1995)]**.

Wood extractives inhibit the formation of hard wood vacuum pyrolysis oil yields. Wood cellulose was found to be the main source of formic acid when pyrolysed in the presence of extractives. Extractives inhibited the formation of levoglucosan formation during the vacuum pyrolysis of lignocellulosic materials. Lignin was found to inhibit the carboxylic acid production and enhanced the oil yield. Extractives caused a 50°C retardation on gas and acetic acid production in the temperature range 250-350°C.

Pakdel H. , C. Roy and C. Amen-Chen (1997) performed a detailed study of the effect of process parameters on the production of phenolic chemicals from bark residues in a batch reactor.

The forestry industry generates large volumes of bark residues. The Quebec forest industry produced an annual surplus of 0.9 Mt in 1996. Renewable biomass (harvest and process residues in forestry and agricultural operations, specific crops grown for fuel and medicinal plants) represents an important source of energy and chemicals.

One kilogram samples of either bark residue or primary sludges from a wood milling operation were placed in a 15L-batch reactor and heated under vacuum conditions. The gases that were produced were trapped in a train of condensers. The first condenser was at room temperature, the second at 0°C in ethylene glycol and the third and fourth condenser at -70°C, in a dry ice and limonene mixture. The non-condensable gases were stored in a 150L metallic cylinder. The air dry bark samples yielded 30.6% oil, 34.1% charcoal, 20.9% water and 14.4% gas. Air dry primary sludges yielded 40% oil, 30.1% charcoal, 18.2% water and 11.7% gas.

Phenolic compounds from pyrolysis oil can be used as a substitute for 50% of the petroleum based phenol adhesives used today **[Pakdel et al. (1997)]**. There is therefore great economic potential in maximising the phenolic yield from biomass. The low syringylic-type phenolic content of softwood bark-derived phenols lowers the economic value of the oil, and the lower value guaiacyclic phenols, such as cresol and phenol, are present in high quantities.

Pyrolysis operating conditions significantly influence the production and composition of phenols. A higher heating rate with thinner bed thickness favours the production of primary phenols. Soaking the plant material in water for 24 hours also increases the phenolic yield, presumably by decreasing the ash and/or extractive content, which catalyticly decompose the phenolic content of the hardwood. In contrast water treatment of softwood decreased phenolic content. Higher particle size and lower pressure are also good for phenol production. The best results were obtained at 450°C and at a heating rate of 10°C/min. It was also suggested that faster heating rates could further improve results.

1. Reactor	6. Pressure gauges
2. Cooling unit	7. Microprocessor
3. Liquid recovery system	8. Manual valves
4. Vacuum pumps	9. Gas sampling valve
5. Gas vessel	
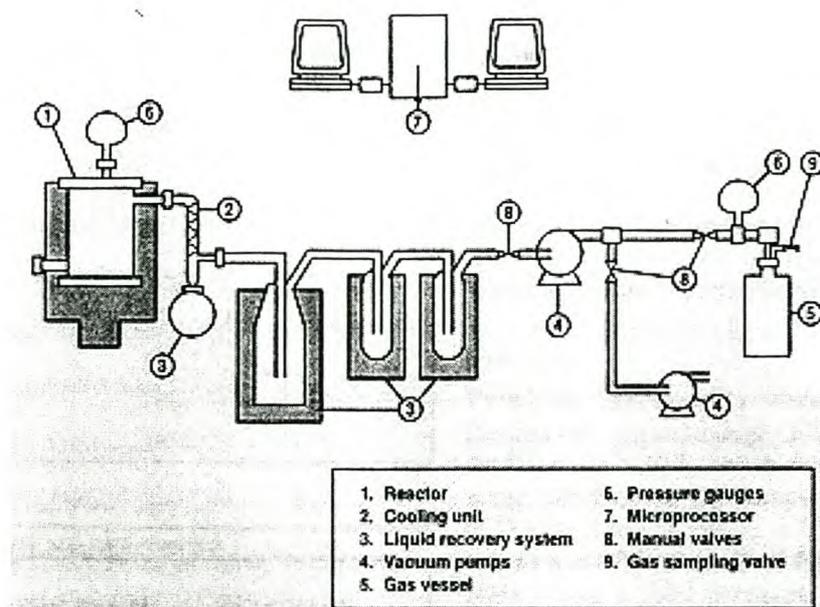
Figure 2. 2 Experimental Batch Reactor Set-up [Pakdel et al. (1997)]

The PDU was further used to test new chemical techniques to determine the qualitative **[Pakdel H., C. Roy (1988), Roy C., H. Pakdel and H.G. Zhang (1994)]** and in some cases the quantitative **[Pakdel H., C. Roy (1987), Pakdel H., H.G Zang and C. Roy (1993), Pakdel et al. (1997)]** chemical compositions of the pyrolytic oils produced.

A study was done by **Pakdel et al. (1987)** to determine the specific carboxylic content of the vacuum pyrolysis oils, specifically the low molecular weight acids. Low molecular weight carboxylic acids are produced in varying proportions during wood carbonation. In the past, the pyroligneous liquors formed during wood carbonation were the only commercial source of acetic acid. The yield of acetic acid obtained by the oven process was 4 to 4.5 wt.% on a dry wood feedstock basis. Formic, propionic, butryric, pentanoic, heptanoic, hexanoic and octanoic acids were also formed, but in smaller quantities.

Since carboxylic acids have very low response factors in gas chromatograph coupled with a mass spectrometer (GC/MS) analysis, the carboxylic acids were first derived to their benzene derivatives. The derived acids were then quantitatively analysed on a GC/MS. The study showed the reliability of the benzylation technique for C1-C7

10

carboxylic acids. The method allows for the identification, separation and quantification of the low molecular weight carboxylic acids as the main constituents of the pyrolysis oil.

The more polar pyrolytic oil components were analysed using a technique described by **Pakdel et al. (1993)**.

Pakdel H., G. Couture and C. Roy (1994) studied the vacuum pyrolysis of bark residues and primary sludges. The experiments were aimed at qualitatively identifying the chemical components of the pyrolytic oil. A fractionation method was used to split the oil into eight fractions, which was then concentrated and analysed by GC/MS. It was shown that carboxylic acids and phenols constitute a large percentage of the chemicals produced. The results showed that a staggering array of chemicals are produced and that the chemical composition is also dependent on the type of plant pyrolysed.

There are three general routes that can be followed for further development of pyrolysis oils: the oils can be fractionated into simple mixtures of components with similar chemical or physical properties, or the pyrolysis products can be refined into more useful chemicals or chemical intermediates. The third method would be to further process the oils to carbon blacks. Knowledge of the chemical composition of the pyrolysis products is a prerequisite for their utilisation as a chemical feedstock.

An example of an upgrading process can be seen in the paper by **Roy et al. (1994)** concerning the catalytic gasification of the aqueous by-product of vacuum pyrolysis. Roy demonstrated the technical feasibility of the catalytic gasification process as a useful step in the recovery of energy from the secondary condensate stream and the cleanup of the by-product water from vacuum pyrolysis of wood.

Work done on continuous reactors by **Roy C., B. de Caumia and P. Plante (1990b)** and **Pakdel et al. (1988)** has paved the way for the next step in the development of vacuum pyrolysis. **Roy C., D. Blanchette, B. de Caumia and B. Labrecque (1992)** have done a conceptual design and evaluation of a biomass vacuum pyrolysis plant.

A molten lead bath in a batch reactor provided the background data for the thermal decomposition in vacuum of a bed of wood particles. The contact time required to achieve the conversion reactions with this system was determined to be 45 minutes, based on a 70mm thick particle bed. This value was then used as the residence time required for a wood particle in a continuous moving bed reactor. The process was designed for a flowrate of 7875 kg/h of wet biomass (50% moisture), using a 14cm thick bed of wood chips on a conveying system. Parameters such as the method of heat transfer in different parts of the reactor were also taken into account.

A heat transfer model revealed that agitation of the moving bed of particles can significantly enhance the heat transfer, thereby reducing the needed residence time of the particles and consequently decreasing the reactor surface area and cost. The influence of pressure on the process economics showed that the optimum pressure was 15 kPa.
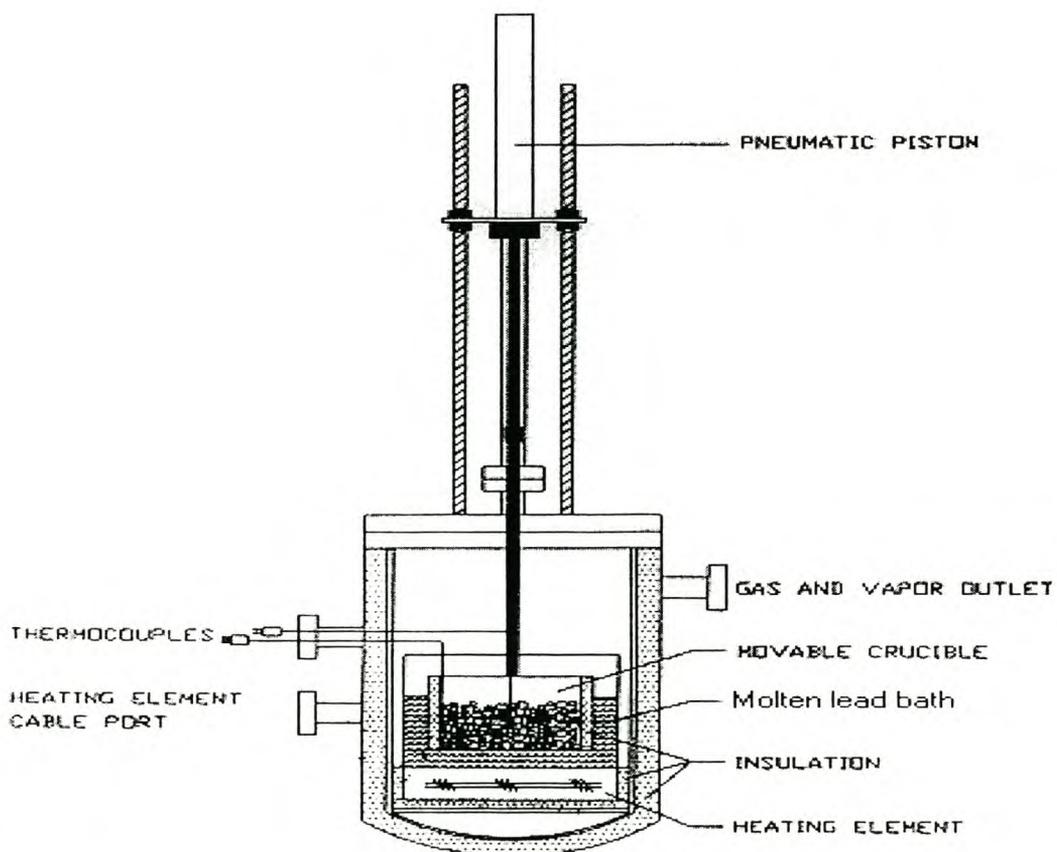
Figure 2. 3 Molten lead bath batch reactor [Roy et al. (1992)]

It was then determined that the manufacturing cost would be $115/t of pyrolysis oil, if the charcoal was sold for $100/t. The capital cost necessary would be M$ 6.37 (1992) for a plant running at 15kPa and 525°C with a capacity of 7875 kg/h.
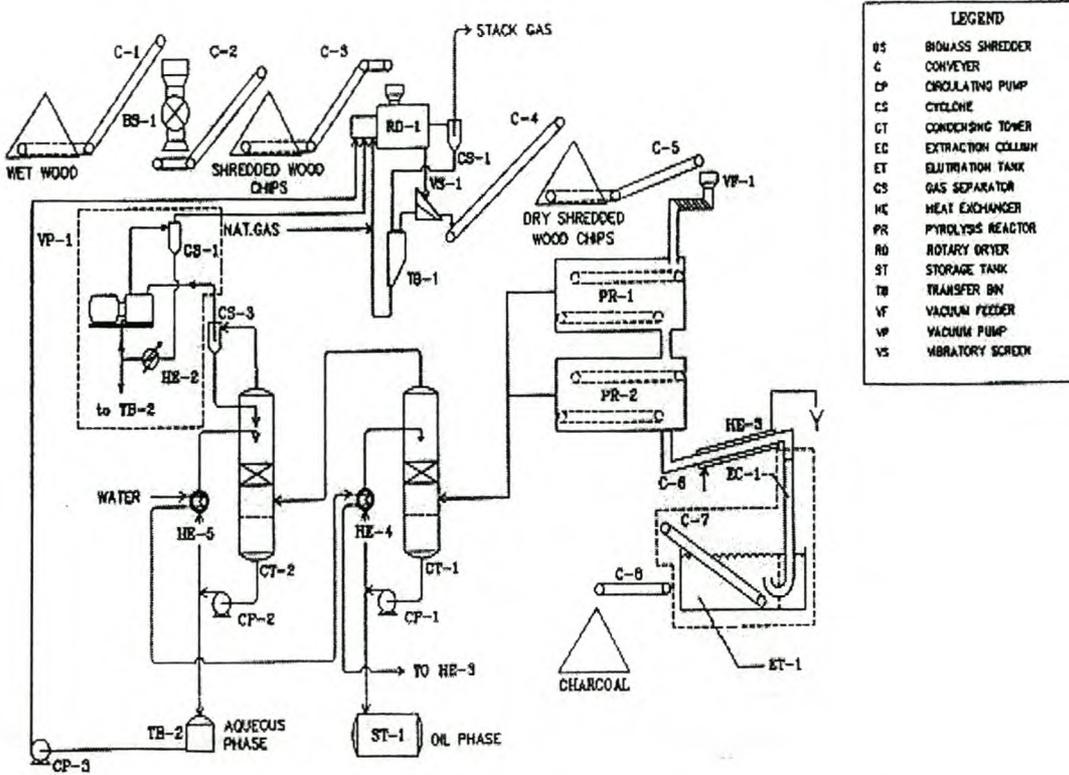
Figure 2. 4 Plant schematic [Roy et al. (1992)]

From these papers it can be seen that there is considerable interest in the production of bio-oil from wood wastes. The process economics appear sound, and with the continued research into new applications and new methods of extracting the valuable chemicals from the vacuum pyrolysis oils, the process seems destined to become a significant contributor to the world chemical industry.

The process can be made even more profitable if the charcoal could be activated to activated carbon. **C. Roy , N.Z. Cao, F. Soutric and Darmstadt H. (1999)** used CO_2 to upgrade vacuum pyrolysed bark derived charcoal. The activated charcoal properties were examined. Thermogravimetric (TG) analysis was done in the first study and a chemical analysis of the char surface in the next.

The TG analysis was done on the activated carbon created from the bark residue (66 % wood, 34 % bark) from different conifers (70% fir, 28% spruce and 2% pine, hemlock spruce and larch), which was pyrolysed at a temperature of 450 °C and a pressure of 20 kPa in a process development unit with a design capacity of 100 kg feed-stock/ h. Furthermore, the same feedstock was pyrolysed in a 1L-laboratory reactor at 1.3 kPa and 100kPa.

Approximately 10-12 mg of finely ground charcoal particles were heated in nitrogen or in nitrogen/steam (3.2 % H2O, 120 ml/min) from 25 to 1000 °C, at a rate of 5 °C/ min. In additional isothermal activation experiments, the charcoal was first heated under the same conditions in nitrogen to the desired activation temperature. Then the flow was changed to nitrogen/steam. Information about the activity of charcoal from vacuum and atmospheric pyrolysis was obtained from its weight loss rate upon heating in nitrogen and nitrogen/steam, respectively. Heating the samples in nitrogen and nitrogen/steam respectively showed that the oxidation of the charcoal sample started above 640°C.

Above 640°C, differences between the two samples upon heating in nitrogen/ steam were observed. Two stages were observed during the differential thermogravimetric (DTG) experiments. The first stage had a linear increase in weight loss, while the second stage showed a significant increase in weight loss with temperature. The second stage started at a higher temperature for atmospheric charcoal as compared to vacuum pyrolysis charcoal. This behaviour was attributed to the presence of carbonaceous deposits on the charcoal surface.

The TG study showed that during pyrolysis hydrocarbons are formed in the gas phase and some of these hydrocarbons condense on the char surface and in the pores. These hydrocarbons then undergo condensation and polymerisation reactions and finally carbonaceous deposits are formed. If pyrolysis is performed at reduced pressure, fewer hydrocarbons are present in the gas phase, fewer hydrocarbons are absorbed and consequently fewer deposits are formed. These deposits restrict the access to the charcoal pore system. The deposits have to be removed by oxidation before "unhindered" oxidation of the charcoal interior becomes possible. Once the deposits

are removed, oxidation will occur at the external and the internal charcoal surface. As the internal surface was considerably larger ($\sim 400 m^2/g$) than the external surface ($\sim 10 \ m^2/g$), the charcoal oxidation after removal of the deposits was considerably faster.

It was concluded that the deposits on the charcoal surface reduce the activation rate. On vacuum pyrolysis charcoal fewer deposits are present than on atmospheric charcoal. Vacuum pyrolysis charcoal should therefore be an attractive feedstock for the production of activated carbon.

2.2.   Plastic wastes

In recent years the importance of municipal waste recycling has started to take precedence over bio-oil production, but once again the innovative use of vacuum pyrolysis can be applied. Although wood and plant wastes make up a large percentage of current municipal waste streams, materials such as plastics and tyre rubber also have to be investigated. The knowledge and experience gained from the vacuum pyrolysis of plant material must now be adapted and applied to varied feedstocks. In order to adapt the technology, a whole new range of experiments on pure and mixed components had to be done.

In the past several different methods were used to pyrolyse plastics and the process has only recently been studied under vacuum conditions. Although the process conditions are different, certain trends, difficulties experienced and strategies employed may still be applicable. The previous techniques also stand as a benchmark against which new processes can be evaluated.

Most of the past processes used thermal catalytic methods to degrade the plastics into a reusable form **[Sekata et al. (1996)** and **McIntosh M.J.,** *G.G. Arzoumanidis and F.E. Brockmeier* **(1998)]. Sakata et al. (1996)** studied the catalytic thermal degradation of municipal waste plastics with the aim of producing fuel oil. A glass reactor was used to thermally degrade the municipal waste plastic into a solid, liquid (condensable with a water-cooled condenser) and gas phase. The experiments were conducted at atmospheric pressures with a N_2 purge at a temperature of 410°C.

Municipal waste plastic (MWP) and simulated municipal plastic (SMP) were degraded with and without a catalyst. It is clear that the catalytic action can greatly improve the system's performance. The simulated waste plastic stream consisted of 37% polyethylene (PE), 17 % polypropylene (PP), 8 % Polyvinyl-Chloride (PVC), 10% poly(ethylene terephthalate) (PET) and 5 % acrylic-butyl styrene (ABS).

The mixed plastics yielded 35 wt. % liquid and 12 wt. % gaseous product, with the remainder being solid and waxlike tarry products left over in the reactor. These solid and waxlike products produced no gases at 410°C.

When PVC is present in the mixture it is necessary to dechlorinate it, as the chlorine containing hydrocarbons formed during the reaction are the precursors of dioxine, a carcinogenic substance. It is therefore necessary to develop an effective dechlorination and degradation process for municipal waste plastics. The dechlorination was achieved by using a temperature programming schedule. The freely bonded water was removed at 120°C for 60 min., and then the dechlorination was performed at 320°C for 20 min, after which the thermal degradation was conducted at 410°C for 300min. It was found that PET leaves a yellow residue consisting of benzoic acid and terephthalic acid. PVC also leaves much coke. The catalyst used was SiO_2/AlO_3, with a 8/2 molar ratio and a surface area of 420 m^2/g. The catalyst is effective for some plastics, but less so for PS and ABS plastics.

McIntosh et al. (1998) studied the recovery of fuels and chemicals through catalytic pyrolysis of plastic wastes. A simulated waste stream of constant composition was pyrolysed at 700°C with different combinations of catalyst and a nitrogen purge to find the best general catalyst. This general catalyst could then be tested further on variable waste streams. It was a small-scale experiment, but 'ASPEN' was used to determine the likely process economics for a large-scale plant.

A combination of ZnO / TiO$_2$ performs best as a catalyst for the recovery of the liquid organic phase. This liquid phase consists predominantly of benzene, toluene, dimethyl heptene, ethyl benzene, styrene, benzonitrile, other volatiles and the high boilers. The liquid organic phase could be split into a fraction boiling below 190°C and another boiling above 190°C. The lower boiling point phase consisted mostly of benzene, toluene, benzonitrile, 2,4-dimethyl-1-heptene, while the higher boiling point fraction contains mostly branched alaphatics of 12-30 carbon atoms per molecule.

Several novel techniques were also developed by researchers such as **Lovett S., F. Berrut and L.A. Behie (1997)** and **R.W.J. Westerhout , J. Waanders, J.A.M. Kuipers and W.P.M van Swaaij (1998). Lovett et al. (1997)** used an ultrapyrolytic technique for the upgrading of plastic wastes and plastic/heavy oil mixtures to valuable gas products. Ultrapyrolytic reactions are run at very high temperature and

for a very short duration. The temperature in these sets of experiments reached 800-965°C and the reaction times were 500-1000ms. Microreactor experiments were performed with polystyrene (PS) and yields of up to 95 wt.% of styrene and benzene were achieved at 965°C and 500ms. Pilot scale experiments were also done on low-density polyethylene (LDPE) and LDPE (5 wt. %) /heavy oil mixtures with residence times of 500ms at temperatures of 830°C. This yielded 55 wt % light olefins. The main products were methane, styrene, benzene, butene and butadiene.

Westerhout et al. (1998) employed a continuously rotating cone reactor for the pyrolysis of polyethene and polypropene. The experiments were conducted at a temperature of 1300°C. Polyethene (PE) and polypropene (PP) plastics were pyrolysed and an alkene yield of 66% was achieved, this is comparable to the 65% obtained in a bubbling fluidised bed (BFB).

Experiments were first conducted with (PE). It was revealed that temperature has the greatest influence on the product spectrum. The yields of ethene and methane both increase sharply with temperature, while yields of propene and butene decrease. When the temperature was too low the gas yields dropped dramatically, because the temperature was too low to take the plastic past the intermediate waxlike products.

The second set of experiments was conducted on polypropene (PP). At low temperatures the main products are propene and butene, but at higher temperatures these products decrease and ethene and methane become the main products. The conclusion is that the reactor temperature has to be set as low as possible to maximise alkene yield. In these reactors factors such as sand flow rate and polymer flow rate also influence the results.

The review of plastic waste recycling by **H. Shent, R.J. Pugh and E. Forssberg (1999)** reveals a definite problem with the handling of mixed plastic waste streams. The composition of several countries' waste streams and also their statistics on plastics recycling were represented. The types of plastics and their production statistics were also shown. Plastics represent 8 wt.% (21% by volume) of the MW in the US and the percentage is growing, especially in industrialised countries. South

Africa is becoming more and more industrialised, and plastics will therefore also become more problematic in the future.

The increased production of plastics has a great impact on the management of MSW (municipal solid waste) by land filling and incineration, as available capacity for the landfill of MSW is declining, and plastics incineration may cause toxic fly and bottom ash, which contain lead and cadmium. The presence of dioxins and difurans in the incineration products also cause problems.

Shent, R.J. Pugh, E. Forssberg (1999), who discussed the origins of plastics, showed that packaging is a significant contributor (33.5%) to the plastic waste stream. A large portion of the packaging waste stream is the so-called 'curbside mix', which contains mostly PET plastic and represents an important recycling opportunity. PVC constitutes about 3 wt.% of the 'curbside mix'. The density difference between PVC and PET is too small for it to be separated by gravity separation. Flotation is discussed as a possible alternative for the separation of PVC and PET.

Chaala A, H. Darmstadt and C. Roy (1997) experimented with vacuum pyrolysis of electric cable wastes. Metal-free cable wastes were pyrolysed at 20 kPa, 450°C and with a heating rate of 10°C/min. The two main products were wax (71 wt.%) and pyrolytic carbon black (21 wt.%). The wax and carbon black were compared with commercial grade materials using Fourier Transform Infrared (FT-IR), Electron Spectroscopy for Chemical Analysis (ESCA), Secondary Ion Mass Spectrometry (SIMS) and X-Ray Diffraction (XRD). Similarly to commercial wax, the pyrolytic wax consisted mostly of alkyl chains. However, it contained more olefinic groups and the alkyl chains were less branched. The surface area of the carbon black was higher than that of the commercial grade of the N500 series. It contained less than 5 wt.% $CaCO_3$, which was the only inorganic detected. The surface chemistry was very close to that of commercial N539 carbon black.

The cable wastes consisted of: 90.8 wt.% cross-linked low density polyethylene (XLPE), a very small quantity of EVA (ethyl vinyl acetate), 4,6 % cable rubber portion (natural rubber) and 4,6 % of other polymers such as chloroprene rubber,

19

ethylene propylene dimer rubber (EPDM), and chlorosulfonated polyethylene (CSM). There were also some additives and fillers.

The gas was condensed at -15°C, -72°C and -72°C. In the first two traps a wax-type product was recovered. The waxes from the first two traps were labelled hard and soft waxes respectively. In the third trap two non-miscible fractions were recovered. The upper and lower layers were labelled light and heavy liquid phases respectively. The yields were: 33.7 wt.% soft wax, 37.6 wt.% hard wax, 21.4 wt.% carbon black, 4.1 % gas, 1.2 and 2 wt.% light and heavy liquid respectively. The thermal decomposition reactions of polyethylene occur after its melting. The reactions are equivalent to the decomposition of long chain length liquid paraffin.

The paper also explains the creation of large macromolecules through backbiting and chain breakage at the very weak carbon-carbon bonding sites at the symmetrical point in long-chain aliphatic molecules. Under low pressure and with short residence times of the vapours in the reactor, the disproportionation of the primary macroradicals is the major reaction explaining the formation of n-paraffins and olefins at 450°C. The lower yields of light organics can be explained by the low cleavage which occurs near the end of the macromolecular chain. Cleavage here refers to the breaking of the polymerised chain molecule at some point in the chain.

The chemical components found in the light liquid phase were ethanol, acetone, methyl acetate, acetic acid, heptane, diphenylbenzenemethanol and others. Analysis was done with GC/MS for the light liquid fraction, FT-IR, NMR for the waxes and XRD for the carbon black.

Chaala A., O.G. Ciochina and C. Roy (1999) did further work on the vacuum pyrolysis of automobile shredder wastes. The pyrolysis oil produced was then tested for its use as a modifier for road bitumen. The vacuum pyrolysis of the shredder wastes was performed at 450°C-500°C and a pressure of 10-20 kPa. The automobile residues consisted of steel, cast iron, forging, plastics foams, rubber, glass, paint, dirt and other materials such as wood, fibrous materials, leather, fluids and lubricants.

GC/MS showed that the pyrolysis oil does not contain any significant amount of sulphur or chlorine derived chemicals. This makes it a low sulphur fuel with a high heating value. The oil contains 33 wt.% monoaromatic compounds, 8.9 % aliphatic, 4.1 % olefinic, 25% alicyclic compounds. The products were 25 wt.% oil and 14 % water (including initial water). Non-condensable gases were 7 wt.% and the solid residue was 54 wt.%, consisting of diverse metals and carbonaceous deposits.

Physiochemical characterisation of pyrolytic oil residue (PR) derived from the vacuum pyrolysis of automobile shredder residues indicated that this material has a composition and behaviour similar to that of petroleum bitumen (PB). It was found that PR possessed a consistency of bitumen with a penetrability grade of 150-200. The addition of PR at various concentrations to PB reduced the thermal susceptibility of the blends and enhanced their rutting resistance. A 10 wt.% PR concentration in the blend exhibited the best performance. A long-term study still has to be done to determine its reliability from an environmental point of view.

Miranda, H. Pakdel, C. Roy, H. Dramstadt and C. Vasile (1999) has done an extensive study of the vacuum pyrolysis of PVC. The study consisted of two parts: Part I studied the kinetics of the pyrolysis reaction, while the detailed chemical analyses were discussed in Part II. A more detailed study of this paper is presented here, as it was very useful in terms of the work done on the co-pyrolysis of PVC and wood (Chapter 7). The purpose of the kinetic study **(Part I)** was to identify each apparent reaction that occurred during the vacuum pyrolysis of PVC. Three stages of weight loss were identified during TG analysis, both under vacuum and nitrogen conditions, whereas most previous studies showed only two stages. The temperature ranges of these stages were 200-230°C, 250-375°C and 375-520°C.

Based on these TG results, a three-apparent-reactions model was proposed. The kinetic parameters and conversion factors have been calculated for each apparent reaction, with this model including all three stages of decomposition. The experiments were conducted at pressures ranging from 2-15kPa and temperatures ranging from 200-520°C. The purpose of the experiments was to recover high yields of useful

products and to minimise harmful emissions during the vacuum pyrolysis of MSW (municipal solid waste) derived plastics.

The powder sample used was a commercial suspension material (grade SE-950EG). The thermal analysis experiments were performed with a TG/DTA system. A 6g sample was used for each experiment and the runs were carried out in a nitrogen (60ml/min) atmosphere and at vacuum (0.6 kPa). Four heating rates (1, 5, 10, 20 °C/min) were also employed. The purpose of the kinetic study was to characterise each possible apparent reaction and to add new elements concerning the mechanisms of the formation of aromatic hydrocarbons and chlorinated compounds. Various models were tested and adapted for the apparent reactions and to obtain the kinetic parameters.

It was observed that at a heating rate of 10°C/min the weight loss for the first heating stage (200-330°C) was 46 wt.%, the second stage (220-375°C) represented 18 wt. % and the third stage (375-512°C) represented a weight loss of 30.3 wt. % with 5.7 wt. % for the final solid residue.

Between 200-375°C the main reaction involves a dehydrochlorination step with subsequent formation of conjugated double bonds in polyene chains. This was supported by the elemental analysis of the residue. The total chlorine remaining in the residue after pyrolysis at 360°C was 0.14 wt. %. The difference between the initial amount of HCl (58.7 wt.%) and the total weight loss at 375°C corresponds with the formation of some hydrocarbons, mainly aromatics such as benzene. Between 375°C and 500°C there is only one DTG peak, which corresponds with the decomposition of the polyene chain formed during the first stage of PVC degradation.

The influence of a nitrogen atmosphere compared to vacuum was also investigated. It was found that the first two heating stages are not extensively influenced, but that the third stage was. In the final stage a lower temperature was needed in vacuum to obtain the temperature of maximum weight loss rate. In addition the reaction in vacuum produced almost 50 wt.% less residue than in a nitrogen atmosphere. The difference in the final percentage of residue formed may be explained by an accelerated release of

volatile compounds formed in the temperature range of 360-500°C of PVC thermal decomposition in vacuum, as some secondary condensation and aromatization reactions are avoided. This also implies that a greater quantity of hydrocarbons can be obtained during vacuum pyrolysis when compared with atmospheric pyrolysis in nitrogen.

According to **Miranda et al. (1999)** the parallel kinetic model was first reported by **Wu et al (1994),** who measured two stages of weight loss. They considered the two stages of weight loss to be composed of four apparent reactions. The first stage consists of two parallel reactions, which produce intermediate pyrolysis products and gases. The volatiles consist of HCl and hydrocarbons. Two other parallel reactions corresponding to the second stage convert the intermediate pyrolysis products into gases and carbonaceous residue. **Wu et al. (1994)** believed that the first stage was determined by the percentage composition of the two species of vinyl chloride bonds i.e. head-to-tail and head-to-head in the PVC sample. A head-to-head configuration indicates that the two like sides of the monomer binded, while a head-to-tail configuration happens when the dissimilar sides of the monomer bind. It has been established that chlorine atoms are less stable in the head-to-head PVC than in the head-to-tail.

In contrast the results presented in this paper indicate that a greater quantity of residue was formed at higher heating rates, while **Wu et al. (1994)** found that the residue decreased with higher heating rate. Based on the parallel model of **Wu et al. (1994),** a three-apparent-reactions parallel kinetic model was proposed in this work, which considers the three stages of weight loss during PVC pyrolysis as resulting from three parallel reactions.

The first reaction considered the formation of HCl from one structural species (P_VC1). As soon as polyene sequences appear as intermediates along the chain, the second process starts and becomes a parallel process, together with the second species of configuration of the initial sample (P_VC2). The second reaction involves the release of the HCl from the second species of PVC and the aromatics formation, i.e. mainly the formation of benzene from polyene already formed. The third reaction entails the

evolution of substituted aromatics, such as toluene and methyl naphthalene from the polyene that has not been used to produce aromatics in the second reaction and polyene formed from PVC_2.

In **Part II** of the work by **Miranda et. al (1999)**, the PVC pyrolysis products were analysed and special attention was given to the effect on the chlorine. The bench scale reactions were conducted at a temperature at the end of each of the heating stages identified in part I of their study. A GC/MS method was developed for the analysis of the chlorinated compounds as well as the hydrocarbons produced during pyrolysis. The reaction pathways of the thermal degradation, under vacuum, of the PVC was also postulated (see figure 2.5). The same sample characteristics and vacuum pyrolysis methods and conditions applied for the second paper.

The HCl was trapped using three methods, a water trap at 0°C, a NaOH trap at -10°C and a CaO column. The water and NaOH traps had to be followed by cold traps at -78°C to capture the water that evaporates under the reduced pressure. The NaOH trap captured 100% of the HCl, while the water trap captured 96.07% and the CaO column only captured 49.59%. The HCl concentration in the NaOH was established by capturing the HCl in NaOH with known concentration and then doing a HCl neutralisation of the excess NaOH by titration.

A thorough knowledge of the organic and inorganic chlorine production is very important, due to the high corrosion potential of HCl and the formation of hazardous chlorinated hydrocarbons. The processing of high chlorine content materials is also undesirable in the petrochemical industry.

Approximately 79.52 wt.% of the initial chlorine was released at a pyrolysis temperature of 260°C, including 78.62 wt.% as HCl and 0.05 wt.% in the organic fraction. 0.85 wt.% was attributed to the losses. A significant quantity of chlorine was left behind in the residue at 260°C. Approximately 99.84 wt.% chlorine was removed at 360°C, including 98.98 wt.% HCl, 0.09 wt.% in the organic fraction. 0.16 wt.% was left behind in the residue and 0.77 wt.% is the loss. At a pyrolysis temperature of 520°C, 99.11 wt.% of the chlorine was released as HCl, 0.11 wt.% was found in the

organic fraction and 0.78 wt.% was lost. The total chlorine in the oil represents 0.063 wt.% on the original polymer basis and 0.194 wt.% on the total oil basis at 520°C. No chlorine was found in the solid residue at 520°C.

The non-condensable gases were less than 0.04 wt.% at 320°C and increased to 0.34 wt.% at a pyrolysis temperature of 520°C. Hydrogen and low molecular weight alkanes and olefins were the most prominent pyrolytic gas components. The gas had a calorific value of 56.15 kJ/mol that could be used as a make-up heat source for the process.

The major product of the pyrolysis condensates was benzene which accounts for 64.33, 64.74 and 17.91 wt.% of the global liquid fraction (i.e. 1.1, 3.24 and 5.80 wt% of the original PVC) at pyrolysis temperatures of 260, 360, 520°C respectively, followed by naphthalene and toluene.

During the early stages (200-260°C), HCl is the major product followed by 1.01 wt.% benzene, 0.17 wt.% naphthalene and 0.03 wt.% toluene on the basis of the original material. The dehydrochlorination of the PVC generates conjugated polyene structures containing both cis and trans configurations as intermediate products. As the temperature increases intermolecular cyclisation becomes a predominant reaction mechanism (360°C). The production of benzene and naphthalene reaches a maximum of 3.24 and 0.62 wt.% respectively. During the third thermal stage, the formation of benzene and other unsubstituted aromatics is inhibited due to the cross-linking of the polyene chain by intermolecular reaction at 360-520°C. Substituted aromatics such as toluene and xylenes with a yield of 8.85 wt.% are the major products produced by intramolecular cyclization reactions and scission of the cross-linked polyene chain during the third stage of pyrolysis. 2.57 wt.% benzene and 0.27 wt.% naphthalene are also produced during the third stage. At pyrolysis temperatures of 360-520°C, cross-linked polyene chains tend to form substituted aromatics rather than char. A sharp increase in the production of substituted aromatics can be perceived above 360°C , with a net yield of 11.06 wt.% on the basis of the original material. The production of toluene and xylenes increased from 0.15 wt.% at 360°C to 1.71 wt.% at 520°C. The

formation of saturated and unsaturated aliphatics also sharply increase above temperatures of 360°C.

Benzene, Naphththalenle, Anthracene+other unsubstituted aromatics

Intermolecular cyclization

-HCl   Intermolecular

PVC → **Linear Cis-Polyene Chain**   **Cross-Linked Polyene Chain**

Transfer

Intramolecular Cyclization and Scission Partial Hydrogenation

Linear Trans-Polyene Chain   Intermolecular Cyclization and Aromatization Dehydrogenation   **Mainly Alkyl Aromatics**

Char

Figure 2. 5 Postulated reaction pathways for PVC thermal decomposition [Miranda et al. (1999)]

The formation of chlorinated hydrocarbons increases with increased pyrolysis temperature up to 360°C, after which it levels off at a total incremental increase of 0.003 wt.% between 360°C and 520°C. The formation of chlorinated aromatics is greater than that of chlorinated aliphatics during the pyrolysis of PVC. Approximately 0.71 wt.% of the chlorinated hydrocarbons produced at 520°C is found in the light liquid fraction. Benzyl chloride is the main chlorine compound formed, followed by chlorobenzene, 3-chloro-1-phenyl-but-2-ene and (2-chloro-2-butenyl) benzene. The chlorine content in the pyrolysis products has several sources. It may be partially derived from dissolved HCl in the aromatic products or it originated from the vapour of HCl produced during the pyrolysis. Part of the organochlorinated compounds may also be due to secondary reactions (condensation reactions) after pyrolysis. In order to minimise the organic chlorinated compounds the HCl should be captured before condensation.

The solid residue was analysed using Brunauer, Emmett and Teller (BET) calorific elemental analysis and ESCA survey spectra techniques. The residue produced at 520°C had a high calorific value of 38MJ/kg with a rather low surface area of $10m^2$/g. The elemental analysis showed that the H/C ratio decreased with increased pyrolysis

temperature. The original PVC sample had an H/C ratio of 1.507. At a pyrolysis temperature of 250-260°C the ratio was decreased to the 1.18-1.1 range due to the dehydrochlorination reaction. The H/C ratio further decreased to 0.95 at 360°C as a characteristic of carbonisation. Char was formed at a ratio of 0.615 at 520°C.

In the ESCA survey spectra of the char at 260, 360 and 520°C it could be seen that the carbon surface concentration increased with increased pyrolysis temperature, whereas the oxygen and chlorine concentrations decreased. The surface concentration of the oxygen was considerably higher than in the bulk, but oxidation of the surface could easily occur and this tended to increase the oxygen content. Since the PVC contains little oxygen it is possible that the oxidation occured during handling and storage. The decrease in oxygen content with increased pyrolysis temperature could be explained by the decrease of surface active sites by aromatization. For the same reason the surface chlorine concentration decreased with increased pyrolysis temperature. Approximately 0.4 and 0.1 mol % of chlorine was found on the surface and in the bulk, respectively, after pyrolysis at 360°C and higher temperatures. Moreover, the instability of chlorine groups at high temperatures will result in the evaporation of the surface chlorine atoms. From the carbon spectra there was an indication that the char became more aromatic with increasing pyrolysis temperature. The oxygen spectra indicated that the oxygen on the surface of the char was mainly in C-OH bonds. The chlorine spectra showed no indications of inorganic chlorine compounds such as Cl^-, ClO_3^- or ClO_4^-. The spectra did show a typical response for organic chlorine compounds such as PVC. Approximately 0.4 and 0.1 mol % chlorine was found on the surface and in the bulk, respectively, after pyrolysis to temperatures of 360°C and higher.

Yuan C. and J. Chen (1998) have investigated the emission of volatile and semi-volatile organic products during the thermal treatment of waste acrylonitrile-butadiene-styrene plastics in a two-chamber combustion process. This study revealed that the major organic degradation products formed during thermal treatment under oxidation conditions, were volatile organic compounds and a small number of monomers were also found. While the major organic compounds generated under pyrolysis conditions were monomers and some volatile organic compounds, aromatic

compounds were also detected in the gas outlet stream. This study also revealed that the mechanism of pyrolysis was end-chain scission.

The emission of organic thermal degradation products increased with primary combustion temperature and decreased with secondary combustion chamber temperature under pyrolysis conditions. The emission of organic products increased with air ratio at 400°C, but the maximum emission of acrolein, acrylonitrile, styrene and benzene was observed with an equal ratio of N_2 and O_2 in the inlet gas stream at temperatures of 500°C and 600°C for the two reaction chambers. It was also revealed that organic degradation products decrease with longer retention times in the reactor, which indicates secondary reactions.

2.3. Used Tyre Rubber

Scrap tyres are a major environmental problem. An estimated 2.5 x 10^9 kg of scrap tyres are generated each year in North America **[C. Roy, A. Rastegar, S. Kaliaguine, H. Dramstadt and V. Tochev (1995)]**. There has therefore for many years been a drive to find a profitable way to recycle the used tyre rubber. Much of the pyrolysis work done on used tyre rubber has been done under atmospheric conditions.

San Miquel G., G.D. Fowler and C.J. Sollars (1998) studied the porosity and adsorption characteristics of the used tyre rubber pyrolytic chars produced in a nitrogen atmosphere. At 500°C the char yield was 42 wt.%, the multipoint Brunauer, Emmett and Teller (BET) surface area was 85 m^2/g and the micropore volume was 0.04 mL/g. Due to the poorly developed micropore structure, the pyrolytic chars exhibited limited aqueous adsorption capacity for small molecular weight molecules, such as phenol. However, the adsorption capacity for species of large molecular weight molecules was much higher. This was attributed to the presence of large mesopore volumes (0.19 mL/g).

Much of the work done on tyre rubber was aimed at carbon black formation and subsequent activation to activated carbon. The activation was achieved using techniques such as superheated steam **[Akbar, A. Merchant and Mark A. Petrich,**

1993] or CO_2 **[Teng H., M.A.Serio, M.A. Wojtowicz, R. Bassilakis and P.R. Solomon 1995]**.

Akbar et al. (1993) pyrolysed tyre rubber in a nitrogen atmosphere and then activated the carbon using superheated steam. The main aim of this work was the conversion of used tyres into activated carbon with surface areas exceeding $500m^2/g$ and with significant micropore structure. It was found that the porosity development during steam activation was similar to that reported for various other chars. A maximum in micropore volume was observed as a function of conversion, but the total surface area increases monotonically with conversion. The article suggests that the activation process consist of micropore formation, followed by pore enlargement. Activated carbons with surface areas higher than $500m^2$ were produced at an activation temperature of 850°C in nitrogen stream containing 40 mol % water. Gasification appears to be chemically controlled because of the surface area enhancement and high apparent activation energy.

Teng et al.(1995) produced activated carbons in an inert atmosphere from pyrolysis chars of used tyres, with surface areas higher than $800m^2/g$ at pyrolysis temperatures of up to 900°C, followed by activation by CO_2. The efficiency of the activation process was greatest when large pieces (~170mg) of tyre rubber were used. It was also found that oxygen pre-treatment of the tyres enhanced both the yield and the area of the carbon product.

Vacuum pyrolysis of used tyre rubber have been researched extensively. The drive has mostly been in the direction of carbon black or activated carbon from the char and valuable or burner oil from the liquid fraction.

C. Roy et al. (1995) did a study on the physiochemical properties of carbon blacks from vacuum pyrolysis of used tyres. The experiments were run in a batch laboratory scale reactor, similar to most of the batch reactors used for wood vacuum pyrolysis, at temperatures ranging from 350°C-700°C and total pressures of 0.3-20.0 kPa. At the optimum organic liquid yield temperature of 420°C and 0.3 kPa the vacuum pyrolysis

yields were: 72 wt.% organic liquids, 23.3 wt.% char and 4.7 wt.% gasses on the original rubber feedstock basis.

The purpose of the study was to recover scrap tyres-derived pyrolytic carbon blacks with good mechanical properties. These properties were determined using proximate analysis (which determines the ash, volatile matter, fixed carbon and water content), elemental analysis, specific surface area, pH, ESCA surface analysis and X-ray diffractograms (XRD). The bulk chemical properties were also determined using chemical solution techniques.

XRD showed the inorganic fillers that were used during the manufacturing of the tyres. Although plants also contain some inorganics, it would be a much lower percentage than for tyres. ZnO and ZnS were found by using XRD, the ZnS was found to be in two phases. The ESCA surface analysis showed that there were some differences between the bulk chemical content and the surface content. In the case of oxygen it was shown that the surface concentration was higher than the bulk concentration. This is probably due to the exposure of the char to oxygen during handling.

The specific area variation with temperature was tentatively explained as follows. Upon increasing the reactor bed temperature from 420°C to 500°C, the excess rubber hydrocarbons from the pores and surface of the particles were pulled out and volatized. In the lower temperature region, this resulted in a sharp rise in the iodine absorption number (which can be directly related to surface area). When the temperature was increased above 500°C, the residual carbonaceous solids were subjected to a series of complex changes, which were the main sources for the substantial decrease in the iodine index. The proximate analysis showed that the pyrolysis reaction was almost completed at 420°C and 0.3 kPa, since the volatile matter, ash and fixed carbon remained constant between 420°C-700°C.

The economics of the vacuum pyrolysis process are very dependent on the value of the carbon black produced **[Roy et al. (1995), Darmstadt et al. (1995)]**. **C. Roy and**

H. Darmstadt (1998) did a study to compare the pyrolytic carbon black produced from used tyre rubber under vacuum conditions with commercial carbon blacks.

From experimental results it was seen that during atmospheric pyrolysis of tyre rubber, char yields of up to 50 wt.% can be achieved, while yields of only 30 wt.% are reported during vacuum pyrolysis at 500°C. This means that during atmospheric pyrolysis considerable amounts of carbonaceous deposits are formed. The lower char yield shows that only small amounts of carbonaceous deposits are formed during vacuum pyrolysis. Furthermore, it was shown by surface specific spectroscopic techniques, such as ESCA and SIMS, that by reducing the pyrolysis pressure, the amount of carbonaceous deposits formed is considerably reduced. The low concentration of carbonaceous deposits on the char from vacuum pyrolysis ensures that these chars are very close in their morphology to commercial grades.

Absorption enthalpies of the commercial and recovered carbon black were almost identical. This indicates that no poisoning or deactivation of the carbon blacks occurs during the recovery process. In contrast to the absorption enthalpies the surface energies of the char were considerably lower than those of commercial carbon blacks. The lower surface energy was explained by the deposition of carbon deposits on the carbon black during the pyrolysis.

The concentration of these deposits can be measured by ESCA spectroscopy. A good correlation was found between the amount of carbonaceous deposits measured by ESCA, and the surface energy. The decrease in surface energy was interpreted as a loss of 'active' sites on the char by formation of carbonaceous deposits. The paper also states that the strength of the active sites before and after the pyrolysis is similar.

The surface energy of char from vacuum pyrolysis is about 1/3 smaller than the surface energy of the commercial back initially present in the tyre. The "active" surface area of char from vacuum pyrolysis should therefore be 2/3 of its BET area. Thus a 100 m²/g char from vacuum pyrolysis should be able to replace a 66 m²/g commercial carbon black.

It can be concluded from these results that vacuum pyrolysis charcoal should have the potential to replace commercial carbon black grades in some applications.

2.4. Co-pyrolysis

The study of the co-pyrolysis of materials is necessary to develop the models for complex mixtures of materials such as municipal waste. Although the study of co-pyrolysis is still in its infancy the following articles give insight into the chemical and physical interactions that occur during pyrolysis and vacuum pyrolysis.

H. Darmstadt, M. Garcia-Perez, A. Chaala and C. Roy (2000b) did a study on the co-pyrolysis of sugar cane bagasse and petroleum residue. The purpose of the study was to determine if the pyrolytic oil derived from bagasse vacuum pyrolysis could be improved by the addition of petroleum residue and to determine the effect on the char formed. The influence on the feasibility of activating the char was also investigated.

Vacuum pyrolysis of sugar cane bagasse yields 20 wt. % char, 34 wt. % oil, 28 wt. % aqueous phase and 18 wt. % gas on an anhydrous basis. It was found that the addition of 15% petroleum residue yielded pyrolytic oil that met the specifications for gas turbine fuel. The addition of the petroleum residue also influenced the yield and properties of the charcoal formed.

Approximately 100 g of the feedstock mixture was pyrolysed in a 1 L batch reactor. The reactor was purged with N_2 and the feedstock was then heated at 12°C/min to 500°C at 1.5kPa. The temperature was held at 500°C for one hour, after which it was allowed to cool. The steam activation of the chars was performed at 850°C for two hours.

The experiments showed that the char yield increased with the addition of the petroleum residue up to a concentration of 15%, but that the char yield decreased for higher concentrations. This shows that there is interaction between the bagasse and the petroleum residue during the pyrolysis. If it is assumed that during co-pyrolysis no interaction occurs between the two feedstock materials, one would expect that the

char yield would change linearly with increasing petroleum residue concentration in the feedstock. The observed char yield, however, was considerably larger than expected. The higher than expected char yield can be explained by the different thermal stabilities of the two feedstock materials. Thermogravimetric (TG) analysis of the bagasse, petroleum residue and a 50% mixture of the two showed that the formation of the bagasse char is almost completed when the pyrolysis of the major portion of the petroleum residue occurs.

Darmstadt et al. (2000) therefore assumed that coke-like products from the petroleum residue were deposited on the bagasse char, thereby increasing the char yield. It was also stated that the deposits might block some of the pores of the bagasse, thereby trapping some of the volatiles. The trapped volatiles would then react to form coke-like deposits within the bagasse char. The presence of the deposits on the char surface was verified using ESCA. The shape of the C_1 peak in the Carbon 1s spectra was used as an indicator of the polyaromatic nature of a carbonaceous sample.

In the spectra of compounds consisting of seven and less condensed aromatic rings (e.g. coronene) the C_1 peaks are symmetrical, whereas for larger polyaromatic systems the C_1 peak becomes asymmetrical . In the spectra of this work, the C_1 peak of the bagasse char was very asymmetrical indicating a graphite-like surface. The C_1 peak became less asymmetrical upon addition of 5% PR to feedstock. After addition of 15 % PR the C_1 peak was practically symmetrical. The C_1 peaks in the spectra of the other co-pyrolysis chars were perfectly symmetrical. This observation indicates that with increasing PR concentration in the feedstock the graphite-like surface of the bagasse char was successively covered with coke-like compounds characterised by less polyaromatic structure. When the PR concentration in the feedstock reached 15 % the entire surface of the bagasse char was covered. At this PR concentration, the maximum char yield was reached. Upon further increase of the PR concentration, the char yield decreased nearly linearly with the decreasing bagasse concentration in the feedstock.

The surface area of the co-pyrolysed char was also lower than that of the bagasse char ($529m^2/g$). This indicates that deposits blocked some of the pores. These assumptions were supported by the properties of the activated carbon produced from the chars. Bagasse char yielded activated carbon with a considerably larger surface area (1947

m²/g) than the co-pyrolysis chars (1047–1300 m²/g). The reason for this was explained as follows: During activation the deposit-free pores in the bagasse char allow unhindered access for the steam to the pores. The existing pores are widened and new ones created. In the case of the co-pyrolysed charcoal the deposits first have to be oxidised before activation can occur. However, activation of co-pyrolysis char from 85 % bagasse and 15 % PR yielded an activated carbon with a high surface area (1300 m²/g). The pore size distribution of this activated carbon was comparable to some commercial grades. It was concluded that co-pyrolysis of bagasse and petroleum residue yields oil and char, which can be used as fuel in turbines and as feedstock for the production of activated carbon respectively.

A simple model for the charcoal formed during the pyrolysis of municipal waste was developed using co-pyrolysis of poly(vinylchloride) with cellulose derived materials.[McGee et al. (1995)]. This simple model does give a relatively good indication of the char yield that could be expected from municipal waste. A 10 wt.% plastic / 90 wt.% cellulose mixture yielded the best correlation with two real-life municipal waste compositions. At 900°C the char yields were 24 wt.% for the wood, 10 wt.% for the PVC, Byker MW yielded 30% and the 90%/10% mixture yielded 30 wt.%. The ash content of the Byker MW was 46% and that of the IOW (Isle of Wight) MW was 33 wt %. The reactivity of the MW chars was significantly below those of the PVC and straw. The reactivity of the 90% straw/ 10% plastic and the IOW MW was the same. The reactivaty of the charcoal was less for the pyrolysed mixture than for the pyrolysed wood on its own. This interaction between the straw and PVC also increases the charcoal yield. This could be because of the HCl released by the PVC at temperatures below 600K.

F. Carrasco, Trois-Rivieres and C. Roy (1992) showed that hydrolysis of the biomass took place when dilute acid was added. Hydrolysis of biomass can be caused by acid treatment or by the acetic acid released during water prehydrolysis (autohydrolysis). Autohydrolysis occurs when water hydrolyses the biomass because of liable acetyl groups present in the hemicellulose that are changed into acetic acid. According to **Carrasco et al.** removal of hemicellulose improves the cellulose yields for acid hydrolysis processes. This was attributed to the increased accessibility of the

cellulose, which was caused by the removal of the hemicellulose and the decreased crystallinity of the cellulose.

Arzoumanidis et al. (1995) also showed that wood can scavenge HCl from CH_3Cl when pyrolysed with PVC. This would then also cause interaction between the HCl released during a co-pyrolysis process and the wood being pyrolysed.

The articles by **McGee et al. (1995), Roy et al. (1990), Darmstadt et al. (1999)** and **Darmstadt et al. (2000)** show that a study of waste needs to be done on a co-pyrolysis basis. This is necessary since the individual components of the waste stream interact and can therefore not be seen as merely the sum of the pyrolysis characteristics of the individual components.

The composition of municipal waste streams varies with the seasons and factors such as location and the local industry also play a role. A general waste composition can be estimated from the following tables, which represent waste streams from several different locations.

Table 2. 1 Municipal waste composition [Helt et al., (1988)]

Waste Component	Fraction [%]
Paper	30-50
Glass	8-10
Metals	7-10
Plastics	1-5
Rubber & Leather	1-3
Wood	1-4
Textiles	1-5
Food Wastes	10-20
Yard Waste	5-20
Other	1-4

Table 2. 2 Municipal waste composition [McGee et al. (1995)]

Waste Component	Fraction [%]
Paper	41
Glass	8
Metals	8
Plastics	7
Rubber-Leather	3
Wood	4
Textiles	2
Food Wastes	8
Other	19

According to **Shent et al. (1999)** the plastic fraction of the MSW (municipal solid waste) is 8 wt.% (21% by volume). The total PVC content of the plastic waste stream is roughly 14-15 wt.%, which equals about 1 wt.% of the total waste stream. **McGee et al. (1995)** showed that a 10 wt.% PVC / 90 wt.% cellulose mixture gives a good estimation of the charcoal yield and reactivity when the pyrolysis is done at atmospheric pressure in a nitrogen atmosphere.

A vacuum co-pyrolysis study of different plastics with varying percentages of plant material should also, after thorough characterisation of the plastics and plant material, elucidate many of the unanswered questions regarding the vacuum pyrolysis of municipal wastes.

Chapter 3: Materials and Methods

3.1 Reactor Set-up

Schematics of the reactors used are shown in figure 3.2 and figure 3.3 and figure 3.1 shows a diagram of the reactor control and data logging set up. The first reactor had a volume of 10 L and was heated by an electrical heating jacket. The reactor was used in previous experiments and provided the basis for the new reactor design.

The reactor in figure 3.3 was used for all the results presented in this thesis. It consists of a 1m long, 60mm OD quartz tube, heated by six well insulated, computer controlled heating elements. The computer control, and data logging were done based on the readings of four type K, 3mm diameter thermocouples, two in the sample, one outside the quartz tube, next to the heating elements and one on the SS pipe exiting the reactor. There was also one Schaevitz, type P2104-0002 differential pressure sensor, which had a range of 0-2 bar (see calibration curve in appendix J)
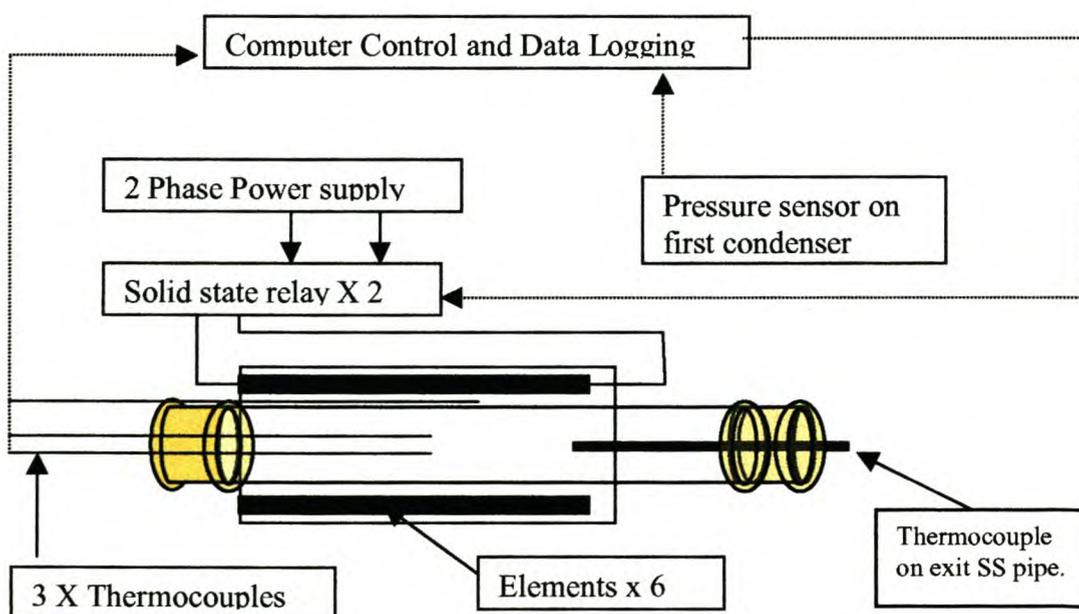
Figure 3. 1 Reactor Control and Data Logging

Figure 3.1 shows the reactor control and data logging set-up. A 486 IBM compatible computer was used with an eagle G70 analogue to digital converting card. The card had eight analogue input and four control channels, of which four input channels and

one output channel were used. The inputs to the card were the two thermocouples in the sample, the thermocouple next to the heating elements and pressure sensor. The control channel gave a 0 V or 10 V output for the control of the solid state relays (SSR). The solid state relays switched the heating elements' power on or off.

The control program was designed to control the heating rate, pyrolysis time and final pyrolysis temperature and to log the temperatures from the four thermocouples and the pressure sensor every ten seconds. Since there were large temperature gradients in the bed during heating, the control program tried to apply a fixed heating rate, using on/off control, up to 15°C below the pyrolysis temperature and then slowly increased the temperature to the pyrolysis temperature. This ensured better temperature uniformity in the bed and less overshoot. The temperature was controlled in a temperature range of about 10°C. More advanced control techniques could have made the bed temperature more constant, but since the bed temperature was taken as an average value between the two thermocouples in the sample, there would have been only a slight increase in accuracy. The readings between the two thermocouples differed by as much as 20-30°C while heating for temperatures below 300°C, but decreased to less than 5°C for the remainder of the heating period. The temperatures were within 2°C-3°C of one another once the pyrolysis temperature was reached.

The experiments were conducted in batch runs with variable pyrolysis times, temperatures and reactor pressures. The pyrolysis temperatures were varied in the temperature range of 300°C to 520 °C, while the reactor pressure ranged from 18 kPa to 50 kPa. The reactor was loaded with samples ranging in weight from 30g-160g. The samples were placed in a cylindrical Pyrex holder, which was then moved into the hot-zone of the reactor. Care was taken to ensure that the whole sample was within the hot-zone. The sample was loaded before heating started after which the reactor was sealed and evacuated to the operating pressure of 18kPa or 50kPa. The stainless steal unions and glass fittings were sealed using silicone grease. Once the operating pressure was reached the programmed heating of the reactor started. A typical run would last between 2 to 3 hours, after which the reactor was allowed to cool for ± 2 hours depending on the pyrolysis temperature employed.

The reactor consisted of a heated chamber connected to a condensation train and a vacuum pump. The pipes leading from the reactor to the condensation train were maintained at 100-120°C to limit condensation before the traps. The vacuum pump removed the organic vapours and gas products from the reactor through the condensation train. The condensable gasses were then condensed in the vacuum traps and recovered as liquid, which were later weighed and analysed. The set-up was allowed to cool under vacuum until the sample temperature reached at least 120°C. The sample holder was then removed and weighed, after which the residue (charcoal) was removed and stored for analysis.

The condensation train in the final set-up consisted of five condensers, the first was held at room temperature, the second and third at -10°C and the last two at -78°C (dry ice temperature). In the first set-up a water-cooled shell-and-tube heat exchanger was also used in the train, but it was found to be more convenient to leave this out of the second reactor. This meant that the condensation started only in the first condenser, limiting losses in the pipes.
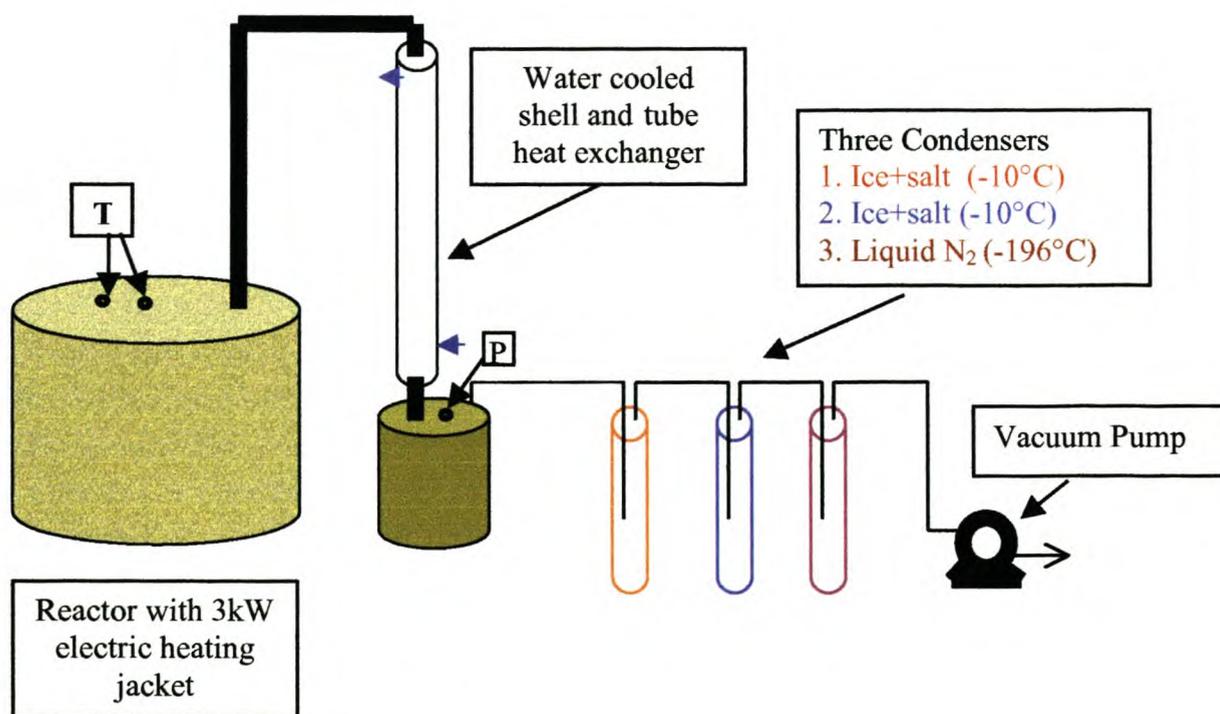
Figure 3. 2 Initial experimental set-up

The first reactor set-up gave problems in that it had air leakage and control problems. This caused a lack of reproducibility in the results and necessitated a redesign. It can also be seen that the second set-up had a different condensation train set-up in that the use of two -78°C traps eliminated the need for liquid nitrogen.

A 16mm stainless steel pipe was installed leading from the brass slide-in cap to the hot zone of the reactor (see figure 3.3). The pipe had a 10mm thick SS disk that slid over it. The disk fitted tightly inside the quartz tube. This ensured that the gasses and vapours would pass through the pipe and not come into contact with the cold walls of the quartz tube outside the hot-zone. The pipe was also heated to 100°C to ensure minimum condensation. The brass fittings were water cooled to ensure that the o-rings did not become too hot. A more detailed engineering drawing of the set-up can be found in appendix K.
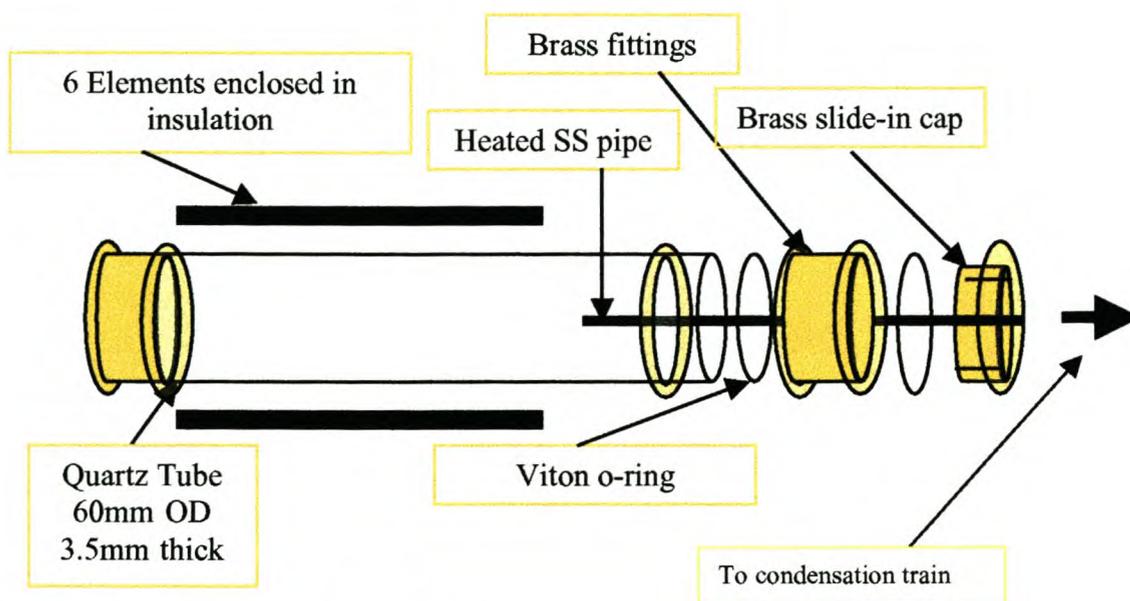
Figure 3. 3 Final experimental set-up

It was found that the final experimental set-up produced results that were accurate to within 2%-3% for the charcoal yields and 4%-5% for the oil yields. The experimental reproducibility is discussed in detail in appendix I.

3.2 Analytical methods

The process produces products in three phases: charcoal, oil and water, and gas. The charcoal, aqueous and tar oil phases were analysed using the following techniques. A more detailed explanation of some of the techniques can be found in appendix C.

3.2.1 Karl Fisher
This is a standard method for the determination of the water content of the aqueous phase. A Metrohm KF Titrino was used for the analysis. The analysis method is explained in appendix C.

3.2.2 Physical Properties and Composition
The physical properties of the charcoal were examined to elucidate some of the trends in the data and also to help with the determination of the economic value of the charcoal.

Ash analysis was done on the samples by heating the samples in air to 600°C and weighing the residue. These were used to form economic estimates of the charcoal value by comparing the samples to commercially sold charcoal.

Volume reduction is a very important indication of the process feasibility if the charcoal cannot be sold because of contaminants. The volume reductions of the samples are calculated as the density of the crushed charcoal compared to the density of the unpyrolysed waste when land filled.

The surface area of the charcoal was determined using the multipoint Brunauer, Emmett and Teller (BET) analysis on a Micrometrics ASAP 2010. This showed whether the charcoal has any potential to be upgraded to activated carbon through steam activation **[Darmstadt et al. (1999)]**. The surface area can also be an indication of reaction pathways, especially when condensation within the reactor is an issue. It can also cast light on some of the processes leading to the changes in yields experienced during co-pyrolysis when compared to the pure samples.

Thermogravimetric analysis (TGA) was also done with a DuPont Instruments 951 Thermogravimetric analyser. It was mostly used to show the differences in feedstock decomposition between aged samples and fresh samples and also to show the changes that occur during co-pyrolysis.

The energy values of the charcoal and oil was determined using a Digital Data Systems CP500 bomb calorimeter. A Ni/Cr wire was used with 0.5g of sample and Benzoic acid as primary standard.

3.2.3   Inorganic Composition

The inorganic composition of some of the charcoal samples was determined to estimate the potential of the charcoal for use as compost or fuel.

The metals in the charcoal samples were analysed using a Liberty Series II radial emission Inductively Coupled Plasma (ICP) spectrometer. The samples were first burned in air for 4 hours at 600°C, to remove the carbon. Afterwards the ash was dissolved in Aqua Regia and diluted with water. With the known ash mass and dilution factor it was possible to quantitatively determine the metal content of the charcoal.

The metal ions were then converted to their metal oxides and the total percentage it represented of the charcoal as a whole was calculated. The sulphur content was determined using a LECO sulphur analyser and was used to classify the grade of the oil and charcoal for fuel purposes.

3.2.4   GC/MS analysis of the oil tar phase

The chemical compounds in the tar oil phase were determined to see if there were any economically valuable chemicals formed.

The tar oil phase was analysed using the method described by **Pakdel et al. (1994)**. This entailed the pre-absorption of the oil onto one gram of Taylor Mesh 80 silica gel. The pre-absorbed oil was then transferred to a 10mm ID glass column filled with 15 grams of silica gel. The column was then sequentially eluted with 150ml of 8 increasingly polar eluants.

The eluants were:

1. Petroleum ether

2. 75% Petroleum Ether + 25% Dichloromethane

3. 50% Petroleum Ether + 50% Dichloromethane

4. 25% Petroleum Ether + 75% Dichloromethane

5. Dichloromethane

6. Ethyl Acetate

7. Methanol

8. 10% Formic acid +90% Methanol

The fractions were then concentrated using a rotary evaporator under decreased pressure. The samples were concentrated until dry and then weighed. The dry samples were then dissolved in 2 ml of the eluate and analysed on a Hewlett Packard G1800A GCD system. A BP1-PONA (100% Dimethyl Polysiloxane, 0.15mm (ID), 0.5 µm (Film), 50 m(length)) column was used. The GC column was heated from 50°C at 10°C/min up to 250°C and kept at 250°C for 15-25 minutes.

Only the first 7 samples were analysed using the GC/MS. The eighth sample was not analysed due to its high polarity and the formic acid which might have damaged the column. Quantitative GC/MS results were obtained by using benzonitrile as internal standard. Since there is such a staggering array of chemicals present in the oil samples only a few response factors for the main chemicals were determined. By using the benzonitrile internal standard it was also possible to do quantitative comparisons between the different samples, even though their response factors where unknown. Benzonitrile was chosen as internal standard because it had a GC retention time which placed it roughly in the middle of the important compounds. It also mixed easily with the solvents and it was not found in any of the oils.

Although most of the main compounds should have been identified by the GC/MS analysis of the oil, there can still be other important compounds that were not identified because of certain factors, such as the GC/MS column and GC/MS detectors used. Some compounds would not easily have passed through the column and the detectors might not easily identify others. Another factor is the time the

detectors are switched off for the solvent peak. The very low concentration of some of the compounds necessitated large sample injections (in the order of 0.8µg), which in turn necessitated long times during which the detector was switched off. Any compound that would have passed through the column in that time would not have been detected.

Chapter 4: Intruder Plant Species

4.1 Introduction

In this study the economic viability of intruder plant species control through the use of vacuum pyrolysis was examined. Three plant species that cause grazing problems in the dryer parts of the country were chosen. These were Kraalbos (*Galenia africane*), Asbos (*Psilocaolon absimile*) and Scholtzbos (*Pteronia pallens*).

Finding an economically attractive method of intruder plant species control would provide the farmers and authorities with an incentive to clear these plants and not only help the environment and increase the potential for grazing, but also make direct profit on their investment.

Even though only three species were studied here, the trends and implications of the study will show the possible advantages for any vegetation-clearing project.

4.2 Vacuum pyrolysis of lignocellulosic materials

Firstly it must be explained that the vacuum pyrolysis of wood is a thermochemical conversion technology; it involves rapid cracking of the complex polymeric structures of the lignocellulosic materials and produces high yields of complex primary oil, rich in oxygen, together with a good quality wood charcoal as by-product. Non-condensable gases and a large percentage of water, depending on the raw material, are also produced as by-products.**[Pakdel et al. (1994)]**

Lignocellulosic materials mainly consist of cellulose, hemicelluloses, lignin, extractives and ash. The relative amounts of these components differ from hardwood to softwood species and from plant to plant. The differences between hardwood and softwood species are much more pronounced than the differences within each category, with the differences within the categories being mainly related to the extractive chemical composition and the ash content. The experiments were conducted on softwood intruder plant species. Mature plants, with their roots attached,

were harvested and then put through a hammer mill. The plants were then stored indoors while the experiments were conducted.
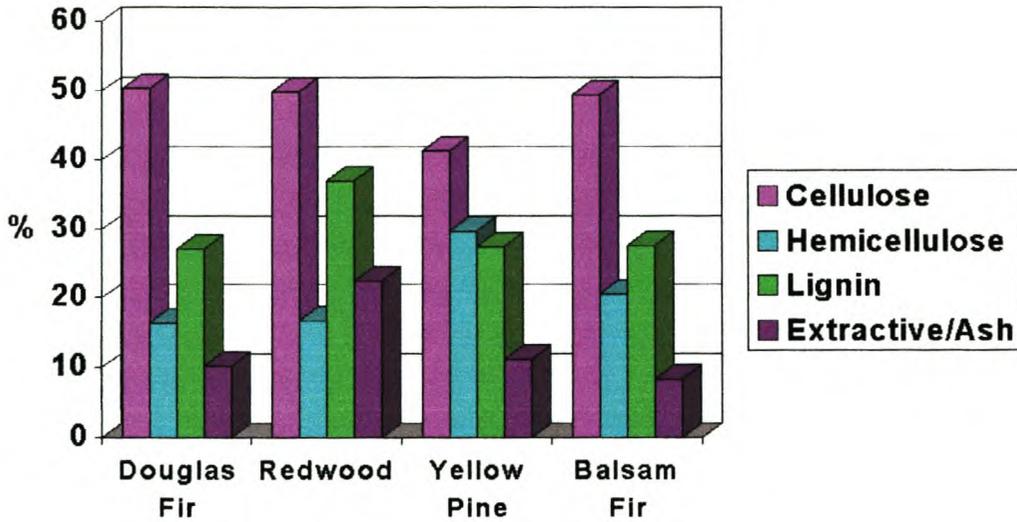
Figure 4. 1: Average Softwood Compositions for a few different trees [Northey (1999)]

In wood, cellulose is part of a fibre reinforced composite in which long cellulose chain molecules organised in thin fibrils constitute the plant reticulum material, held together and protected by hydrophobic lignin acting as binder and encasement.
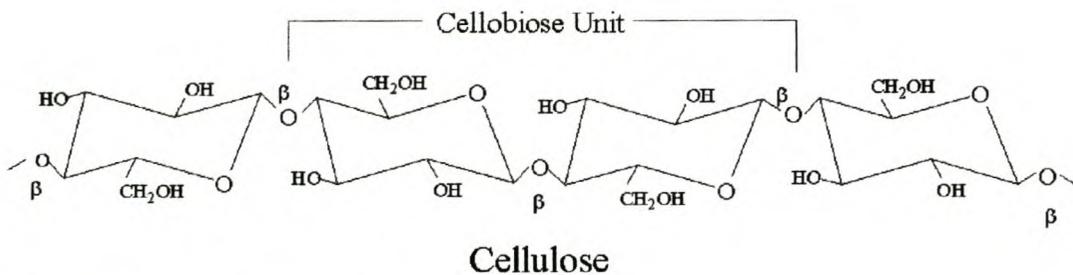
Figure 4. 2: Cellulose Structure [Northey, (1998)]

Cellulose is an isotactic β-1,4-polyacetal of cellobiose (4-O-β-D-glucopyranosyl-d-glucose). The base unit, cellobiose, consists of two glucose molecules. For this reason cellulose can be considered a (syndiotactic) polyacetal of glucose. The elemental composition of cellulose are 44.4% C, 6.2% H and 49.4% O **[Elvers B., S. Hawkin, G. Schulz (1991)]**.

The other important components of wood are hemicelluloses and lignin. Lignin is a phenolic polymer; it is the glue that holds the fibres together. Hemicellulose and lignin consist of several different chemicals.

Hexoses

β-D-Galactopyranose   β-D-Glucopyranose   β-D-Mannopyranose

Pentoses

α-L-Arabinopyranose   β-D-Xylopyranose   α-L-Arabinofuranose
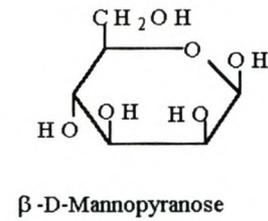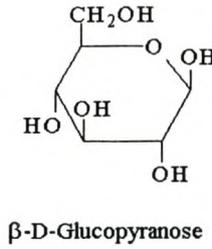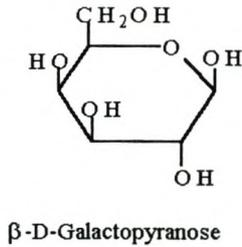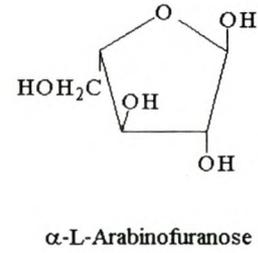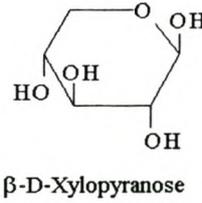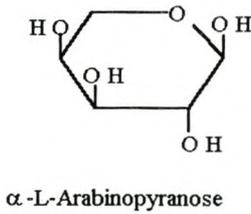
Figure 4. 3 Chemical components of Hemicellulose [Northey, (1998)]

Lignin Source	Grass	Softwood	Hardwood
ρ-Coumaryl Alcohol (No Methoxyl)	10-25%	0.5-3.5%	Trace
Coniferyl Alcohol (1 methoxyl)	25-50%	90-95%	25-50%
Sinapyl Alcohol (2 Methoxyls)	25-50%	0-1%	50-75%

Figure 4. 4 Lignin components [Northey, (1998)]

The chemicals that are liberated during the vacuum pyrolysis process are removed from the reactor by a vacuum pump. This minimises recondensation reactions and the time the compound spends at the elevated temperature. Some of the compounds do undergo fractionation in the reactor and this, combined with the variability of the compounds that can be liberated from the main lignocellulosic structure, causes a staggering array of chemicals to be formed during the pyrolysis process. A small fraction of the compounds may be removed without modification, as will be seen later when the chemical composition of the oil tar fraction is discussed.

The main economic factor in the simplest vacuum pyrolysis process is the charcoal yield and ash content. The higher the total energy value and the lower the ash content, the higher the value of the charcoal. In the simplest process the oil and non-condensable gasses will be used as a make-up energy source for the process, whereas with a more integrated approach where the oil is either upgraded to a fuel or separated into high value chemicals, the economics of the process could be greatly improved.

4.3 Background

The most important aspects of chapter 2 are summarised in this section to give a quick overview of the topic. Previous work done on plant vacuum pyrolysis focused mostly on wood mill wastes. These are mostly hardwood shavings and bark **[Pakdel et al. (1994), Roy et al. (1988)]**, and would therefore produce significantly different yields of charcoal and oils.

In the paper by **Roy et al. (1988)**, a study was made of the processing of wood chips in a semi-continuous multiple-hearth vacuum pyrolysis reactor. The objectives of the study were to determine engineering data and to test the configuration and operation of the reactor before scale-up could be attempted. The results of this study led to the design and subsequent performance study of a 30kg/h vacuum pyrolysis process development unit.

Roy et al. (1992) discussed the conceptual design and evaluation of a biomass vacuum pyrolysis plant, and concluded that in the case where the oil and gases are used as makeup heat source, the selling price of the charcoal would determine the cost

effectiveness of the plant. Based on batch reactions where the batch reactor was dipped in a molten lead bath, it was determined that for a bed thickness of 70mm, a contact time of 45 minutes would be required. Roy also showed that 15kPa would be the most economic pressure at which to operate a vacuum pyrolysis reactor.

Research was also conducted to increase the charcoal and oil yields and also the yields of specific chemicals in the oils. The process parameters that have been studied are the feedstock, temperature, pressure, particle size, heating rate, moisture content, ash content, extractive content and the pyrolysis time **[Roy et al. (1990b), Pakdel et al. (1987) and Pakdel et al. (1997)]**. The variables that were found to have the greatest effect on charcoal and oil production are the feedstock, temperature, pressure and pyrolysis time. These parameters were varied in the present study of the vacuum pyrolysis of intruder plants. Additionally the effects of feedstock ageing on charcoal and oil production have also been studied.

4.4 Results

The experiments were conducted to determine the most profitable operating conditions for the vacuum pyrolysis of intruder plants. From these experimental results it would then be possible to determine the economic feasibility of vacuum pyrolysis as a processing technique.

4.4.1 Effects of Pyrolysis Temperature

The experiments were conducted at temperatures ranging from 350°C to 520°C, with the reactor pressure at 18kPa or 50 kPa. The 50g-100g samples were heated at ±10°C/min and were kept at the pyrolysis temperature for 30, 60 or 120 minutes. A mechanistic representation of wood vacuum pyrolysis can be seen in appendix D, section 2.

Figures 4.5 and 4.6 show the yields of charcoal and oil for the three plant species over the temperature range 350°C to 520°C at 18 kPa reactor pressure, a heating rate of ±10 °C/min and a pyrolysis time of 60 minutes.

Vacuum Pyrolysis of Intruder Plant Species: Charcoal
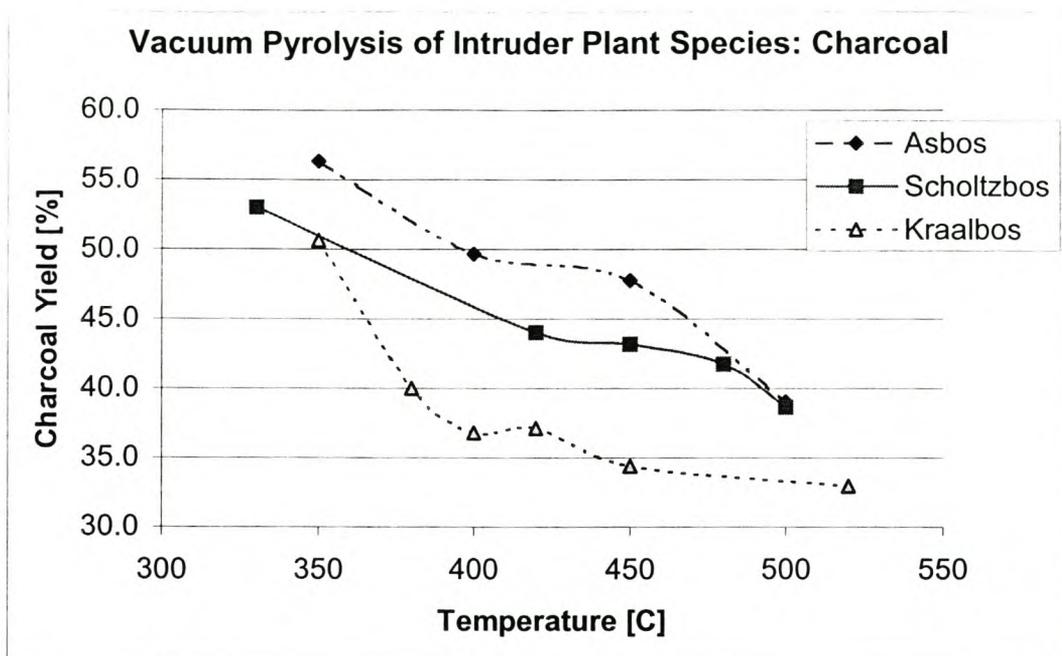
Figure 4. 5 Intruder plant species charcoal   (water free basis)

From figure 4.5 and 4.7 it can be seen that there are significant differences between the plant species in both oil and charcoal yields. The differences in the oil composition will be discussed later in this chapter.
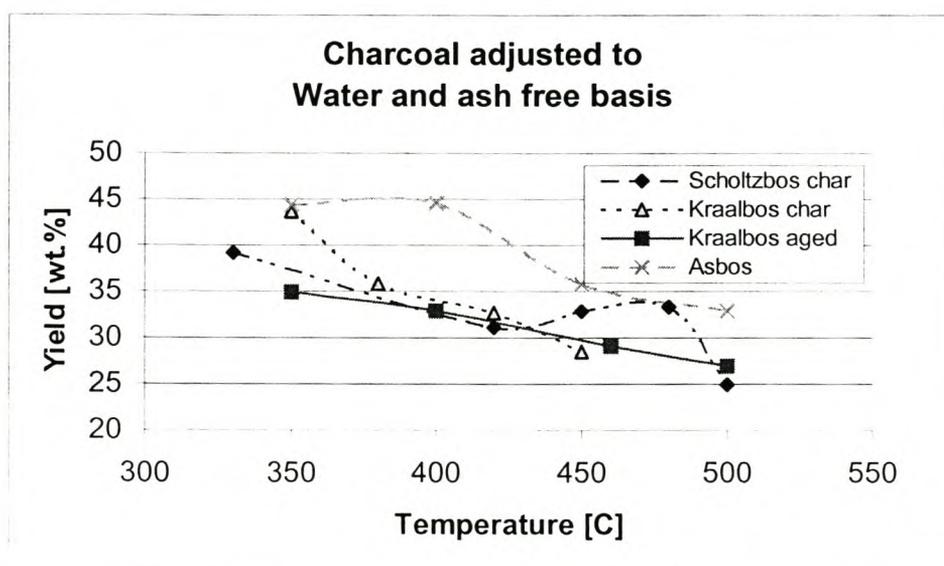
Figure 4. 6 Charcoal yield adjusted to a water and ash free basis for experiments at 18kPa and a pyrolysis time of 60 min.

One of the main reasons for the differences in charcoal yield between the species is the difference in ash content. In the figure 4.6 the charcoal yield values are adjusted to an ash free basis so that the differences in ash contents does not effect the yield.

Figure 4.6 clearly shows how closely related the different plant species are, with the only exception seeming to be the Asbos. It must be noted though that the Asbos sample used for the 350°C experiments had a water content of 50%, while the samples for the 400°C, 450°C and 500°C experiments had a water content of 8%. The fact that the 350°C and 400°C experiments yielded basically the same charcoal yield on an ash and water free basis indicates that some experimental error occurred during the 350°C experiment since it should have a much higher yield (see section 4.4.6). It is possible that air might have leaked into the reactor.

It was assumed that the reason why Kraalbos and Scholtzbos behave in a similar fashion when pyrolysed, was that they have very similar compositions (see figure 4.1). The cellulose, hemicellulose and lignin content of the plants must be almost the same; this is to be expected since they are both softwoods. Since these similar combinations of wood components react similarly to heating in vacuum, the charcoal yields differ only slightly and the differences can be attributed to the differences in the extractives and the slight differences in the basic wood contents from plant to plant.

The large difference in charcoal yield for Asbos would probably be because of its exceedingly high ash content. The Asbos feedstock had an ash content of 19.85%, while that of the Scholtzbos was 8.33% and the Kraalbos 4.92%.

Pakdel et al. (1997) reported the results in table 4.1 for the vacuum pyrolysis of softwood species at ±5 kPa.

Table 4. 1 Yields for the vacuum pyrolysis of softwoods reported by Pakdel et al. (1997)

Feedstock	Pyrolysis temp. [C]	Moisture [wt.%]	Ash [wt.%]	Heating rate [C/min]	Bed Thickness	Char [wt.%]	Liquid [wt.%]	Gas [wt.%]
Softwood sawdust	525	4.8	0	2	20cm	17.3	73.6	9.0
Softwood sawdust	525	5.4	0	10	20cm	16.4	69.9	13.7
Softwood bark	525	6.1	1.9	10	20cm	29.5	57.1	13.4
Softwood wet bark	525	42.4	0.1	10	20cm	17.2	56.8	26.0
Softwood bark powder	525	4.1	3.3	10	20cm	30.9	52.2	16.9

The operating conditions during the experiments by **Pakdel et al. (1997)** were significantly different than those employed during this study and the total liquid yields were reported instead of separate oil and pyrolytic water yields. The first two results are for feedstocks containing no ash and can therefore be compared to the ash free basis results in figure 4.6. Pakdel reported charcoal yields of 17.3% and 16.4% on a water free basis compared to the 25% and 27% of Scholtzbos and aged Kraalbos respectively. The reported values of Pakdel are lower than those reported in this study, but this would have been caused by the fact that a pressure of 2 kPa was applied and that this would have significantly decreased the charcoal yield in comparison to the 18kPa employed in this study. The softwood bark powder had a yield of 30.9%, which also compares favourably to the yield of 33% of the aged Kraalbos. These two values compares so well because the feedstocks had moisture and ash contents that were very close to one another.
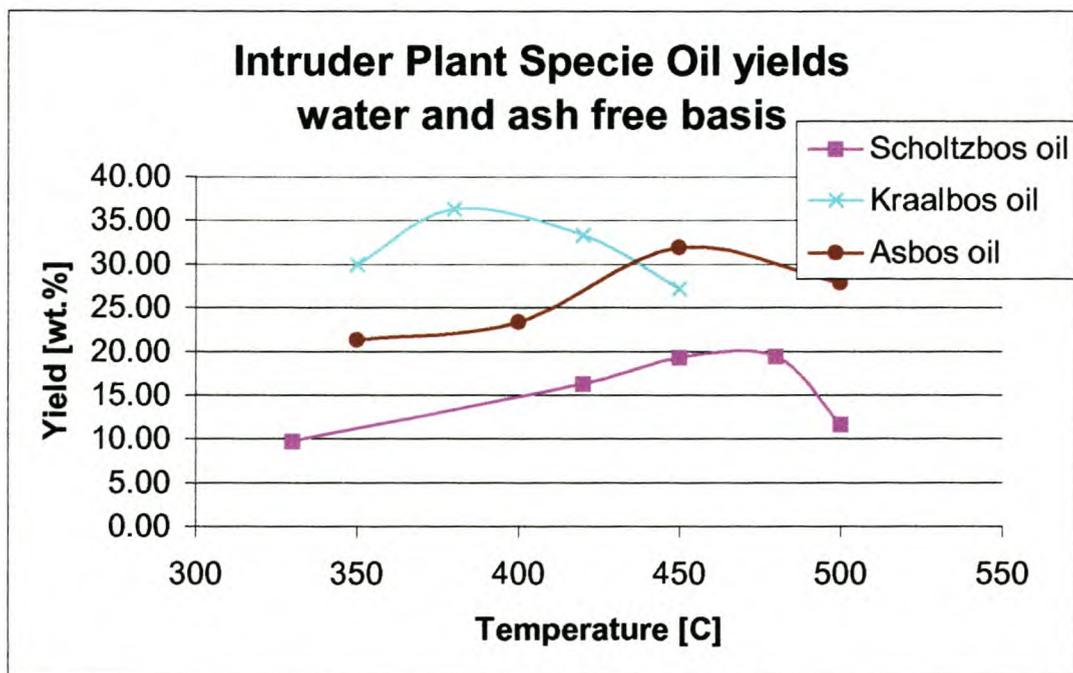
Figure 4. 7 Intruder plant species oil yields (water and oil free basis)

Even though the adjusted charcoal yields are very much the same between the plant species, there are still significant differences in oil yields. It has been shown that the ash and water content of wood have effect on the oil yield and on the composition of the oil for atmospheric pyrolysis **[Gray et al. (1985)]**. This suggests that the differences in ash content may to some extent be responsible. **Gray et al. (1985)** also

52

showed that some ash components catalyse decomposition reactions. This would then cause more shorter chain non-condensable gases to be formed, which would cause lower oil yields.

Even when the oil yields are adjusted so that the ash content has no influence, Kraalbos still has a much higher maximum oil yield than either Scholtzbos or Asbos. This would support the hypothesis that the ash catalysed the decomposition of the wood to form non-condensable gases, instead of condensable longer chain vapours which would contribute to the oil yield.

It is noteworthy that Kraalbos reaches its maximum oil yields at a much lower temperature than Scholtzbos or Asbos. This indicates a difference in the way their wood structure decomposes. **Roy et al. (1990b)** showed that the extractives and even the cellulose fibre orientation affects the oil yield. There could therefore be many reasons for these differences in maximum oil yield temperature. Even so it is interesting that the two plants with the higher ash content need higher temperatures to reach their maximum oil yield temperature.

Figure 4.5 shows that the charcoal yield decreases with increasing temperature. There were initially high weight losses between consecutive pyrolysis temperatures, but at higher temperatures the decrease in charcoal yield slowed down significantly. The high rate of weight loss at the lower temperatures could be attributed to the liberation of the components in wood that are least thermally stable. These would be in order from least stable to most stable: the extractives, hemicellulose and lignin, with the cellulose degrading last of all. Cellulose degrades at temperatures between 250°C and 350°C.

At the lower temperatures more, shorter chain length non-condensable compounds are formed. This occurs because there is less energy available in the system to liberate compounds from the wood structure, and this causes more of the less complicated shorter chain length compounds to be released than the longer chain compounds, since less energy is necessary to release these compounds than would be needed to release the more complicated compounds. The endothermic nature of the pyrolysis

process should also cause less of the structure to be degraded at lower temperatures. The higher yield of short chain length molecules could also be due to the nature of the wood structures, which degrade at the lower temperatures. These structures would consist of less complicated compounds and would therefore also yield compounds of lower complexity and therefore lower boiling points.

At the higher temperatures the compounds of lower complexity would also be degraded, leading to the creation of non-condensable gases, but more of the more complicated structures will also be degraded because of the higher energy in the system. The degradation of the more complex structures would then lead to the higher production of condensable vapours and the subsequent higher oil yield. As the energy in the system increases with increased temperature, more heavy compounds are therefore released, until the maximum oil yield temperature is exceeded. Beyond this temperature, 480°C for Scholtzbos, there is too much energy in the system and more shorter chain length compounds are liberated from the wood structure. At the same time more of the longer chain compounds that have been released, are split into shorter chain compounds, because there is too much energy in the system for the compounds to remain whole during their residence time in the reactor.

The values in figure 4.8 were calculated with the thermodynamic equilibrium program. C_2H_6 was the most complicated compound formed at equilibrium conditions and was therefore used to gain greater understanding of the effect of temperature on the vapours in the reactor. Figure 4.8 shows how the equilibrium yield of C_2H_6 changes with temperature. The C_2H_6 was due to gas phase reactions and not due to the liberation of compounds from the cellulose structure, as is the case for vacuum pyrolysis. It can be seen that higher temperatures lead to more gas phase collisions and a higher mass of elements in the gas phase, which then leads to a higher yield of C_2H_6. At temperatures higher than the maximum yield temperature more C_2H_6 was destroyed than created, and the yield therefore decreased. The maximum yield of C_2H_6 was achieved between 380°C and 420°C, which indicates the temperature where it is most stable. At temperatures above 420°C there is too much energy in the system and it starts to break down again.

Even though the vacuum pyrolysis process does not operate at equilibrium conditions, parallels can be drawn between the influence of temperature on the yield at equilibrium conditions and the influence of temperature on the creation of more light compounds from secondary reactions. Using a thermodynamic program it was possible to predict the solid and gas phase products over the temperature range of 350°C to520°C and at the pressure of 18kPa.

Chemical Equilibrium with Applications (CEA) was the computer program used to determine the equilibrium yields. The program is used to determine equilibrium compositions of complex mixtures with applications in rocket performance, shock, detonation and several other types of problems. It works on the principle of minimising the Gibbs free energy and was developed by Bonnie J. McBride and Sanford Gordon at the Lewis Research Centre for NASA. An example program output file can be seen in appendix H.

The major difference between the programmed conditions and the actual experiments was that the program gave equilibrium yields, while the actual experiment was not operating at equilibrium conditions. Further, the computer program could not simulate the removal of the gases and vapours during the actual experiment. The yields from the program was also for graphite carbon and not for charcoal. The program does, however, give a useful indication of the expected influence of parameters such as temperature, water content and pressure.

The curve (figure 4.8) is an indication of the way in which the gas phase reactions would proceed in the vacuum pyrolysis reactor. Longer residence times of the vapours in the reactor and higher temperatures would cause the products to be closer to the equilibrium yields. The figure shows that the complex compounds liberated during the vacuum pyrolysis process would have been increasingly broken down and would have undergone more side reactions as the temperature increased above the maximum oil yield temperature.
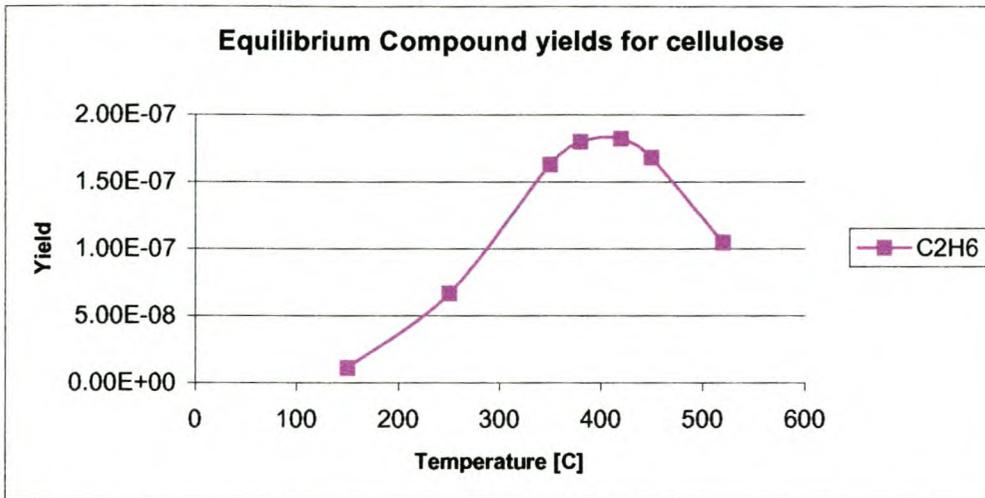
Figure 4. 8 Equilibrium compound yields for the decomposition of cellulose

If compounds are more likely to undergo secondary reactions at higher temperatures, the implication is that if the pressure was decreased, the maximum oil yield temperature would be higher. This would be the case, because more complicated compounds would be able to survive if the residence time of the vapours in the reactor was decreased. It would of course depend on whether more longer chain compounds would be formed in relation to the increase in shorter chain length compound production at the elevated temperature. **Pakdel et al. (1997)** found that lowering the pressure led to higher phenol production.

Figure 4.9(a) illustrates that there are more light compounds formed below and above the maximum oil yield temperature, which in turn causes lower oil yields.

(a)

(b)
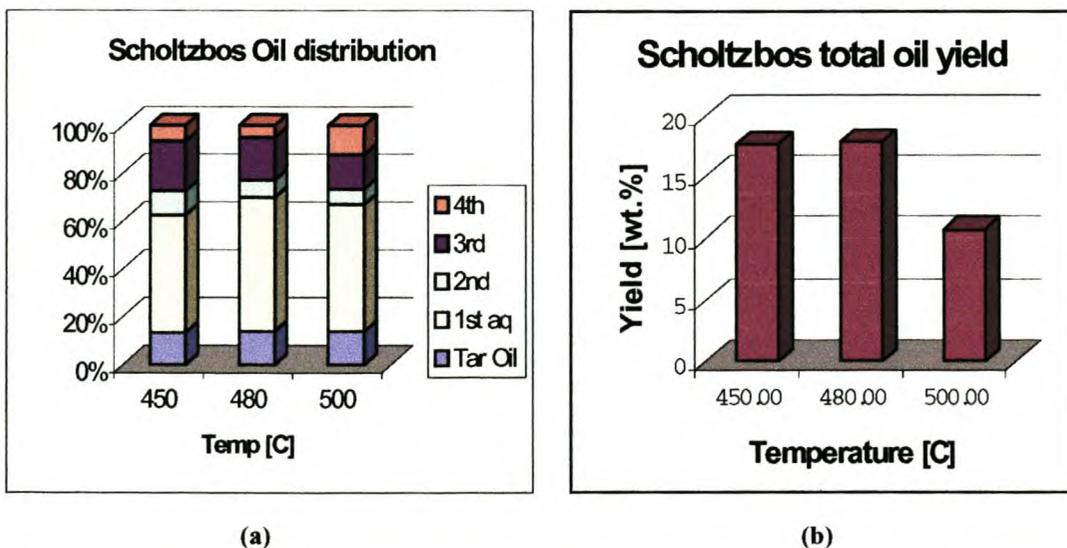
Figure 4. 9 (a) Scholtzbos oil condensation distribution over the four condensers. (b) Scholtzbos total oil yield

Figure 4.9(a) shows the condensation distribution of the condensable oils over the five condensers. The oil fraction was condensed in the room temperature trap, the 1st aq fraction refers to the aqueous phase in the first -10°C condenser, 2nd was the second -10°C trap, with 3rd and 4th referring to the two -78°C condensers. This figure shows the oil condensation distribution over the temperature range of 450°C to 500°C.

Figure 4.9(b) shows the maximum oil yield for Scholtzbos to be at 480°C. Even though the differences seem small there is a higher percentage of light compounds at 450°C and 500°C than at 480°C. It can also be seen that at 500°C there was significantly more condensation in the last condenser, which implies that even more basic compounds and therefore more non-condensable gases were formed. This is consistent with the expected trend of increased energy input above the maximum oil yield temperature, equalling higher yields of progressively less complicated compounds. It must also be noted that the higher the condensation in the last condenser, the more gases will not be condensed at all.

4.4.2   Effect of pyrolysis time

The next parameter investigated was the vacuum pyrolysis time. Samples of each of the intruder plant species were kept at the pyrolysis temperature for 30, 60 and 120 minutes respectively. This will give a good indication of the pyrolysis time that will be required in industry, depending on what charcoal properties are required.

Longer pyrolysis times produce less charcoal and more oil. Longer pyrolysis time also decreases the volatile matter in the charcoal, which has important implications for upgrading to activated carbon. When activating carbon, lower volatile matter content usually results in shorter activation times and higher final surface area.
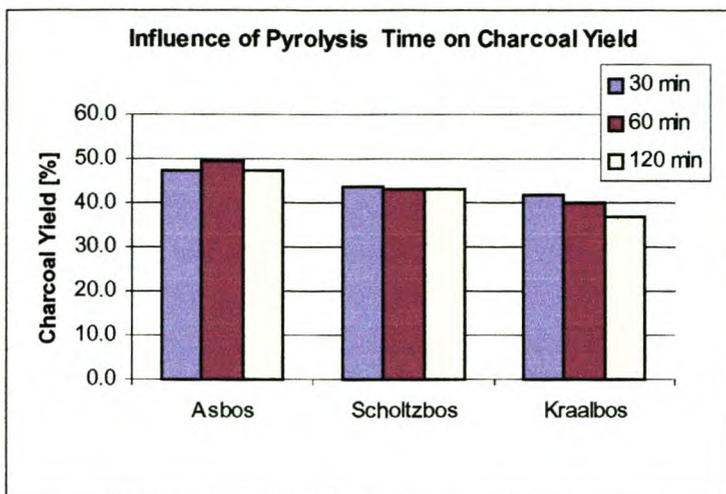
Figure 4. 10 Influence of pyrolysis time on charcoal yield
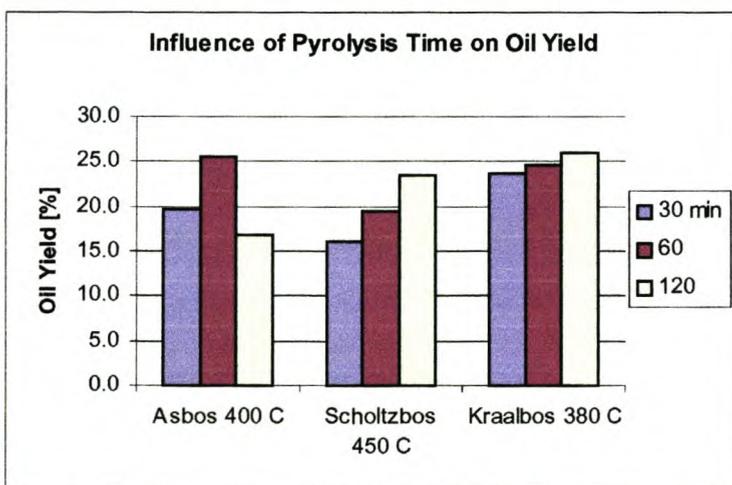
Figure 4. 11 Influence of pyrolysis time on oil yield

The different sets of experiments for the three plants were done at the maximum oil yield temperature of the different plants. The results would therefore show the most economical pyrolysis time that should be used if the oil yield were to be maximised. Figure 4.10 shows the decreased charcoal yield with increased pyrolysis time, and figure 4.11 illustrates how the oil yield increases with increased pyrolysis time. The charcoal yield decreases, as more volatile matter is removed the longer the sample is kept at temperature. This trend will of course level out as the remaining volatile matter is driven off. This is also the reason why the oil yield increases, as the volatile matter condenses and forms more oil.

The lower than expected oil yield for the Asbos in figure 4.11 indicates that the feedstock might have aged in the month between the 60 minute and 120 minute experiments, or that an experimental error occurred.
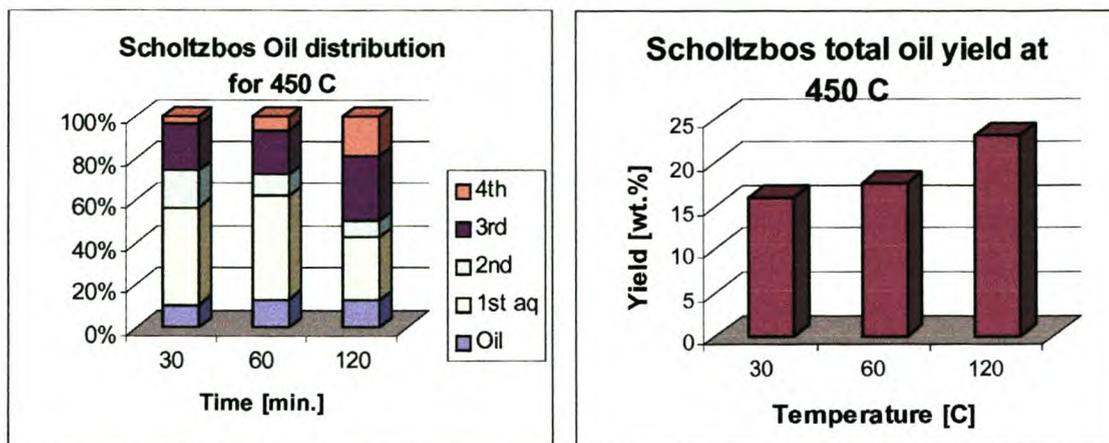
Figure 4. 12 (a) The condensation distribution for Sholtzbos at 450°C for different pyrolysis times. (b) Schotlzbos total oil yield at the different pyrolysis times.

Figure 4.12(a) shows the increase in oil yield as a percentage of the total condensable fraction as the pyrolysis time was increased. It also clearly shows that the portion of the condensable fraction that condenses in the last two condensers also increases with increased pyrolysis time. This indicates the formation of relatively higher yields of light compounds as the pyrolysis time increases.

This is the trend that was expected, since the condensable gases released after long pyrolysis times would be the products from the carbonation of some of the recondensed vapours or vapours that were trapped deep inside the particles. In either case the products would have spent long periods inside the reactor and would therefore have undergone more side reactions, which would cause more shorter chain molecules to be formed.

Figure 4.12 also shows that the oil fraction increased with increasing time, which indicates that the extended pyrolysis time also helps to release some longer chain compounds. These compounds would originate from trapped vapour that was slowly released and/or from further structural degradation of the wood structure.

59

4.4.3 Effects of reactor pressure

Roy et al. (1992) found 15 kPa to be the most economic pressure at which to run a continuous biomass vacuum pyrolysis plant. To test if the reactor pressure has comparable effects on the intruder plant species as it had on the hardwood species tested in the study by Roy et al., the following set of experiments was conducted.

A reactor pressure of 50kPa was used to study the effect reactor pressure has on the charcoal yield. The oil yield could not be studied, as there was too much condensation in the reactor at 50kPa to make the mass measurements meaningful.
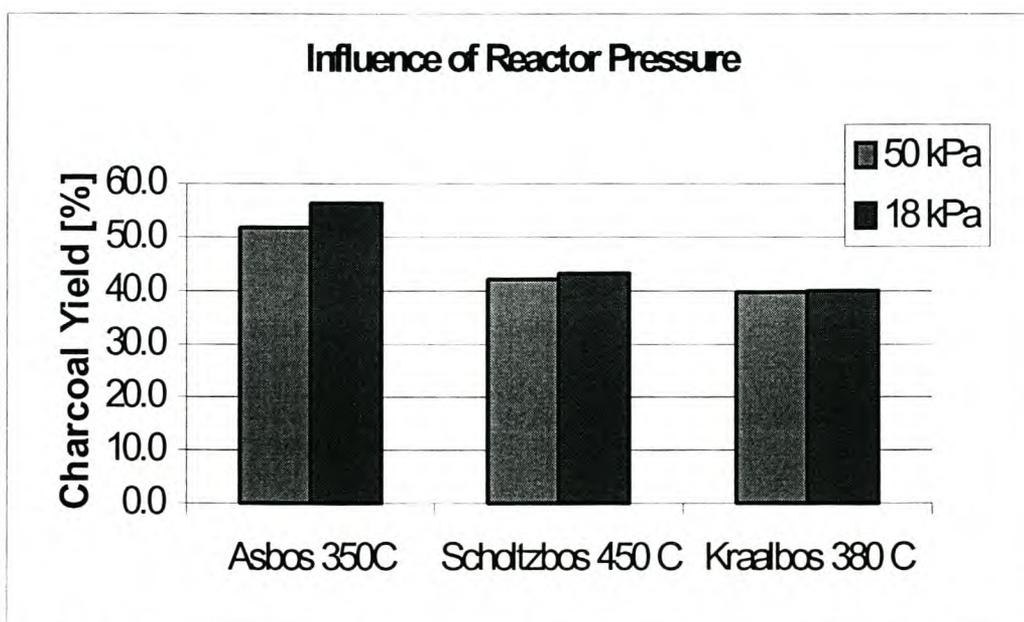
Figure 4. 13 Influence of reactor pressure on charcoal yield for a 60min. pyrolysis time.

Figure 4.13 illustrates the effect of increased reactor pressure on charcoal yield for the three intruder plant species. It can be seen that the 50kPa charcoal yield is consistently lower than the 18kPa charcoal yield. This is a counter intuitive result, since it is commonly accepted that at higher pressures there will be more recondensation reactions which would lead to more of the vapours becoming trapped on the charcoal, thereby increasing the charcoal yield. The condensation of vapours on the surface of the charcoal would lead to carbonation of the oils and subsequent blocking of the pores. This would cause the vapours to become trapped in the wood particles, where they would also be carbonised, adding to the charcoal mass. These reactions would

still occur, but some other mechanism has to have a greater influence, since the charcoal yields are consistently higher for the lower pressure values than for the higher pressure values.

One possible explanation could be that the remaining oxygen in the system was the cause. Since the reactor commences filled with air and is only evacuated at the start of the experiment, it therefore means that the reactor would still be partially filled with oxygen when the pyrolysis temperature is reached. This would cause oxidation reactions that would drastically lower the charcoal yield. There would be more oxygen present at the higher pressure.

Table 4. 2 Theoretical mass loss due to oxygen remaining in the reactor

Pressure	mol O2	Mass loss
18kPa	0.013	0.078g
50kPa	0.043	0.259g

It was assumed that the main reaction would be $C + O_2 \rightarrow CO_2$. There would therefore be a 12g-weight loss in carbon for every 2 moles of oxygen present.

One way to determine whether the yield was due to the oxygen, would be to compare the higher pressure charcoal to the low pressure charcoal to see whether a higher percentage of ash was present, indicating more carbon loss. Since mostly carbon would be lost if the wood reacted with O_2 giving CO_2, the mass percentage decrease should be less than the ash percentage increase. For Asbos there was a 10% decrease in charcoal yield with increased pressure, with a corresponding 33% increase in ash. Since the ash is also an indication of the amount of burnable matter present in the sample, a decrease in burnable matter would increase the amount of ash. It also follows logically that oxygen present in the system at pyrolysis temperatures would decrease the amount of burnable matter by burning some of the burnable matter during pyrolysis. It would therefore seem that the higher oxygen content in the reactor for the 50 kPa experiments is at least partly responsible for the lower charcoal yield when compared to the 18 kPa experiments.

Table 4. 3 Comparison of the charcoal yields for high and low pressures, with the charcoal yields adjusted to the values it would have been if there had not been any oxygen in the reactor.

Sample	Pressure	Char yield	% Difference	Adjusted Char yield	% Difference
Asbos	18kPa	56.3		56.7	
	50Kpa	51.8	8.87	52.4	8.04
Sholtzbos	18kPa	44.0		44.1	
	50kPa	41.4	6.34	41.8	5.42
Kraalbos	18kPa	38.9		39.1	
	50kPa	39.1	-0.49	39.8	-1.96

From table 4.3 it can be observed that for all the plant species except Kraalbos the difference between the charcoal yields decreased when the mass loss due to oxygen was added to the yield. This indicates that the oxygen content does play a role, but that there must still be other factors involved, since the charcoal yields for the 50kPa experiments are still much lower than the 18kPa experiments. The reason why the effect of the oxygen had a greater influence on the Kraalbos experiments is that less of the sample was used for the experiments, and there was therefore a higher relative amount of oxygen per gram of sample.

Another or parallel effect could be that, as expressed by Le Chatelier's rule, the reaction would be forced in the direction of higher molar gas yield due to the lower pressure. Forcing the reaction to produce more moles of gas would force the reaction to create more short chain molecules. These would increase the final charcoal yield, since fewer carbons and more hydrogen molecules would be released in relation to lower weight compounds. In effect this means that more short chain compounds lead to lower weight losses than would have been the case if fewer moles of long chain molecules were released, as would theoretically be the case for higher pressures. The higher oil yields for lower pressure experiments would occur because the longer chains can survive the shorter residence time, while the long chain molecules under-go side reaction because of the longer residence times for the high pressure experiments.

The thermodynamic equilibrium program was used to determine whether the theory regarding Le Chatelier's rule could be true. The results in figure 4.14 indicate that for temperatures below 460°C the 15 kPa graphite yield was lower than the 55 kPa yields. The change in the trend for temperatures higher than 460°C was probably due to the

very sudden increase in CO formation experienced during the low pressure run. By using the yields at the thermodynamic equilibrium, the effects of the changing vapour residence times are negated by basically changing the residence times for both to infinity. This then allows the true effects of the reactor pressure to be observed.
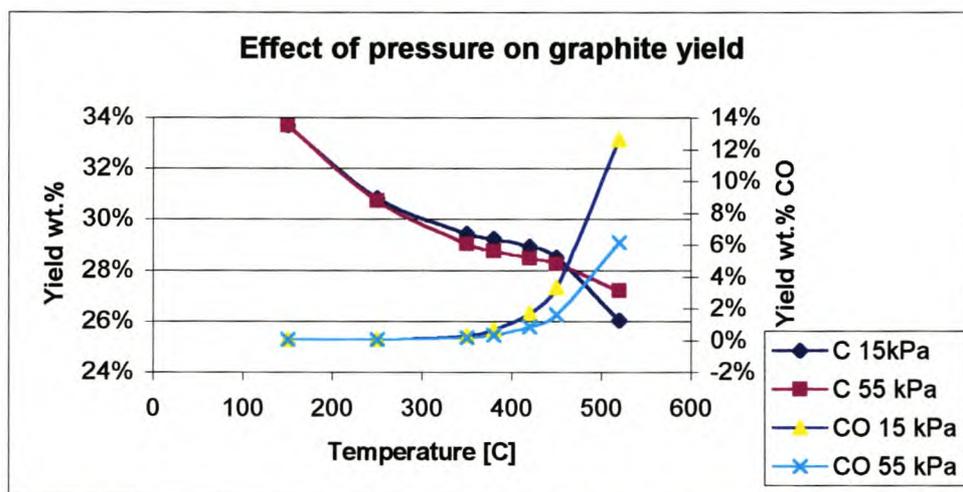
Figure 4. 14 Effect of pressure on the equilibrium graphite and CO yields

The higher graphite yield for the 15 kPa run supports the theory that the lower pressure promotes the creation of less complex molecules, which in turn leads to less weight loss. Figure 4.15 shows that the formation of CO_2 was enhanced at the lower pressure, and even though it was the most abundant compound, the graphite yield for the lower pressure was still higher. Since CO_2 contains a carbon atom and was the most abundant compound, it would be the compound that would have decreased the graphite yield the most. This shows that the preferential formation of the less complex compounds at the lower pressure had a pronounced influence on the graphite yield, because it was still the highest even though the CO_2 formation was higher.

From the equilibrium yields in figure 4.15 and figure 4.16 it can be seen that H_2 was promoted as the less complex product, while the CH_4 and C_2H_6 (most complex organic compounds formed) yields were suppressed at lower pressures. The higher production of H_2 in the lower pressure run would have caused less carbon containing compounds to form, and would therefore have aided in causing the higher graphite yield.
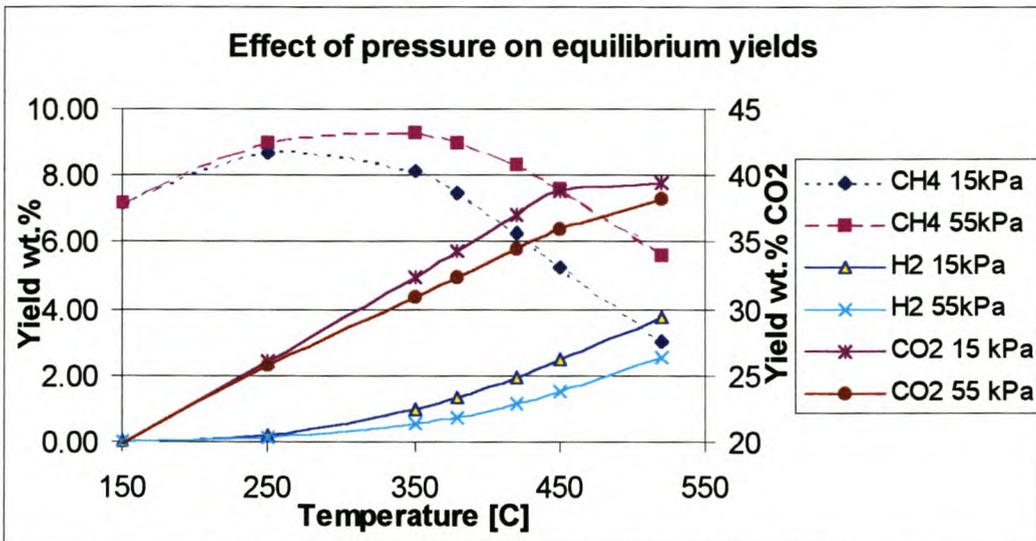
Figure 4. 15 Effect of pressure on the equilibrium yields of H_2, CO_2 and CH_4
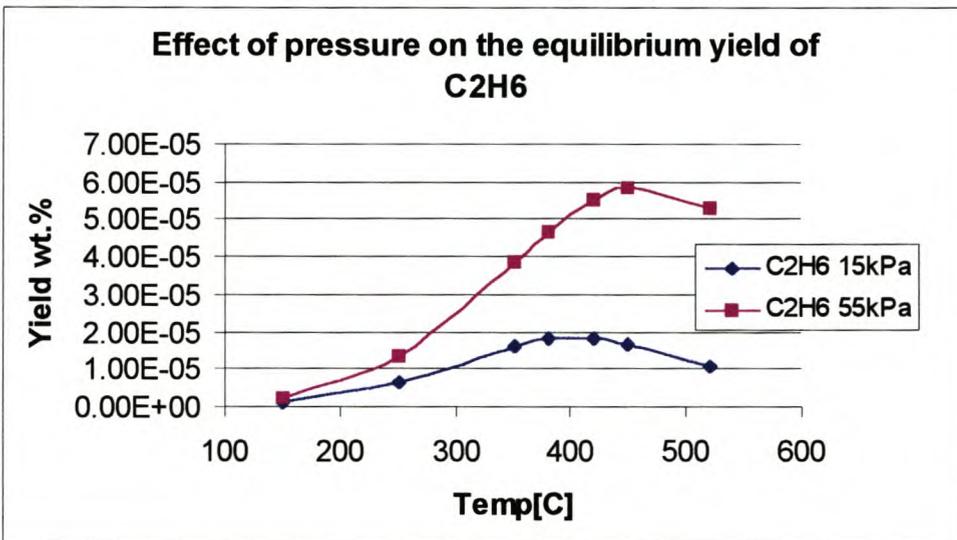
Figure 4. 16 Effect of pressure on the equilibrium yield of C_2H_6

Even though the yield of C_2H_6 was very low it was still important, as it was the most complex compound formed under equilibrium conditions. The effect of the pressure also appears to be more pronounced in the more complex compounds, with the C_2H_6 maximum yield increasing by more than 420%, while the CH_4 increased by only 96%. This also appears to support the theory that the higher pressure would favour the formation of higher complexity compounds more than less complex compounds.

From the analysis of the products formed from the equilibrium reactions, it appears that the favoured formation of less complex compounds did contribute to the higher charcoal yields of the plant charcoals.

64

4.4.4 Physical characteristics of the vacuum pyrolysis charcoal

One of the main factors influencing the selling price of the charcoal and therefor the economics of the process, is the charcoal's ash content. Charcoal is classified according to the energy value, ash, heavy metal and other contaminant content. Figure 4.17 shows the ash content of the intruder plant species charcoal at different vacuum pyrolysis temperatures when pyrolysed at 18kPa for 60 minutes.
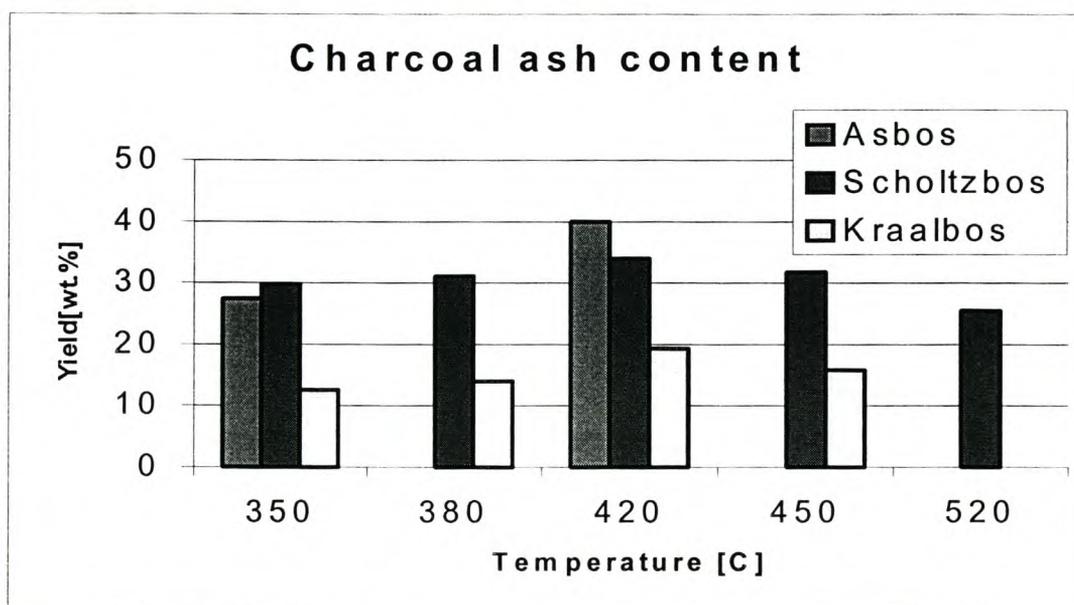
Figure 4. 17 Ash content of the intruder plant species charcoal at various vacuum pyrolysis temperatures

The ash content of some of the plant charcoals compare favourably with the 10%-17% ash content of charcoal that can be bought for home cooking fires. A more thorough investigation of the effect of ash on the process economics can be found in chapter 8.
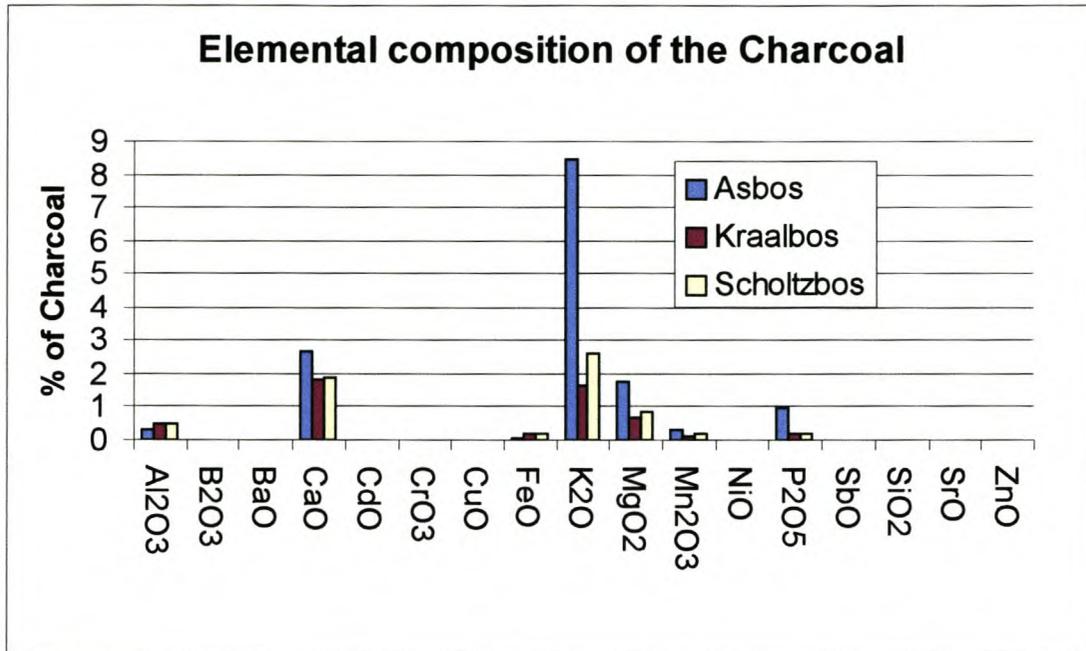
Figure 4. 18 Elemental composition of intruder specie charcoal

Figure 4.18 shows the elemental composition of the plant charcoal. The elemental composition was determined by the method described in chapter 3. The elements shown here are given as quantitative values, but only about 60% of the total ash elements were identified. One of the main elements not shown here is Silicon. Silicon does not easily dissolve in Aqua Regia and could therefore not be properly analysed.

From figure 4.18 it was observed that K, Ca, Mg and P were the main elements found in the plant specie charcoal. None of the elements poses a problem for the usage of the charcoal as a fuel.

Table 4. 4 BET surface areas of the vacuum pyrolysis charcoals

BET surface analyses		
Sample	Temperature [°C]	Area m^2/g
Asbos	450	2.4
	500	
Scholtzbos	450	5.5
	500	6.8
Kraalbos	450	12.4
	500	5.36

The BET surface analysis shows that the charcoals have very low surface areas. Typical surface areas of up to $400m^2/g$ have been reported by **Darmstadt et al.**

66

(2000). The reason for the low surface areas was the high volatile matter contents of the samples. The volatile matter content was so high that great difficulty was experienced during the degassing process that formed part of the analysis.

The reason for these charcoals having such low surface areas is that the pyrolysis temperature was too low. This left too much volatile matter still trapped in the pores, preventing access to the pore structure. It also indicates that the temperature was too low for proper pore formation to start. These factors all led to low surface areas. Higher pyrolysis temperatures would be necessary if the charcoal were to be upgraded to activated carbon.

The energy values of the feedstock, commercial products, charcoal and oil were determined.

Table 4. 5 Feedstock and commercial product energy values

Sample	MJ/kg
Kraalbos	16.3
Scholtzbos	16.8
Ethosha brickets	20.4
Etosha charcoal	27.6
Charca brickets	24.9

Table 4. 6 Energy values of the vacuum pyrolysis products

Sample	Pyro time [min]	Pressure [kPa]	Pyro temp [C]	Charcoal MJ/kg	Oil MJ/kg
Scholtzbos	60	18	450	19.5	26.9
Asbos	60	18	450	12.9	-
Kraalbos					
Fresh	60	18	380	24.3	21.6
	60	18	420	25.0	21.6
	60	18	450	25.0	21.8
	30	18	380	23.0	24.8
	120	18	380	23.9	-
	60	50	380	25.5	-
Kraalbos					
aged	120	18	380	25.8	-
	60	18	500	24.8	24.0

It can be seen that energy values of the charcoal and oil were significantly higher than the feedstock energy values, with the exception of Asbos, which had a lower energy value. Asbos had a low energy value because it had such a high ash content. The pyrolysis conditions and pyrolysis time do not seem to influence the energy value of the charcoal or oil to such a great extent. This implies that the process can be operated at relatively mild temperatures and higher pressures without unduly influencing the products value. The volatile content of the charcoal might however be an important factor depending on the application it will be used for. The energy values of the charcoal (see tables 4.5 and 4.6) compares favourably with those of the commercial products and should therefore have comparable economic value.

It was determined that the initial feedstock air dry water contents were 8.6% for Asbos and 7.27% and 6.56% for Kraalbos and Scholtzbos respectively.

The sulphur analysis also showed that the plant charcoals had sulphur content below 0.3%. (See appendix G)

4.4.5   Effects of feedstock ageing

The last variable to be investigated was the effect of feedstock ageing on the charcoal and oil yields. The second set of experiments was done six months after the initial set, and the feedstock (Kraalbos) was kept in the same bag, indoors, the whole time.

During this time, biological respiration of living cells, chemical reactions, and attack by micro-organisms degraded the wood. The extent of the wood degradation depends on many factors, the most important being the duration of storage, the storage conditions, the climate and type of wood **[Elvers et al. (1991)]**.

In the storage of very fresh wood the respiration of nutrients still present in the wood continues, which generates heat. After this increase in temperature, fungi and bacteria attack the wood. Apart from microbial oxidation, chemical auto-oxidative and hydrolytic degradation also occur. In auto-oxidation the wood components react with atmospheric oxygen and frequently forms organic acids. Substances which primarily undergo auto-oxidation are the wood extractives, especially unsaturated fatty acids,

resin acids, and terpenes. The hydrolysis of carbohydrates releases acetic acid from the hemicelluloses, which causes further hydrolysis.

Fungi and bacteria have the most destructive effects on the wood. Most of the micro-organisms that destroy wood have an optimum temperature of between 25°C and 50°C, with the most damaging having an optimum temperature of 30°C. The optimal moisture content for attack is 24-32%. Since fungi do not attack very moist wood, it is advantageous to store wood in a saturated state.

Degradation is accompanied by the loss of strength of the wood and individual wood components. Discoloration of the wood may also occur. As a rule of thumb a wood loss of 1% per month of storage can be expected. Microbial attack not only results in the loss of wood substance, but also in the reduction of the degree of polymerisation of the cellulose **[Elvers et al. (1991)]**. Brown rot causes the cellulose and hemicellulose to be degraded by organic attack, but the lignin is left unchanged. When white rot occurs, all the structures are degraded and a white residue can be seen. Here brown rot most likely occurred, which changed the wood's colour to brown and shrunk it. **[Elvers et al. (1991)]**

In the article by **Lynd et al. (1999)** it was said that biological attack dissolved the hemicellulose from the wood structure, leading to pore formation and overall better access to the cellulose structure.

It was found that the feedstock moisture content increased from 4% to 9% during storage. This represents a high increase in moisture content, but a value of 9% is still low and should not unduly decrease the charcoal yield or increase the oil yield (see section 4.4.6).
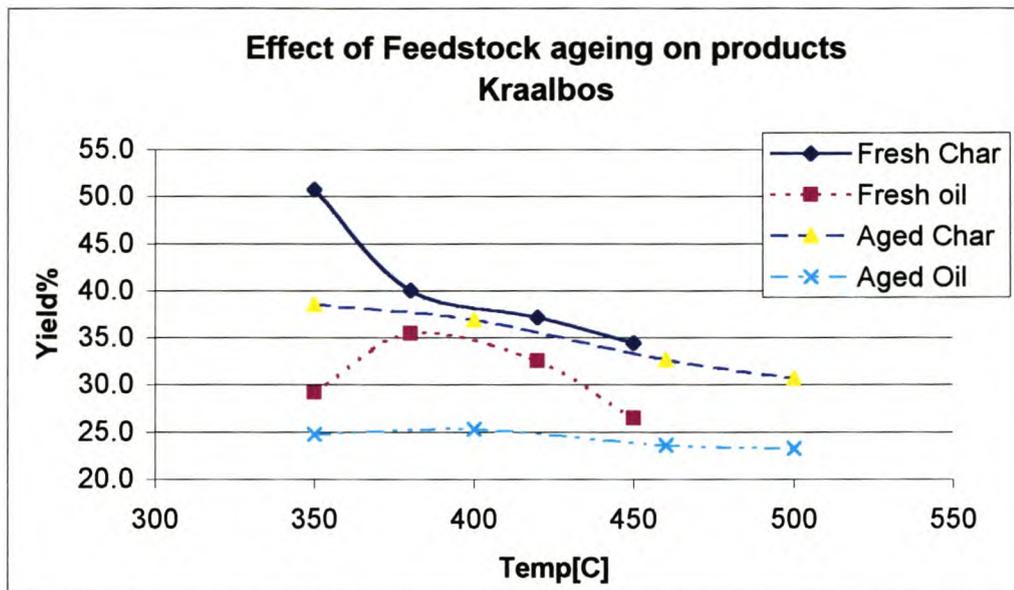
Figure 4. 19 Effect of feedstock ageing on vacuum pyrolysis products

Figure 4.19 shows the difference in charcoal and oil production between the fresh and aged wood samples. There is an initial large difference between the charcoal yields, but above 380°C the difference becomes quite small, but constant. The aged wood oil yields were much lower than the fresh wood yields.

The difference in charcoal yields for 350°C can be explained by the aged wood's releasing of gases and vapours at a lower energy value than the fresh wood. That would imply that the degraded structure of the aged wood facilitated the decomposition of the wood at lower temperatures (see figure 4.21). The difference in the method of decomposition can also be seen when the TGA plots in appendix F are studied. The fresh wood decomposes in two main stages, with the first representing a much higher weight loss. The aged wood decomposes in three stages, with the first stage and last two stages representing roughly equal losses in weight.

Gray et al. (1985) and **Pakdel et al. (1997)** suggested that water decreases wood crystallinity and viscosity at fusion temperature (temperature at which a polymer melt of the thermoplastic cellulose and lignin start to form **[Gray et al. (1985)]**), which in turn requires a lower volatilisation temperature. It is feasible to assume that, since biological attack lowers the degree of polymerisation of the cellulose, it would also decrease the crystallinity and therefore viscosity of the wood, which would have the same effect as suggested by Gray et al. and Pakdel et al. for water. The starting of the

decomposition at lower temperatures, as can be seen in figure 4.22, supports this assumption.

Even though the differences between the charcoal yields are small at temperatures above 380°C, there was still a very definite difference in oil yield. This shows that, even though the mass loss is similar, the way in which the mass was lost has changed. The only way in which basically the same weight can be lost, while the oil yield drops significantly, is if much more of the released products were in the form of short chain non-condensable gases, instead of longer chain vapours that would be condensed as oil.

Comparing figures 4.20 and 4.21 it can be seen that there are significant differences in both the oil composition and also the structure from which the vapours were released.

(a)   (b)
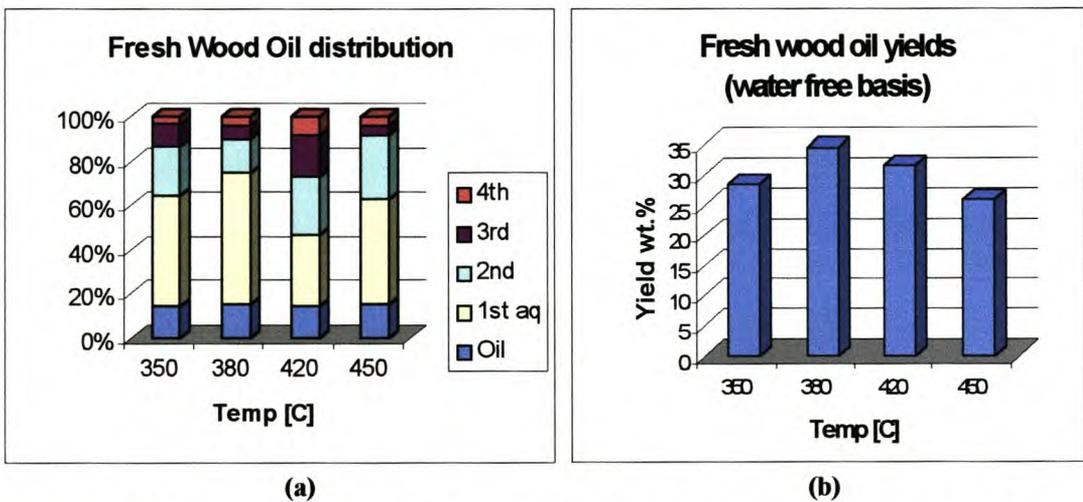
Figure 4. 20 (a) Fresh wood oil condensation distribution.   (b) Fresh wood total oil yields

(a)   (b)
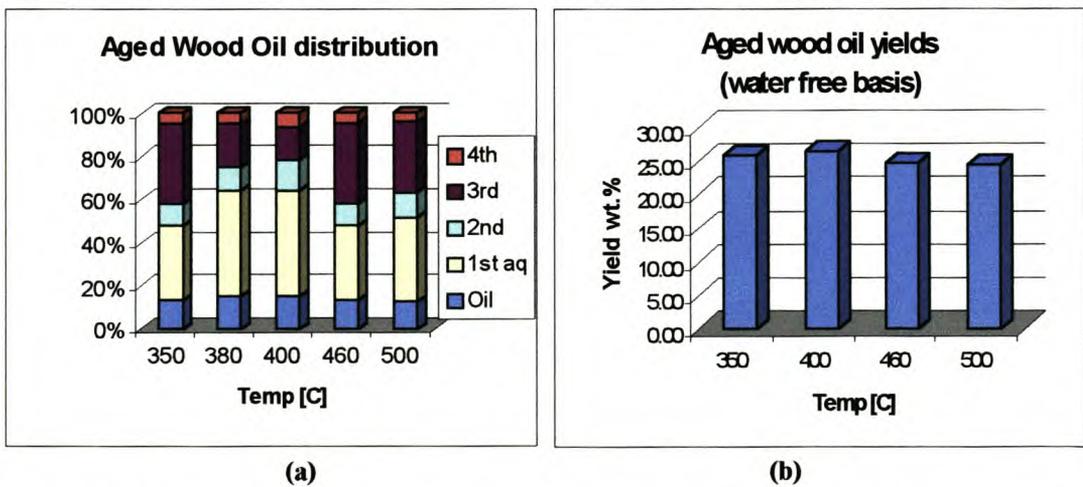
Figure 4. 21 (a) Aged wood oil condensation distribution. (b) Aged wood oil yields

The fresh wood has significantly lower percentages of shorter chain length compounds, this is apparent from the fact that there is much less condensation in the last two condensers for the fresh wood experiments. The temperatures of the vacuum traps (numbers 1 through 4) were explained under figure 4.9.

The nature of the gases is apparent from the vacuum trap it condensed in, as lighter compounds are trapped at lower temperatures and would therefore be trapped in one of the lower temperature vacuum traps. Therefore, if figure 4.20(a) and 4.21(a) show that a larger percentage of the condensable fraction of the evolved gas and vapours condense in condensers 3 and 4, it implies that a higher percentage of the vapours are lighter compounds. The fresh wood also has significantly higher oil yields (see figure 4.19).

The lowering of the degree of polymerisation of the cellulose and the creation of pores by the biological attack on the hemicellulose should lead to higher oil yields, but instead the oil yield decreases drastically. The pores should increase the diffusion rate of the degradation products out of the wood structure, thereby lowering the retention time of the vapours in the reactor. This would then limit side reactions and therefore yield more long chain compounds.

The fact that this is not the case indicates that some other effect dominates in the creation of non-condensable gases over condensable vapours. One reason for this effect could be that due to the ageing of the wood some of the wood components, mainly the extractive, react with the atmosphere. This is what causes the discoloration in wood. The aged wood would therefore have a higher oxygen content than fresh wood. The higher oxygen content would then lead to the formation of more CO_2 and CO, which lowers the charcoal yield and also lowers the oil yield, in that these gases are not condensed as oil.

It could also be that the lowering of the degree of polymerisation of the cellulose structure was not very severe, and that the advantages associated with it in terms of oil production would also be small in comparison to the disadvantages of the higher oxygen content.

The effects of the biological attack on wood can be better understood if they are compared to the effects of the HCl attack on wood during the co-pyrolysis experiments of chapter 7. From chapter 7 it can be seen that the acid treatment of the wood by the release of HCl gas greatly improves the oil yield. It is the same aged wood used in these experiments that was used for the co-pyrolysis experiments in chapter 7. The acid treatment also lowers the degree of polymerisation of the cellulose and it also creates and enlarges pores by dissolving the hemicellulose. The only added effect was that the acid treatment also dissolved the lignin, which caused the wood fibres to become less compact and in so doing increased the diffusion rate of the degradation products. This effect alone, however, should not be enough to enhance the oil yield so significantly if the cellulose and hemicellulose were not also degraded further. From figure 7.4 it can be seen that the degree of polymerisation of the cellulose was further decreased in that the volatilisation temperature was further reduced. A lower volatilisation temperature is an indication of a lower degree of polymerisation. The only effect not present was that of the increased oxygen content, as the same feedstock was used.

All these factors increased the oil yield for the co-pyrolysis experiments. This indicates that the cellulose structure was not degraded to such a great extent by biological attack alone, and also that the pore creation was not so severe as to be of enough benefit to offset the higher oxygen content. It can be seen that the biological attack was not severe, since the acid treatment of the wood could have such a pronounced effect. This would not have been possible if the structure was already mostly degraded. It would therefore seem that the higher oxygen content of the aged wood should be the main cause of the lower oil yield for the aged wood experiments.

It might be possible to increase the oil yield of the aged wood by increasing the heating rate. This would decrease the time at lower temperatures and therefore the short chain compound yield. **Pakdel et al. (1997)** showed that the phenolic yield of wood can be increased if the heating rate was increased.

Less of the light compounds would be formed, as less time would be spent at the lower temperatures where there is not enough energy to liberate complex compounds. Because of the degraded structure of the aged wood, the resulting higher flux of

vapours would find it easier to reach the surface of the particle, thereby making it possible for the longer chain compounds to survive at the elevated temperatures, as the residence times would be short enough.

The oil yield for the aged wood remains almost constant over the whole temperature range. This implies that, as more of the structure was degraded to vapours and gases, the amount of non-condensables had to increase to remove the extra mass from the system without increasing the oil yield.

Another explanation could be that the oil yield remains the same, because the total condensable mass that was liberated from the charcoal was liberated before 350°C, and the rest of the released mass was released as non-condensable gases from then on. This would then imply that the aged wood structure could not yield condensable gases above 350°C. It must be remembered that with a heating rate of 10°C/min one would expect that the temperature would rise above 350°C before the structure could be fully degraded. Therefore the constant oil yield must be due to increased light compound formation. The relation between the mass loss and the increased light compounds would be such that the final yield remains constant. It is logical that there will be a temperature above which no condensable gases can form, but it seems to be above 520°C

The condensable fractions composition in terms of which the gases condensed would then also have to remain constant, as the whole condensation process would stop at that maximum condensation temperature. Since no such trend was evident from figure 4.16, it therefore follows that the maximum temperature for condensable gas production was not reached.

Further insight into the problem could be gained by studying figure 4.22, in which the pressure and temperature versus time are plotted. Firstly it must be noted that the pressure in the reactor for the aged wood ranges from 17.5 to 20 kPa, while the pressure for the fresh wood ranges from 19 to 25. It can therefore be seen that the release of the vapours and gases from the aged wood happens more gradually than in the case of the fresh wood.
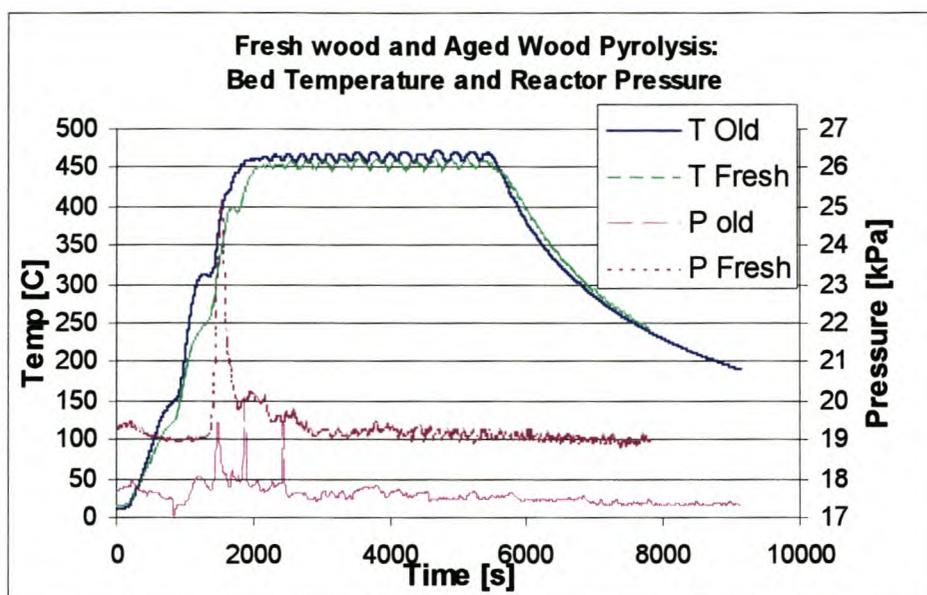
Figure 4. 22 Fresh wood and aged wood vacuum pyrolysis: Bed temperature and Reactor Pressure

The fresh wood shows a sharp rise of 6 kPa in reactor pressure as the temperature reaches 260°C, while the aged wood starts showing a much slighter rise of only 2.5 kPa between 180°C and 450°C. The pressure rise for the fresh wood was a large spike, which lasted 540 seconds and had already disappeared by 400°C, followed by smaller peaks that persisted for another 1100 seconds. The aged wood showed many small spikes, which persisted for 2000 seconds after the initial pressure rise. This indicates a definite change in the way the vapours are released, and therefore the basic structure from which it was released. The more gradual release of the gases would be partly because of the creation of pores through the biological attack. In the case of the aged wood the liberation of gases and vapours started much faster and continued more steadily than can be observed in the case of the fresh wood. In the case of the fresh wood the gases and vapours were liberated abruptly, after which it continued very much like the aged wood.

It appears as if the degradation of the wood structure lowers the energy needed to liberate compounds from the wood. As has been mentioned before, Pakdel et al. (1997) and Gray et al. (1985) suggested that the lowering of the crystallinity and viscosity of wood could lead to the release of the volatiles at lower temperatures.

75

The release of the volatiles at lower temperatures does not have the same positive effect it had on the co-pyrolysis experiments, because the biological attack does not create such a significant amount of pores. This leads to more vapour evolution in the wood structure, but without the same easy access to the particle surface. The result is a slower diffusion rate and therefore the creation of more non-condensable gases as the vapours undergo secondary reactions.

Another factor contributing to the higher production of non-condensables was that the decomposition of the aged wood started at a lower temperature. This would have liberated more, shorter chain molecules, as less energy was available, and with rising reactor temperature the chain length would have increased. This behaviour causes more short chain compounds to be formed, as can be seen in Figure 4.17, and this should be one of the reasons why less oil is formed during vacuum pyrolysis of the aged wood.

In the case of fresh wood a higher energy value has to be reached before decomposition starts. The fresh wood structure resists decomposition up to a higher temperature, at which point there is enough energy present to liberate longer chain compounds, lowering the amount of gases formed and increasing the oil yield. The higher liberation temperature would also have the negative effect that the compounds have a higher likelihood of undergoing secondary reactions, but for these low temperatures the advantages seem to outweigh the disadvantages.

4.4.6   Effects of feedstock moisture content

The effect of the feedstock moisture content is important, because it would dictate the degree of pre-processing needed to get a useful feedstock. Plants usually have moisture contents in the range of 40%-50%, while most of the experiments were done with 10% moisture content feedstock. Higher moisture content feedstock consumes more energy, as the water has to be evaporated first. It also creates more of the unwanted aqueous phase. Industrial vacuum pyrolysis processes usually receive feedstock at 50% moisture and then dry the feedstock to 10% moisture before pyrolysis. **[Roy et al. (1992)]**

From figure 4.6 it can be seen that the aging of the Kraalbos had only a slight decreasing effect on the charcoal yield, so the charcoal yields can be compared, assuming that only the moisture content has changed. The Asbos was also only two months old, compared to the six months of the Kraalbos, when the second set of experiments was done.
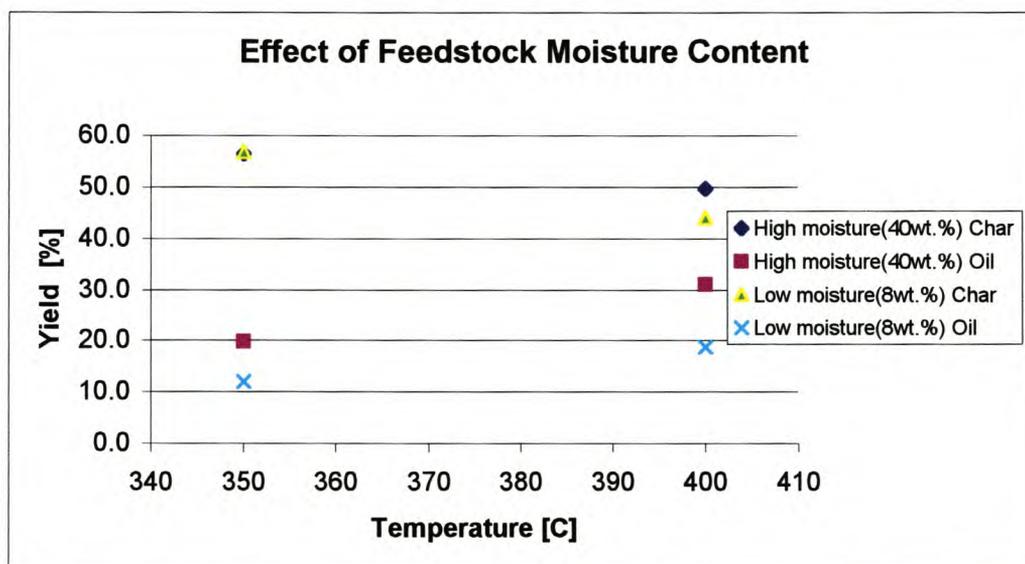
Figure 4. 23 Effect of moisture content on the charcoal and oil yields of Asbos (water free basis).

The 350°C experiment was done at a slightly higher pressure because of changes made to the reactor set-up. This would increase the charcoal yield and decrease the oil yield, but the effect should be minimal, as the pressure was only slightly higher.

Figure 4.23 shows that the high moisture feedstock leads to higher oil and charcoal yields. Although the 350°C charcoal yield appears to be the same for high and low moisture feedstocks, the higher pressure of the low moisture experiment has to be taken into account. This would have increased the charcoal yield, and therefore the low moisture charcoal would have had a lower charcoal yield.

As mentioned before, **Gray et al. (1985)** and **Pakdel et al. (1997)** suggested that water decreased wood crystallinity and viscosity at fusion temperature, which would therefore require a lower volatilisation temperature. **Carrasco et al. (1992)** states that water prehydrolysis (autohydrolysis), which occurs when the water present in the sample hydrolyses the wood at increased temperature, leads to hemicellulose

77

decomposition and the lowering of the degree of crystallinity of the cellulose. The water would also allow the wood to swell, which would permit rapid diffusion of the gases and vapours formed inside the wood particles.

These effects should lower the temperature at which vapours are released and also decrease the vapour residence time inside the reactor. Both these effects should therefore lead to higher oil yields and lower charcoal yields. Figure 4.23 shows that the oil yield did increase as expected. Contrary to what the physical effects of water would have lead us to expect, though, **Gray et al. (1985)** found that for atmospheric pyrolysis reactions the presence of moisture in wood increased the charcoal yield by as much as 5%.

The expected increase in oil yield indicates that the lower volatilisation temperature because of the lowered crystallinity and viscosity did occur. Figure 4.24 also indicates the lower temperature for the start of volatilisation for the high moisture sample. This indicates that another separate factor leads to the increase in charcoal yield.

The vacuum applied to the reactor enhanced this factor. A 5% increase in charcoal was measured for atmospheric pyrolysis, while a 12.9% increase was observed for the 400°C vacuum pyrolysis experiment. This indicates that the vapour and gas evolution, and therefore recondensation reactions, cannot be blamed. If the higher oil and therefore vapour yield (see figure 4.23) was to blame, the effect would be less pronounced for the vacuum pyrolysis experiments. This would be so since vacuum pyrolysis is much more effective at the fast removal of vapours from the reactor than atmospheric pyrolysis, thus leading to fewer recondensation reactions.

This was, however, not the case, since the charcoal yield increase was even more pronounced than for the atmospheric pyrolysis. In the section dealing with the effects of pressure on leather waste vacuum pyrolysis in the following chapter, it was shown that the lowering of the pressure had little effect on the residence time of the vapours inside the particles.

Ruling out recondensation reactions as reason for the higher charcoal yield, indicates that the cause should be sought in structural changes, apart from the lowering in viscosity and volatilisation temperature at fusion temperatures caused by the water.
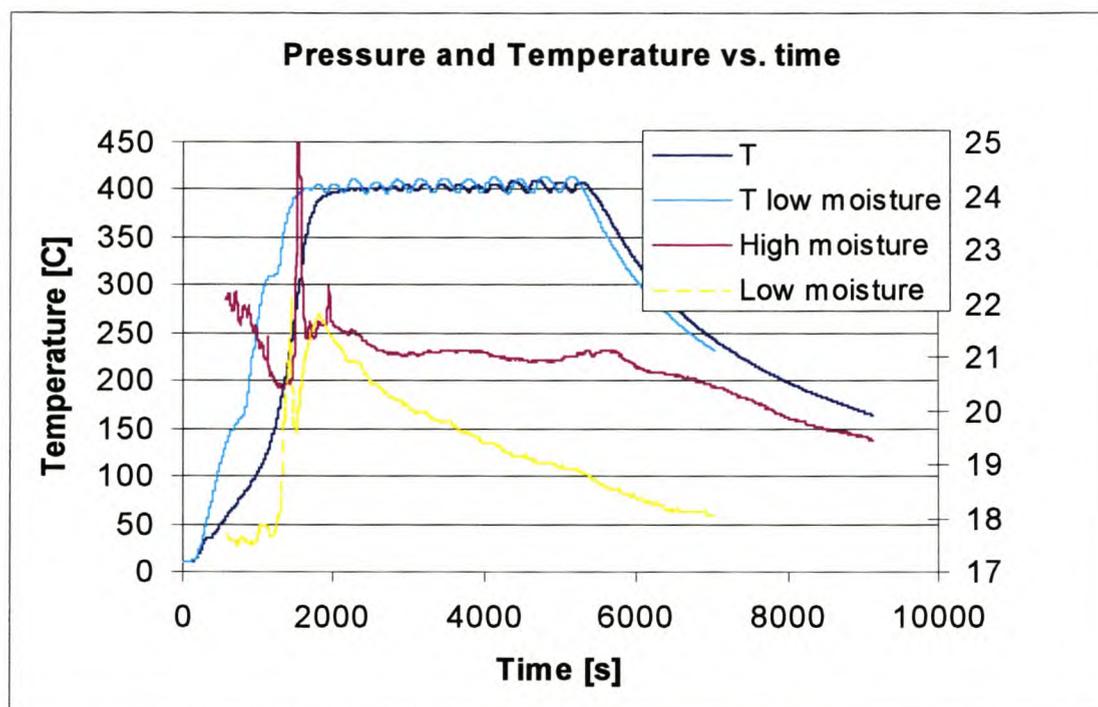
Figure 4. 24 Reactor pressure and temperature versus time for high and low moisture wood.

The pressure versus time plot in figure 4.24 should elucidate some of the structural changes caused by the higher moisture feedstock. From figure 4.24 it can be seen that the low moisture content wood's first gas evolution pressure peak starts 50°C lower than the high moisture peak. Note that the heating rate of the low moisture run was higher than the high moisture run. The first gas evolution peak of the low moisture wood starts at 300°C, while the high moisture peak starts at 250°C. This shows that a lower volatilisation temperature was needed for the high moisture wood, which supports the theory that the crystallinity and viscosity of the wood decreased.

Figure 4.24 shows that the initial gas evolution peaks for the high and low moisture content experiments are both in the range of 4.5kPa, but that the low moisture content experiment had a secondary prominent peak of 2kPa that lasted for at least 2000 seconds. The second peak represents a large mass of liberated vapours and gases,

which indicates that more mass was liberated during the low moisture experiments than during the high moisture experiments.

One way in which less mass could be released from the feedstock, while more oil is formed, would be if more of the released vapours were condensable gases. It appears therefore that the high moisture feedstock releases a higher percentage of its liberated mass in the form of long chain condensable gases. Its lower volatilisation temperature also allows more of the released long chain compounds to exit the reactor before side reactions can occur. This then allows for a higher oil yield, with a corresponding lower loss in charcoal mass. It could also be that some of H_2O present in the sample does not evaporate before the reaction temperature is reached and would therefore react with the biomass. The oxygen atom would cause more of the charcoal mass to be lost to CO_2, while the two hydrogen atoms would react to hydrolyse the biomass. The hydrolysis of the biomass would then lead to the creation of more organic compounds and therefore higher oil yields.

The effect of an increased charcoal yield was enhanced by vacuum pyrolysis, because the higher gas formation for the low moisture feedstock can be removed from the reactor before recondensation reactions occur that would have increased the charcoal yield in the case of atmospheric pyrolysis. The increased charcoal yield would then have decreased the percentage difference between the two charcoal yields to only 5%. This suggests that water changes the wood structure in a way that promotes the stability of the wood during thermal degradation.

Similar changes in wood structure occurred during the vacuum pyrolysis of aged wood, as discussed in section 4.4.5 and for the co-pyrolysis of PVC and wood, as discussed in chapter 7. Although the charcoal yield was lower for the co-pyrolysis and aged wood experiments than for the pure and fresh wood experiment, the lower yield can be explained by the harsher nature of the structural changes of the wood during co-pyrolysis and biological ageing. It was, however, found that at temperatures exceeding 500°C the co-pyrolysed wood was more stable than the pure wood, in that its rate of weight loss was lower than that of the pure wood and therefore it yielded

more charcoal. There are indications that the same could be true for aged wood, but the fresh wood was not pyrolysed at high enough temperatures to test the theory.

The increased charcoal yield at high temperatures indicates that after the initial mass loss the structure becomes more stable than would have been the case for the low moisture or pure wood experiments. The less severe nature of the structural changes allows less of the structure to be lost for the moisture experiments and it therefore has a higher yield than the low moisture wood. The released mass for both the high moisture and co-pyrolysed feedstocks is mostly long chain condensable gases, which in turn results in higher oil yields.

Figure 4.25 shows the results from the thermodynamic computer program used to predict the yields at the thermodynamic equilibrium. Cellulose was used as a simplified feedstock for wood and the ash content was varied depending on the water content to keep the cellulose mass constant. Unlike the actual experimental values, the program predicted that water would lower the carbon yield, the reason being that the program gave equilibrium results that yielded only carbon. The water would lower the carbon yield by oxidising the carbon with the oxygen in its structure.
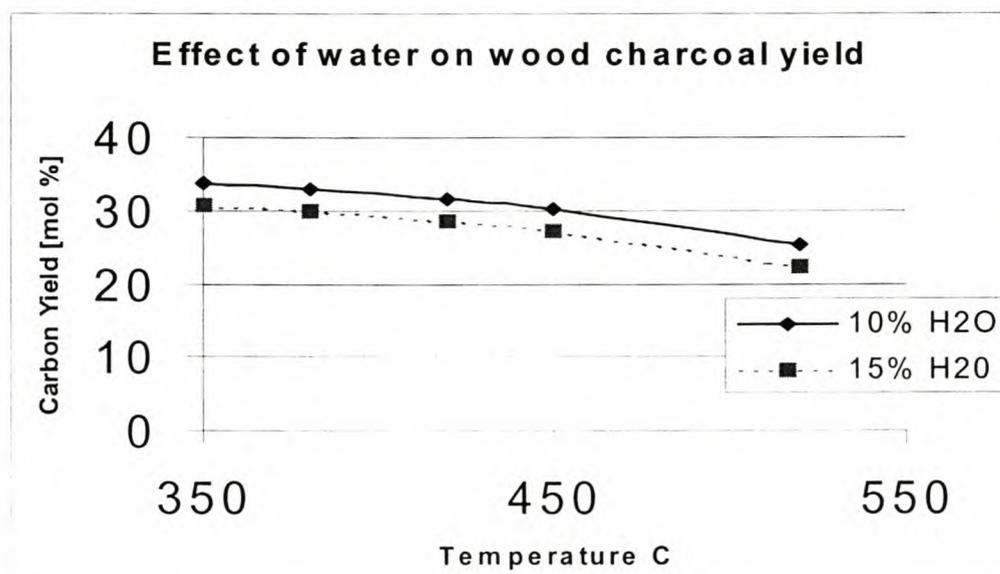
Figure 4. 25 Effect of water content on the carbon yield at the thermodynamic equilibrium

At higher heating rates the higher water content could lead to lower charcoal yields because of the presence of the oxygen and two hydrogen atoms in the water molecule.

The oxygen would cause oxidation of the charcoal and the subsequent formation of CO and CO_2, while the hydrogen would hydrolyse the biomass and cause more organic compounds to be formed. Higher heating rates would also bring the reactions closer to the thermodynamic equilibrium and therefore closer to the predicted values. However, at heating rates as low as 10°C/min. the water would mostly evaporate and be removed from the reactor before oxidation reactions with the feedstock could occur.

The results obtained in this study correspond and support Gray and Pakdel's assumptions and offer an explanation for the previously unknown factors that caused the higher charcoal yield when lower yields were expected.

4.4.6   Oil analysis

The oil analysis was done using the techniques specified in the materials and methods chapter (Chapter 3). Only the tarry oil fractions were analysed using GC/MS. A (by no means exhaustive) list of compounds found in the oil can be seen in Appendix B. The compounds listed in appendix B were all compounds identified with a certainty of more than 80%. The more detailed quantitative analysis will be presented and discussed here.

The large number of compounds identified in the tar fraction precludes the quantitative analyses of all the compounds. The compounds listed in table 4.7 were quantitatively analysed, but it is possible to estimate the response factors of many of the other compounds.

Table 4. 7 Components quantitatively identified [yield in % of dry, ash free feedstock mass]

Components	Asbos	Kraalbos	Scholtzbos	Pakdel et al. (1997)
Acetic acid	0.230	n.d	0.029	-
2-Propanol	0.025	n.d.	0.003	-
Eugenol	0.007	0.002	0.011	0-0.2
o-cresol	0.001	0.001	n.d.	0-0.04
Xylenol	0.003	n.d.	0.010	0-0.04
Guaiacol	0.004	n.d.	0.062	0.05-0.31
Benzene, 1,2,3-trimethyl-	0.002	n.d.	0.001	-

Vanillin	n.d.	0.009	0.005	n.d.
Benzaldehyde, 4-hydroxy-3,5-dimethyl	n.d.	0.006	0.001	-
furfuryl alcohol	n.d.	0.003	0.006	-
6-Methoxyeugenol	n.d.	0.054	0.001	n.d.
p-cresol	n.d.	0.004	0.013	0-0.04
1,2-Benzenediol	0.029	0.056	0.044	-
Phenol	0.287	0.130	0.608	0.03-0.05
Phenol, 2,6-bis(1,1-dimethylethyl)	0.047	0.010	0.008	-

Comparing the yields to the values obtained by **Pakdel et al. (1997)**, it can be seen that he reported phenol yields in the range of 0.01 % to 0.24%. Comparative yields were obtained for guaiacol, 6-methoxyeugenol and acetic acid. The phenol yield of 0.6 percent for Scholtzbos was particularly high. It must however be noted that Pakdel analysed the total liquid fraction and not just the tar oil fraction as was done in this study.

The acetic acid yield should be much higher, as it is one of the main compounds found in pyrolysis oils, but because of its short retention time in the GC/MS it could only be detected in the fraction 7, where methanol was used as eluant. Its relatively high yield does indicate its abundance, though.

Using the assumption that compounds with the same major functional groups will have close to the same response factors, it is possible to tentatively quantify many of the other compounds. Although it would be better to have the response factors for all the compounds, this method does allow a better indication of the yields than assuming a response factor of one. In table 4.8 the estimated response factors were used to calculate the oil yields of some of the more abundant compounds and of those whose response factors could be inferred with some confidence.

Table 4. 8 Compound yields using inferred response factors [dry, ash free basis]

Components	Asbos	Kraalbos	Scholtzbos
Cyclohexanone	1.301	0.111	0.299
Benzaldehyde, 4-hydroxy-3,5-dimethyl	n.d.	0.006	0.001
Phenol, 3-methyl-	0.020	n.d	0.017
Syringol	0.075	0.225	0.044
Ethanol, 2-butoxy-	0.114	0.022	0.027
Cyclohexene, 1-methyl-4-(1-methylene)	0.166	0.002	0.002
Benzene, ethyl-	0.299	0.003	0.020

Benzene, 1,4-dimethyl-	0.460	0.004	0.013
Benzene, 1,3-dimethyl-	0.308	n.d.	0.043
Benzene, methyl-	0.719	0.008	0.021

Cyclohexanone was the dominant component for Asbos. Even if the yield contains an error of 50%, it would still make it an important compound. Asbos also produced high yields of benzene, methyl and benzene, ethyl. Kraalbos can be noted for its high syringol content.

Analysis by HPLC would allow for the detection of the heavier phenols, which could not be detected on the GC/MS. These would be phenols like gallic acid and others that could be expected to form during the vacuum pyrolysis of wood.

It must be noted that many of the compounds have furan and pyran as mayor functional groups. Referring to the structural representation (figure 4.26 and 4.27) of these two compounds, it can be seen that they most likely originated from cellulose and hemicellulose, as can be seen in figures 4.2 and 4.3.
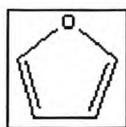
Figure 4. 26 Furan
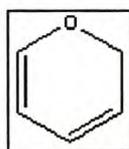
Figure 4. 27 Pyran

The pyran could be from either the cellulose or the hemicellulose, but the furan has only four carbons and the only 4-C compound found in hemi-cellulose is arabinofuranose, a pentoses. This would then most likely be the source of most of the furan groups.
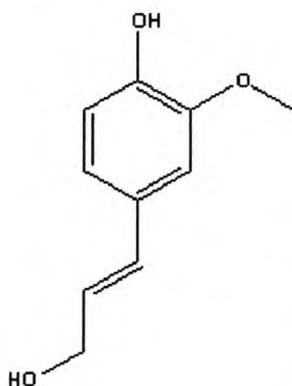
Figure 4. 28 Coniferyl Alcohol

The only difference between coniferyl alcohol, p-coumaryl alcohol and sinapyl alcohol is the methoxy group. Sinapyl alcohol has another methoxy in the meta position, while coumaryl alcohol has no methoxy groups. (Refer back to figure 4.4)

Studying figure 4.4 and 4.25, it can be seen that most of the benzene and phenol groups would most likely have originated from the lignin fraction of the plants, and specifically from the coniferyl alcohol that constitutes 90-95% of softwood lignins (see figure 4.4). **Pakdel et al. (1997)** also observed that the structure of certain types of phenolics in the oil were similar to the lignin basic methoxy-phenyl-propane units.

According to **Pakdel et al. (1997)** the depolymerisation of lignin by thermal degradation produces various phenolic compounds. Pakdel goes on to say that some phenols are primary pyrolysis products and are produced by the cleavage of β-O-4 aryl ether bonds in lignin (see figure 4.30(b)), and that some of the others are created through the secondary reactions of guaiacol and syringol.

Since lignin is a phenolic polymer it is interesting to inspect some of the proposed linkages that exist in hard and softwoods.

Linkage	Dimer Structure	Softwood %	Hardwood %
β-O-4	Arylglycerol-β-aryl ether	50	60
α-O-4	Noncyclic benzyl aryl ether	2-8	7
β-5	Phemylcoumaran	9-12	6
5-5	Biphenyl	10-11	5
4-0-5	Diaryl ether	4	7
β-1	1,2 Diaryl propane	7	7
β-β	Linked through side chains	2	3

Figure 4. 29 Proposed lignin linkages in softwoods and hardwoods. [Northey (1998)]

- **Aryl**: Any organic group derived from an aromatic hydrocarbon by the removal of a hydrogen atom, for example C_6H_5- (phenyl radical, from benzene).

Figure 4.30 (a) and (b) explain the nomenclature used in the linkages referred to in figure 4.29.

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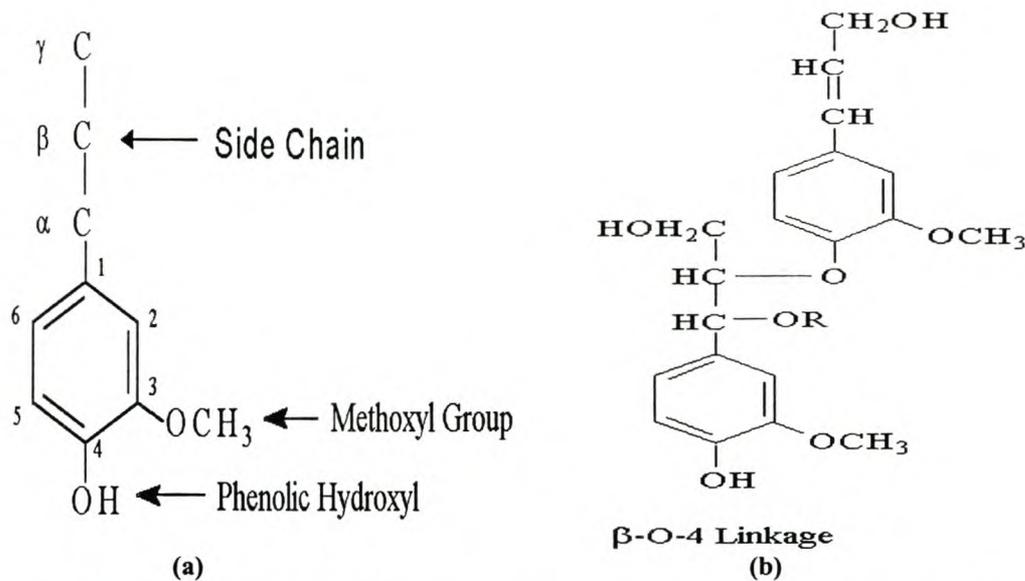
Figure 4. 30 Structural representation of (a) Nomenclature used (b) β-O-4 aryl ether [Northey (1998)]

It must of course be remembered that side reactions, recondensation reactions, chain splitting and many other reactions can occur during the pyrolysis process. These reactions could lead to the formation of almost any compound, and therefore the exact origins of a compound cannot be stated with certainty.

4.5 Conclusions

The study of the vacuum pyrolysis of intruder plant species showed that it is possible to produce economically valuable, high energy charcoal (avg. 24 MJ/kg) and oil (avg. 25 MJ/kg) products. It was found that the charcoal from plants with ash contents below 10% compares favourably with commercial products. The charcoal from both Kraalbos and Scholtzbos can be sold on equal footing with commercial products, but the ash content of Asbos was too high and led to very low energy values.

Depending on the selling price of the charcoal and oil, different vacuum pyrolysis conditions would be used to optimise either the charcoal or oil yield, or the economically most favourable combination of the two. The effects of pyrolysis temperature, time, reactor pressure, feedstock water content and feedstock age on the charcoal and oil yields were investigated. It was found that, as expected, the charcoal yield was highest at the lowest pyrolysis temperature of 350°C and highest pressure of

50kPa, but because of the high volatile content of these charcoals they would be of use only to industries wanting fast burning charcoals. The charcoal yields appears to level off above 450°C, which indicates that most of the volatile matter would have been removed and in terms of input energy it would not be profitable to increase the temperature above 450°C with a pyrolysis time of 60 minutes. A lower temperature can be used if longer pyrolysis times are employed, as this allows the volatiles more time to be removed.

It also appears as if the maximum oil yield temperature might be affected by the ash content of the feedstock. This can be seen from figure 4.7, where the ash content of the Scholtzbos and Asbos species were 8.33% and 19.85% respectively, and their maximum oil yield temperatures ranged from 450°C to 480°C. On the other hand, the ash content of the Kraalbos was 4.94%, and its maximum oil yield temperature was only 380°C. If the maximum oil yield was the main economic factor, then the reactor would have to be operated at 450°C-480°C for Scholtzbos and Asbos, and 380°C for Kraalbos.

It was also found that the rise in feedstock oxygen content during ageing decreases the charcoal and oil yields of plant material. Higher moisture feedstocks produce more charcoal and oil when compared to low moisture feedstocks. It appears that the structural changes that occur when water is pyrolysed with wood promote the resistance of the wood to thermal degradation. The structural changes also lead to the liberation of more long chain compounds and subsequent higher oil yields.

The study showed that plant-clearing projects could benefit from using vacuum pyrolysis to produce charcoals and oils.

Chapter 5: Leather Waste

5.1 Introduction

Leather wastes present an economic and environmental problem in that the leather cuttings are contaminated with various chemicals and heavy metals, mainly chrome and sulphur. This necessitates land filling in lined dumping sites at great cost. Dumping costs for a medium-sized tannery could run up to a R1000 000 a year.

Any process that could turn this hazardous, costly waste into either a valuable product or at least achieve significant reductions in volume would be welcomed as an economic and environmentally sound alternative to land filling. Vacuum pyrolysis is such a process. Volume reduction is one of the process's main advantages, and it is probable that the charcoal and oil yields would have economic value.

A medium sized tannery produces 190m^3 of waste cuttings each week. This represents a significant market for the emerging technology of vacuum pyrolysis and could lead to enormous savings. Vacuum pyrolysis would also be very advantageous to the environment compared to land filling and other waste disposal techniques.

5.2 Background: Leather tanning process

Tanned leather consists mostly of a protein called collagen, since this is the main component of the dermis layer used for tanning. The tanning process also introduces other contaminants. The main contaminants in tanned leather are Cr and S, but there are also many other chemicals left on the leather cuttings when they are landfilled. These contaminants necessitate the special handling required for the leather wastes. In order to identify the possible contaminants that may be present in leather waste, it is necessary to discuss the tanning process and identify the chemicals used.

It is the section between the epidermis and the flesh layer that is important to tanners. This section is called the dermis and consists mainly of densely interwoven fibrous tissue. This tissue is made up of a protein called collagen. The chemical formula for

the protein collagen is: C_2H_5-NO-C_5H_9-NO-C_5H_{10}-NO_2. It can be seen that collagen has a complex structure and would therefore also yield a range of compounds through the vacuum pyrolysis process.

The skins arrive at the tannery in their cured form. This can be achieved through various methods, such as drying or salting. The skins are then prepared for the tanning process through the following steps:

- **Soaking** - The first operation is to soak the skins. This operation, as do most of the following operations, involves chemicals. Each batch is put in a drum and processing starts by soaking in cold water to which **detergent**, **salt** and **biocide** are added. The drum is turned occasionally and the water is changed if it becomes heavily contaminated. The process is finished when the water remains clean, and the skins have been re-hydrated. The whole process can be speeded up by one or both of the following methods: 1) Heating the water and 2) Adding **enzymes**.

- **Liming** - The cleaned skins still have their hair on. This must now be removed together with the hair roots and the epidermis, in order to expose the grain layer. **Sodium sulphide** or **sodium hydrosulphide** is added to the soaked skins. After approximately an hour, these chemicals would have penetrated deeply into the hair and grain of the leather, causing the breakdown of the keratin, the main protein constituent of the hair and epidermis. Strong alkalis such as **lime** and **caustic soda** are then added, enhancing the breakdown that actually dissolves the hair root and epidermis. No damage is done to the collagen (dermis) part of the skin by the liming. Another effect of the liming process is the removal of the inter fibrillary proteins.

- **Washing** - The skins are washed to remove excess lime and materials loosened during the previous stage.

- **Fleshing** - The adhering fat and tissues on the bottom of the skin form a significant barrier to the penetration of subsequent chemicals. The removal of the fat and tissues is carried out using a fleshing machine.

- **De-liming** - The liming operation has made the skins very alkaline. In order to begin tanning, the alkalinity has to be reduced considerably. The chemical used for this is **ammonium chloride**.

- **Bating** - Bating is carried out in order to soften the skin even further through the enzymatic removal of muscle fibres. Bacterial enzymes are used during this stage.

- **Scudding** - This is the final process prior to the actual tanning. By placing the skins on a rounded board and by running a rounded, blunt knife over the grain, any remaining hair root, skin pigmentation and surface fat are squeezed out of the skin.

The next step is to tan the leather. There are many substances that are able to interact with pelt to bring about the required properties. They fall into a number of broad categories:

- **Mineral Tans**-These include compounds of **chromium, zirconium, aluminium** and **iron**. (The use of **chromium salts** has dominated the tanning industry in recent decades and this remains the most widespread method of tanning today, although there is growing pressure in the developed countries for replacement with materials with a less harmful environmental impact).

- **Vegetable Tans**-Extracts from many hundreds of plant species have been shown to have a tanning effect. They contain large **poly-phenolic molecules**, which act by displacing the bound water from the protein and taking up many of the exposed hydrogen bonding sites.

- **Synthetic Tans ("Syntans")**-Originally these were the results of the chemical industry's attempts to copy naturally occurring vegetable tans. The category has now grown to include a huge variety of products with widely varying properties. Some of them are used as sole tanning agents, for example in the production of white leather, but mostly they are now used as modifiers in combination with other tanning materials.

- **Aldehydes-formaldehyde** and **glutaraldehyde** are used commercially. Chamois leather production, which involves the treatment of pelt with raw cod oil, is an example of this type of tanning, as complex aldehydes are created by oxidation of the oil during the tanning process. **[Unknown author, (2001b)]**

There are many other materials that have some tanning properties, but are not used in commercial leather production, generally because they are too expensive or are hazardous to handle.

Formic acid is also used in the leather processing industry as a de-liming agent and neutraliser, and to tan, de-hair, and plump hides. **[Unknown author, (2000a)]**

The leather studied in this chapter was treated using the chromium sulphide method.

5.3 Results

Leather waste makes up 1%-3% of municipal solid waste and this study should be a first step into incorporating it in a model for the vacuum pyrolysis of such wastes. **[Mcgee et al. (1995)]**

The specific leather waste studied here comes in two forms: fine and coarse. The reason for this is that the cuttings originate from two different stages in the process, but their chemical properties are the same. The fine cuttings are 20mm-200mm long, 2mm-5mm wide and 0.1mm-0.2mm thick while the coarse cuttings are 300mm-600mm long, 70mm-110mm wide and 2mm thick. The cuttings were pyrolysed as is.

Table 5.1 shows the yields of the charcoal, oil, water and non-condensable gases. The oil yield value contains both the tar and aqueous phase yields, with the aqueous phase

containing 10% to 15% of the oil. The hp in the left-hand column indicates the runs done at 50kPa.

Table 5. 1 Results from the Vacuum pyrolysis of the leather waste

Samples	Temp [C]	Heating Rate [C/min]	Pyro time [min]	Pressure KPa	Char %	oil total %	Pyro water %	Non-cond. gases %
Leather								
Fine	350	4.9	60	18	48.8	18	27	12
	412	4.9	60	18	32.3	25	42	2
	445	8.0	60	18	33.2	21	38	14
	520	5.0	60	18	27.7	21	50	4
hp	350	8.9	60	52	54.7			
hp	350	10.6	60	46	54.9			
hp	350	4.8	60	48	57.2			
Coarse	350	5.0	60	18	49	21	25	8
hp	345	5.0	60	50	53			

The losses that occur during the process of collecting the oil are included in the non-condensable gas yield percentage. It is therefore only a qualitative indication of the gases produced, with the actual value being lower than the value shown. It can, however, be seen that there are only very small percentages of gas coming off from the process. This would be advantageous, as it reduces the emission problems of the process and shows its clear advantage over conventional pyrolysis or incineration.

5.3.1 Effects of temperature

Figure 5.1 shows the effect of temperature on the fine leather cuttings.
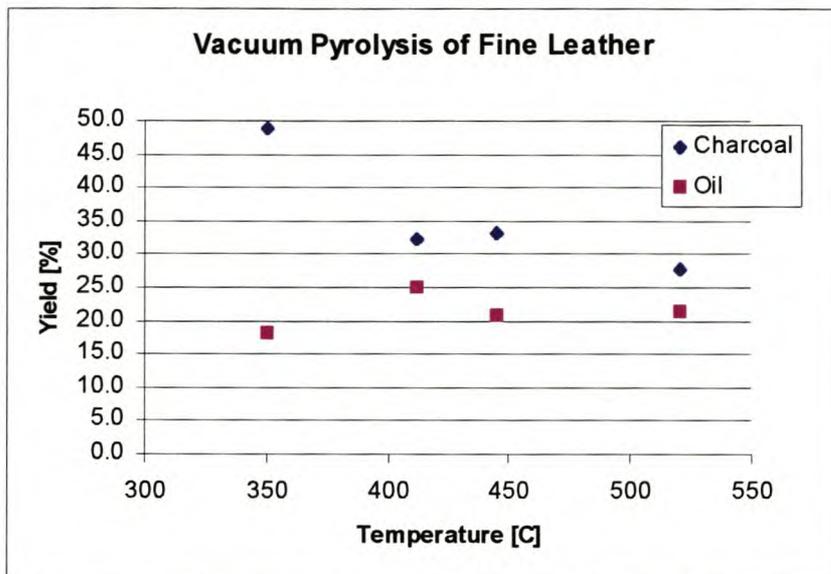
Figure 5. 1 Influence of temperature during the vacuum pyrolysis of fine leather cuttings

The leather samples were heated at a heating rate of 5°C/min and a reactor pressure of 18kPa was used. A heating rate of 5°C/min instead of 10°C/min was used, because the leather cuttings conduct heat slower than the wood particles, leading to high temperature gradients in the bed. The temperature was held constant at the pyrolysis temperature for 60 minutes. The pyrolysis of the leather cuttings follows the same trend as the intruder plant species. The charcoal yield decreases sharply at the lower temperatures and then levels off above 413°C. The oil yield remains nearly constant, but with a maximum at 413°C.

The mechanism of weight loss remains basically the same as for the lignocellulosic materials, except that the main component broken down in the thermochemical conversion reaction was collagen. From figure 5.2 the nature of the compounds formed when the collagen was broken down can be deduced. It can be seen that the yields in all the traps were much higher for the maximum oil yield temperature of 413°C. It can also be seen from the values of the 3rd and 4th vacuum traps that relatively high yields of light compounds were formed. Compared to plants, the yields of light compounds from the decomposition of leather leads were slightly higher (about 35% of the condensed vapours, compared to 30% for plants at 450°C) and the oil yield was also slightly higher (20% compared to 15% of the condensed vapours for plants). The aqueous yields of plants and leather were both about 45% at 450°C.

93
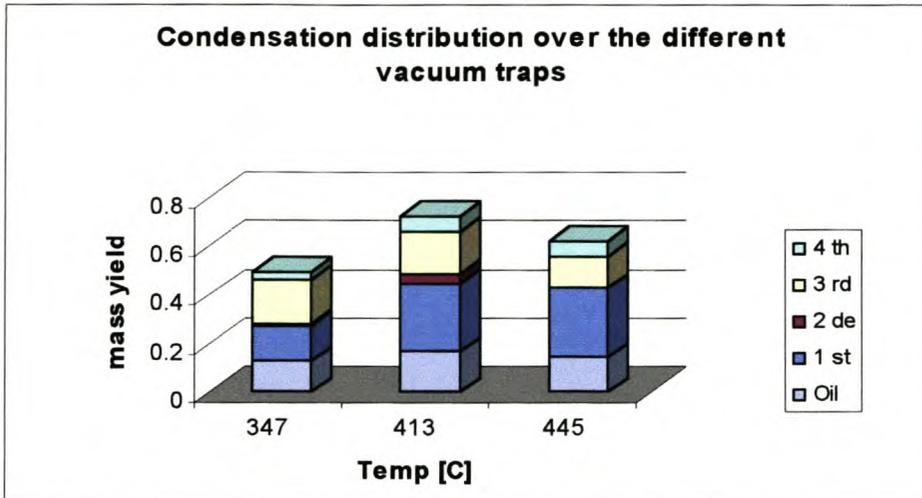
Figure 5. 2 Condensation distribution over the different vacuum traps for the vacuum pyrolysis of leather at different temperatures.

5.3.2   Effect of heating rate

Figure 5.3 shows the influence of heating rate and pressure on the charcoal yields. The figure shows that the charcoal yield decreases with increased heating rate. **Pakdel et al. (1997)** stated that a higher heating rate facilitated the heat transfer between the hot walls of the reactor and the particles, which leads to higher oil yields. This was for the production of phenolics from wood, but the principle stays the same.
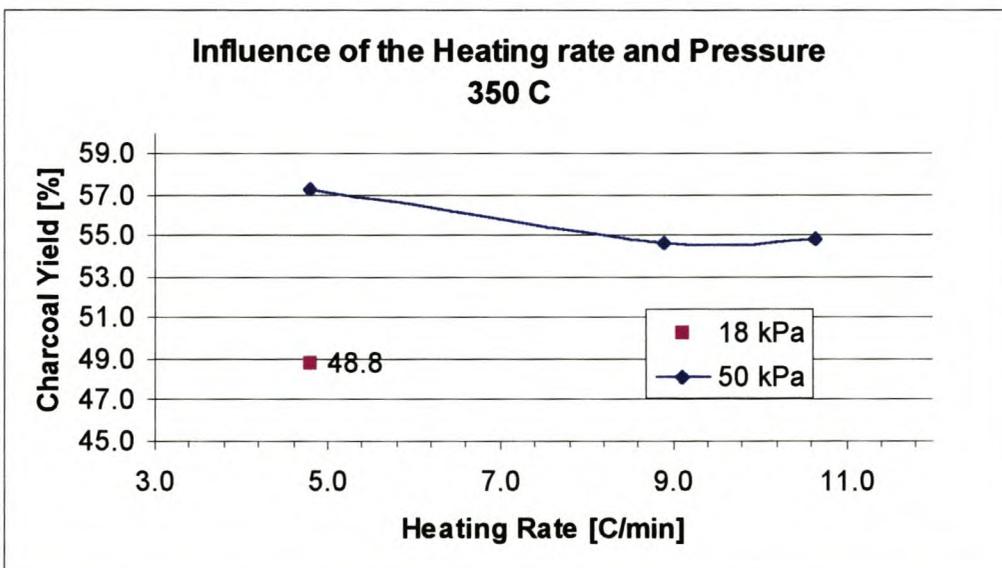
Figure 5. 3 Influence of heating rate and pressure on the charcoal yield at 350°C.

One of the reasons why the charcoal yield decreases with increased heating rate is that not all of the water in the sample would have time to evaporate at the lower

temperature. The remaining water would then react with the charcoal, and the oxygen in the water would lead to oxidation reactions and therefore higher mass loss.

Another reason could be that at higher heating rates the leather structure would not have time to completely degrade at lower temperatures, as it would in the case of slower heating rates. This would lead to the degrading of the structure at higher temperatures where there would be enough energy to liberate longer heavier components, which would lead to higher weight loss than would have been the case if shorter lighter compounds were released at the lower temperatures.

The heating rate experiments were conducted at 50kPa and the effect of the heating rate on the oil could therefore not be studied.

5.3.3 Effect of particle size

It can be seen from figure 5.4 that there are only minor differences in charcoal yield between the coarse and fine particles. This is significant, because it implies that pyrolysing fine and coarse cuttings together would not change the characteristics of the process significantly.

It must be noted that the density of the sample is influenced by the particle size, and this should cause the mixture of fine and coarse particles to yield more oil than the fine cuttings alone. The reason for the higher oil yield is that the mixture has a lower bed density than the fine cuttings alone, and this would lower the residence time of the vapours in the bed.
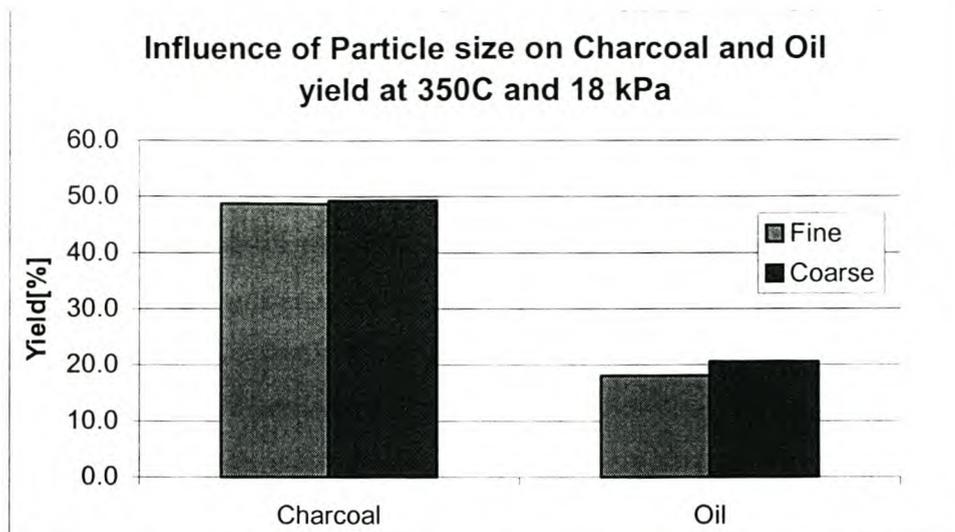
Figure 5. 4 Influence of particle size on charcoal and oil yield at 350°C and 18kPa reactor pressure.

The slightly higher charcoal yield for the coarse particles can be explained by considering the longer path the gases and vapours have to travel to escape the particle, thereby increasing the residence time and increasing the chance of further reaction that would increase the charcoal yield.

The higher oil yield of the coarse leather cuttings indicates the advantages of a less densely packed bed. **Pakdel et al. (1997)** showed that the thinner the bed thickness is and the less densely the particles are packed, the higher is the oil yield. The reason for this is that the thinner the bed is and the lower the density, the shorter the residence time of the vapours in the sample would be, and there would accordingly be a lesser chance for further reaction resulting in higher oil yields and lower charcoal yields. Thus, even though the residence time of the vapours inside the coarse particle is longer than it is in the case of the fine particles, the much lower bed density overcomes the disadvantages and thereby leads to a higher oil yield. The vapours trapped within the longer pathways of the coarse particles lead to higher charcoal yields. On the other hand, vapours trapped within the sample of the fine particles lead not only to an increase in charcoal yield, but also to the creation of more short chain non-condensable gases as the vapours react further, thereby lowering the oil yield.

Since both of the samples undergo charcoal yield increases because of recondensation reactions, it must be accepted that almost all of the vapours trapped within the particle

enhance the particle weight, while only some of the vapours that undergo secondary reactions in the bed increase the charcoal weight. A large fraction of the vapours in the bed only reacts further to form more non-condensable gases and therefore does not increase the charcoal weight. It must also be noted that the heated section of the reactor, through which the vapours must travel, extends past the area occupied by the sample and any further reaction outside the bed could not contribute to the charcoal yield.

The significance of the charcoal yield will only become apparent when the volume reduction and economic value of the charcoal over the temperature range are investigated. This will be discussed later in the section 5.3.5.

5.3.4   Effect of particle size and pressure

The effects of the particle size and pressure were investigated to determine the importance of the pressure on the process yields. Studying the two variables at the same time also gave more insight into the mechanisms governing the charcoal and oil productions.
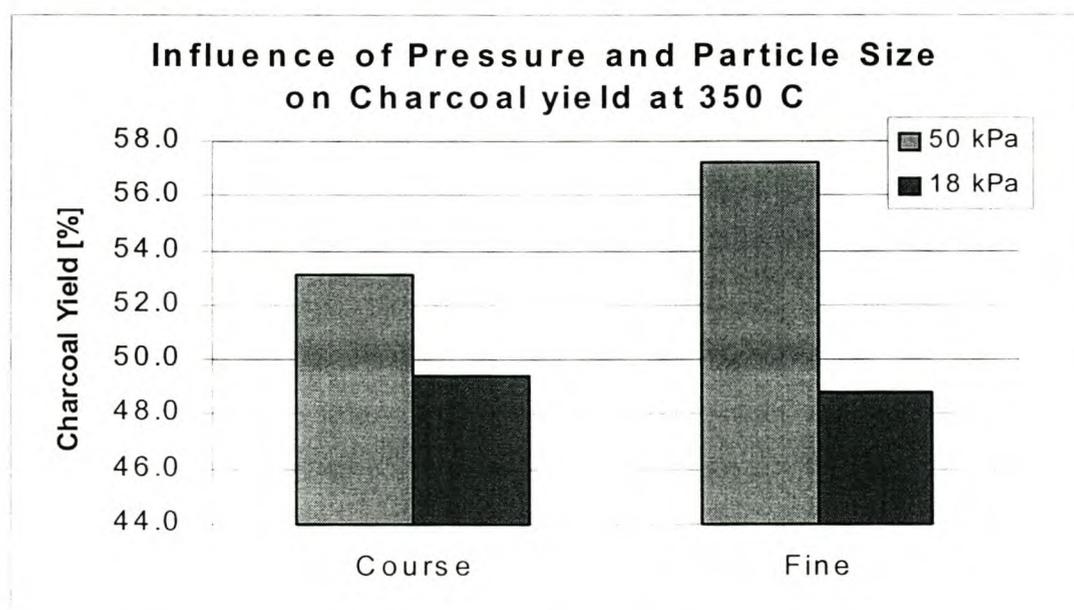
Figure 5. 5 Influence of reactor pressure and particle size on the charcoal yield at 350°C

Figure 5.5 shows the differences in charcoal yields between the different leather cuttings at 50kPa and 18kPa reactor pressure and a heating rate of 5 °C/min. The samples were kept at the pyrolysis temperature for 60 minutes before being allowed too cool in the reactor.

The effect of the higher pressure for both the coarse and fine particles was an increase in charcoal yield. At higher pressures the vapours are not removed from the reactor at a fast enough rate and some of the vapours undergo further reactions, which increase the charcoal yield. Some of the vapours recondense on the charcoal, where it is then carbonised. This increases the charcoal yield and decreases the surface area by blocking some of the pores. The blocking of the pores also leads to the trapping of vapours inside the particles, which then leads to further reactions and ultimately to the increase of the charcoal weight.

It is postulated that the reason why the fine leather has a lower charcoal yield than the coarse leather at 18kPa, but has a higher yield than the coarse leather at 50kPa, is because of two competing mechanisms with three variables. These variables are the particle size, pressure and bed density. The bed density and particle size are linked in that the smaller particles have a higher bed density.

The two competing mechanisms consist of two different factors, giving rise to resistance in the free movement of the gases and vapours, and which therefore leads to longer residence times of the vapours and gases inside the reactor. The first resistance comes from the particle size, or rather the path distance the gases have to travel to reach the particle surface. The longer gas path length associated with the larger particles of the coarse leather cuttings would increase the residence times of the gases and vapours. This would therefore allow more time for further side reactions to occur.

The second resistance to the free movement of the vapours is the bed density. Higher density fine leather beds, compared to the coarse leather beds, would also lead to longer residence times. The fine leather also has a higher surface area per weight and

would therefore be able to release more vapours in a shorter period of time; this would aggravate problems associated with the gas hold-up in the denser bed.

The two mechanisms are a combination of these two resistances and, as will shortly be explained, the pressure is the variable that dictates which of the two resistances has the most influence. At the higher pressure of 50kPa, the greater gas evolution rate, coupled with the inability of the vacuum pump to remove the vapours quickly from the denser fine leather bed, are the ruling factors. This then causes the fine leather to have the greater charcoal yield when compared to the coarse particles at 50kPa. The greater charcoal yield is caused by the higher degree of side reactions and condensation reactions associated with the longer residence time of the vapours and gases at the higher pressure.

At the lower pressure (15kPa), where the greater gas evolution rate of the fine leather can be extracted quickly enough from the dense bed, it is the longer residence time within the coarse leather particles which ends up being the ruling factor. This then causes the coarse leather to have the higher charcoal yield at 15kPa. The rapid removal of the vapours from the bed therefore limits the recondensation and side reactions in the bed. The lower pressure does not, however, influence the residence time of the vapours in the particles, and therefore causes the longer path distance in the coarse particles to lead to side reactions causing higher charcoal yields.
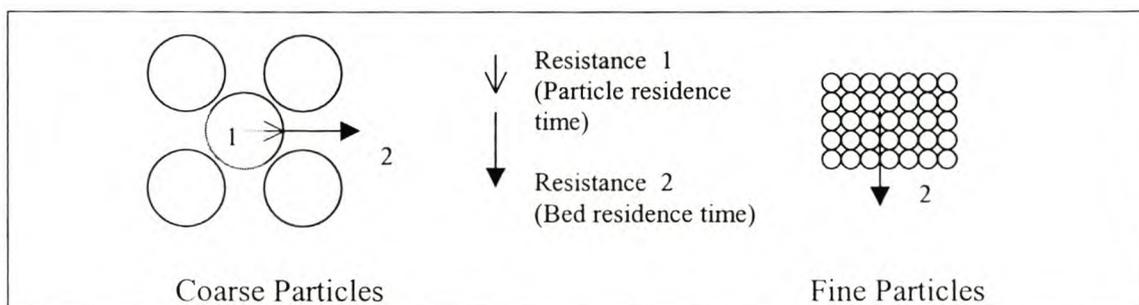
Figure 5. 6 Diagram of the two resistances which influence the charcoal yield

Figure 5.5 also shows that the influence of the pressure is much more noticeable for fine leather. It was assumed that this was the case because the pressure had a much greater influence on the residence time of the gases in the bed than on the gases still in the particles. The assumption is that the residence time of the degradation products

inside the particles is dependent only on the vapour pressure of the degradation products inside the particle and therefore independent on the reactor pressure.

Therefore, since resistance one is kept constant as the pressure changes for either fine or coarse leather separately, only the effect of the bed residence time is seen. This therefore shows the dominance of resistance two for the fine particles, and resistance one for the coarse particles.

The above indicates that the maximum mass loss at a specific temperature would be achieved at the lowest pressure. Economic factors, such as the cost of a vacuum pump that can maintain lower pressures, now have to be considered. The most economic pressure must be combined with the most economic temperature to achieve the cheapest running conditions with the best volume reducing results. **Roy et al. (1992)** showed 15kPa to be the most economic pressure for a biomass process, but further analysis will be needed for a leather feedstock. The best operating conditions would depend on the goals that must be achieved, volume reduction vs. charcoal production.
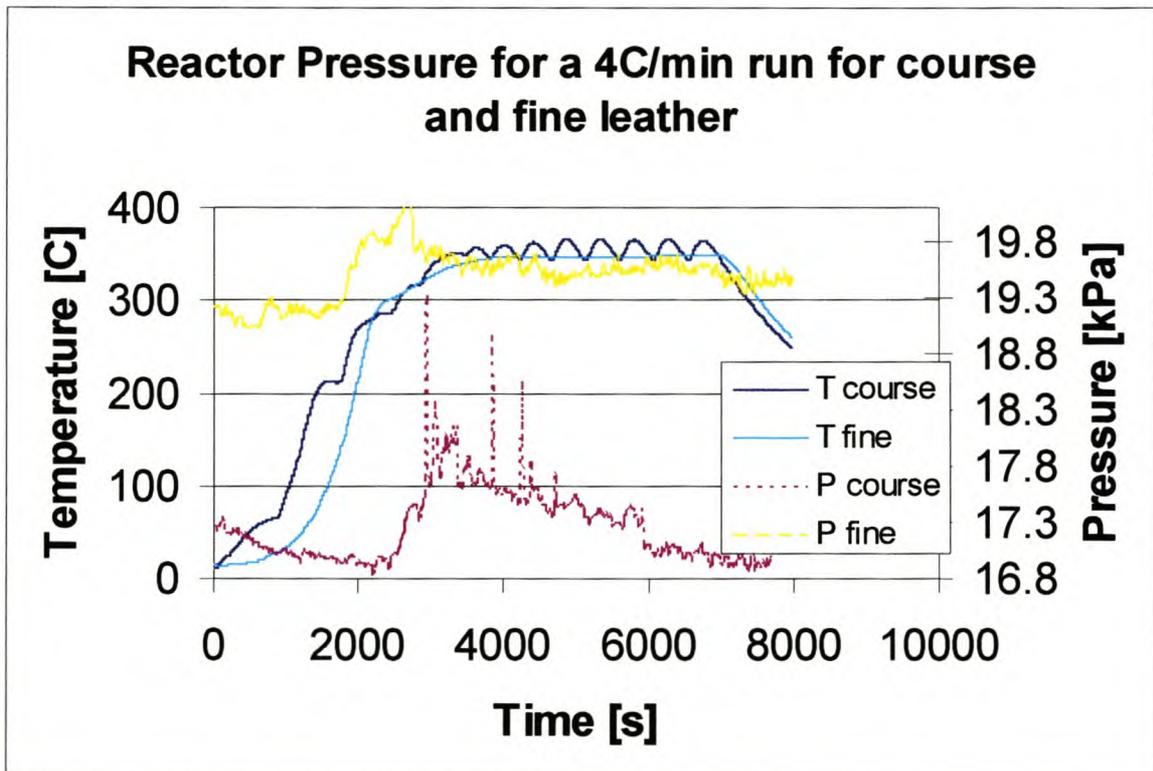
Figure 5. 7 Reactor pressure for a coarse and fine leather 350°C run at 4 °C/min

Figure 5.7 shows the difference between the reactor pressures for coarse and fine leather for the whole 350°C run. The leather was heated at 4°C/min. to a temperature of 350°C and the pressure was recorded throughout. It must be noted that the difference in starting pressure for the fine and coarse leather was dependent on the reactor set-up and the condition of the vacuum pump for the runs. No conclusions should be made based on the offset. The difference between the two runs was only 2kPa and would therefore have had only a very small effect on the yields. The scale used for the pressure in figure 5.7 also gives a distorted view of the pressure difference between the runs. The small scale was used so that the size of the gas evolution peaks could be studied better. However it is interesting to note that the gas evolution starts at a lower temperature for the fine leather, but proceeds much faster than the coarse leather. The fine leather begins to decompose at 210°C, while the coarse leather only starts to decompose at 300°C.

The fact that the coarse leather had a slightly higher pressure increase than the fine leather was surprising. The higher surface area of the fine leather should have caused it to have a higher gas evolution rate, but as it started at a lower temperature, the gas flux was probably spread out over more time, thereby lowering the resulting peak.

The delay in the gas evolution for the coarse leather indicates that the fine leather decomposes more easily. It follows then that more energy is necessary to liberate the gases from the coarse leather. Once the initial resistance was overcome, the leather could decompose and as there was a delay, the material that could be decomposed at the higher temperature was more, resulting in the higher flux.

5.3.5   Volume reduction

Volume reduction would be one of the main advantages of the process if the charcoal cannot be used as a fuel. This will be the case for many tanneries, as the leather contamination is determined by the choice of tanning process. Most of the tanneries would have been in operation from before the latest more stringent environmental laws were passed, and they would therefore most probably be using a process that would result in unusable charcoal.
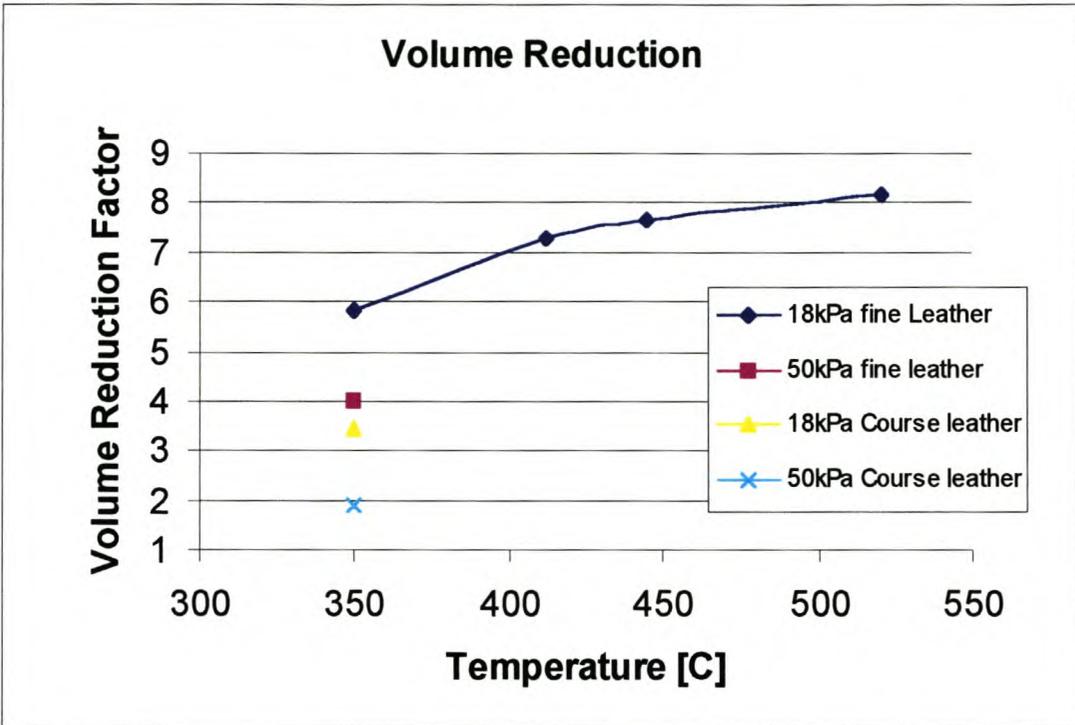
Figure 5. 8 Influence of temperature on the volume reduction of fine and coarse leather

The temperature at which process will operate will be determined by the relation between the higher energy cost of higher temperatures and the increase in volume reduction with increased temperature. The charcoal yield and selling price will be the main driving force behind the process if the charcoal can be sold as a fuel.

The volume reductions shown in figure 5.8 are in relation to hypothetical dumping densities of the virgin feedstock. These densities were assumed to be close to the measured densities of the leather stored in the laboratory. The dumping density of the coarse leather was assumed to be 281 kg/m^3 and the fine leather was assumed to be 161 kg/m^3.

Figure 5.8 shows the volume reduction achieved between 350°C and 520°C. Excellent volume reductions are achieved for the fine leather, with moderately good reductions achieved in the case of coarse leather cuttings. Volume reductions of up to a factor eight seems possible for fine leather at 520°C and 18kPa pressure. A reduction factor of 3.5 for coarse leather at 350°C and 18kPa seems promising, and if it were to follow the same trend as the fine leather, then a reduction factor of 5.5 should be feasible at

520°C and 18kPa. The reduction factor depends to a great extend on the volume of the virgin feedstock under land filling conditions.

From table 5.2 it can be seen that the volume reduction achieved was consistently lower for the 50kPa runs. The density of the charcoal increased by 28% when the pressure was decreased from 50kPa to 18kPa for fine leather, while the increase was 56% for coarse leather. The coarse leather also had a higher density at 50kPa, while the fine leather had the higher density at 18kPa. The density difference between the coarse and fine leather charcoal for a specific pressure is very small, which indicates that the leather particle size does not have a large influence on volume reduction. The main influence is the dumping density of the different leathers.

Table 5. 2 Effects of temperature, pressure and particle size on charcoal density

Sample		Temp [C]	Pressure	heating rate	Crushed Density [kg/m3]
Fine		347	18kPa	5	939
		413	18kPa	5	1177
		445	18kPa	8	1236
		520	18kPa	5	1317
	hp	335	48kPa	5	580
Coarse	hp	345	50kPa	5	526
		350	18kPa	5	958

The answer as to why the density was lower for higher pressures might be found in the fact that the effect was more pronounced in the case of the coarse leather. The question that arises, is what influences the density of the charcoal. The fine leather crushes much more easily than the coarse leather, and this might therefore give rise to the difference between the coarse and fine leather. The consistently higher densities of the lower pressure chars indicate that the charcoal particles have a denser structure. As the chars are all crushed very fine the difference should be in the charcoal particle structure.

At 18 kPa the crushed coarse leather has a higher density than the crushed fine leather. This indicates that the charcoal structure changes with varying particle size. Earlier it had been shown that there were significantly more vapours trapped within the coarse particles compared to the fine particles. These recondensation reactions

which occur inside the particles block the pores and lead to further recondensation and reaction within the particle. This should cause the particles to be denser.

At 50 kPa the fine leather has the higher density, but the difference was less pronounced. There is more condensation on the surface of the fine leather because of the higher density of the bed. This would also lead to pore blockage and therefore higher density than the coarse leather. Pressure changes have less of an effect on coarse leather, which allows the fine leather to achieve the greater density at the higher pressure.

5.3.6 Physical properties of the charcoal

The physical properties of the charcoal will determine whether there are possible economically beneficial applications for the charcoal. The ash content is one of the main factors influencing the economic value of charcoal.
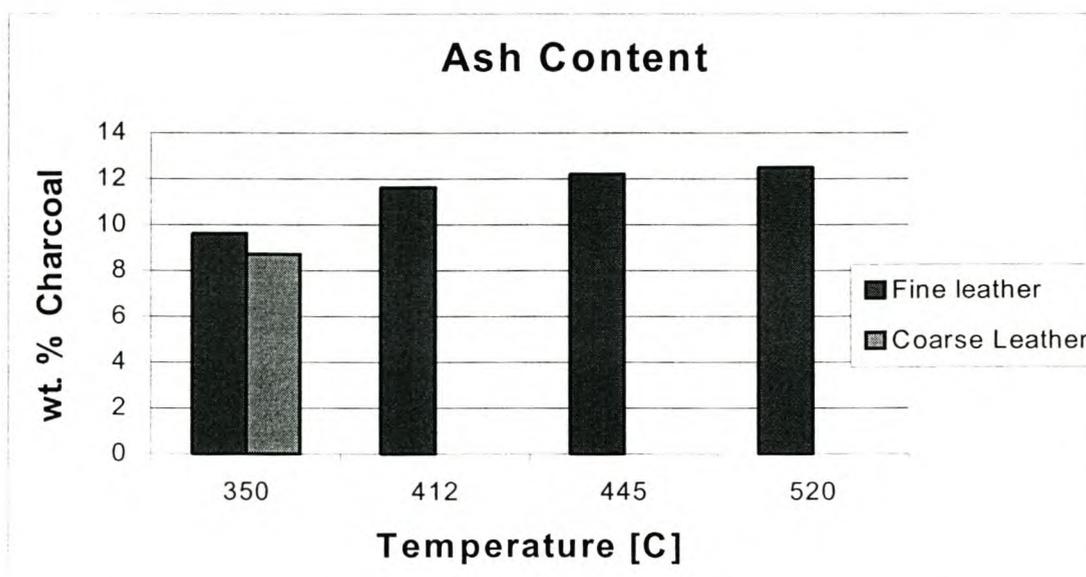
Figure 5. 9 Ash content of the charcoal for the fine and coarse leather.

Figure 5.9 shows that the charcoal has relatively low ash percentages when compared to the 12%-17% ash content of commercial charcoals. Unfortunately it can be seen from table 5.3 that the ash contains very high levels of Cr., which would preclude its use as a fuel or fertiliser. The toxicity of the chromium depends largely on its state of ionisation, with chromium (VI) being the most toxic. Chromium (VI) is classified as a

type B hazardous waste, while chromium carbonyl is a type C or D waste. Chromium(III)chloride falls under toxic hazardous group 3, with a maximum allowed Estimated Environmental Concentration (EEC) of 4.70 ppm and a maximum dumping of 7121.00g/ha/m allowed. The preferred technology for the disposal of the chromium(III)chloride is recovery or immobilisation, precipitation followed by landfilling is also allowed.

Table 5. 3 Metal content of the leather waste charcoal from the 520°C experiment

	Cd	Cu	Pb	Cr	Zn	Fe	Mn	Mg	Al	As
mg/l	0.13	2.27	1.78	33061	0	142.6	0.79	98.54	90.73	0.41
% of ash	0.00	0.01	0.01	99.18	0.00	0.43	0.00	0.30	0.27	0.00
% of charcoal	0.00	0.00	0.00	12.40	0.00	0.05	0.00	0.04	0.03	0.00

This indicates that, unless the chrome can be removed from the charcoal, the vacuum pyrolysis process would be used for its volume reduction capabilities, with the process economics depending on the reduction in landfilling costs.

Another important element to consider is sulphur. The charcoal value would increase with decreased sulphur content.
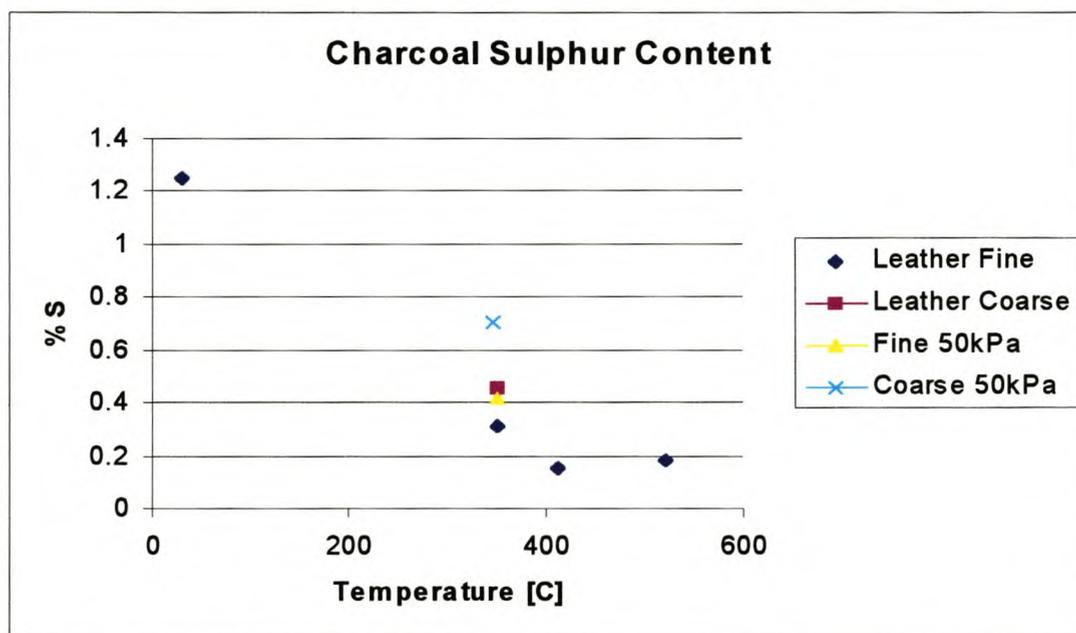
Figure 5. 10 The sulphur content of the charcoal at different pyrolysis temperatures

Even though the high Cr. content of the charcoal precludes its use as a fuel or fertiliser, it is interesting to note that it has a low sulphur content. The virgin leather has a sulphur content of 1.25%, and it can be seen that the sulphur content falls rapidly to about 0.2% of the charcoal mass. The sulphur liberated during the process will have to be removed before it enters the atmosphere.

Luckily this is relatively easy, as sulphur's boiling point is 444.6°C, which would allow the oil vapours to stay in the gas phase while the sulphur could be condensed and so be removed from the gas stream. This effect could also be seen in the experimental reactor where the sulphur condensed in the pipes before it reached the condensers.
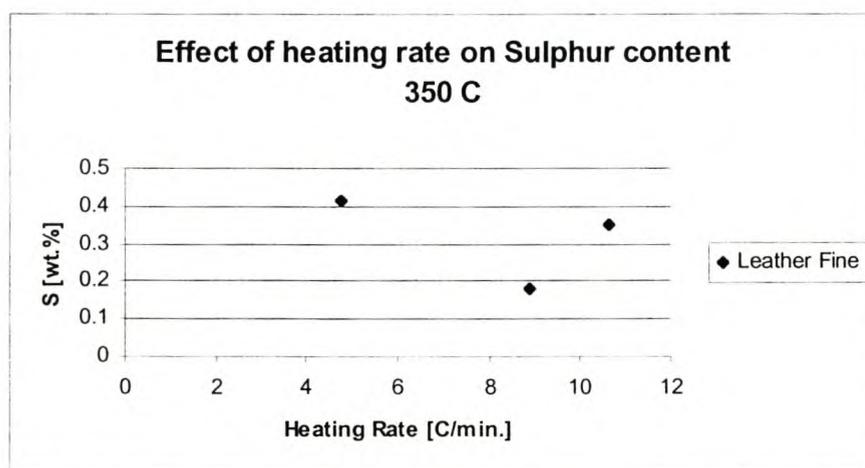
Figure 5. 11 Effect of heating rate on charcoal sulphur content

Figure 5.11 suggests that a higher heating rate would result in lower levels of sulphur in the charcoal. The experiment conducted at the heating rate of 11°C/min appears to have suffered an experimental error. In figure 5.3 it can also be seen that the 11°C/min experiment appears to deviate from the expected curve. Even though there are some doubt concerning the 11°C/min. value, it can still be seen that the sulphur content decreases with increased pyrolysis temperature. A higher heating rate would result in a more violent release of gases and vapours from the degrading leather structure. This could then lead to better access to the interior of the leather particle, resulting in the easier release of the sulphur trapped within the particle.

The energy values of the charcoal and oil produced through the vacuum pyrolysis of leather are shown in table 5.4. The energy value of 26.7MJ/kg of the oil was even higher than the energy values of the oil produced through the vacuum pyrolysis of the intruder plant material. Its sulphur content was also relatively low (0.450%) and would classify it as a low sulphur fuel, unfortunately the nitrogen content of the oil was found to be 6.637%. This is a very high value and would make it difficult to sell the oil as a fuel. The 19.8MJ/kg energy value of the charcoal compares favourably with commercial charcoals (20MJ/kg-27MJ/kg), but because of the high chrome content it can not be used as a fuel unless the chrome can be extracted.

Table 5. 4 Energy values of the leather product charcoal and oil

Sample	Pyro time [min]	Pressure [kPa]	Pyro temp [°C]	Charcoal MJ/kg	Oil MJ/kg
Fine Leather	60	18	445	19.8	26.7

5.3.7 Oil composition

The oil composition was determined using the method described in chapter 3. This was only a qualitative analysis and the relative abundance of the compounds does not take the detector response variations or variations in the injected volume into account. It is, however, likely that the compounds with relative yields in excess of one would be consequential.

From the extensive list in table 5.5 it can be seen that leather, as a complex feedstock on the molecular level, yields complex and varied compounds. The high sulphur content of the leather also transcends to the compounds in that there are sulphated compounds such as N,N-DIMETHYLSULFAMOYLCHLORIDE, but most of the sulphur condenses before it reaches the oil condensers.

Earlier in the chapter it was mentioned that the leather consists mostly of the protein collagen, which has the chemical formula $C_2H_5\text{-}NO\text{-}C_5H_9\text{-}NO\text{-}C_5H_{10}\text{-}NO_2$. It can be seen from table 5.5 that there are many nitrogen containing compounds. Compounds

such as 6-methyl-2,2'-bipyridine 1-oxide; 1,2-benzene-dicarboxylic acid, 3-nitro; benzenepropanenitrile; N-(Dimethyl-Thiophosphinyl)-3-amino and benzene-acetonitrile. The oils' high nitrogen value of 6.6% also reflects this.

If benzene, methyl as the seemingly most abundant compound was said to have a relative value of 10 then:

Table 5. 5 Qualitative Oil analysis [Benzene, methyls' relative value taken as 10]

Most abundant compounds [yield >5] Benzene, methyl-; Benzene, 1,3-dimethyl- ;6-Methyl-2,2'-bipyridine 1-oxide ; Benzene, 1,4-dimethyl- ;Heptane ;Cyclohexene, 1-methyl-4-(1-methylene) ;Benzene, ethyl- ;
Yield >1 1,1-D2-CYCLOPROPABENZENE ;1,2-Benzenedicarboxylic acid ; TETRACOSAMETHYLCYCLODODECASILOXANE ;3-ISOPROPOXY-1,1,1,7,7,7-HEXAMETHYL ;1-Propanol ;Heptane, 3-methyl- ;Ethanol, 2-butoxy- ; Cyclohexanone ;Bornylene ; 1,2-Benzenedicarboxylic acid, 3-nitro ;N,N-DIMETHYLSULFAMOYLCHLORIDE ;Benzenepropanenitrile;.gamma.-Terpinene ; N-(DIMETHYLTHIOPHOSPHINYL)-3-AMINO ; Octane ;Benzeneacetonitrile ; Phenol ;Benzene, 1,2-dimethyl- ;
Yield >0.3 Phenol, 3-methyl-; Benzene, 1,2,4-trimethyl- ;Hexane, 1,1'-oxybis- ; Benzene, 1-ethyl-2-methyl- ; 2-Pentene, 2,3,4-trimethyl- ;Benzene, 1,3,5-trimethyl- ;Dodecane ; Heptane, 2,5-dimethyl- ; Cyclohexane, 1-methyl-2-propyl- ;Acetic acid ;Pentane, 3-ethyl- ;
Trace Benzene, 1-methyl-4-(1-methylethyl ;3,9-DIAZATRICYCLO-[7.3.0.0(3,7)]-DODECANE ; Cyclohexane, 1,1-dimethoxy- ;Heptane, 2,4-dimethyl- ;Phenol, 4-methyl-;2-Piperidinone ;1H-Pyrrole ;Octane, 2,4,6-trimethyl- ;Acetic acid, ethyl ester; Acetamide ;Styrene ;Acetic acid, butyl ester ;2(1),4(1)-Dideutero-2,4,6-trimethyl ; Benzene, 1,2,3,5-tetramethyl- ;Benzene, 1,2,3,4-tetramethyl- ;Benzene, 2-ethyl-1,4-dimethyl- ;3-Buten-2-ol, 2,3-dimethyl- ;3-Phenyl-.lambda.3-phosphorine ;Heptane, 3,5-dimethyl- ;Oxirane ;.DELTA.-4-CARENE ;Tridecane ;Eicosane ; Undecane, 3,7-dimethyl- ;Benzene, 1-ethyl-2,3-dimethyl- ;1-Hexanol, 2-ethyl- ;Pyridine ;cis-1,3-Dideuterio-1,3-cyclohexand ;Tetradecane;

5.4. Conclusions

The economic advantage of the vacuum pyrolysis process for the leather industry would be the volume reductions that can be achieved. As the charcoal was heavily

contaminated with chrome, the process would be operated at the conditions that minimise the charcoal yield while maximising the oil yield. This would require operating the reactor at 420°C, 18kPa pressure and with a feedstock heating rate of 9°C/min. This would result in a factor 7 reduction in volume and an oil yield of close to 25% on a dry feedstock basis. The oil had a heating value of 26.7MJ/kg and the charcoal's heating value was 19.7MJ/kg. The high nitrogen content of the oil does pose problems, but further study would be needed to determine if the nitrogen content could be reduced or if there are uses for such a high nitrogen oil.

The relatively high energy value of the charcoal and its low ash content of 11.5% would have made it ideal for use as fuel charcoal, but its high chrome content of more than 10% makes it impractical. If it were possible to extract and possibly reuse the chrome from the charcoal, it would be possible to sell the charcoal and reduce the cost of the process even further. It would then also completely do away with the need for landfilling and would also reduce the cost of the chrome needed for the process. This would make the process very economically and ecologically attractive and therefore necessitates further research into the possible extraction of chrome from leather waste charcoal.

Chapter 6: Sewage Sludge

6.1 Introduction

What is sewage sludge? Sewage sludge is not sewage. It is one of the final products of the treatment of sewage at a sewage (wastewater) treatment plant. After treatment to break down the organic matter and kill disease organisms, the remaining fine particles ultimately become sludge. America produces 6 million dry tons of sewage per year, but the activated sludge production is much higher. The reason for the high sludge production is due to the organic waste streams from various industries that supplement the sewage sludge in the wastewater treatment plants.

The nature of the sewage sludge necessitates dumping in a lined landfill. This makes disposal of the sludge very costly (R900 000 / day for the Capetown municipality) and any process that could either reduce the cost of the landfilling significantly or upgrade the waste to an economic product would be very well received. This is where vacuum pyrolysis becomes relevant: With its low gas emission and high volume reduction capabilities it should be the perfect solution to this waste problem.

6.2 Results

Vacuum pyrolysis makes it possible to reduce the volume of the sludge by several factors and the charcoal could also be used as fuel if the sulphur content is low enough, or as fertiliser, depending on the phosphate and trace mineral content. It would therefore represent an environmentally friendly alternative to landfilling, and could even turn the waste into a commodity.

The following set of batch experiments was conducted to determine the feasibility of using vacuum pyrolysis to process sewage sludge. The samples had a weight of 150g and the experiments were run at 18 kPa over the temperature range of 300°C to 500°C. The influence of the pyrolysis time was also investigated, as this would determine the necessary residence time for a commercial reactor.

Table 6. 1: Sewage sludge vacuum pyrolysis yield (water free basis)

Temp [C]	Heating Rate [C/min]	Pyrolysis Time [min]	Pressure kPa	Charcoal %	Total oil %	Total water %	Non- Condens. Gases %
300	7-9	60	18	71	12	3	12
400	7-8	60	18	53	33	3	4
450	10	60	18	49	34	4	8
500	11-12	60	18	47	37	3	9
400	10-11	30	18	54	34	5	4
400	12-13	120	18	51	32	8	6

The total oil yield represents the oil in both the tar and aqueous phase. It was also assumed that the tar phase contained almost no water.

6.2.1   Effects of temperature

The effect of the reactor temperature had to be studied to determine the process condition that would be employed in an industrial reactor. Figure 6.1 illustrates the effect of reactor temperature on the charcoal and oil yields.
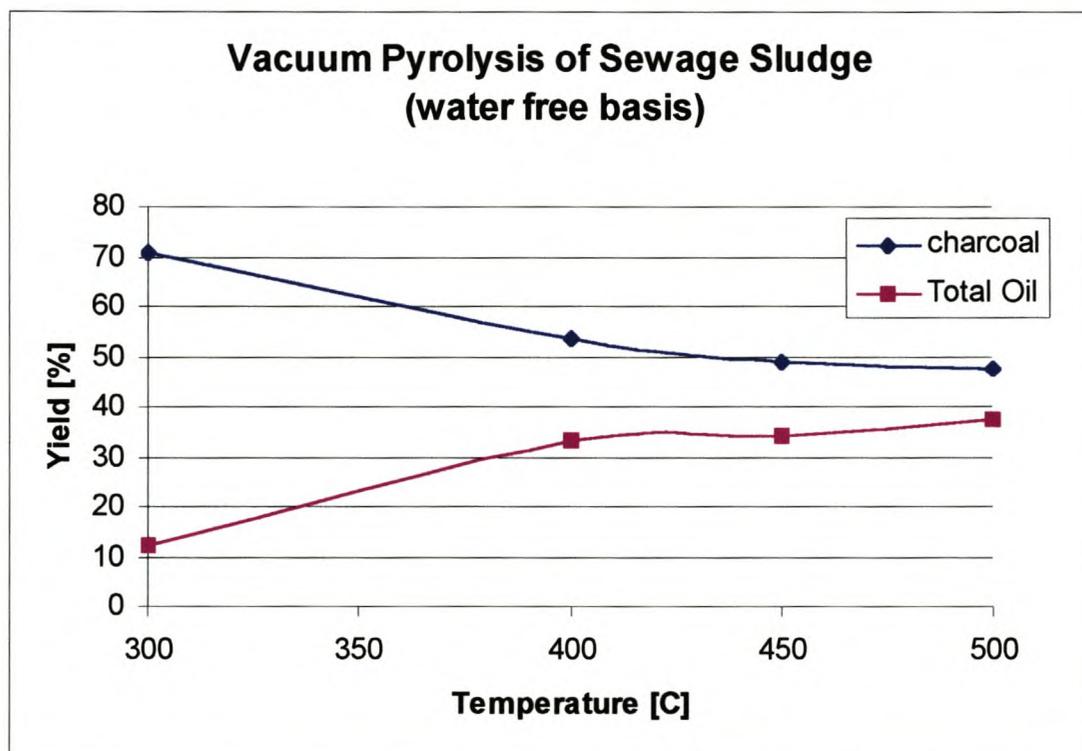
Figure 6. 1 Charcoal and oil yields for the vacuum pyrolysis of sewage sludge

The charcoal yields decrease with increased temperature, while the oil yield increases. Even though it cannot be seen here, the previous experiments on plant material have shown that the oil yield will start decreasing above a critical temperature. The reasons for this effect have been discussed in detail in previous chapters. For the sludge this temperature is higher than for the plant material.

The temperature at which the process will be run will depend on whether the volume reduction or the charcoal selling price dictates the economics. Both the oil and charcoal yields change relatively little between 400°C and 500°C. This would also make energy cost an important factor in deciding on the operating temperature.

6.2.2   Effect of pyrolysis time

Figure 6.1 shows that the sludge loses most of its volatile matter before reaching 400°C. Beyond this point there was only a small decrease with increased temperature. The rate at which the sludge loses the volatile matter will dictate the residence time of the sludge in a continuous reactor and therefore the cost of such a reactor.
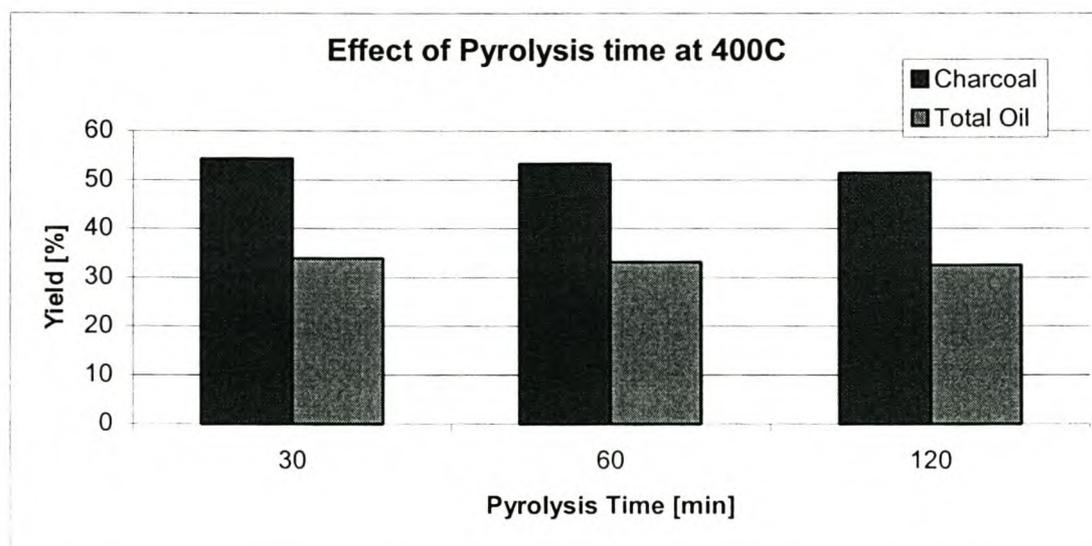
Figure 6. 2 The effect of the pyrolysis time on the charcoal and oil yields at 400°C

From figure 6.2 it can be seen that the pyrolysis time does not have a very significant influence on either the charcoal or oil yields. The charcoal yield decreases slightly, as

were no significant changes in the yields was because most of the volatile matter had been driven off before 30 minutes. The fact that the charcoal yield decreases so marginally with increased pyrolysis time shows just how small the remaining volatile matter content was. This indicates that an industrial process would need only a short residence time, and this would certainly decrease the cost of the process. The slightly higher charcoal yield at 30 minutes indicates incomplete pyrolysis; the original structure would therefore still be partly unreacted.

The small decrease in charcoal is not reflected by a subsequent increase in oil yield. This indicates that the remaining volatiles can only be removed by a longer or higher energy input, and volatiles then also only forms short chain non-condensable gases, which does not influence the oil yield.
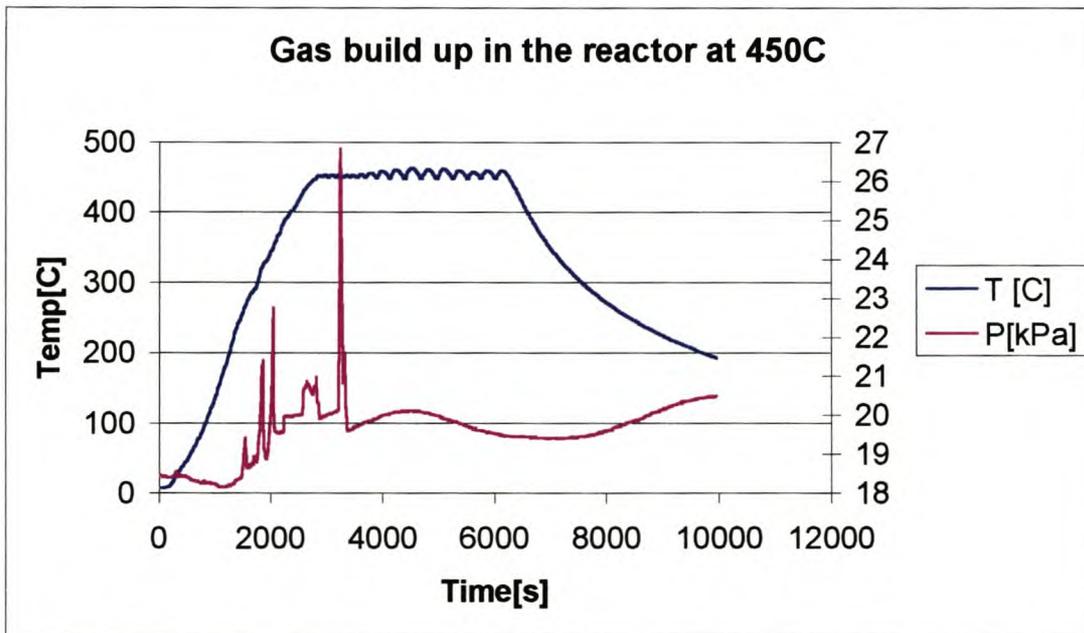
Figure 6. 3 Gas build up in the reactor during the experiment for the 450°C run.

The pressure inside the reactor is an indication of the gas build up and therefore the rate of gas evolution. The rate of gas evolution is all closely linked with mass loss and it can therefore be seen that the highest rate of weight loss occurs during heating and for the short while after the pyrolysis temperature was reached. The spikes in the pressure indicate the decomposition of certain materials, and seem to be characteristic for the material being pyrolysed. The decomposition of the sludge appears to start at

pressure indicate the decomposition of certain materials, and seem to be characteristic for the material being pyrolysed. The decomposition of the sludge appears to start at 250°C and to be mostly finished after 3500 seconds. The high rate of weight loss at the lower temperatures indicates that the sludge easily releases its volatile material. This is then also a reason why only a short pyrolysis time was needed to basically finish the vacuum pyrolysis reaction.

Decreasing the size of the spikes might be necessary if the high gas build up within the reactor leads to condensation reactions. The heights of the spikes are also an indication of the residence time of the vapours inside the reactor, with high gas build ups leading to longer residence times and more non-condensable gases.

6.2.3   Physical characteristics of the charcoal

The physical characteristics of the charcoal would determine its future economic potential and are therefore very important in determining the feasibility of the process. General characteristics dictating the economic potential of charcoal are, among others, the nature and degree of contaminant content and its energy value.

From table 6.2 it can be seen that the low moisture content of the feedstock also helps to make it a good feedstock for vacuum pyrolysis. The low water content leads to less aqueous oil products and also lower energy consumption for the process. The aqueous phase can be difficult to manage due to the multitude of organic compounds present. In the experiments it was found that the aqueous phase contained approximately 90% water. The aqueous phase was not analyzed further.

Table 6. 2 Table of the physical characteristics of the feed material and charcoal

Feed Material	Temp [C]	Pyrolysis Time[min]	Ash %	N %	Water %
Sewage Sludge			28.10	3.956	9.51
Charcoal	300	60	54.96	4.205	0
	400	60	40.88	3.463	0
	450	60	-	-	0
	500	60	33.69	3.111	0
	400	30	41.3	3.489	0
	400	120	38.71	3.397	0

The nitrogen content of the feedstock is actually lower than that of the charcoal at a pyrolysis temperature of 300°C. The lower nitrogen content is probably due to the water and volatiles with low nitrogen content lost at this low temperature, thus concentrating the nitrogen in the rest of the sample. As the temperature was increased the nitrogen content decreased linearly. The nitrogen content also decreased linearly at a constant temperature for longer pyrolysis times.

The ash content of the charcoal samples is very high, which would preclude its use as a fuel. The high trace mineral, nitrogen and phosphate content might however make it usable as compost. The economics of the process will be discussed in chapter 8. The decrease in the ash content for increased temperature and pyrolysis time indicates that some of the metal components are lost to the gas phase during the experiments. Since the ash analysis of the samples were conducted at 600°C for 4 hours temperature or time at the elevated temperature should not allow for the differences since any compound that would be effected by it would be lost during the ash analysis. It therefore appears that it might be the lower pressure of the vacuum pyrolysis process that causes the metals with high vapour pressures to be lost to the gas phase. One such compound could be phosphor, it was one of the most abundant elements found at 400°C, but during the compost analysis of the 500°C charcoal it was only present in trace amounts.

Figure 6.4 shows that ICP analysis results for the 400°C charcoal. The charcoal sample was burnt in normal atmosphere at 600°C for four hours, after which the ash was dissolved in Aqua Regia. The fraction of the ash that did not dissolve was assumed to be SiO_2. The sodium could not be tested due to problems with the ICP, but from the compost analysis later on in the section it can be seen that it is present in significant amounts.
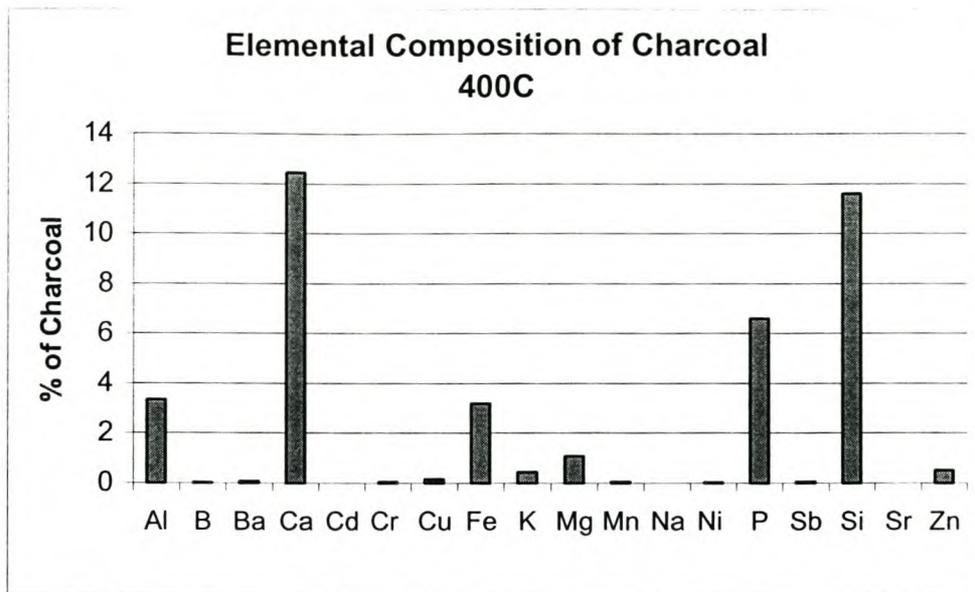
Figure 6. 4 Elemental content of the 400°C charcoal

Using figure 6.4, it is possible to estimate the metal oxide as weight percentage of the charcoal. It was done by taking the concentration of each metal and then calculating the ash content from these values. The results are shown in table 6.3. From the table it can be seen that CaO, P_2O_5 and Al_2O_3 are the dominant ash components.

Table 6. 3 Estimate of the Metal oxide composition as a percentage of the charcoal at 400°C

Elements	B_2O_3	CuO	CaO	CrO_3	ZnO	FeO	Mn_2O_3	MgO_2	Al_2O_3	K_2O	P_2O_5	SiO_2	NiO	BaO
% of charcoal	0.05	0.18	14.76	0.08	0.55	3.48	0.12	2.11	5.36	0.44	12.7	0.92	0.03	0.08

The high ash content of the charcoal indicates that the degree of volume reduction that can be achieved with the process will be important. Figure 6.5 shows the volume reductions that were achieved at the different temperatures vacuum pyrolysis temperatures and also for the different pyrolysis times.
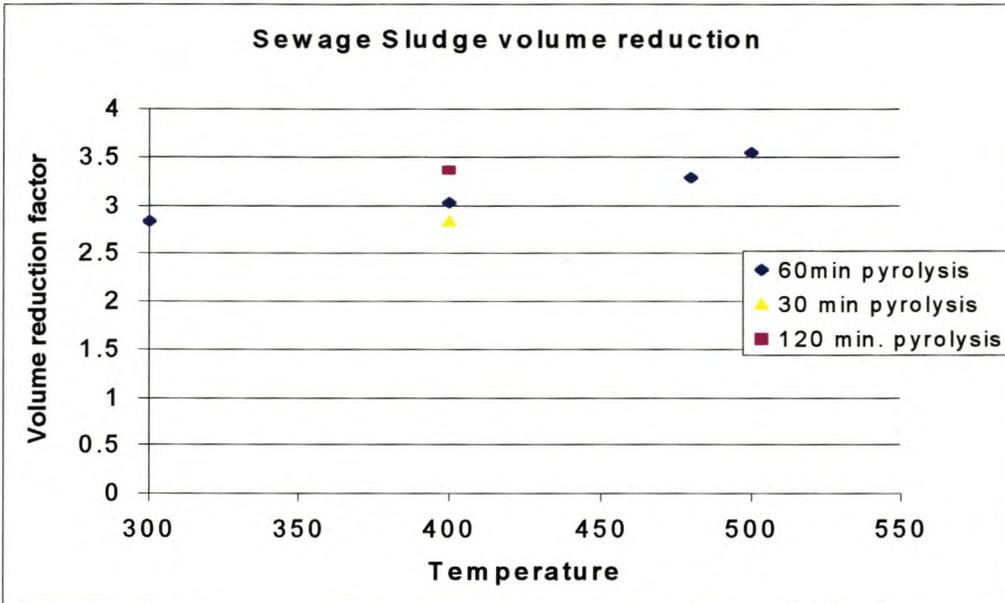
Figure 6. 5 Volume reduction of sewage sludge by vacuum pyrolysis

As could be expected, the volume reduction increases as the temperature increases. With the volume reduction factors in the range of 3.5, it can be seen that the process definitely can bring a significant reduction to the costs of landfilling.
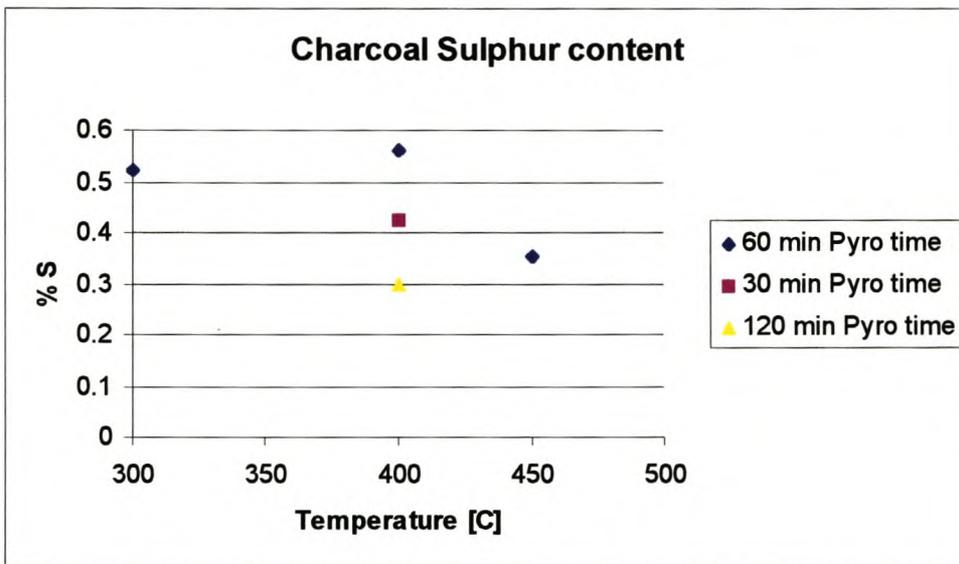
Figure 6. 6 Sulphur content of the charcoals at varying temperatures and pyrolysis times.

Figure 6.6 reveals no definite trend for the charcoal's sulphur content, but the sulphur values are very low and should present no problem in most applications. The oil product produced by the 450°C experiment contained 2.03% sulphur, which would

classify it as a high-sulphur oil. The oil also had a very high nitrogen content of 5.6%, this could pose problems if the oil was to be used as a fuel.

Table 6. 4 Energy values of the sewage sludge vacuum pyrolysis products

Sample	Pyro time [min]	Pressure [kPa]	Pyro temp [C]	Charcoal MJ/kg	Oil MJ/kg
Sewage Sludge	60	18	450	8.545	30.857

Table 6.4 shows that the charcoal had a very low energy value, but that the oil had a high energy value that would make it suitable for use as a fuel. The energy value of the sludge oil was significantly higher than the energy values of either the leather or plant oils (26MJ/kg and 24MJ/kg respectively). It should however be possible to lower the sulphur content of the fuel by designing the system to trap the sulphur before it reaches the oil condensers.

The sewage sludge charcoal was also analysed for its possible application as compost. From table 6.5 it can be seen that the resistance of the charcoal was 880 ohm. This is quite high, considering that some composts have values as low as 100 ohm. The value is an indication of the salt content of the compost, and a higher value is an indication of better compost. The nitrogen content was found to be 3.08%, which is high for compost and would also help to make it better than most composts. Another advantage of using vacuum pyrolysis would be that the ethical and social objections that have been raised against the use of sewage sludge, in the unpyrolysed form, on organic farms should be negated. All bacteria, and even any resemblance to the original feedstock are destroyed during the process and any harmful chemicals such as insecticides, which have been found in some sludges, are also destroyed.

Table 6. 5 Compost analysis of 420°C, 120min. pyrolysis time sewage sludge charcoal

pH KCL	Resistance Ohm	Moisture %	N %	F	K	Ca	Mg	Na	Mn	Cu	Zn	B
7.2	880	0.55	3.08	3	59	1208	79	339007	244	802	2283	59

The charcoal was not perfect, however. Problems existed, in that the phosphate content was very low and the sodium content was exceedingly high. The copper and zinc values were also higher than the ideal. The phosphate content can be very easily

adjusted by adding super phosphate at minimal cost. The high sodium, zinc and copper content is not such a large problem. Application in, for example, nurseries, where large quantities of water is used, these minerals would be leached out of the ground and would therefore not be problematic. In the case of other applications the amount used and regularity of use would just have to be monitored, so as not to create a build up of these minerals in the ground. The sludge charcoal compost could also be mixed with compost with low Na, Zn and Cu concentrations, which would then yield compost without any of the abovementioned problems. It would therefore seem as if the charcoal could be used as a composting material. This will have significant economic benefits for the process. The economics of the process will be discussed in detail in chapter 8.

The BET surface analysis of the charcoal for the 500°C experiments showed a surface area of 75m^2. This is quite a high surface area value and might have qualified the charcoal for steam activation to activated carbon if it were not for the high ash and metal contents.

6.2.4   Oil analysis

A tentative analysis of the tar fraction of the oil phase shows a great variety of chemicals. This is only to be expected for any process where vacuum pyrolysis is applied to a complex feedstock. The chemicals presented here are only those that could be identified with an accuracy of more than 70%. It must also be noted that the yields shown here are only the percentage of the area under the respective peaks in relation to the total area of all the peaks. No corrections for the difference in detector sensitivity towards different chemicals where made, so the values are only an indication of the yields.

Table 6. 6 Qualitative report on the chemicals found in the tar fraction of the oil phase.

[+- 12 %] Cyclohexanone ;
[>7%] Hexane, 2-methyl-; Hexane, 3-methyl-;
[>2%] Heptane; 2(5H)-FURANONE ; 2-Furanmethanol; 1H-Indole; Phenol, 4-methyl-; Pentane, 3,3-dimethyl-;
[> 1%] Tetradecane; 1,2-Benzenedicarboxylic acid, 3-nitro; Phenol, 2-methoxy-4-(1-

propenyl)-; Benzene, ethyl-; Benzene, methyl-; Benzene, 1,1'-(1,3-propanediyl)bis; Hexadecane, 2-methyl-; Cyclopropane, (1-methylethenyl)-; Cyclohexane, 1-methyl-2-propyl-; Phenol, 2-methoxy-; Acetic acid, ethyl ester; Hexatriacontane; Hexadecane ;

[>0.5%] Benzene, 1,3-dimethyl- ; Phenol; Pentadecane; 2-Cyclopenten-1-one, 2-hydroxy-3-methyl ; Butane, 2,2,3-trimethyl- ;1-Propanol; 1-Dodecene; Acetamide; 5-Octadecene, (E)- ; dl-Limonene; Ethanol; 2-Furanmethanol; 2-Butenoic acid, (E)-; Benzene, (1-butyloctyl)-; Benzenepropanenitrile; 1-Undecanol; 1,6-ANHYDRO-BETA-D-GLUCOPYRANOSE; Benzene, 1,2-dimethyl-; Benzene,(1-methylethenyl)-Benzene, 1-ethyl-3-methyl-;

[>0.1%] Acetic acid; Phenol, 2-ethyl-; Acetic acid, propyl ester ; Ethanol, 2-butoxy-; Cyclohexene, 1-methyl-5-(1-methylene); Benzenemethanol, 4-methyl-; Styrene ; Furan, 2,5-dihydro-; 2-Cyclopenten-1-one, 3-methyl-; Butanal; Acetamide; 2-Pyrrolidinone;

As can clearly be seen, this staggering array of chemicals represents a great deal of work to be analysed in detail, but the main components can be seen to be those with yields between 1% en 14%. Further study of the exact yields of the main components could disclose further economic advantages of the process.

It must be noted that a chemical such as 1,6-ANHYDRO-BETA-D-GLUCOPYRANOSE is an example of a chemical that was removed from the reactor without modification. This chemical is the basic building block of cellulose and its presence in the oil indicates that the feedstock contains high amounts of cellulose. It also shows that with a short enough gas retention time in the reactor, it would be possible to extract very complex chemicals from waste materials.

The chemical 1H-Indole is characterised as having a strong faecal odour, this would account for the smell associated with the process and would necessitate proper off-gas handling to prevent complaints. Fortunately the gas will mostly be condensed in the low temperature condensers and burning the rest of the gas would solve any odour problems.

6.3. Conclusions

The purpose of this study was to determine whether vacuum pyrolysis can be used to reduce the cost associated with the handling of sewage sludge. Presently sewage sludge is treated as a hazardous waste that has to be disposed of in very costly lined landfills. The results of the physical analysis of the sludge charcoal have revealed that

the charcoal can be used as compost. The sludge charcoal compost would have to be mixed with normal compost to lower the concentration of the Na, Zn and Cu, but the high nitrogen and low resistance of the sludge charcoal would then probably result in a more valuable end product than either compost on its own.

The charcoal yield would therefore be the main economic variable and to maximise profits, the charcoal yield would have to be maximised. Although the charcoal yields are the highest at the lower temperatures, the charcoal must still be usable as compost. The problem with the low temperature charcoals was that they contain more volatile matter that would have a negative impact on the charcoal's ability to function as compost. It would therefore be best to operate the process at 450°C, where the charcoal yield has levelled off and where it has therefore lost most of its volatiles. This would then change a hazardous, environmentally problematic waste into a commodity product. It might not only decrease the cost of handling the waste, but even make it profitable.

Another advantage of the process was the volume reductions achieved. A volume reduction factor of 3.5 was achieved at 500°C and 18 kPa reactor pressure, and would be the main advantage of the vacuum pyrolysis process if the sludge could not be used as compost.

Selling the charcoal and oil for fuel would be another use for the products, but the high ash content of 40% results in very low energy values for the charcoal (8 MJ/kg charcoal) and therefore precludes its use as a fuel. The oil does, however, have a high energy yield of 33MJ/kg and would have economic value as either a make up heat source for the process or to be sold as a high sulphur fuel. The high nitrogen content (5.6 wt.%) of the oil might pose problems if the oil were to be sold as a fuel. The oil also contains a few economically valuable compounds such as cyclohexanone and phenol that could also make the process more economically attractive.

The only negative effect the process is that, although only a small non-condensable gas yield results from the process, the gas does have a noxious odour. This would necessitate proper off-gas treatment and would therefore make the process less profitable.

Chapter 7: Co-Pyrolysis

7.1 Introduction

Co-pyrolysis is the study of the interaction between different materials when they are pyrolysed in a complex mixture. This study was undertaken to try and understand the interactions that occur during the co-pyrolysis of PVC and plant material. Greater understanding of these interactions would later allow for the modelling of such processes, which would lead to better reactor designs and subsequent economic advantages. A relevant industrial example of co-pyrolysis would be the vacuum pyrolysis of municipal solid waste (MSW).

7.2 Background

A short summary of some of the articles discussed in chapter 2 is given here in order to provide a quick overview of the literature. Several articles have shown that mixtures of materials cannot be modelled as the sum of the individual materials **[McGee et al. (1995)]**, **[Roy et al. (1990)]** and **[Darmstadt et al. (2000)]**.

Roy et al. (1990) showed that the different components of wood (cellulose, hemicellulose, lignin and extractives) interact. Wood extractives exhibit a significant inhibiting effect on hard wood vacuum pyrolysis oil yields. Wood cellulose was found to be the main source of formic acid when pyrolysed in the presence of extractives. Extractives inhibited the formation of levoglucosan during the vacuum pyrolysis of lignocellulosic materials. Lignin was found to inhibit the carboxylic acid production and enhanced the oil yield. Extractives also caused a 50°C retardation on gas and acetic acid production in the temperature range 250-350°C.

The article by **Darmstadt et al. (2000)** showed the interaction between sugar cane bagasse and petroleum residue. It was shown that, contrary to the expected no interaction, the charcoal yield did not decrease linearly but showed a marked increase when petroleum residue was added. It was shown that the petroleum residue increased the charcoal yield by causing deposits to form on the bagasse during the vacuum

pyrolysis process. This then also blocked the pores on the bagasse, trapping more of the volatiles inside the particles. The trapped volatiles would then react to form coke-like deposits within the bagasse charcoal, increasing the charcoal yield

McGee et al. (1995) showed that the HCl released from PVC during pyrolysis interacts with cellulose if the two materials are pyrolysed together. His study showed that a 90% cellulose/ 10% PVC mixture yielded less charcoal below 600K and a higher charcoal yield above 600K, when compared to cellulose in the form of straw.

7.3 Results

The vacuum co-pyrolysis of PVC and wood (Kraalbos) was investigated as a possible simplified model for the vacuum pyrolysis of MSW. PVC and wood were chosen, because **McGee et al. (1995)** suggested a simple model for the charcoal formed during the pyrolysis of municipal waste as the atmospheric co-pyrolysis of poly(vinylchloride) with cellulose derived materials. This simple model does give a relatively good indication of the char yield that can be expected from municipal waste. A 10 wt.% plastic / 90 wt.% cellulose mixture correlates best with two real-life municipal waste compositions. The charcoal yields under similar conditions for MSW from two different towns in England correlated very well to the charcoal yield of the PVC / cellulose mixture.

In this chapter a similar set of experiments was conducted, but the co-pyrolysis was performed under vacuum conditions, and instead of cellulose, plant material (Kraalbos) was used. By applying the same principles employed in the article by **McGee et al. (1995)**, it should be possible to predict the charcoal yield for MSW under vacuum pyrolysis conditions.

7.3.1   PVC

The first step in accessing the effect of vacuum co-pyrolysis was to pyrolyse each of the materials separately in vacuum. Sheet PVC cut into ribbons of 3mm long, 2mm wide and 2mm thick were used. Figure 7.1 shows the results of the vacuum pyrolysis

at 22kPa and a pyrolysis time at the pyrolysis temperature of 60 minutes. The pressure was slightly higher, because two NaOH traps were installed inline to protect the vacuum pump from the HCl vapours.
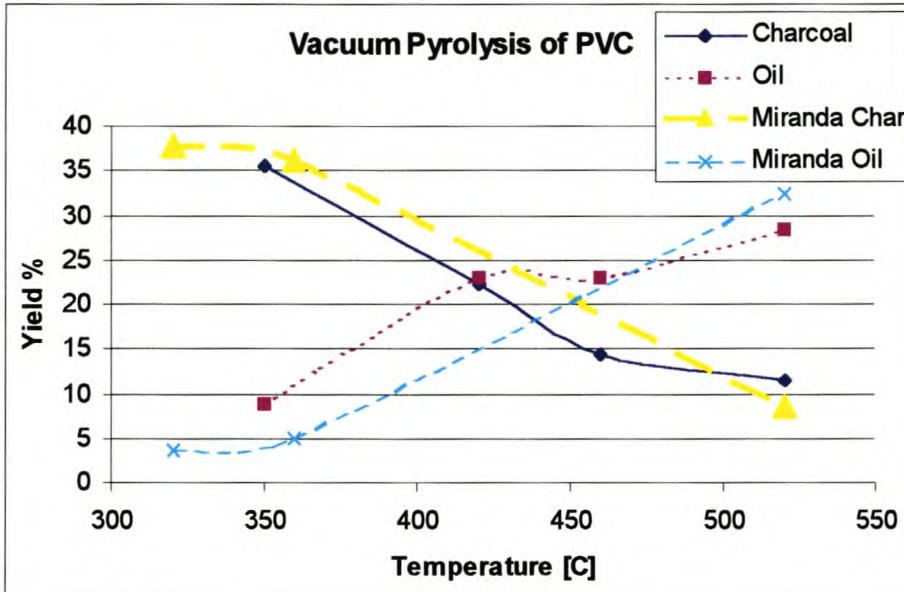
Figure 7. 1 Charcoal and oil yields for the vacuum pyrolysis of PVC

The figure corresponds very well to the values obtained by **Miranda et al. (1999)**, with the small differences in yield attributed to the lower pressure used in that study. Miranda et al. ran her experiments at 2kPa and held the pyrolysis temperature stable for 40 minutes.

Miranda et al. (1999) showed that almost 100% of the HCl was released from the PVC at a temperature of 350°C. In other words, the HCl would have reacted with the plant material at a temperature below 350°C and would then have been removed from the reactor by the vacuum. The HCl would therefore have behaved as an acid hydrolysis pre-treatment of the wood, after which the vacuum pyrolysis would have proceeded on the modified structure of the wood for all the runs. **McGee et al. (1995)** theorised that one of the main reasons why independence between the two materials cannot be assumed is that HCl is released from PVC. It was also hypothesised that the HCl might be a catalyst for certain acid hydrolysis reactions in the cellulose.

The acid hydrolysis of the wood should be comparable to the same process used in the paper industry. Although only a small mass of HCl is created, as only 58% of the

124

PVC is released as HCl, and the contact time was very short, the temperature at which it happens is much higher than the temperatures in the paper industry. The higher temperature should lead to much higher reaction rates, and with the similar chemicals involved there should therefore still be similarities in the reactions.

During the paper industry's hydrolysis process, the cellulose fraction is converted to glucose and the hemicellulose fraction is converted to a mixture of hexoses and pentoses (xylose, mannose, glucose, galactose, and arabinose). Lignin, which is predominantly embedded between the wood fibres as a binder and in the outer cell wall layers, as well as hemicellulose are largely dissolved out of the fibre matrix during chemical digestion in the pulp industry. Lignin is not very soluble during hydrolysis. Consequently it precipitates, and hence can be separated from the soluble sugars. Acid hydrolysis normally occurs in two stages. During the first stage, weak acids break the hemicellulose into its sugar components. During the more severe second stage a strong acid treatment is used to hydrolyse the cellulose component of the feedstock to glucose, a six-carbon sugar [*Unknown author, (2000)*].

7.3.2 Kraalbos

The Kraalbos had to be pyrolysed separately to enable a comparison to be made between the predicted product yields for the co-pyrolysis of Kraalbos and PVC, and the actual experimental values. The following table shows the product yields for the aged wood vacuum pyrolysis experiments

Table 7. 1 Products for the aged Kraalbos vacuum pyrolysis experiments (dry feedstock basis)

Temp [C]	Heating Rate [C/min]	Pyro time [min]	Pressure kPa	Char %	oil total %	Pyro water %	Non-cond. Gases %
350	10.0	60	18	38.5	24.7	28.8	10.1
400	10.0	60	18	36.8	25.25	27.3	12.9
460	10.0	60	18	32.6	23.6	37.7	8.1
500	10.0	60	18	30.7	23.2	33.5	14.0

Figure 7.2 shows the effect of temperature on the charcoal yield and oil yield of the aged Kraalbos.
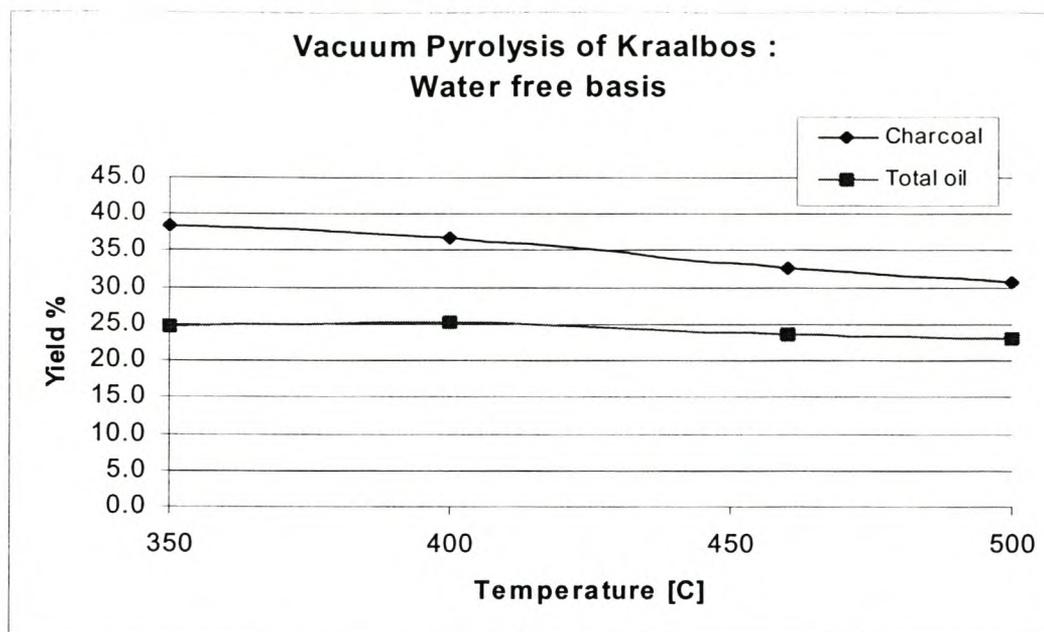
Figure 7. 2 Charcoal and oil yield for the vacuum pyrolysis of aged Kraalbos

The second feedstock that was used in the co-pyrolysis experiments was aged Kraalbos. There is a possibility that the ageing of the Kraalbos has made it more vulnerable to chemical attack by HCl when compared to a fresh sample.

The focus in this chapter will be on the changes in the expected yields for the charcoal and oil and not on the general susceptibility of wood to HCl attack in this environment. The MSW feedstock would have many more variables affecting its yield, so the changes caused by wood ageing should not have too great an effect on the realism of the simulated MSW. Ageing might even be a possible factor in future municipal waste treatment.

7.3.3 Co-pyrolysis of Kraalbos and PVC

The final step in the study of the interactions that occur during the vacuum co-pyrolysis of the PVC and Kraalbos, was to do several experiments with samples containing 10% PVC and 90% Kraalbos. Table 7.2 shows the experimental conditions and product yields for the co-pyrolysis experiments.

Table 7. 2 Products from the vacuum co-pyrolysis of PVC and Kraalbos (Dry feedstock basis)

Temp [C]	Heating Rate [C/min]	Pyro Time [min]	Pressure kPa	Char %	Oil total %	Pyro water %	Non-cond. Gases %
350	10	60	18	38.2	34.1	15.5	14.6
380	10	60	18	36.2	32.4	20.8	12.9
420	10	60	18	31.1	32.9	21.9	16.1
460	10	60	18	29.7	42.4	19.3	11.1
520	10	60	18	28.4	35.6	25.6	12.5

From table 7.1 and 7.2 it can be observed that the pyrolysis water increases with increased temperature. This is to be expected, as certain secondary reactions would lead to the formation of water, and secondary reactions increase with increased temperature. A mechanistic explanation for the vacuum co-pyrolysis of PVC and wood can be seen in appendix D, section 3.
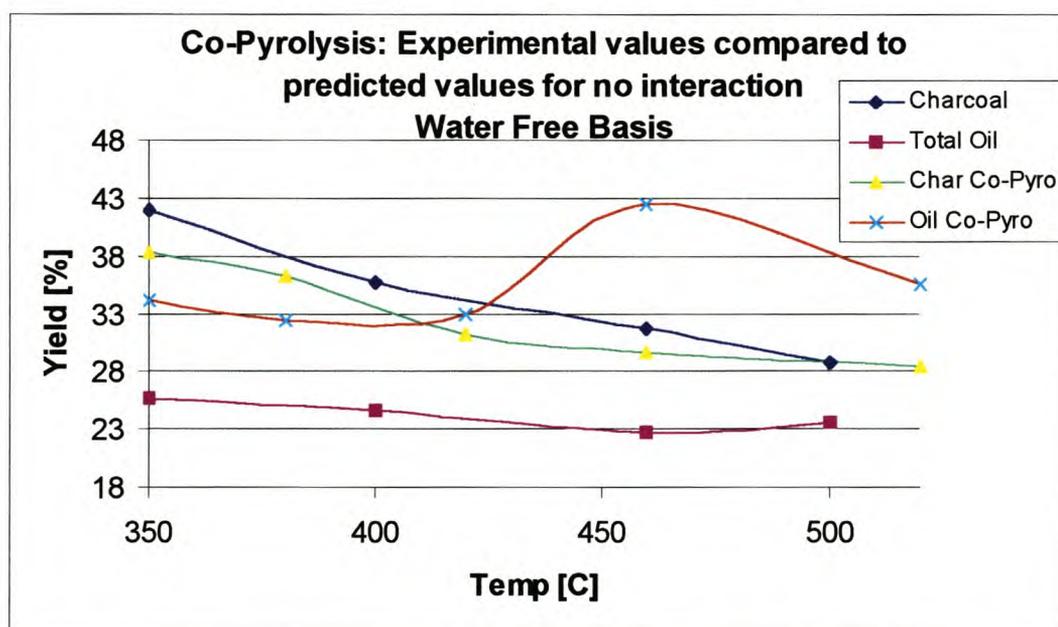
Figure 7. 3 Comparing the experimental values to the predicted values for the case were it is assumed that no interaction takes place between the different materials.

It is immediately apparent that there are definite differences in charcoal and oil yields when compared to the no interaction predictions. There was a relatively constant lower charcoal yield between 350°C and 460°C for the co-pyrolysis charcoal, after

which the two yields converged at 500°C. It appears that the co-pyrolysis charcoal's weight loss evens out faster than the predicted values, with the predicted values appearing to suggest that the charcoal would continue decreasing past 520°C at a much faster rate.

McGee et al. (1995) noticed the same trend at 380°C for atmospheric pyrolysis, with lower charcoal yields for the PVC/cellulose mixture than for pure cellulose below 380°C and higher yields above 380°C. McGee's atmospheric TG analysis of the mixture and pure cellulose showed that the mixture had a higher rate of weight loss below 380°C, and a slower weight loss rate than pure cellulose above 380°C. No explanation was given for this phenomenen, but it was speculated that acid hydrolysis of the cellulose structure might be involved.

Further TGA analysis showed that using a higher percentage of PVC in the co-pyrolysis sample caused the structure to degrade to a greater extent. (see Appendix E) It could also be seen that the individual peaks, of the derivative of the weight loss, were also enhanced. This indicates that higher weight loss rates occur for higher PVC concentrations, which is to be expected if the HCl was the main contributing factor. Comparing the aged Kraalbos TGA plot in appendix F with the aged Kraalbos/ PVC plots in appendix E, it can be seen that the way in which the weight was lost had changed considerably.

The oil yield appears to be significantly higher for the co-pyrolysis runs. This suggests that the structure of the wood has been affected in a way that expedites the liberation of long chain chemicals from the wood structure and lowers the retention time of the vapours. This causes the longer chains to survive the journey through the hot zone of the reactor without reacting to form short chain gases.

In the article by **Lynd et al. (1999)** it was stated that the dissolution of the hemicellulose from the wood structure leads to pore formation and overall better access to the cellulose structure. The statement related to biological attack on biomass, but the principle should hold for any process that dissolves the hemicellulose out of the wood structure. Such an effect would shorten the time vapours spend inside

the wood particles and would therefore help to lower the reactor retention time of the vapours. **Carrasco et al. (1992)** attributed the improvement in cellulose yields during the second stage of biomass acid hydrolysis, to the better access allowed to the cellulose because of the removal of hemicellulose and the decrease in cellulose crystallinity due to dilute acid prehydrolysis.

The dissolution of some of the lignin by the released HCL would also allow for rapid diffusion of the degradation products from the wood, because the lignin acts as the glue that holds the fibres together. Its removal would therefore afford easier access to the cellulose structure. A lower retention time for the vapours would be reflected in a reactor pressure versus temperature figure. The peaks should be less pronounced, indicating less pressure build up and therefore shorter vapour retention times.
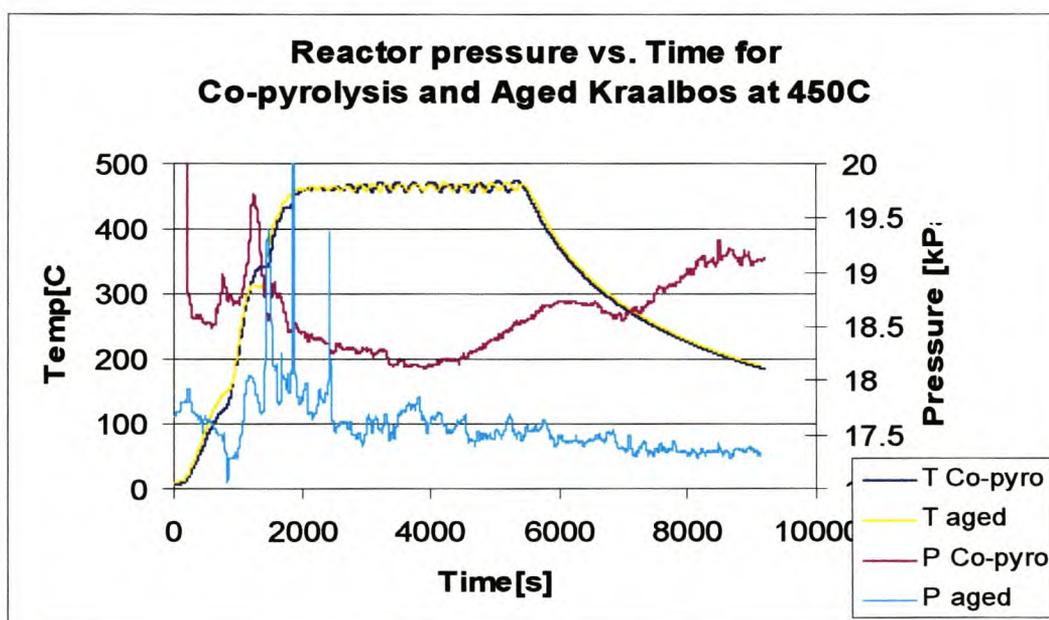
Figure 7. 4 The reactor pressures and temperatures of aged Kraalbos and Co-pyrolysis experiments versus time for a pyrolysis temperature of 460°C.

The difference in starting pressure was due to the difference in the vacuum pump operation on the day, as well as the set-up of the equipment, and is of no significance. What is important is the relative height of the peaks between the two experiments.

Figure 7.4 shows that the heating of the samples proceeded basically identically, but that the pressure build-ups inside the reactor were quite different. As expected, the co-pyrolysis run had more even and less intense peaks. This seems to confirm the

hypothesis that the chlorine gas helps to lower the retention time of the vapours through some mechanism (probably the creation of pores in the wood particle structure or by weakening the structure in such a way that the vapours are released more gradually). The gradual release of the vapours and gases would prevent surges of gas that would cause the reactor pressure to rise and cause longer retention times.

The co-pyrolysis experiment also showed an earlier start in reactor pressure rise, which indicates that a structural change causing more gradual vapour release seems possible. As was seen in the case of the aged wood when compared to a fresh sample, it appears as if the structure once again became less resistant to thermochemical degradation at lower temperatures.

It would therefore seem likely that the HCl changes the structure of the cellulose, in addition to liberating the hemicellulose and lignin before 350°C. **Gray et al. (1985)** and **Pakdel et al. (1997)** suggested that water decreases wood crystallinity and viscosity at fusion temperature, which in turn requires a lower volatilisation temperature. **F. Carraso and C. Roy (1992)** showed that the hydrolysis of cellulose could be improved by using a two-stage hydrolysis method. During the first stage dilute acid hydrolysis was used to improve access to the cellulose for the second concentrated acid hydrolysis. **Carraso et al. (1992)** attributed the improvement to the increased accessibility caused by the removal of the hemicellulose and decreased cellulose crystallinity. This would also be the result of the acid hydrolysis reactions that occur during co-pyrolysis.

The cellulose structure was degraded, and this should have the same effect as the dilute acid treatment and water treatment. The volatilisation temperature would therefore be lowered, which would lead to the earlier start of the vapour production. The structural changes in the cellulose would account for the higher than expected charcoal yield above 460°C. The higher yield indicates that the final structure becomes more stable when compared to aged wood for the same temperature. The faster weight loss of the co-pyrolysis run at temperatures below 460°C indicates the expediting of the loss of some of the components of the wood structure. The hemicellulose and lignin should also cause faster weight loss, as their partial digestion

by the acid hydrolysis would make it easier for them to be volatilised. The lower degree of polymerisation of the cellulose would also make it easier for it to degrade at lower temperatures.

From literature **[Elvers et al. (1991)]** it is known that hemicellulose and lignin are easily digested by acid hydrolysis, and it is known that the extractives can be removed from wood at relatively low temperatures (in the range of 200°C-250°C), leaving only cellulose.

All the glycosidic links of cellulose are vulnerable to acid hydrolysis and the presence of gluco-pyranose in the oil indicates its degradation. It was found that 5 times more gluco-pyranose formed during the co-pyrolysis experiments than during the pure Kraalbos experiments. This shows that the cellulose structure was degraded by the HCl gas, leading to structural changes that would be partly responsible for the more gradual vapour and gas release. The higher gluco-pyranose yield also indicates that higher yields of complex compounds were made possible by the acid treatment.

The formation of benzenedicarboxylic acids during the co-pyrolysis experiments is a sure indication of acid induced reactions. No benzenedicarboxylic acids were formed during the vacuum pyrolysis of Kraalbos or any of the other plants. The 5 % yield, on a water free feedstock basis, also shows the severity of the acidic attack. A 5 % yield represents the highest yield recorded for any of the compounds present in the samples.

According to **Pakdel et al. (1997)** benzenediol and benzenetriol are demethylation products of primary phenolic compounds. The lower gas retention time and the degraded structure of the cellulose during the co-pyrolysis experiments decreased the occurrence of this side reaction, which led to lower yields of benzenediol and benzenetriol.

Table 7. 3 Benzenediol yield compared on a per gram of oil basis

Compound	Kraalbos	Co_pyro
1,4-Benzenediol	0.2655	0.1414
1,2-Benzenediol	1.0735	0
1,4-Benzenediol, 2-methyl-	0.1804	0
	1.5194	0.1414

As can be seen from table 7.3 the benzenediol yield decreased ten fold for the co-pyrolysis when compared to the pure Kraalbos experiment. This shows that the much lower occurrence of side reactions was greatly responsible for the higher oil yield of the co-pyrolysis experiments.

There might also be another factor that would increase the oil yield in co-pyrolysis experiments. **Puncochar et al. (2000)** showed that metals catalyse the formation of chlororinated dioxins and furans during pyrolysis, while **Gray et al. (1985)** established that ash and added calcium catalysed the conversion of tar into aqueous products. **Pakdel et al. (1997)** also stated that metals catalytically decompose phenolics. During the co-pyrolysis experiments HCl was formed which could have reacted with the surface of the metals present in the samples. This would then have deactivated the metal's surface and would therefore lessen the catalytic effect it had. This would allow for more vapours to be formed in relation to gases, increasing the oil yield. The lower benzenediol formation shows that fewer side reactions occurred, and it is possible that the lower catalytic potential of the deactivated metals were also partly responsible.

To see if the HCl could affect the metal surfaces the thermodynamic equilibrium computer program was once again used to study the hypothetical equilibrium process yields.
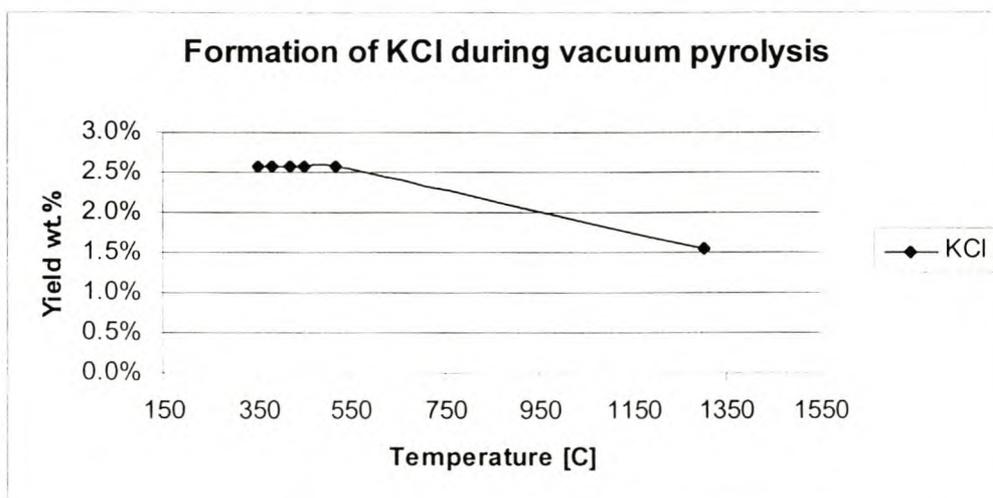
Figure 7. 5 Formation at equilibrium conditions of KCl during vacuum pyrolysis

As can be seen from figure 7.5 some KCl would be formed at the thermodynamic equilibrium. This indicates that KCl will to some extent be deposited on the metal surfaces, which should deactivate the metal surface and reduce its catalytic effect. The reduction in the catalytic effect would therefore lead to higher oil yields.

Studying the condensed oil distribution should help to show that more oil and less non-condensables were formed. Figures 7.6 (a) and (b) show the differences in condensed oil distribution for the different pyrolysis temperatures for aged and co-pyrolysed wood. By studying these figures it was be possible to make deductions regarding the nature of the vapours and gases formed and therefore also the process which led to their formation.

(a)   (b)
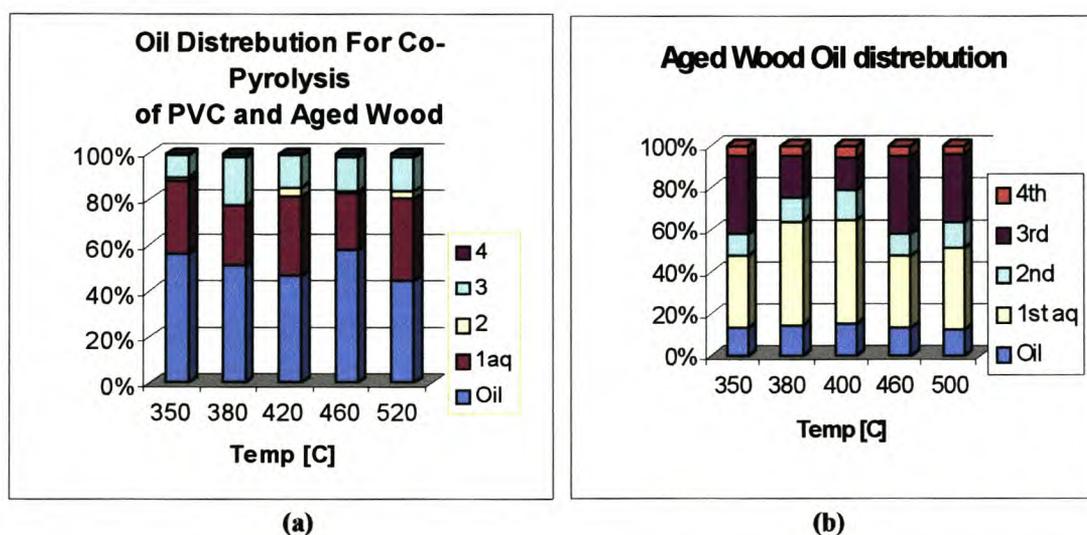
Figure 7. 6 Oil distribution for (a) the co-pyrolysis of PVC and Aged wood, and (b) the pyrolysis of pure aged wood

Figure 7.6(a) and (b) show the condensation distribution of the condensable oils over the five condensers. The oil fraction was condensed in the room temperature trap, the 1 aq fraction refers to the aqueous phase in the first -10°C condenser, 2nd refers to the second -10°C trap, with 3rd and 4th referring to the two -78°C condensers. It follows that the lower the temperatures required to condense the vapours, the shorter is the compound's chain length. Consequently higher percentages of the oils condensing in the colder condensers indicate the formation of more light molecules.

It is immediately apparent that a much higher percentage of the total oil yield for the co-pyrolysis experiments were condensed as oil and that there was almost no

condensation in the last trap. When this is compared to the pure aged wood vacuum pyrolysis runs, it can be seen that there were significant percentages of the vapours condensed in the last condenser for the pure wood experiments. This indicates that in the case of the wood experiments a high percentage of the oils are formed as short chain length molecules, and the differences between the two experimental runs show the effect that HCl has on the aged wood structure.

The HCl released by the PVC at temperatures below 350°C caused the wood structure to change in such a way that more longer chain molecules and more oil in total were formed. The more complex chemicals also had a better chance of passing through the reactor without modification, as the reactor temperature was lower.

The changes in the structure also caused the charcoal yield to be lower for the co-pyrolysis experiments. This would also contribute to the higher oil yield, as more of the wood structure was decomposed to form vapours and gases. Even though more of the charcoal structure degrades at the lower temperatures for the co-pyrolysis experiments, the difference in charcoal yield between the two sets of experiments is still much lower than the rise in oil yield. This indicates that the co-pyrolysed wood structure also degrades in a different way than the aged wood structure, which in turn could also point to changes in the wood structure itself.

All these facts seem to indicate that the decreasing of the wood crystallinity and viscosity because of the acid hydrolysis of the cellulose, and pore formation because of the digestion of the hemicellulose are the main reasons for the higher oil yield for the co-pyrolysis experiments.

The BET surface area analysis in table 7.4 shows that the charcoal from the 520°C co-pyrolysis experiment has a surface area of $88m^2$. This is significantly better than the $5.4m^2$ and $6.8m^2$ surface areas of the 500°C plant experiments. It has been noted before that the surface areas of the charcoals from the plant experiments are very small, the reason being that a large quantity of volatiles is still present in the sample. These volatiles block the pores and thereby decrease the surface area.

Table 7. 4 BET surface areas for the co-pyrolysis and plant charcoals

BET surface analyses		
Sample	Temperature [°C]	Area m^2
Co-Pyrolysis	450	11
	500	88
Kraalbos	450	12.4
	500	5.36
Scholtzbos	500	6.8

Comparing the surface areas of the Kraalbos charcoal with the co-pyrolysis charcoal for the 450°C runs, it can be seen that the values are nearly identical. Both had surface areas in the range of 11-13m^2. This indicates the incomplete pyrolysis of both samples. The low surface area for the 450°C experiments for both samples shows that, while the pure wood charcoal still contained volatiles at 500°C, the co-pyrolysed charcoal had already finished its pyrolysis reactions. It was therefore free of volatiles, and so allowed access to its pore structure, thus resulting in a higher surface area. The much higher surface area of the co-pyrolised charcoal at 500°C also suggests that the acid treatment affected the charcoal structure on the macroscopic level. It appears that pore formation did occur, as was suggested by the pressure vs. time graph (figure 7.4). This tentatively supports the hypothesis of pore formation due to the acid dissolving the hemicellulose.

A surface area of 88m^2 was high enough to make the charcoal a candidate for steam activation to activated carbon. Activation experiments would, however, first need to be done before the feasibility could be determined.

Apart from the interest in the interaction between PVC and wood and the effects this interaction had on the vacuum pyrolysis products, there was also another reason to study the vacuum co-pyrolysis of wood and PVC. PVC is one of the most troublesome wastes to handle since it releases HCl during heating and causes several other problems. One of the greatest problems is the creation of chlorinated dioxins and furans. The paper by **Puncochar et al. (2000)** states that metals present in the ash and fly ash catalyse the formation of these chlorinated dioxins, but that the catalytic efficiency of the metals surfaces can be reduced by the formation of metal sulphates

through concentrated sulphuric acid treatment. The paper also stated that the Deacon reaction contributes to the dioxin formation. The reaction causes more of the HCl to convert to chlorine gas, which leads to higher yields of dioxins.

$2\ HCl + \frac{1}{2}\ O_2 = Cl_2 + H_2O$ (Deacon reaction, starts >400°C)
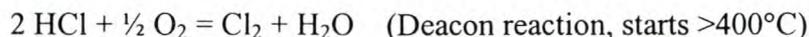
Vacuum pyrolysis would have the advantage of firstly working at much lower temperatures than incinerators and atmospheric pyrolysis (400°C-520°C compared with 1300°C), which would cause less of the metals to be able to catalyse the dioxin formation. This would be because the lower temperature would slow the rate of reactions and less of the metals would be in the gas phase where they are the most reactive. The Deacon reaction would also occur to a much smaller extent since the vacuum pyrolysis process operates in a very low oxygen content atmosphere. Even though atmospheric pyrolysis also operates in a low oxygen atmosphere the much higher reaction temperatures would still lead to the creation of more dioxins.

Most of the chlorine released during the vacuum pyrolysis process would therefore be in the form of HCl instead of chlorine. This would lead to less dioxin and furan formation and although the process equipment would still have to be stainless steel to cope with the corrosive HCl gas; and proper off gas treatment would still be necessary to properly remove the HCl from the gas stream, it should still be a much better solution than incineration or atmospheric pyrolysis.

One of the main possible applications for vacuum pyrolysis on mixtures of PVC and plant material would be municipal solid waste (MSW). The assumption that municipal waste can be represented by a 10% PVC/ 90% cellulose feedstock **[McGee et al. (1995)]** was tested using the thermodynamic program. Figure 7.7 reveals that the curves of the simulated MSW (using the MSW composition reported by **McGee et al. (1995)**) and the PVC/ cellulose mixture follows the same trend. It also shows that the simulated MSW does have a slight positive offset compared to the PVC/ cellulose mixture.
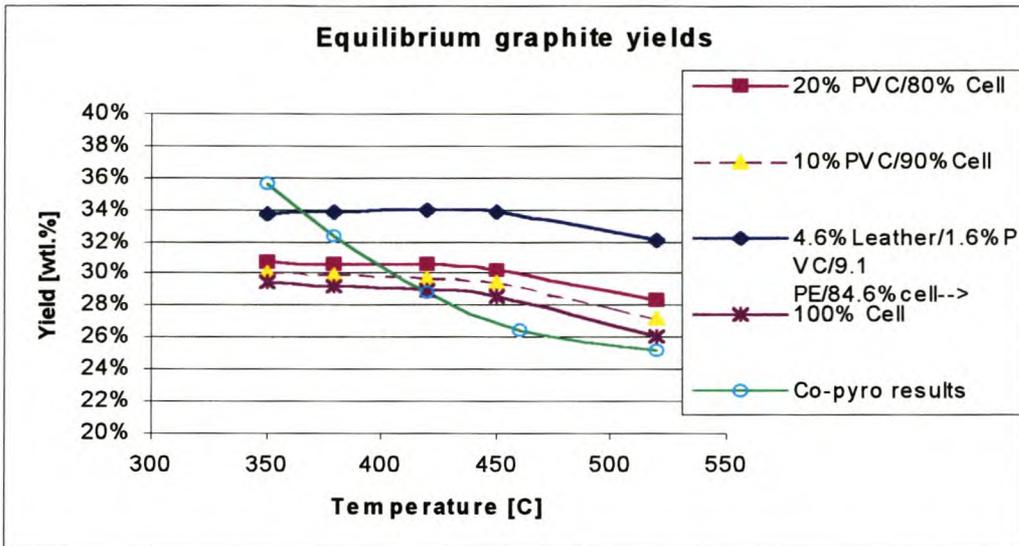
Figure 7. 7 Equilibrium graphite yields for simulated MSW and PVC/ cellulose mixtures (ash free basis)

The graphite equilibrium yields did not follow same trend as the charcoal yields for the co-pyrolysis experiments, but this is to be expected since the charcoal does not consist only of graphite and the co-pyrolysis reactor is not a closed system. It is interesting to see that the co-pyrolysis charcoal yield at 520°C was very close to the predicted graphite yield. This implies that the co-pyrolysis experiment was close to the theoretical equilibrium, this would only be for the charcoal and not for the gases, since the gases were removed from the reactor.

The predicted yields of the 10% PVC / 90% Cellulose mixture were between 20% and 11% (decreasing difference with increased temperature) less than the simulated MSW yields. This can be seen as a fairly good correlation since the pyrolysis process from which the 10%PVC/ 90% Cellulose mixture approximation was first developed, and the vacuum pyrolysis processes, are not process that operates close to equilibrium conditions. The similar trend between the MSW and the simulated PVC/cellulose mixture were also encouraging.

7.3.4 Co-Pyrolysis Oil analysis

The tarry oil fraction of the 460°C pyrolysis experiment was analysed to determine the chemical composition of the oil and to study the difference in oil yields achieved

137

between the aged wood and co-pyrolysis experiments. The list of all the chemicals found in the co-pyrolysis oil and the comparison between the co-pyrolysis oil components and the aged wood components can be found in appendix B. Table 7.5 and 7.6 shows the results from the quantitative analysis of the tarry oil fractions. Using an internal standard and then determining the GC/MS response factors of the compounds in relation to it enabled the determination of the quantitative results.

Table 7. 5 Quantitative compound yields [dry feedstock basis]

Compound	Yield % Co-Pyro	% Kraalbos
1,2-Benzenedicarboxylic acid, 3-nitro <nitro-Phthalic acid> + other substituded Phthalic acids	5.00	n.d.
1-Propanol	0.09	0.003
Phenol, 2,6-bis(1,1-dimethylethyl)	0.04	0.01
Phenol, 2-methoxy- <guaiacol>	0.04	n.d.
p-cresol	0.03	0.004
Benzene, 1,2,3-trimethyl-	0.002	0.001
Benzaldehyde, 4-hydroxy-3-methoxy- <vanillin>	0.02	0.001
Phenol	0.01	0.13
o-cresol	0.01	0.001
Xylenol	0.01	n.d.
1,4-Benzenediol	0.01	0.054
1,1'-Biphenyl	0.003	n.d.
Phenol, 2,6-dimethoxy-4-(2-propenyl) <6-methoxyeugenol>	0.07	0.051

It is clear that the co-pyrolysis experiment yielded more phenols than the Kraalbos or any of the other plants.

The response factors used for the quantitative determination of the results in table 7.6 could not be determined, and they were therefore inferred by assuming that the response factor would be close to the values determined for chemicals with similar functional groups. Although this is not a very accurate method, it does allow for better values than using a response factor of one.

Table 7. 6 Compound yields using inferred response factors [dry feedstock basis]

Compound	Yield	
	Co-Pyro	Kraalbos
Cyclohexanone	0.28	0.104
Cyclohexene, 1-methyl-4-(1-methyle	0.08	0.002
Benzene, methyl-	0.06	0.008
Acetic acid, ethyl ester	0.10	
Phenol, 2,6-dimethoxy-	0.14	
Ethanol, 2-butoxy-	0.06	
Benzene, ethyl-	0.04	0.003
Benzene, 1,2-dimethyl-	0.03	0.004

It was observed that 28.8mg per kg of dry feedstock, biphenyl was recovered in the oil fraction for the 460°C co-pyrolysis experiment. Biphenyl is a dangerous chemical that can cause serious environmental problems.

The main compound formed during co-pyrolysis was benzenedicarboxylic acid (phthalic acid). The phthalic acid mostly had other functional groups attached, such as 3-nitro and dioctyl. The formation of benzenedicarboxylic acids is unique to the co-pyrolysis experiments and is proof that a high degree of acid hydrolysis occurs. Thus the released HCl does have a significant effect on the chemical bonds of the wood structure.

The total yield of all the phthalic acid components was close to 5 % of the initial dry feedstock weight. Comparing this value to the percentage yields achieved for the other compounds, it can be seen that this is almost a factor 10 higher than the second most abundant compound. Acid hydrolysis of compounds containing alcohols and aldehydes can lead to the formation of carboxylic acids. Lignin being the main source of aromatic compounds in the pyrolysis oil appears to be the most likely source of the phthalic acid. The phthalic acid would have been created through acid hydrolysis reaction of the lignin.

From table 7.6 it can be seen that the co-pyrolysis yields are once again much higher. This is mostly because of the higher oil yield for the co-pyrolysis experiment, but other factors such as the higher percentage of more complex compounds formed also played a role.

7.4 Conclusions

This chapter of the thesis is different from the others in that it was not specifically designed to determine the economic advantages of co-pyrolysis. The aim of the study was to elucidate the interaction between PVC and plant material, and the possible future application in MSW vacuum pyrolysis. It was found that adding PVC to plant material during vacuum pyrolysis could increase the product yields. The charcoal yield decreased from 32.6% to 29.7% on dry feedstock basis at the maximum co-pyrolysis oil yield temperature of 460°C, but the oil yield increased substantially to 42.4% from 23.6% at 460°C. The energy value of the charcoal was slightly higher than the charcoal at 27.9MJ/kg, and the oil had basically the same energy value of 24MJ/kg. This indicates that hydrolysing biomass feedstocks before pyrolysis, as has been done for years in the bioprocessing of plant material, could lead to much higher product yields and therefore increased profits. The most important issue that needs to be addressed before commercial applications could become possible, is the nature and degree of chlorine contamination of the charcoal, oil and off gases that occurs during such a process.

The main aim of the study of the PVC and plant material vacuum co-pyrolysis was to determine what the effects and extent of the interaction in the mixture was. It was found that the significant increase in oil yield and slight decrease in charcoal yield could mainly be attributed to the hydrolysis of the hemicellulose and cellulose. The hydrolysis of the hemicellulose led to pore formation and subsequent better access to the cellulose in the particles, which lowered the vapour residence time in the particles and thereby reduced the degree of side reaction that occurred. Lowering the degree of side reaction then led to higher oil yields. Hydrolysis of the cellulose lowered the degree of crystallinity of the cellulose and so reduced the temperature at which it degraded, which allowed the vapours to be released at a lower temperature. The lower temperature at which the vapours were released also led to a reduction in the degree of side reactions that occurred. The decrease in the degree of crystallinity of the cellulose also changed the nature of the compounds released from the cellulose structure and led to the release of longer chain compounds, which also increased the oil yield.

Another factor that could have contributed to the higher oil yield was the possible reduction in the catalytic effect of the ash present in the plant material. **McGee et al. (1995)** showed that the ash present in wood catalyses the formation of aqueous products and in so doing reduces the oil yield. A thermodynamic equilibrium program was used to show that metal chlorides were formed at the temperatures at which the vacuum pyrolysis process operated (350°C-520°C), and that this reduced the catalytic effect of the ash. This was found to be at least partly responsible for the increased oil yield found during vacuum co-pyrolysis of PVC and plant material.

The article by **Puncochar et al. (2000)** indicates that vacuum pyrolysis might decrease troublesome dioxin and furan emissions, created during the incineration of PVC, because of its lower operating temperature and the low oxygen content of the atmosphere in the reactor. The exact dioxin and furan content of the oil and gas phases would however first have to be determined before comparisons could be made.

The assumption that MSW can be represented as a mixture of 10% PVC and 90% cellulose was tested using the thermodynamic equilibrium computer program. It was found that although the equilibrium graphite yields differ, the overall trend appears to be the same. This coupled with the experimental results obtained by **McGee et al. (1995)** indicates that the mixture can be used as a simplified representation of MSW.

It seems that the study of the co-pyrolysis of PVC and plant material could reveal advantages of the industrial application of vacuum pyrolysis in the future. The most important question that would have to be addressed before commercial applications could become possible would concern the nature and degree of chlorine contamination of the charcoal, oil and off gases that occurs during such a process.

Chapter 8: Preliminary Process Economics

8.1 Introduction

As with any engineering solution to a real world problem, the economics of the process plays a dominant role. As the vacuum pyrolysis process was studied in relation to the field of recycling, the environmental impact has to be considered, especially with new and harsher environmental laws being passed continually.

Roy et al. (1992) did a conceptual design of a continuous wood vacuum pyrolysis plant and found that the selling prices of the charcoal and the oil were the most important economic factors. Roy calculated that if a 7875 kg/h (50% moisture biomass) vacuum pyrolysis plant were to be erected, the production cost per ton of oil would be R1000 if the selling price of the charcoal were R900 per ton (January 2001 basis). These costs are a good indication of the production cost of a large biomass plant, but the applications for biomass vacuum pyrolysis in South Africa would probably start at a much smaller level. If the oil were to be used for its fine chemical content, the process economics would be greatly improved.

The charcoals' economic viability was determined by comparing the charcoal from the vacuum pyrolysis process with commercially available charcoal brickets and charcoal. The comparisons were conducted on the basis of ash and sulphur content and their respective calorific values. Possible future economic advantages of the process will also be discussed. Factors such as the upgrading of the charcoal to activated carbon and the upgrading of the oil to valuable chemicals will be considered.

8.2 Intruder Plant species

The aim of the vacuum pyrolysis of the plant species was to see if it would be possible to make intruder plant clearing projects financially viable. The charcoal and oil produced from the intruder plants would allow these projects to generate money, instead of being only a necessary expense. The intruder plant specie charcoal does not contain any noteworthy contaminants that could cause problems in terms of its use as a fuel. Figure 8.1 shows the sum of charcoal and oil yields for the different plants at 18kPa reactor pressure and with a pyrolysis plateau time of 60 minutes.
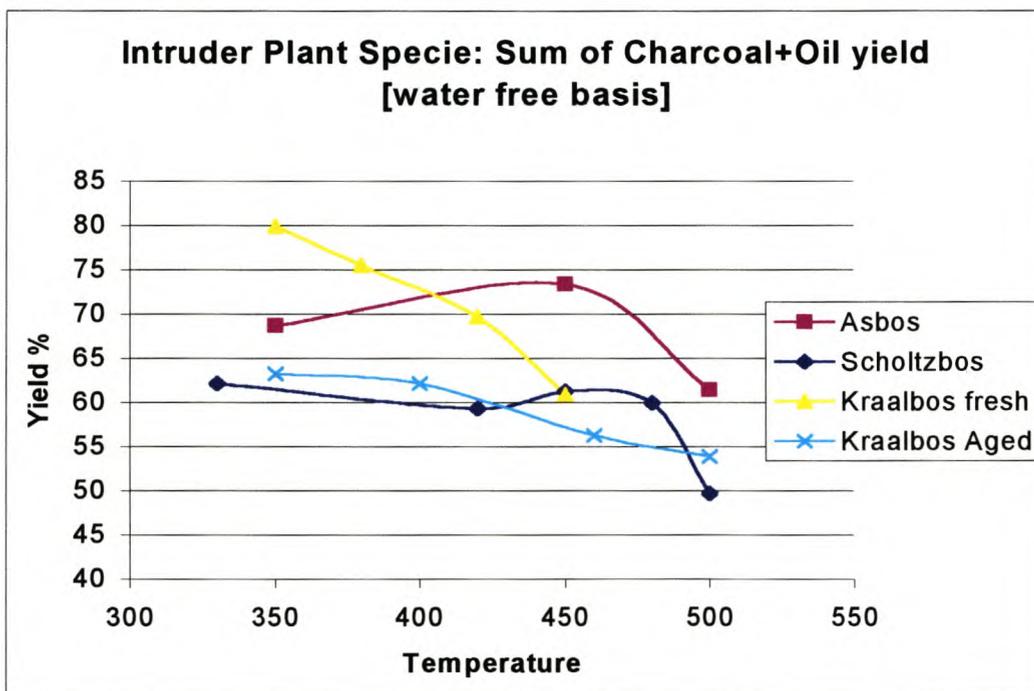
Figure 8. 1 Sum of the Charcoal and oil yields for the intruder plant species. [water free basis]

The sum of the charcoal and oil yields gives an indication of the possible economic value of the products if the charcoal and oil could be sold or used in a way that would affect the process economics. The most economic temperature will be determined on a combination of charcoal yield / energy value basis. This will ensure that the most economic vacuum pyrolysis temperature will be chosen.

Table 8. 1 Energy values of the plant products

Sample	Pyro time [min]	Pressure [kPa]	Pyro temp [C]	Charcoal MJ/kg	Oil MJ/kg
Scholtzbos	60	18	450	19.4	26.9
Asbos	60	18	450	12.9	-
Kraalbos Fresh	60	18	380	24.3	21.6
	60	18	420	25.0	21.6
	60	18	450	25.0	21.8
	30	18	380	23.0	24.8
	120	18	380	23.9	-
	60	50	380	25.5	-
Kraalbos aged	120	18	380	25.8	-
	60	18	500	24.8	24.0

The energy values of the Kraalbos and Scholtzbos compare very well with the values obtained by **Pakdel et al. (1994).** Roy found that the vacuum pyrolysis of primary sludges and bark yielded charcoal with 22.2 MJ/kg and 28.1 MJ/kg respectively. It also yielded oil with an energy value of 25.1 MJ/kg and 30.9 MJ/kg respectively. It can be seen from table 8.1 that the oils have high energy values and combined with their low sulphur contents of 0.47% would qualify it as a low sulphur furnace oil. The general retail price of furnace oil is R1.42 per litre.

Table 8. 2 Energy values of the plant feedstocks and commercial charcoals

Sample	MJ/kg
Feedstocks	
Kraalbos	16.3
Scholtzbos	16.8
Commercial products	
Etosha Charcoal	27.6
Etosha Brikets	20.4
Charca Brikets	24.9

The energy values of all the charcoal products except Asbos are also in the same energy range as the commercial products. The energy values of the charcoals stay relatively constant over the temperature range. Therefore, if the process economics depend mostly on the charcoal, it would be best to work at the lowest pyrolysis temperature studied. Figure 8.1 indicates that this temperature should be 350°C, as the charcoal yield was at a maximum at this temperature and the energy costs associated with the process would also be low. From figure 8.1 it can be seen that the maximum yield of the sum of the oil and the charcoal is at 350°C, except for Asbos, which has a slightly higher yield at 450°C.

From table 8.1 it can also be seen that the energy value of the charcoal was not very sensitive to the pyrolysis time of reactor pressure. A lower reactor time and higher pressure would lead to a charcoal containing a high percentage of volatiles, which could be problematic in some applications of the charcoal. The shorter reaction time would lead to smaller reactors and the higher pressure would make it possible to install cheaper vacuum pumps.

Figure 8.2 shows the sulphur content of the intruder plants and commercial charcoal.
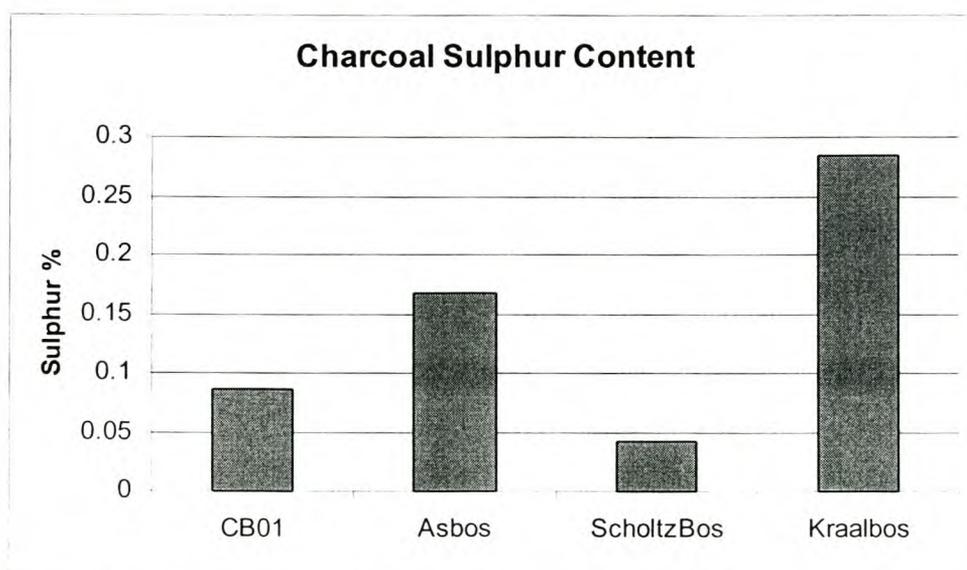
Charca Brikets (CB01) represents the commercial charcoal.

Figure 8. 2 Plant charcoal sulphur content

The very low sulphur values make the charcoal ideal as an energy source. Even though the Kraalbos has a higher sulphur value, the value is still low enough to allow the coal to be used. All three the plants had nitrogen contents in the range of 1%, which was basically the same as the commercial products.

The only other major factor that had to be considered was the charcoal ash content. The following figure shows the ash content for the vacuum pyrolysis charcoal at different temperatures for the three plant species.
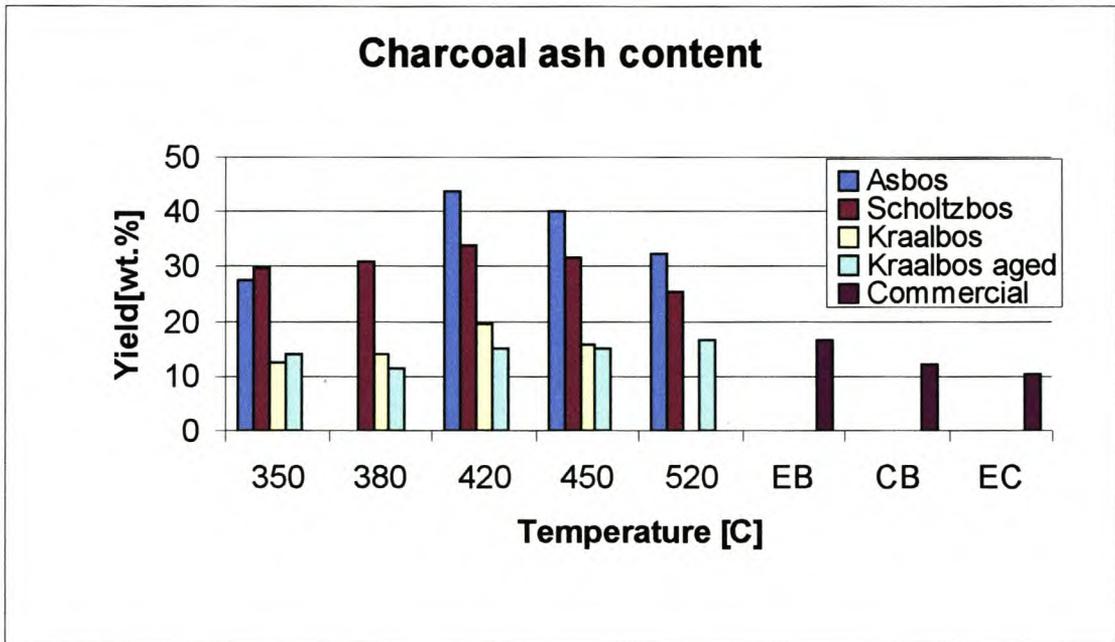
Figure 8. 3 Charcoal ash content

The commercial charcoals were Ethosha brikets (EB), Ethosha charcoal (EC) and Charca brikets (CB). Figure 8.3 shows that Kraalbos has an ash content that is even lower, at some temperatures, than the commercial products, making it perfect for the commercial application of vacuum pyrolysis. Scholtzbos has an ash content that is almost double that of the commercial products. Asbos, on the other hand, has an ash content of between 100% and 160% more than the commercial products. The higher ash content lowers the energy value of the charcoal, and would therefore be worth less as a fuel. It should still be of use to the braai industry, home-cooking and other home applications, though.

Table 8. 3 Selling price per kilogram of commercial charcoal

Product name	Price per kilogram
Etosha Charcoal	R2.70
Etosha Brikets	R3.38
Charca Brikets	R5.00

The Kraalbos and Scholtzbos charcoals can definitely compete with the commercial brands of charcoal available and would therefore have a commercial selling price between R3000-R5000 per ton, but the high ash content and low energy value of the Asbos makes it less desirable as a feedstock.

The oil analysis in chapter 3 showed that there are several valuable compounds present in the oil in meaningful concentrations, but the technology to produce fine chemicals from the oils are not yet developed enough to use it in small scale processes. There would, however, be significant economic advantages in doing so. From table 8.4 the possible economic value of some of the oils can be seen. The selling price of the compound off course fluctuates significantly depending on the grade and demand for the compound. The prices listed here are for the selling price of chemically pure reagents and not for industrial grades, the actual values would therefore be less than half of the listed value. The prices are also for small quantities and not for industrial scale sales.

Table 8. 4 Selling price of some of the major compounds found in the oil

Compound	Selling Price	Selling price Per unit
Acetic acid	R700/25L	R28/L
Acetic acid ethyl ester	R1000/25L	R40/L
Cyclohexanone	R130/ L	R130/L
Benzene, Ethyl	R140-R300/ L	R140-R300 /L
Benzene, Methyl	R100-R210/ L	R100-R210 /L
Phenol	R140-R700/L	R140-R700/L
Phenol,1,2-dimethyl	R770-R910/kg	R770-R910/kg
p-Cresol	R110/ 500g	R220/kg
Eugenol	R5600/18kg	R311/kg
6-Methoxyeugenol	R210/g	R210/g

| 1,2-Benzenediol | R1000/ 5kg | R200/kg |
| o-Cresol | R240/ kg | R240/kg |

A short summary of the uses of some of the chemicals found in the pyrolysis oils is given below. **Phenol** is used in making plywood, pharmaceuticals, adhesives, plastics, rubber and as a general disinfectant in solution for toilets, etc. It is used in dyes and in solution for petroleum refining. It is also used in paints as a germicide and as a disinfectant against vegetative bacteria and certain viruses. **Acetic acid** is an important compound in the manufacture of cellulose acetate, plastics, dyes, insecticides, pharmaceuticals and textile printing. **Aniline** is used in the manufacture of rubber, dyes, photographic chemicals and pharmaceuticals. **Cresol** is needed as a disinfectant, in resins, ore flotation, textile scouring agent and synthetic food flavours. **Cyclohexanol** can be used for soap, insecticides, nylon, resins, lacquers, paint, varnish, finishes, removers and polishers. **Cyclohexanone** is important in the manufacture of woodstains, paint and varnish remover, spot remover and polish; lube-oil additive, solvent, degreasing metals, leveling agent in dyes and organic synthesis. **Meta-Benzene dicaboxylic acid** can be used as an additive in the industry of PET fibre and high graded paints. **2-Butoxy-Ethanol** is found in surface cleaning products. **Syringol, Vanillin, Eugenol, 6-Methoxyeugenol** and **Methyl Benzene** and most of the substituted phenols are used in the perfumery industry and/or flavour industry. **Xylenol** is found in some pesticides and herbicides.

The feasibility of the vacuum pyrolysis of plants for the production of charcoal would depend on the cost of the reactor and the size of the application. Higher production capacities would make the process more profitable. As has been stated before, according to **Roy et al. (1992)** a selling price of R900 per ton of charcoal would result in a production cost of R1000 per ton of oil. Although a selling price of more than R900 per ton of charcoal should be attainable, the economic viability would probably depend on the selling price of the oil. The high energy value of the oil does make it attractive as an energy source, and it would therefore seem as if the process would be economically attractive on a larger scale. The feasibility of smaller scale production would, however, have to be investigated further.

8.3 Leather wastes

The vacuum pyrolysis of leather wastes was done with volume reduction as the main aim. The reason for this was twofold, firstly the dumping costs for a mid-sized tannery can be as much as R1 000 000 per year and secondly, the leather waste charcoal was heavily contaminated with chrome.

The volume reduction was achieved in that a certain weight loss was achieved, depending on the vacuum pyrolysis temperature employed, and by increasing the density of the charcoal by crushing. The charcoal was very brittle and only mild pressure was necessary to turn the charcoal into a powder. Figure 8.4 shows the volume reductions achieved by the vacuum pyrolysis of charcoals at different temperatures, pressures and for the two different particle sizes. The volume reductions shown in figure 8.4 are in relation to hypothetical dumping densities of the virgin feedstock. The dumping density of the coarse leather was assumed to be 281 kg/m^3 and that of the fine leather as 161 kg/m^3 (the basis for the assumption was explained in chapter 5).
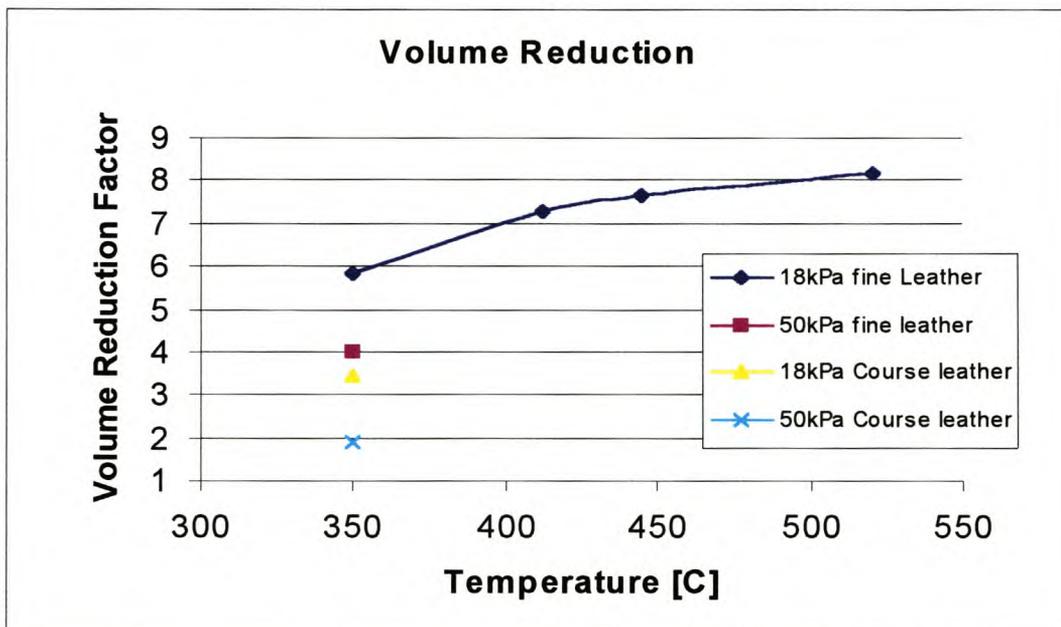
Figure 8. 4 Relation between volume reduction and temperature for 60min. pyrolysis times.

149

the savings would be R850 000 per year in reduced dumping costs. The operating cost of the vacuum pyrolysis process would of course have to be deducted from this value, but the savings should still be substantial. The pressure used in the process would depend on the increase in production cost due to a higher vacuum, compared to the increase in savings because of the higher volume reduction.

Table 8. 5 Metal content of the leather waste charcoal from the 520°C experiment

	Cd	Cu	Pb	Cr	Zn	Fe	Mn	Mg	Al	As
Mg/l	0.13	2.27	1.78	33061	0	142.6	0.79	98.54	90.73	0.41
% of ash	0.00	0.01	0.01	99.18	0.00	0.43	0.00	0.30	0.27	0.00
% of charcoal	0.00	0.00	0.00	12.40	0.00	0.05	0.00	0.04	0.03	0.00

From table 8.5 it can be seen that the very high chrome content of the charcoal would preclude its use as a fuel and would still relegate it to being dumped in a lined landfill. There is, however, another option that could be considered. Chrome is a valuable metal and its use in the form of chromiumsulfide is one of the major cost factors in the tanning industry. The charcoal contains 12% chrome, and it might therefore be economically feasible to extract the chrome for reuse. Depending on the method of chrome extraction, it might still be possible to use the charcoal afterwards or during the extraction. This would have the advantage of completely negating the need for landfilling, which would make the process extremely attractive on an economic and environmental basis.

The leather contains 1.25% sulphur, while the charcoal produced at 400°C contains only 0.2%. Therefore the sulphur content decreases from 12.5g/kg to 0.5g/kg, indicating that 12g of sulphur per kilogram of feedstock either condenses in the system or was released in the off-gas. The high boiling point of sulphur fortunately makes it easy to condense before it comes in contact with the condensed oil or is released into the atmosphere.

The high energy value of the oil product (26.7MJ/kg) would make it a good fuel. The sulphur content of the 450°C oil was 0.45%, which would classify it as a low sulphur furnace fuel. The only problem could be the very high 6.64% nitrogen content of the oil. This might make the fuel unusable and therefore turn it into a liability. Other

options would then have to be investigated to either purify the valuable compounds from the oil or to use the oil as a make-up heat source and install a very good scrubbing system.

The significant volume reductions achieved by the vacuum pyrolysis process at relatively mild temperatures, and the extensive potential market, shows that waste leather would be an excellent application of the technology. The possibility of chrome regeneration and the complete negation of the need for landfilling makes this an application that has to be investigated further.

8.4 Sewage Sludge

The vacuum pyrolysis of sewage sludge will be economically useful for industry if it can significantly reduce the dumping cost of the problematic solid waste by either volume reduction or by turning the charcoal derived from the waste into a valuable commodity.

Unfortunately the charcoal was too contaminated with metals and had much too high an ash content (up to 50% and more) to be considered as a fuel. Fortunately large volume reductions were achieved and the high ash content could also qualify the charcoal as a composting material.

Firstly the volume reduction can be studied in figure 8.5.

Sewage Sludge volume reduction
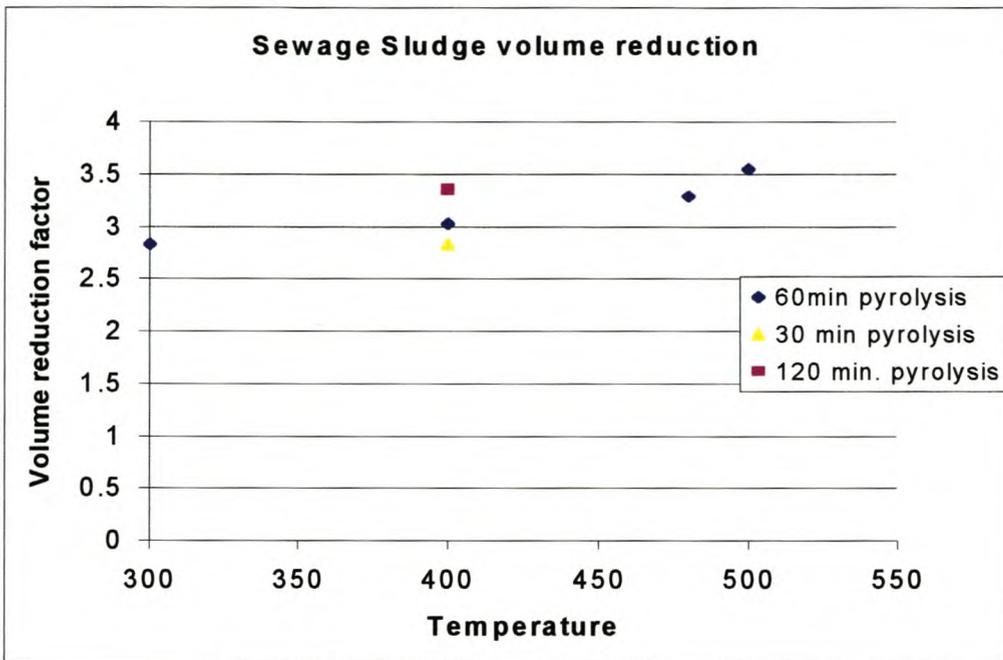
Figure 8. 5 Sewage sludge volume reduction

It can be seen that volume reductions of a factor 3 to 4 can significantly decrease dumping costs, and using the oil as a make-up heat source would lead to further savings. The oil from the 450°C experiment had a high energy value of 30.857 MJ/kg, but it also contained 5.6% nitrogen and 2.03% sulphur. The high energy value would have qualified the oil as a high sulphur fuel, but the high nitrogen content could pose problems.

In chapter 5, section 3.5.3 it was shown that the sewage sludge could be used as a composting material. Even if selling the sludge charcoal as compost did not cover the running cost of the process, it must be remembered that a costly waste product will now be turned into a commodity product that would reduce the cost of handling the sludge by many factors. Depending on the selling price and demand for the sludge charcoal compost, it might even be possible to make a profit from the process. This would turn a hazardous waste product that costs millions of rands per year to dump, into an environmentally friendly, profitable commodity.

8.5 Co-Pyrolysis

The co-pyrolysis of PVC and wood was studied with the purpose of better understanding the interaction between materials when pyrolysed. It was found that the addition of 10% PVC to the pure wood sample decreased the charcoal yield at temperatures below 500°C and increased the yield above 500°C. The oil yield was drastically increased by the addition of the PVC and it also led to the production of a new compound, namely benzenedicarboxylic acid and substituted variations on it. The yield of the benzenedicarboxylic acid and substituted variations was in the range of 5 % of the dry feedstock mass (12% of the oil yield), making it significant in terms of the economic evaluation of the process. The retail price of benzenedicarboxylic acid, 3-nitro (the main substituted product) is R3000 for 2.5 kg. This shows that it is a specialist product with limited uses, but it can be very valuable if a market can be found.

Table 8. 6 Energy values of the vacuum pyrolysis charcoals

Sample	Pyro time [min]	Pressure [kPa]	Pyro temp [C]	Charcoal MJ/kg	Oil MJ/kg
PVC	60	18	520	34.0	-
Kraalbos aged	120	18	380	25.8	-
	60	18	500	24.8	24.0
Co-Pyrolysis	60	18	380	27.9	-
	60	18	460	26.0	23.2
	60	18	520	-	24.3

The energy values presented in the table are even higher than the pure wood pyrolysis values. This indicates that the energy yield of the process can be increased by the addition of the PVC.

Table 8. 7 Total energy produced per kilogram of feedstock

Sample	Pyrolysis temp. [C}	Char yield %	Oil yield %	Char MJ/kg Charcoal	Oil MJ/kg Oil	Total MJ/kg Feedstock	Energy % increase
Co-Pyrolysis	460	28	40	26.0	23.2	16.5	28.2
	500	27	30	26.0	24.3	14.0	16.3
Aged Kraalbos	460	31	22	24.8	24.0	12.8	
	500	29	22	24.8	24.0	12.3	

It can be seen that a 28 % increase in energy yield was possible with the addition of the PVC at 460°C. Even for a vacuum pyrolysis temperature of 500°C there would still be a 16% increase in total energy yield (assuming that the oil and charcoal energy values stayed the same for the aged Kraalbos between 460°C and 500°C).

It must first be determined whether the charcoal and oil contains high amounts of HCl, but the increase in energy might make it possible to cover the cost of an off gas system. The chlorine content of the charcoal and oil would be the determining factor in the possible application of PVC as a catalyst in a wood vacuum pyrolysis application.

Chapter 9: Conclusions and Recommendations

9.1 Conclusions

9.1.1   Plant material

- The study showed that plant-clearing projects could benefit from using vacuum pyrolysis to produce charcoal and oil from the cleared plants.

- The charcoal and oil produced from the plants with ash content below 10% have energy values of 20 - 27 MJ/ (kg oil or charcoal). This compares favourably to the 24.8MJ/kg energy value of the commercially available Charca Brikets.

- The ash content of the wood feedstock determines whether it will produce charcoal that can compete with commercial products. The commercial products had charcoal ash content values in the range of 10%-17%, while the plant charcoals had values ranging from 10%-40%. Kraalbos and Scholtzbos charcoals had ash contents low enough to allow the charcoal to have sufficiently high energy values, but Asbos was unusable with an ash content of 40%

- The process pyrolysis temperature, time and reactor pressure will depend on the characteristics demanded of the product. The maximum charcoal yield was achieved at 350°C and 50kPa with a 30-minute reaction time. This however led to charcoal with very high volatile matter content. A reactor temperature higher than 450°C, with a pyrolysis plateau time of 60 minutes, should be employed if charcoal with lower volatile content were needed. The maximum oil yield temperature for each plant must be used if maximum oil yield were the aim of the vacuum pyrolysis process. The maximum oil yield temperature of Kraalbos was 380°C, while that of Asbos and Scholtzbos were 450°C and 480°C respectively. The pressure must also be kept as low as possible and the pyrolysis time must be at least 60 minutes.

- It appears that the rise in feedstock oxygen content during aging decreased the charcoal and oil yields and led to the formation of more non-condensable gases.

- Higher moisture content feedstock produces more charcoal and oil than low moisture feedstocks. It appears that structural changes occur because of the autohydrolysis reactions, which promotes the stability of the wood to thermal

degradation. It also leads to the liberation of more long chain length molecules, which condenses more easily and leads to higher oil yields.

9.1.2 Leather Wastes

- The tanning industry would benefit greatly from using vacuum pyrolysis to handle its leather wastes.

- High volume reductions of up to a factor 5-8 are possible for both fine and coarse leather cuttings.

- Although the charcoal has a high energy value, it is contaminated with 12% chrome, which precludes its use as fuel. The charcoal and oil has energy values of 19.7MJ/kg and 26.7MJ/kg respectively.

- The oil has a low sulphur content of 0.45%, but its high nitrogen content of 6.6% could pose problems.

- If the chrome could be recovered from the charcoal, the need for landfilling could be totally negated and the chrome could be reused in the tanning process.

9.1.3 Sewage Sludge

- Vacuum pyrolysis could be used to turn the hazardous waste sludge into compost, which would definitely reduce the costs of handling the waste.

- The charcoal can be used as compost if super phosphate is added and the compost is used in an application where high quantities of water is applied to the ground (e.g. nurseries). The compost could also be mixed with other composts with very low copper and sodium content to produce a more widely usable composting material.

- At 450°C the oil yield was 35% on a dry feedstock basis. The oil has an energy value of 30.9MJ/kg and might be used as a high sulphur (2.03 wt.%) heating fuel. The high nitrogen content of 5.6 wt.% might unfortunately necessitate a different approach to dealing with the oil.

- Significant volume reductions were achieved, which would greatly reduce the cost of landfilling this hazardous waste.

- Its high ash content causes the charcoal to have a very low energy value and this, combined with the contaminants present in the charcoal, makes it unsuitable for use as a fuel.

9.1.4   Co-pyrolysis

- The addition of PVC to wood feedstock enhances the total energy value of the vacuum pyrolysis products by 16%-28%. This happens through the significant increase of the oil yield and also through the slight increase in the energy value of the oil and charcoal. The co-pyrolysis charcoal and oil had energy values of 26MJkg and 24MJ/kg respectively.

- The co-pyrolysis of PVC and wood (aged Kraalbos) produces less charcoal, but much more oil than was predicted for a scenario where it was assumed that no interaction between the feedstocks would occur.

- It was found that acid hydrolysis of the wood constituents, caused by the released HCl from the PVC, was responsible for the change in yields.

- It also appears as if the released acid digests some of the wood components, leading to pore formation and therefore high surface area charcoals.

- This study once again shows the importance of the interaction between different materials when pyrolysed together and underscores the need for further research into municipal waste recycling by vacuum pyrolysis.

- It appears that it could be possible to reduce greatly the hazardous furan and dioxins produced during the thermal decomposition of PVC and other wastes by using vacuum pyrolysis instead of incineration or atmospheric pyrolysis. The lower operating temperature employed and the lower oxygen content causes the reduction in the furan and dioxin formation. It would however be necessary to test this theory by doing a study of the furan and dioxin content of the oil and gas phase of a vacuum pyrolysis process compared to the other process.

9.2 Recommendations

A thorough study of the process economics for a small-scale vacuum pyrolysis process should be done to determine whether it could be operated at a profit. Further study of the possibility of chrome extraction and reuse from leather waste charcoal could also lead to huge savings for the industry.

Determination of the chlorine content of the charcoal and oil would make it possible to see whether PVC can be used as a catalyst for wood vacuum pyrolysis processes. It also opens the question as to whether acid pretreatment of wood wastes could lead to higher profits for vacuum pyrolysis processes. Studying the dioxin and furan content of the oil and gas phases during vacuum co-pyrolysis would show whether these hazardous emissions could be reduced compared to other processes.

The vacuum pyrolysis set-up can be improved by heating the stainless steel pipe, leading from the hot-zone in the reactor to the vacuum traps, to a temperature higher than 160°C-200°C. This would limit the condensation of oils in the pipes and improve the reproducibility of the oil yield.

Nomenclature

1. ABS   Acrylic-Butyl Styrene
2. BET   Brunauer, Emmett and Teller
3. BFB   Bubbling Fluidised Bed
4. CSM   Chlorosufonated Pollyethylene
5. DTG   Dynamic Thermogravimetric analysis
6. EPDM   Ethylene Propylene Dimer Rubber
7. ESCA   Electron Spectroscopy for Chemical Analysis
8. EVA   Ethyl Vinyl Acetate
9. FT   Fourier Transform
10. IR   Infra Red
11. GC   Gas Chromatograph
12. ICP   Inductively Coupled Plasma
13. LDPE   Low-Density Polyethylene
14. NMR   Nuclear magnetic resonance
15. MS   Mass Spectrometer
16. MSW   Municipal solid waste
17. MWP   Municipal Waste Plastic
18. PVC   Poly(Vinylchloride)
19. PE   Petroleum Ether
20. PET   Poly(Ethylene Terephthalate)
21. PR   Pyrolytic oil Residue
22. PB   Petroleum Bitumen
23. PDU   Process Development Unit
24. SEM   Scan Electron Microscope
25. SIMS   Secondary Ion Mass Spectrometry
26. SMP   Simulated Waste Plastic
27. TGA   Thermogravimatric Analysis
28. XLPE   Cross-Linked Low-Density Polyethylene
29. XRD   X-ray Difractograms

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Appendix A

Experimental Results

Experimental Results   Table A.1

Water Free Basis

Samples		Temp [C]	Heating Rate [C/min]	Pyro time [min]	Pressure kPa	Char %	oil total %	Pyro water %	Non-cond. gases %	Ash %	N %
Asbos		500*					18.6	8.3	42.7	30.4		
		460*					33.3	11.8	29.6	25.2		
		444*					42.0	7.1	43.1	7.9		
	p	350	10	60	50	51.8				39.74	
		350	10	60	18	56.3	19.6	30.9	7.4	27.45	
	\\	400	10	60	18	49.7	30.9	18.6	7.1	43.57	
		450	10	60	18	47.8	25.6	18.7	11.7	40.01	
	\\	400	10	120	18	48.3	16.1	26.6	11.5	30.84	
		500	10	60	18	39.0	22.3	28.7	12.7	32.4	
		400	10	120	18	47.1	16.9	28.5	10.4	29.8	
		400	10	30	18	46.7	19.8	26.0	10.8	23.5	
		400	10	60	18	44.0	18.7	24.0	16.3	18.8	1.349
Scholtzbos		420*					31.5	10.0	44.4	14.1		
		400*					40.5	11.0	23.7	24.8		
		494	60.0	1	18	64.2	2.3	14.5	21.0		
		330	12.0	60	18	53.0	9.1	9.7	25.7	29.76	
		420	13.1	60	18	44.0	15.3	17.1	19.6	31.02	
		450	11.9	60	18	43.2	18.0	15.2	18.3	33.91	
		480	12.1	60	18	41.7	18.2	18.9	18.3	31.66	
		500	10.4	60	18	38.7	11.0	19.5	27.1	25.42	
		450	14.0	60	18	43.4	19.5	14.9	18.5	39.72	
	\\	450	11.4	30	18	42.3	16.2	18.8	19.1	29	0.784
		450	12.0	120	18	43.1	23.6	15.8	15.3	27.54	
	p	450	10.0	60	50	42.2				31.73	
		450	10.0	30	18	43.4	21.1	17.6	16.3	32.6	
Kraalbos		350	11.6	60	18	50.7	29.2	27.0	-4.3	12.48	
		380	12.3	60	18	40.0	35.4	21.5	5.1	13.98	
	2	400	10.0	60	18	36.8	25.25	27.3	12.9	15.1	
		420	12.1	60	18	37.1	32.5	26.4	5.7	19.33	
		450	12.2	60	18	34.4	26.4	24.7	14.5	15.86	

Samples		Temp [C]	Heating Rate [C/min]	Pyro time [min]	Pressure kPa	Char %	oil total %	Pyro water %	Non-cond. gases %	Ash %	N %
Kraalbso		380	12.4	30	18	41.7	23.7	23.2	12.2	23.95	
	\\	380	12.9	120	18	36.8	19.5	20.4	23.4	19.64	
	p	380	10.0	60	50	40.2					
		380	10.0	60	18	39.7	24.7	24.7	12.5	11.3	
	2	520	10.0	60	18	33.0	32.2	19.3	17.7	22.4	
		380	10.0	120	18	34.9	26.0	35.6	5.5	12	
	2	350	10.0	60	18	38.5	24.7	28.8	10.1	13.8	
	2	460	10.0	60	18	32.6	23.6	37.7	8.1	15.2	0.763
	2	500	10.0	60	18	30.7	23.2	33.5	14.0	16.4	
Leer fyn		350	4.9	60	18	48.8	18.1	27.1	12.3	9.61	
		412	4.9	60	18	32.3	24.9	42.0	2.1	11.6	
	\\	445	10.0	60	18	29.7	16.7	94.7	-36.4	11.8	
		445	8.0	60	18	33.2	20.8	38.0	14.3	12.18	
	p	350	8.9	60	52	54.7	13.9	7.3	32.9	8.83	
	p	350	10.6	60	46	54.9				9.14	
	p	350	4.8	60	48	57.2				8.92	
		520	5.0	60	18	27.7	21.3	50.3	4.2	12.5	
Growwe Leer		345	5.0	60	50	53.1				9.66	
	\\	350	5.0	60	18	51.9	13.9	23.1	8.1	9.61	
		350	5.0	60	18	49.4	20.6	24.5	8.4	8.7	
Slyk		400	10	60	18	53.3	33.1	2.7	3.9	29.3	3.463
		300	10	60	18	70.7	12.0	3.0	11.6	40.88	4.205
		500	10	60	18	47.3	37.2	3.4	8.6	33.69	3.111
		400	10	30	18	54.3	33.8	4.7	4.5	41.3	3.489
		400	10	120	18	51.4	32.5	7.6	6.2	38.71	3.397
		450	10	60	18	49.0	33.9	4.3	8.2	56.6	
PVC		350	10	60	24	35.5	8.9	0.0	55.6	0.09	
		420	10	60	24	22.1	22.9	0.0	55.0		
		460	10	60	24	14.3	22.9	0.0	62.7		
		520	10	60	24	11.4	28.4	0.0	60.1	0.33	

Samples	Temp [C]	Heating Rate [C/min]	Pyro time [min]	Pressure kPa	Char %	oil total %	Pyro water %	Non-cond. gases %	Ash %	N %
Co-Pyro	350	10	60	18	38.2	34.1	15.5	14.6	12.5	
	380	10	60	18	36.2	32.4	20.8	12.9	16.3	
	420	10	60	18	31.1	32.9	21.9	16.1	13.1	
	460	10	60	18	29.7	42.4	19.3	11.1	16.4	
	520	10	60	18	28.4	35.6	25.6	12.5	16.6	
Tire Rubber	400x*				48.0	43.1	2.3	9.0		
	420x*				43.0	54.0	2.8	4.0		
	420x*				43.0	51.2	2.7	7.0		
	420x*				43.0	48.4	2.5	9.0		
	450x*				38.0	55.8	2.9	6.0		
	500x*				36.0	58.3	3.1	6.0		
	430*			45	38.8	38.5		22.7		

* Experiments on initial reactor

x   Done by Reine Knoetze (Final Year Lab Project)

p   Experiments done at 50kPa pressure

// Probable experimental error

2   Aged feedstock

Appendix B

Detailed Oil Analysis

Table B.1 GC standard Response factors

Compounds	Avg. Strd RF
vanillin <benzaldehyde,4-hydroxy-3-methoxy->	0.59
2-methyl-1-butanol	0.61
hydroquinone <benzene 1,4 diol>	0.37
3,4 dimethylphenol	0.58
acetophenone <ethanone, 1-phenyl->	0.65
guiaiacol <phenol,2-methoxy>	0.47
1-pentanol	0.58
furfuryl alcohol <2-furanmethanol>	0.42
2,6 dimethoxy phenol	0.00
2,3 dimethyl phenol	0.64
4 hydroxy benzaldehyde	0.42
1-dodecanol	0.58
5-isopropyl-2-methyl phenol	0.95
Eugenol<phenol,2-methoxy-4-(2-propenyl)>	0.45
phenol, 2-(1,1-dimethyletheyl)	0.51
Pentanoic acid	0.33
Propanoic acid	0.21
135 trimethylbenzene	1.22
124	0.00
Hexanoic acid	0.00
o-creasol	0.85
By-Phenyl	0.94
p-cresol	0.54
phenol	0.73
benzoic acid	0.16
acetic acid glacial	0.46
benzene	1.08
benzaldehyde	0.64
propan-2-ol	0.81
tetrahydrofuran	0.92
methyl cyclohexan	1.41

Analysis of the oil in the last -70C condenser Table B.2

Aged Kraaibos 520C Components	Yield	Co-pyrolysis 500C Components	Yield
Benzene, methyl-	4.99	2-Furancarboxaldehyde	0.57
2,3-Butanedione	4.40	Ethane, 1,1,2-trimethoxy-	0.30
2-Butanone	3.37	2-Pentanone, 3-methyl-	0.19
2-Propanone	1.63	2-Propanone	0.08
3-Pentanone, 2-methyl-	1.00	Cyclopentanone	0.07
Acetonitrile	0.74	Propanal, 3-(methylthio)-	0.04
Benzene	0.71	2-Propenoic acid, 2-methyl-, methy	0.04
Benzene, 1,3-dimethyl-	0.70	Disulfide, dimethyl	0.04
Propanoic acid, methyl ester	0.66	Propane, 1,1-dimethoxy-	0.04
2-Butenal	0.56	N,N-DIETHYL-3-BUTENYLAMINE	0.03
Acetic acid, methyl ester	0.55	Benzaldehyde	0.03
2-Pentanone	0.54	2-Propanone, 1-chloro-	0.03
Benzene, ethyl-	0.50	2-Propen-1-ol	0.03
Butanal, 3-methyl-	0.42	3-Pentanone, 2,4-dimethyl-	0.03
Propanal, 2,2-dimethyl-	0.42	2-Butenal	0.03
2-Furancarboxaldehyde	0.41	Ethanol	0.03
Butanoic acid, methyl ester	0.40	Butanal, 3-methyl-	0.03
Furan, 2,5-dimethyl-	0.37	1-Butene, 2,3-dimethyl-	0.02
1H-Pyrrole, 1-methyl-	0.36	2-Furanmethanol	0.02
1,3,5,7-Cyclooctatetraene	0.36	Styrene	0.02
Butanal, 2-methyl-	0.32	1-Hexanol, 2-ethyl-	0.02
Phenol	0.31	CYCLOPENT-2-EN-1,4-DIONE	0.01
Nonane	0.25	Propanoic acid, methyl ester	0.01
Propanenitrile	0.23		
2-(2-PROPENYL)-FURAN	0.16		
Furan, tetrahydro-	0.14		
Benzaldehyde	0.13		
Cyclotetrasiloxane, octamethyl-	0.11		
Cyclopentene, 4,4-dimethyl-	0.10		
3-Hexanone, 4-methyl-	0.09		
Benzenemethanol	0.08		
Phenol, 2,6-dimethoxy-	0.08		
Cyclohexene, 1-methyl-4-(1-methyle	0.07		
Phenol, 2-methoxy-	0.07		
Decane	0.06		
Anisole-2,4,6-D3	0.05		
Cyclobutanol	0.04		
Cyclopentasiloxane, decamethyl-	0.04		
O-TOLYL VINYL SULFIDE	0.04		
2-Hexene, 2,5-dimethyl-	0.03		
2-Propenenitrile	0.03		
Furan, 3-methyl-	0.02		
Octane	0.02		
Phenol, 4-ethyl-2-methoxy-	0.02		
2-Cyclopenten-1-one, 2,3,4-trimeth	0.01		

Intruder Plant Specie Oil Analysis   Table B.3

Asbos Components	Yield	Components	Yield	Components	Yield
Cyclohexanone	30.35	Phenol, 2,6-bis(1,1-dimethylethyl)	0.56	Benzene, 1-ethyl-2,3-dimethyl-	0.14
Benzene, methyl-	16.78	Benzene, 1-methyl-2-(phenylmethyl)	0.52	Hexane, 1-(hexyloxy)-2-methyl-	0.14
Benzonitrile	16.71	2-Propanol	0.47	Sabinene	0.14
Heptane	11.70	Butane, 2-methyl-	0.45	2-Cyclopenten-1-one, 3-methyl-	0.13
Benzene, 1,4-dimethyl-	10.19	Butane, 2,2,3,3-tetramethyl-	0.43	Benzene, 1-methyl-4-(1-methylethyl	0.13
Benzene, 1,3-dimethyl-	6.84	.gamma.-Terpinene	0.38		
Heptane, 3-methyl-	6.55	1,2-Ethanediol	0.37		
Benzene, ethyl-	5.92	Tetradecane	0.36		
Cyclohexene, 1-methyl-4-(1-methylene)	4.27	Phenol, 3-methyl-	0.34		
Pentane	4.11	4,7,7-Trimethylbicyclo[3.3.0]octan	0.32		
Octane	3.90	Benzene, 1,3,5-trimethyl-	0.31		
Ethanol, 2-butoxy-	2.39	1H-Indole	0.30		
Acetic acid	2.31	CYCLOHEXANE, 1,2-DIMETHYL-	0.29		
Hexane, 2,5-dimethyl-	1.56	Ammonia	0.29		
Heptane, 2,5-dimethyl-	1.47	Phenol	0.29		
Undecane, 5-methyl-	1.33	9-Octadecenamide, (Z)-	0.29		
3,4,5-TRIMETHYL-HEPTANE	1.30	Benzene, 1-ethyl-3-methyl-	0.27		
Acetic acid, ethyl ester	1.17	Tridecane	0.27		
1-Propanol	1.14	Acetaldehyde, hydroxy-	0.27		
(Z)-Octadec-9-en-18-olide	1.13	Pentane, 2,3-dimethyl-	0.27		
Heptane, 2,4-dimethyl-	1.07	1,2-Benzenediol	0.25		
1-Pentene, 2,3-dimethyl-	0.98	Benzene, 1-ethyl-2,4-dimethyl-	0.22		
Hexane, 2-methyl-	0.88	Benzene, 1,3-diethyl-	0.20		
Hexane, 3-methyl-	0.87	Propane, 2,2-dimethoxy-	0.19		
Decane	0.86	Phenol, 4-ethyl-2-methoxy-	0.19		
Benzene, 1,2-dimethyl-	0.83	Pentadecane	0.18		
Pentacosane	0.74	5-METHOXY-1-AZA-6-OXABICYCLO	0.17		
Dodecane	0.74	Benzene, 1-methyl-3-(1-methylethyl	0.16		
Phenol, 2,6-dimethoxy-	0.70	Ethanol	0.16		
l-Phellandrene	0.68	1-Decanol	0.16		
Heptane, 2,6-dimethyl-	0.62	Benzene, 1-ethyl-2-methyl-	0.15		
Octane, 4-methyl-	0.56	1-Tetradecene	0.15		

171

Kraalbos Table B.4 Components	Yield	Components	Yield	Components	Yield
Cyclohexanone	5.71	2,4,6-Trimethyl-1,3-benzenediamine	0.20	2-Butene, 1,4-diethoxy-	0.07
Phenol, 2,6-dimethoxy-	4.62	Benzaldehyde, 4-hydroxy-3,5-dimeth	0.20	Phenol, 3-methoxy-	0.07
3-Methoxy-pyrocatechol	1.47	Tridecane	0.19	2-Furanmethanol	0.06
Phenol,2,6-dimethoxy-4-(2-propenyl)	1.19	2-Methoxy-4-methylphenol	0.19	3-Pyridinol	0.06
1,2-Benzenediol	1.07	1,4-Benzenediol, 2-methyl-	0.18	Cyclopentane, 1-methyl-2-propyl-	0.05
Ethanol, 2-butoxy-	1.01	1H-Inden-1-one, 2,3-dihydro-	0.18	Phenol, 2-ethyl-	0.05
2-Propanamine	1.00	2-ETHYL-3-METHOXY-2-CYCLOPENTENONE	0.17	Phenol, 2-methoxy-	0.05
2,4-Dimethyl-3-(methoxycarbonyl)-5	0.95	Hexadecane	0.16	1,3-Pentadiene, 2,4-dimethyl-	0.04
1-Propanol	0.91	Benzenemethanol, 2-hydroxy-	0.16	Hexadecane, 2,6,10,14-tetramethyl-	0.04
2H-Pyran-2,4(3H)-dione, 3-acetyl-6	0.91	Propane, 2,2-dimethoxy-	0.15	Hydroxylamine, O-decyl-	0.04
2,6-Dimethyl-3-(methoxymethyl)-p-b	0.82	2H-1-Benzopyran-2-one	0.15	Phenol, 2-methoxy-4-(2-propenyl)-	0.04
Butanoic acid, pentyl ester	0.71	Guanidine	0.14	3-OCTYNE-2-ONE	0.04
Methane, dichloro-	0.65	2-Furancarboxaldehyde, 5-(hydroxymethyl)	0.14	Ethanol	0.04
Formic acid, 1-methylethyl ester	0.53	Ethanone, 1-(4-hydroxy-3,5-dimetho	0.14	Phenol, 2-methyl-	0.03
1,2-Benzenedicarboxylic acid, dioc	0.43	Cyclohexene, 1-methyl-4-(1-methylene)	0.14	Nitrogen oxide (N2O)	0.03
2-Cyclopenten-1-one, 2-hydroxy-3-m	0.43	Benzene, (1-methylethyl)-	0.13	2-Furancarboxaldehyde	0.03
Benzene, methyl-	0.42	1,3-Cyclopentanedione	0.13	1,2-Ethanediol, monoacetate	0.03
2,6-DIMETHYL-4-OXA-ENDO-TRICYCLO	0.41	Phenol	0.13	Phenol, 2,5-dimethyl-	0.03
Decane	0.40	Bornylene	0.13	N-Methylethane- and 1-methylethane	0.03
1,2-Ethanediol	0.34	ETHYL CYCLOPENTENOLONE	0.13	Cyclopropane	0.02
Phenol, 2-methoxy-4-(1-propenyl)-	0.33	Phenol, 4-methyl-	0.12	1,3-Pentadiene, (Z)-	0.02
Phenol, 2,6-bis(1,1-dimethylethyl)	0.31	Benzene, 1,4-dimethoxy-	0.12	Heptane, 3-methyl-	0.02
1,6-ANHYDRO-BETA-D-GLUCOPYRANOS	0.30	Tetradecane	0.12		
4,7,7-Trimethylbicyclo[3.3.0]octan	0.29	Benzene, ethyl-	0.11		
Benzaldehyde, 4-hydroxy-3-methoxy-	0.28	1,6-Methanofluorene	0.11		
Ethanol, 2,2'-oxybis-	0.28	1,2-Cyclopentanedione, 3-methyl-	0.11		
Ammonia	0.27	dl-Limonene	0.10		
1,4-Benzenediol	0.27	Benzene, 1,2-dimethyl-	0.09		
Benzoic acid, 2-nitro-	0.25	4-Hexen-3-one, 4,5-dimethyl-	0.09		
Phenol, 4-ethyl-2-methoxy-	0.24	4-METHYL-1,2-BENZOQUINONE	0.08		
Ethanone, 1-(4-hydroxy-3-methoxyph	0.24	Phenol, 2-methoxy-4-propyl-	0.08		
2(3H)-Furanone, dihydro-	0.24	Naphthalene, 2-methyl-	0.08		
O-TOLYL VINYL SULFIDE	0.23	TRIDEUTEROACETONITRILE	0.08		
Benzene, 1,4-dimethyl-	0.21	Acetic acid, ethyl ester	0.08		

Scholtzbos Table B.5 Components	Yield	Components	Yield	Components	Yield
Cyclohexanone	21.6	3-ISOPROPYL-2-(1-PYRROLIDINYL)-1-C	0.34	Cyclohexene, 1-methyl-4-(1-methylene)	0.13
Benzene, 1,3-dimethyl-	2.97	3-Methoxy-pyrocatechol	0.32	Octadecane	0.13
Phenol, 2-methoxy-	2.15	4,7,7-Trimethylbicyclo[3.3.0]octan	0.32	Octacosane	0.13
Ethanol, 2-butoxy-	1.74	1,3-Benzenediol	0.30	SOLERON	0.13
Benzene, methyl-	1.52	Heneicosane	0.30	1-Pentadecanol	0.13
Phenol, 4-ethyl-2-methoxy-	1.37	Benzene, 1,2,3,5-tetramethyl-	0.29	Phenol, 2-ethyl-	0.12
1-Propanol	1.29	2-METHOXY-4,5,6-TRIMETHYLPYRIMIDI	0.29	dl-Limonene	0.11
Phenol, 2,6-dimethoxy-	1.29	Benzene, 1,2,4-trimethyl-	0.27	Hexadecane	0.11
Benzene, ethyl-	1.23	2-(Dimethylhydrazono)butanal	0.27	2-Propanone, 1-(acetyloxy)-	0.11
1,2-Benzenediol	1.18	Acetamide	0.26	Ethanone, 1-(2,6-dihydroxy-4-methoxy)	0.10
1,2-Ethanediol	1.00	Methane, dichloro-	0.25	Phenol, 2-methoxy-4-propyl-	0.10
Acetic acid	0.97	1,2-Benzenediol, 3-methyl-	0.24	1-HYDROXY-2-BUTANONE	0.09
Phenol, 2-methoxy-4-(1-propenyl)-	0.94	XYLENE	0.22	Butanoic acid, 3-methyl-	0.09
Benzene, 1,4-dimethyl-	0.92	Octane	0.21	2-Furancarboxaldehyde, 5-methyl-	0.09
Phenol, 3-methyl-	0.90	Benzaldehyde, 4-hydroxy-3-methoxy-	0.21	2,3-DIMETHOXYTOLUENE	0.09
2-Methoxy-4-methylphenol	0.87	Phenol, 2,6-bis(1,1-dimethylethyl)	0.21	3-ETHYLCYCLOPENT-2-EN-1-ONE	0.08
Benzene, 1,4-dimethoxy-	0.85	Ethanone, 1-(4-hydroxy-3-methoxyph	0.20	Cyclopentanone, 2-(3,3-dimethylbut	0.07
ACETOPHENONE, 2'-METHOXY-	0.83	2-Propanol	0.20	Benzene, 1,2,3-trimethyl-	0.07
2,4,6-Trimethyl-1,3-benzenediamine	0.81	Methyl cinnamate	0.20	2-Furancarboxylic acid, methyl ester	0.06
Ammonia	0.71	Cyclohexene, 1-methyl-5-(1-methyle	0.20	3-Octyne	0.06
Phenol	0.61	2H-Pyran-2,4(3H)-dione, 3-acetyl-6	0.19	2-Cyclopenten-1-one	0.06
Acetic acid, ethyl ester	0.59	Phenol, 2-methyl-	0.18	Benzene, 1,3,5-trimethyl-	0.06
Ethanol, 2,2'-oxybis-	0.56	2-Furanmethanol	0.18	Benzene, 1-methyl-4-(1-methylethyl)	0.05
2,6-DIMETHYL-4-OXA-ENDO-TRICYCLO	0.54	Ethene, fluoro-	0.18	Benzene, 1-methyl-3-(1-methylethyl)	0.05
Phenol, 3-ethyl-	0.52	2-Cyclopenten-1-one, 3-methyl-	0.17	Benzaldehyde, 4-hydroxy-3,5-dimethyl	0.05
Phenol, 4-methyl-	0.50	Benzene, 1-ethyl-3-methyl-	0.16	Disulfide, diethyl	0.04
Benzene, 1,2-dimethyl-	0.48	1,3-Benzenediol, 5-methyl-	0.16	2(5H)-Furanone, 5-methyl-	0.04
Phenol, 2,4-dimethyl-	0.44	Heptacosane	0.16	3,4,5-TRIMETHYL-HEPTANE	0.04
2-Cyclopenten-1-one, 2-hydroxy-3-m	0.41	1,3-Cyclopentanedione	0.16	1H-Isoindole-1,3(2H)-dione, 3a,4,7	0.04
Tetradecane	0.40	2,4-Dimethyl-3-(methoxycarbonyl)-5	0.15	Butanal	0.04
1-Decene	0.38	Hexatriacontane	0.15	Acetic acid, butyl ester	0.04
Tridecane	0.38	ETHYL CYCLOPENTENOLONE	0.15	2,6-Dimethyl-3-(methoxymethyl)-p-b	0.04
Benzene, 2-ethyl-1,4-dimethyl-	0.38	Phenol, 3-(1-methylethyl)-	0.13	Silane, ethenyltrimethyl-	0.04
Phenol, 2-methoxy-4-(2-propenyl)-	0.34	Dotriacontane	0.13	Phenol, 2,6-dimethoxy-4-(2-propenyl)	0.03

173

Co-pyrolysis Table B.6

Components	Yield	Components	Yield	Components	Yield
1,2-Benzenedicarboxylic acid, 3-nitro	200	Benzaldehyde, 4-hydroxy-3-methoxy-	0.28	Pentadecane	0.106
1,2-Benzenedicarboxylic acid, bis(octyl)	8.6	Phenol	0.27	Methanamine, N-methyl-	0.102
Cyclohexanone	7.42	1-Decanol	0.26	Benzene, 1-methyl-4-(1-methylethyl)	0.097
Cyclohexene, 1-methyl-4-(1-methylene)	2.47	Ethanone, 1-(2,6-dihydroxy-4-methoxy)	0.26	Benzenepropanoic acid, methyl ester	0.094
1,6-ANHYDRO-BETA-D-GLUCOPYRANOS	1.94	Dodecane	0.25	Hexadecane	0.094
Benzene, methyl-	1.58	Benzene, 1,4-dimethoxy-	0.25	9-Eicosene, (E)-	0.09
Acetic acid, ethyl ester	1.54	2,6,6-Trimethyl-3-methylenecyclohexane	0.24	2H-1-Benzopyran-2-one	0.088
Phenol, 2,6-dimethoxy-	1.5	2-Propanol	0.24	3-Pentanol, 3-methyl-	0.088
Ethanol, 2-butoxy-	1.48	2H-Pyran-2,4(3H)-dione, 3-acetyl-6	0.23	3-Buten-2-one, 3-methyl-	0.087
1-Propanol	1.37	9-Octadecyne	0.22	1-Hexadecanol	0.081
XYLENE	1.19	2-Methoxy-4-methylphenol	0.21	Phenol, 2,6-dimethoxy-4-(2-propeny	0.079
Cyclohexane, 1,1-dimethoxy-	1.02	Octacosane	0.2	Benzaldehyde, 4-hydroxy-3,5-dimeth	0.078
Propane, 1,1-dimethoxy-	0.93	4,7,7-Trimethylbicyclo[3.3.0]octan	0.19	Benzene, 1,3,5-trimethyl-	0.076
Benzene, ethyl-	0.82	Oxirane	0.19	1,1'-Biphenyl	0.074
Benzene, 1,2-dimethyl-	0.79	3,4-Dihydropyran	0.18	Ethanol	0.071
Butanal, 3-hydroxy-	0.71	Naphthalene, 2-methyl-	0.18	[1'-13C]-Octyne	0.067
Methyl palmitate	0.7	Naphthalene, 1-methyl-	0.17	Propane	0.066
1,4-Cyclohexanedione	0.62	Phenol, 2-methyl-	0.15	Benzene, 2-ethyl-1,3-dimethyl-	0.063
Phenol, 2,6-bis(1,1-dimethylethyl)	0.6	Phenol, 2,4-dimethyl-	0.15	2-Pentanol, 2-methyl-	0.061
Hydrazine, 1,2-dimethyl-	0.55	Ethanone, 1-(4-hydroxy-3-methoxyphenyl)	0.15	Cyclodecene	0.059
.gamma.-Terpinene	0.55	Cyclohexene, 1-methoxy-	0.15	Acetic acid, butyl ester	0.059
Phenol, 2-methoxy-	0.54	1,4-Benzenediol	0.14	Hexane, 2-methyl-	0.058
Decane	0.51	dl-Limonene	0.14	Nonane, 3-methyl-	0.055
Hexatriacontane	0.51	Decanoic acid, methyl ester	0.14	Propanamide	0.054
Methane, dichloro-	0.46	Ammonia	0.13	Undecanoic acid, 10-methyl-, methyl	0.053
Phenol, 4-methyl-	0.44	2-Propanone, 1-hydroxy-	0.13	Cyclopentane, methyl-	0.047
Benzene, 1,4-dimethyl-	0.4	6-Methyl-2,4-di-tert-butyl-phenol	0.13	Butanedioic acid, dimethyl ester	0.047
2,5-DIMETHOXYTOLUENE	0.35	ETHYL CYCLOPENTENOLONE	0.13	Benzene, 1,2,4-trimethyl-	0.046
Propane, 2,2-dimethoxy-	0.35	2-Phenylthiobutanal	0.13	4a(2H)-Naphthalenecarboxylic acid,	0.042
9-Octadecenamide, (Z)-	0.34	.ALPHA.-TERPINOLENE	0.12	Pentanedioic acid, dimethyl ester	0.041
Benzene, 1,3-dimethyl-	0.33	Tridecane	0.12	Heptadecanoic acid, methyl ester	0.041
Tinuvin P	0.32	17-Pentatriacontene	0.11	Ethanol, 2,2'-oxybis-	0.041
10-Octadecenoic acid, methyl ester	0.31	9H-Fluorene	0.11	Benzoic acid, 4-hydroxy-3-methoxy-	0.039
Nonane, 3-methyl-5-propyl-	0.29	Azulene	0.11	Heptane	0.037
Phenol, 4-ethyl-	0.28	Naphthalene, 1,6-dimethyl-	0.11	Naphthalene, 2-ethyl-	0.037

Comparason of the yields of the three alien plant species

Components	Asbos	Kraalbos	Scholtzbos	Components	Asbos	Kraalbos	Scholtzbos
Cyclohexanone	30.35	5.71	21.64	Ethanol	0.16	0.03	n.d.
Benzene, methyl-	16.78	0.42	1.52	Bornylene	0.12	0.13	n.d.
Benzene, 1,4-dimethyl-	10.19	0.21	0.92	Hexadecane	0.10	0.16	0.11
Benzene, 1,3-dimethyl-	6.84	n.d.	2.97	2,4,6-Trimethyl-1,3-benzenediamine	0.08	0.20	0.81
Heptane, 3-methyl-	6.55	0.02	n.d.	Phenol, 2-methoxy-4-propyl-	0.08	0.08	0.10
Benzene, ethyl-	5.92	0.11	1.23	2-Methoxy-4-methylphenol	0.08	0.19	0.87
Cyclohexene, 1-methyl-4-(1-methylene)	4.27	0.14	0.13	Heneicosane	0.07	n.d.	0.30
Octane	3.90	n.d.	0.21	Phenol, 2-methoxy-4-(2-propenyl)-	0.07	0.04	0.34
Ethanol, 2-butoxy-	2.39	1.01	1.74	Phenol, 2-ethyl-	0.05	0.05	0.12
Acetic acid	2.31	n.d.	0.97	Naphthalene, 2-methyl-	0.05	0.08	n.d.
3,4,5-TRIMETHYL-HEPTANE	1.30	n.d.	0.04	Benzene, (1-methylethyl)-	0.03	0.13	n.d.
Acetic acid, ethyl ester	1.17	0.08	0.59	Phenol, 2-methyl-	0.02	0.03	n.d.
1-Propanol	1.14	0.91	1.29	Methane	0.05	n.d.	0.03
Heptane, 2,4-dimethyl-	1.07	n.d.	0.02	Phenol, 2,4-dimethyl-	0.05	n.d.	0.44
Decane	0.86	0.40	n.d.	Phenol, 2-methoxy-	0.04	n.d.	2.15
Benzene, 1,2-dimethyl-	0.83	0.09	0.48	Benzene, 1,2,3-trimethyl-	0.03	n.d.	0.07
Phenol, 2,6-dimethoxy-	0.70	4.62	1.29	Benzene, 1,4-dimethoxy-	n.d	0.12	0.85
Phenol, 2,6-bis(1,1-dimethylethyl)	0.56	0.31	0.21	2,6-DIMETHYL-4-OXA-ENDO-TRICYCLO(	n.d	0.41	0.54
2-Propanol	0.47	n.d.	0.20	Benzaldehyde, 4-hydroxy-3-methoxy-	n.d	0.28	0.21
1,2-Ethanediol	0.37	0.34	1.00	ETHYL CYCLOPENTENOLONE	n.d	0.13	0.15
Tetradecane	0.36	0.12	0.40	dl-Limonene	n.d	0.10	0.11
Phenol, 3-methyl-	0.34	n.d.	0.90	Benzaldehyde, 4-hydroxy-3,5-dimethyl	n.d	0.20	0.04
4,7,7-Trimethylbicyclo[3.3.0]octan	0.32	0.29	0.32	Ethanol, 2,2'-oxybis-	n.d	0.28	0.56
Phenol	0.29	0.13	0.61	Ethanone, 1-(4-hydroxy-3-methoxyphenyl)	n.d	0.24	0.20
Benzene, 1-ethyl-3-methyl-	0.27	n.d.	0.16	Phenol, 2,6-dimethoxy-4-(2-propenyl)	n.d	1.19	0.03
Tridecane	0.27	0.19	0.38	2,6-Dimethyl-3-(methoxymethyl)-p-b	n.d	0.82	0.04
1,2-Benzenediol	0.25	1.07	1.18	2,4-Dimethyl-3-(methoxycarbonyl)-5	n.d	0.95	0.15
Propane, 2,2-dimethoxy-	0.19	0.15	n.d.	2,3-DIMETHYL-2-CYCLOPENTEN-1-ONE	n.d	0.06	0.06
Phenol, 4-ethyl-2-methoxy-	0.19	0.24	1.37	1,3-Cyclopentanedione	n.d	0.13	0.16
Benzene, 1-methyl-3-(1-methylethyl	0.16	n.d.	0.05	2-Cyclopenten-1-one, 2-hydroxy-3-m	n.d	0.43	0.41
2-Cyclopenten-1-one, 3-methyl-	0.13	n.d.	0.17	2H-Pyran-2,4(3H)-dione, 3-acetyl-6	n.d	0.91	0.19
Benzene, 1-methyl-4-(1-methylethyl	0.13	n.d.	0.05	2-Furanmethanol	n.d	0.06	0.18
Octadecane	0.13	n.d.	0.13	3-Methoxy-pyrocatechol	n.d	1.47	0.32
Benzene, 1,2,3,5-tetramethyl-	0.12	n.d.	0.29	Phenol, 4-methyl-	n.d	0.12	0.50
Benzene, 2-ethyl-1,4-dimethyl-	0.10	n.d.	0.38				

175

Table B.8 Comparison between Co-pyrolysis and Aged Kraal

Components	Yield	
	Co-pyrolysis	Kraalbos
1,2-Benzenedicarboxylic acid, 3-nitro	177.00	
Benzonitrile	11.70	10.20
1,2-Benzenedicarboxylic acid, bis(octyl)	8.60	90.85
Cyclohexanone	7.42	5.71
Cyclohexene, 1-methyl-4-(1-methylethyl)	2.47	0.14
1,6-ANHYDRO-BETA-D-GLUCOPYRANOSE	1.94	0.30
Benzene, methyl-	1.58	0.42
Acetic acid, ethyl ester	1.54	0.08
Phenol, 2,6-dimethoxy-	1.50	4.62
Ethanol, 2-butoxy-	1.48	1.01
1-Propanol	1.37	0.91
Benzene, ethyl-	0.82	0.11
Benzene, 1,2-dimethyl-	0.79	0.09
Phenol, 2,6-bis(1,1-dimethylethyl)	0.60	0.31
Phenol, 2-methoxy-	0.54	0.04
Decane	0.51	0.40
Methane, dichloro-	0.46	0.65
Phenol, 4-methyl-	0.44	0.12
Benzene, 1,4-dimethyl-	0.40	0.21
Propane, 2,2-dimethoxy-	0.35	0.15
Benzaldehyde, 4-hydroxy-3-methoxy-	0.28	0.28
Phenol	0.27	0.13
Benzene, 1,4-dimethoxy-	0.25	0.12
2H-Pyran-2,4(3H)-dione, 3-acetyl-6	0.23	0.91
2-Methoxy-4-methylphenol	0.21	0.19
4,7,7-Trimethylbicyclo[3.3.0]octan	0.19	0.29
Naphthalene, 2-methyl-	0.18	0.08
Phenol, 2-methyl-	0.15	0.03
Ethanone, 1-(4-hydroxy-3-methoxyphenyl)	0.15	0.24
1,4-Benzenediol	0.14	0.27
dl-Limonene	0.14	0.10
Ammonia	0.13	0.27
ETHYL CYCLOPENTENOLONE	0.13	0.13
Tridecane	0.12	0.19
Hexadecane	0.09	0.16
2H-1-Benzopyran-2-one	0.09	0.15
Phenol, 2,6-dimethoxy-4-(2-propenyl)	0.08	1.19
Benzaldehyde, 4-hydroxy-3,5-dimethyl	0.08	0.20
Ethanol	0.07	0.03
Ethanol, 2,2'-oxybis-	0.00	0.28

Appendix C

Analytical Techniques

Analytical Techniques

Thermogravimetric analysis (TGA)

The TG analysis were performed on a DuPont Instruments 951 Thermogravimetric analyser. The apparatus used a horizontal differential system balance mechanism. About 17mg of sample was placed on the scale and then heated at 10°C/minute in a nitrogen atmosphere. The sample was heated to 520°C and then held at the temperature for two hours, after which it was allowed to cool in the nitrogen atmosphere to room temperature. The nitrogen flow rate was kept constant at 50ml/minute for the whole experiment. Weight and temperature readings were stored on computer and the weight versus temperature and the derivative of the weight loss per unit time was plotted for use in the thesis.

Karl-Fisher analysis

Karl-Fisher analysis is a standard test for water content determination. A Metrohm KF Titrino was used to do the analysis and standardised Karl-Fisher reagent was used during the analysis. The reagent was standardised using distilled water, where after approximately 2-8 µg of sample was injected. The water content was automatically determined as a percentage of the injected sample.

Brunauer, Emmett and Teller (BET) analysis

A Micrometrics ASAP 2010 was used to do the BET surface area analysis. The samples were first degased in a vacuum at 300°C. This ensured that all the volatiles have been removed so that the analysis would not be influenced by gases developing during the analysis. For most of the samples only the surface areas were determined using nitrogen absorption with a four point analysis method. The micropores were also investigated for some of the samples. This requires a much longer analysis time since the gas has to penetrate to the much finer internal micropores.

Appendix D

Mechanistic Postulate for the vacuum
pyrolysis process

Mechanistic postulate for the formation of charcoal, vapours and gases during vacuum pyrolysis

Many heat transfer models exists for the vacuum pyrolysis process, but only one mechanistic model by **J. Reina, E. Velo and L. Puigjaner (1998)** could be found as to how the charcoal, vapours and gases form. The following postulate was deduced from results obtained in this thesis along with observations made in literature.

D1. Proposed Mechanisms

D1.1 Vapour and gas evolution and charcoal formation

The formation of vapours and gases and the degree to which recondensation reactions occur, depends on the way the vapours evolve and the residence time of the vapours in the sample bed. **Darmstadt et al. (1999)** showed that during the pyrolysis of wood hydrocarbons are formed in the gas phase and that some of these hydrocarbons condense on the charcoal surface and in the pores. It was shown in chapter 5, section 5.3.4, that there are two resistances to the free movement of the vapours and gases. These were the resistances experienced by the vapours inside the particle and during the vapour movement through the sample bed. It was shown that the residence time of the vapours inside the particles was only influenced by the particle size and structure and by the vapour pressure inside the particle. The reactor pressure seemed to have very little influence on the vapour residence time inside the particle, but was the ruling factor influencing the residence time in the particle bed. **Pakdel et al. (1997)** showed that a thinner bed thickness and lower bed density led to higher phenolic yields during the vacuum pyrolysis of wood.

Thermally induced degradation of the feedstock particle structure leads to the formation of vapours and gases inside and on the surface of the particle.
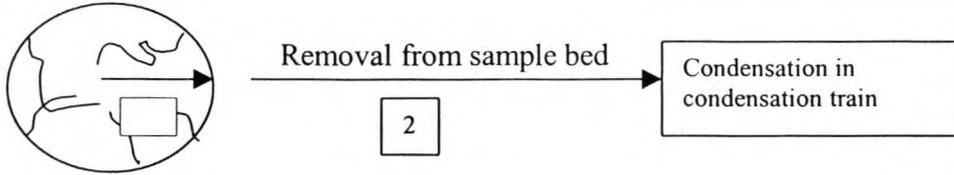
Feedstock particle

Numbers 1 and 2 represents the resistance to the free movement of the degradation products in the particle and sample bed respectively.

- The diffusion rate of the degradation products inside the particles depends only on the vapour pressure inside the particle and the particle structure and not on the pressure in the sample bed. The movement of the gases inside the bed depends on the bed density and the reactor pressure. This was deduced from the results obtained in chapter 5 section 5.3.3.

- The longer the residence time of the vapours inside the reactor the higher the degree of side reactions that occur, leading to lower oil yields and higher charcoal yields.

D1.2 Wood decomposition mechanism

Pyrolysis of wood (200°C to 900°C) **[Reina et al. (1998)]**

```
          → Gas              →  Gas
          |                  |    ↑
Wood  →      Intermediate   →  Tar
          |                  |    ↓
          → Tar              →  Char
```
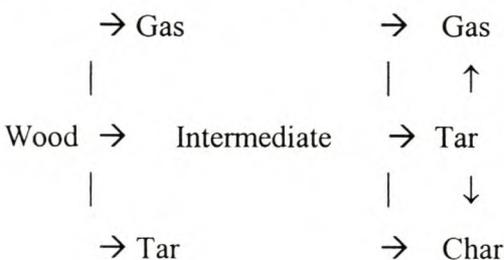
This shows that the wood firstly decomposes to Gas, Tar and an intermediate, then in the second stage the intermediate decomposes to Gas, Tar and char. The tar that was formed

in the second stage can also decompose to gas or form char through some side or recondensation reaction.

1. In the first stage a high degree of conversion is reached through both the cracking of macromolecules (cellulose and lignin), which produces a decrease in the polymerisation degree, and the thermal decomposition of the remaining organic compounds. Most of the volatile compounds are released in this stage. The intermediate was produced through the depolymerisation of the cellulose and lignin and represents an organic compound of relatively low molecular weight. The lignin is more resistant to thermal decomposition and causes an increase in the activation energy in the last part of stage one.

2. The second stage proceeds at higher temperatures and represents a much smaller weight loss. In this stage the weight loss was attributed to the cracking of the residual organic components that decomposed to produce gases and chars.

Proposed mechanism for the vacuum pyrolysis of wood

$$
\begin{array}{ccccc}
 & \rightarrow \text{Gas} & & \rightarrow \text{Gas} \\
 & | & & | & \uparrow \\
\text{Wood} \rightarrow & (\text{depolymerised Intermediate})_1 & \rightarrow & \text{Oil} \\
 & | & & | & \downarrow \\
 & \rightarrow \text{Vapour} & & \rightarrow \text{Char}
\end{array}
$$
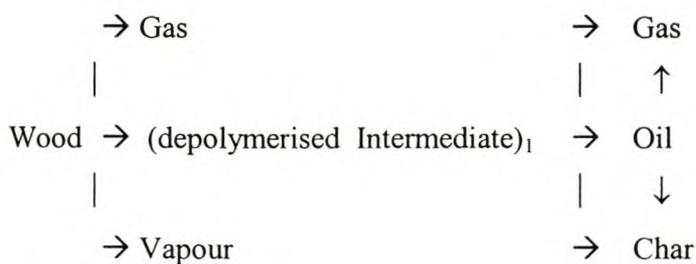
The mechanism is basically the same for vacuum pyrolysis except that the lower pressure allows more of the released volatiles to be in the form of vapour instead of gases. The vapour can be condensed and can therefore be as oil. The formation of gases and vapour are also enhanced over the formation of char. This leads to lower char yields for the vacuum pyrolysis process when compared to atmospheric pyrolysis, as was also stated by **Miranda et al. (1999) and Roy et al . (1992).** The oil (tar) yield was also significantly higher for the vacuum pyrolysis process. Figure F.2 shows the TGA plot for the

decomposition of fresh Kraalbos in N_2 atmosphere. It can be seen that the wood decomposes in two stages, with the first stage liberating most of the mass before 380°C, followed by a less severe second stage commencing above 400°C. **Miranda et al. (1999b)** showed that the vacuum thermal decomposition of PVC follows the same trend, but with higher mass losses for the individual stages, as atmospheric decomposition.

D1.3 Proposed mechanism for the vacuum co-pyrolysis of PVC and wood

Miranda et al. (1999) proposed the mechanism presented in chapter 2, figure 2.5, for the decomposition of PVC. The following is a simplified representation of it.

>200°C<350°C   >350°C

→ Gas +vapours   → Gas +vapour

| | ↑

PVC   →   Linear Cis-Polyene Chain→ Cross-linked polyene chain

| | ↓

→ HCL   →   Char
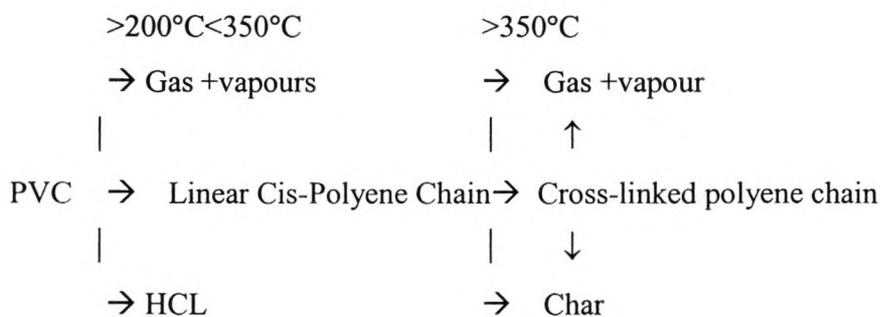
Since only 10% of the feedstock was PVC it was only the HCl that significantly influenced the wood decomposition.

The following is the proposed mechanism for the co-pyrolysis of PVC and Wood.

```
        >200°C                                    >350°C
                                                  → Gas + vapour          →   Gas
            + HCL                                 |                       |    ↑
Wood  →  (depolymerised Intermediate)₂ →  (depolymerised Intermediate)₃ →Oil
      |              ↑ + HCl                                              |    ↓
      → (depolymerised  Intermediate)₁                                   →   Char


 +HCL


           Dissolves hemicellulose → pore formation
```
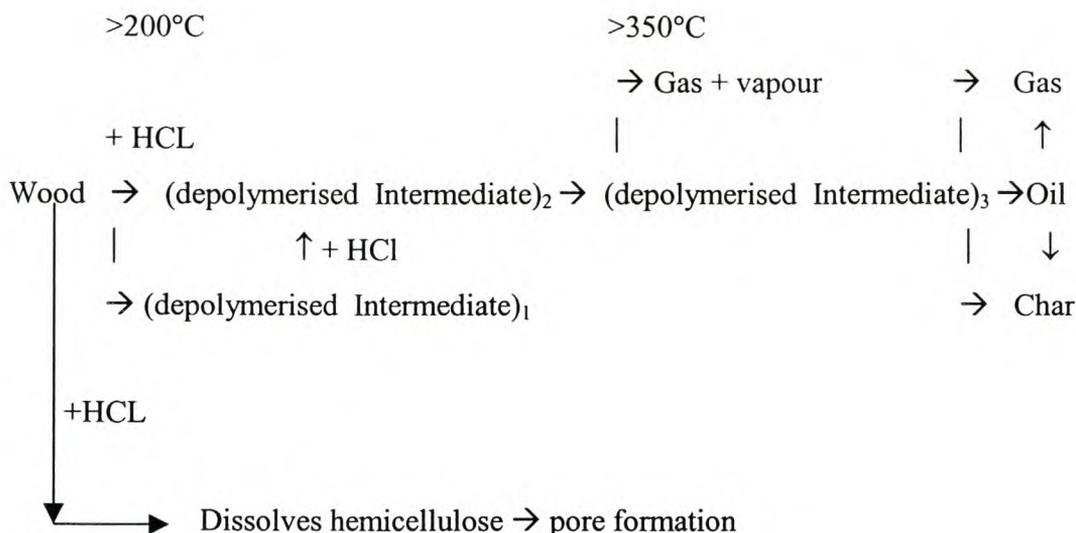
It can be seen that the mechanism consists of three stages, during the first stage intermediate$_1$ and intermediate$_2$ forms. Intermediate$_1$ represents the thermally degraded wood structure and intermediate$_2$ the acid hydrolysed wood structures. Stage two commences above 350°C when most off the HCl has already been released. Intermediate$_3$ consists of the further thermally degraded structures of both intermediates 1 and 2. The last stage commences at high temperature (in the rage of 420°-520°C) and represents the final weight loss stage. From figures E1, E2 and E3 of the TGA plots, of the atmospheric thermal decomposition of PVC/cellulose mixtures, it can be seen that three weight loss stages are present. This supports a three stage mechanism.

The major difference between the intermediate formed by the thermal degradation of the wood during the vacuum pyrolysis of wood (depolymerised intermediate$_1$), and the intermediate formed during the vacuum co-pyrolysis of wood and PVC (depolymerised intermediate$_2$); was the much greater extent to which the cellulose as a whole was converted to a depolymerised intermediate during co-pyrolysis. It can be seen from the mechanistic representation, of the co-pyrolysis experiment, that intermediate$_1$ was still

184

formed due to thermal degradation. Intermediate$_2$ was formed, directly from the wood structure and from intermediate$_1$, through acid hydrolysis reactions. In the chapter covering the vacuum co-pyrolysis of PVC and wood it was found that 5 times more glucopyranose was formed during the co-pyrolysis experiment when compared to the wood pyrolysis experiment. This implies that 5 times more of the cellulose structure was depolymerised during the co-pyrolysis experiment.

The higher oil yield during the co-pyrolysis experiments was caused by several factors. Firstly the higher degree to which the wood cellulose and lignin were depolymerised favoured and increased the vapour production over the gas production. Secondly the pore formation caused by the dissolved hemicellulose **[Lynd et al. (1999)]** increase the diffusion rate of the degradation products and in so doing lowered the vapour retention time **[Carraso et al. (1992)]** and increased the oil yield. **[Pakdel et al. (1997)]**

The co-pyrolysis experiments exhibited a lower charcoal yield than the pyrolysis experiments for temperatures below 500°C. This was due to the higher degree and extent of the reduction in the degree of polymerisation of the wood structures, which led to the liberation of more of the wood structure. It does appear that the charcoal yield of the co-pyrolysis experiment will be higher than the pure wood experiment for temperatures exceeding 500°C. **McGee et al. (1995)** found the same trend for atmospheric co-pyrolysis experiments at temperatures exceeding 380°C. It was assumed in this thesis that the reason for this was that although the initial structure degrades more readily, the remaining wood structures were changed in a way that made them more thermally stable.

More nitrogen atmosphere TGA experiments need to be done and it is also essential that TGA experiments are conducted in vacuum. It would also be necessary to conduct experiments where the experiments are stopped at the temperature boundaries of the proposed mechanism. The charcoal could then be analysed to determine the effect the cellulose had on it. These experiments would test the theory and would show if it is feasible.

Appendix E

TGA results for the co-pyrolysis experiments

Sample: 7% PVC/93% Kraalbos aged
Size: 17.8360 mg
Method: Wian
Comment: 50ml/min N2 1mg PVC, res kraalbos

TGA

File: C:WIAN.4
Operator: WA
Run Date: 12-Oct-00 08:52
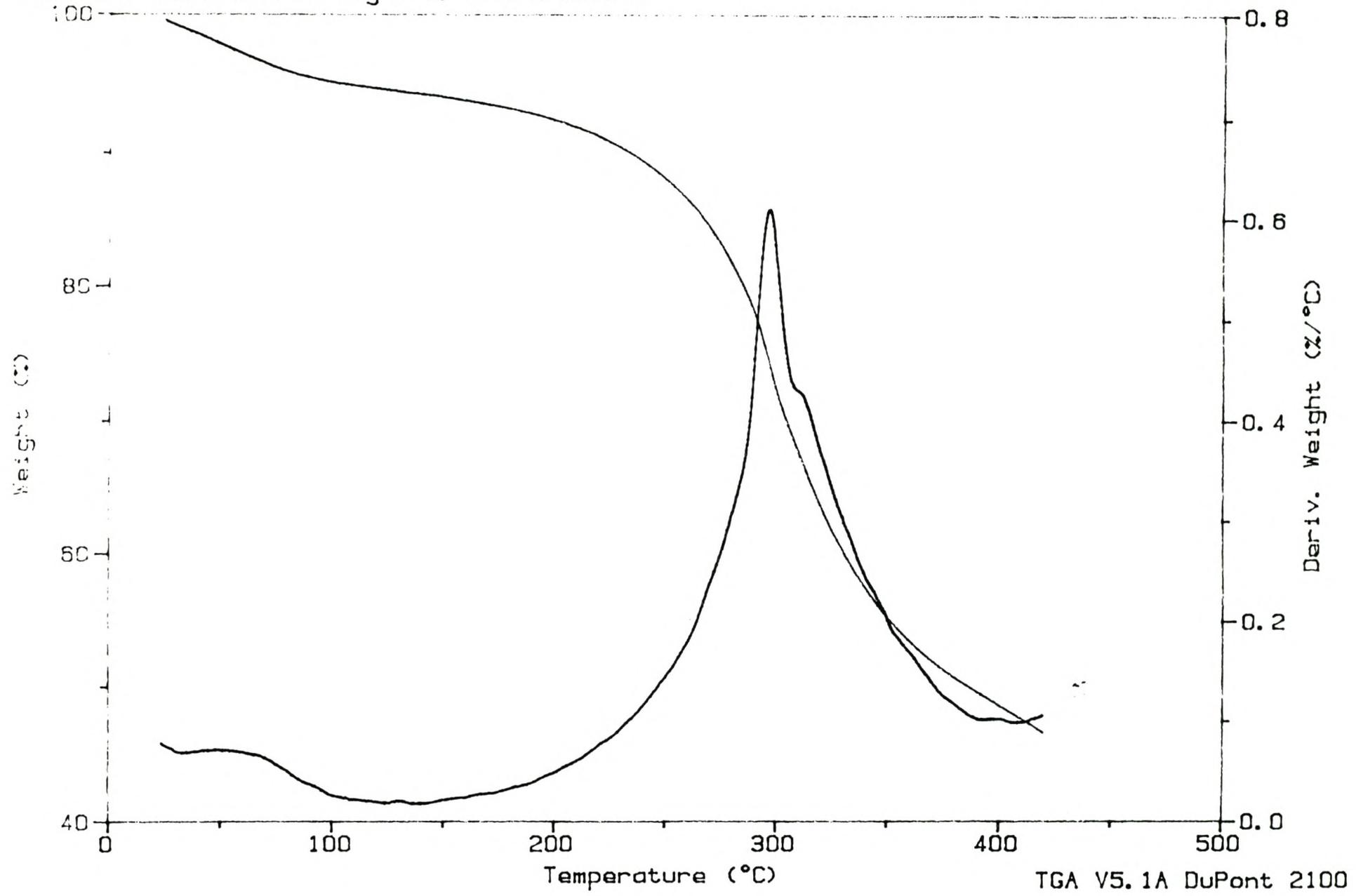
TGA V5.1A DuPont 2100

Sample: 12% PVC/88% Kraalbos aged
Size: 15.5270 mg
Method: Wian
Comment: 50ml/min N2 2mg PVC, res kraalbos

TGA

File: C:WIAN.3
Operator: WA
Run Date: 11-Oct-00 18:45

TGA V5.1A DuPont 2100
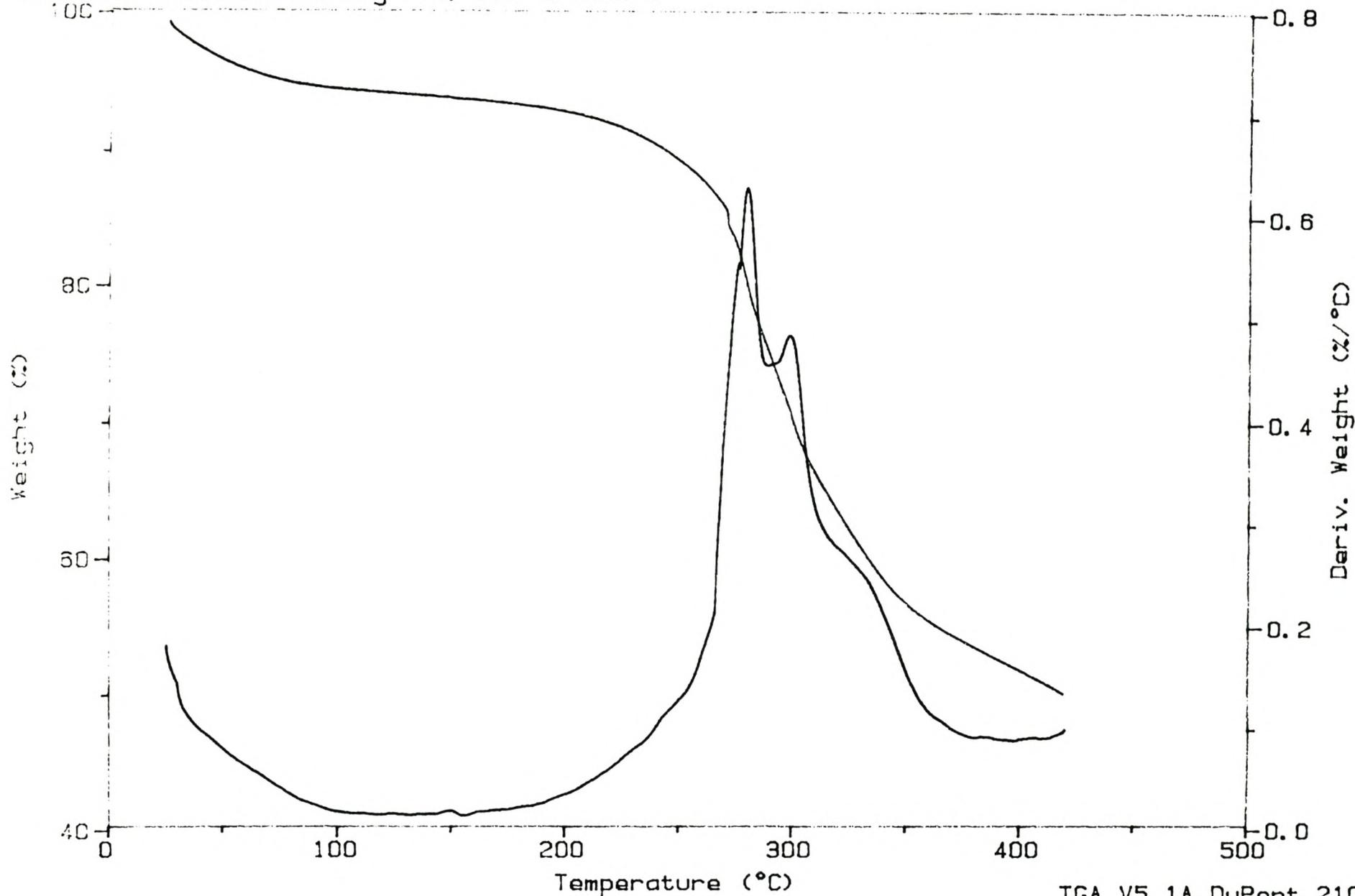
Sample: 18% PVC/82% kraalbos, aged   File: C.WIAN.8
Size: 11.8310 mg
Method: Wian
Comment: 50ml/min N2

TGA

Operator: WA
Run Date: 16-Oct-00 09:16
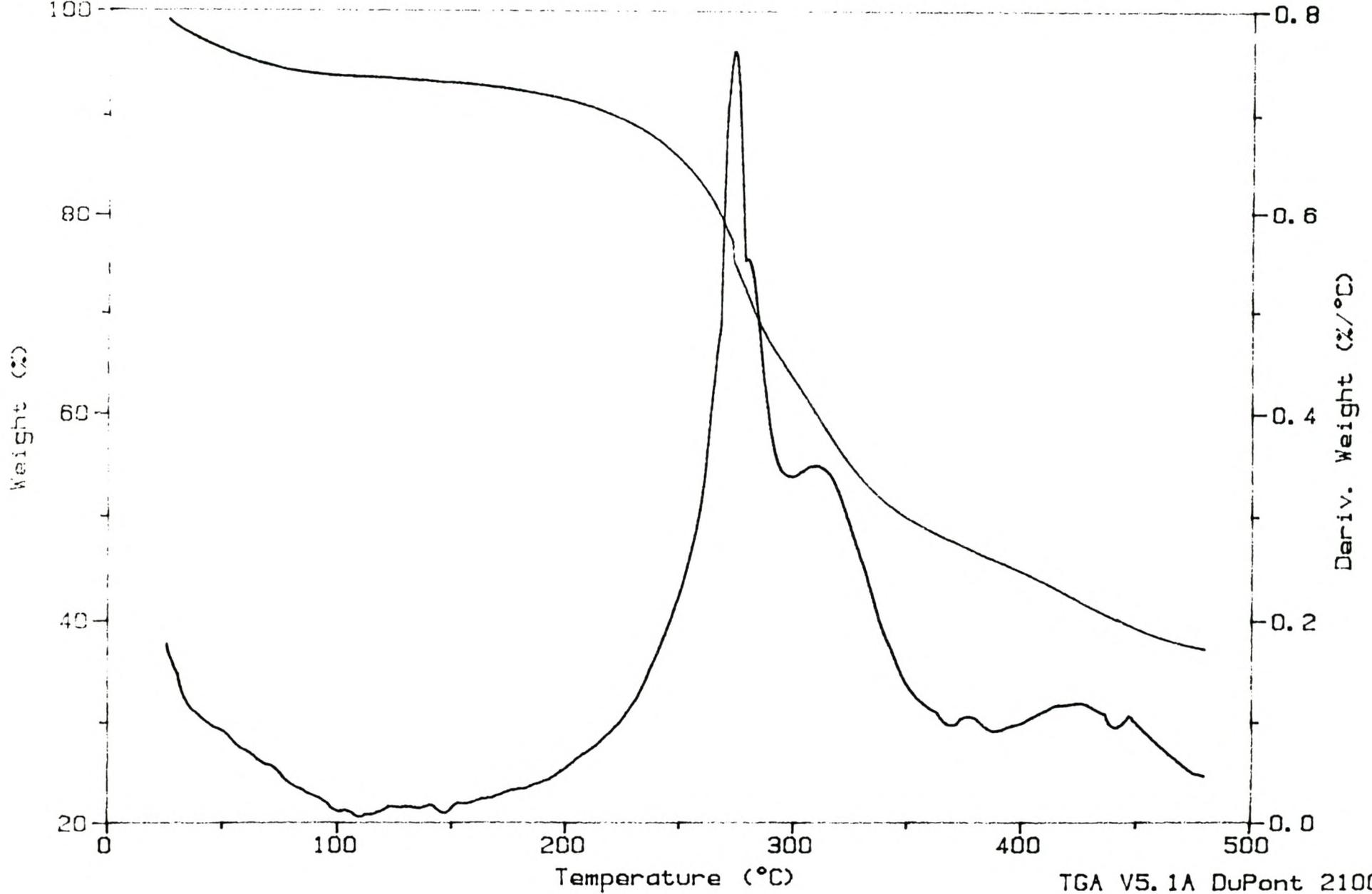
TGA V5.1A DuPont 2100

Appendix F

TGA results for the wood pyrolysis
experiments

Sample: Kraalbos aged
Size: 14.2930 mg
Method: Wian
Comment: 1st run

File: C:WIAN.1
Operator: WA
Run Date: 11-Oct-00 15:02

TGA

TGA V5.1A DuPont 2100

191
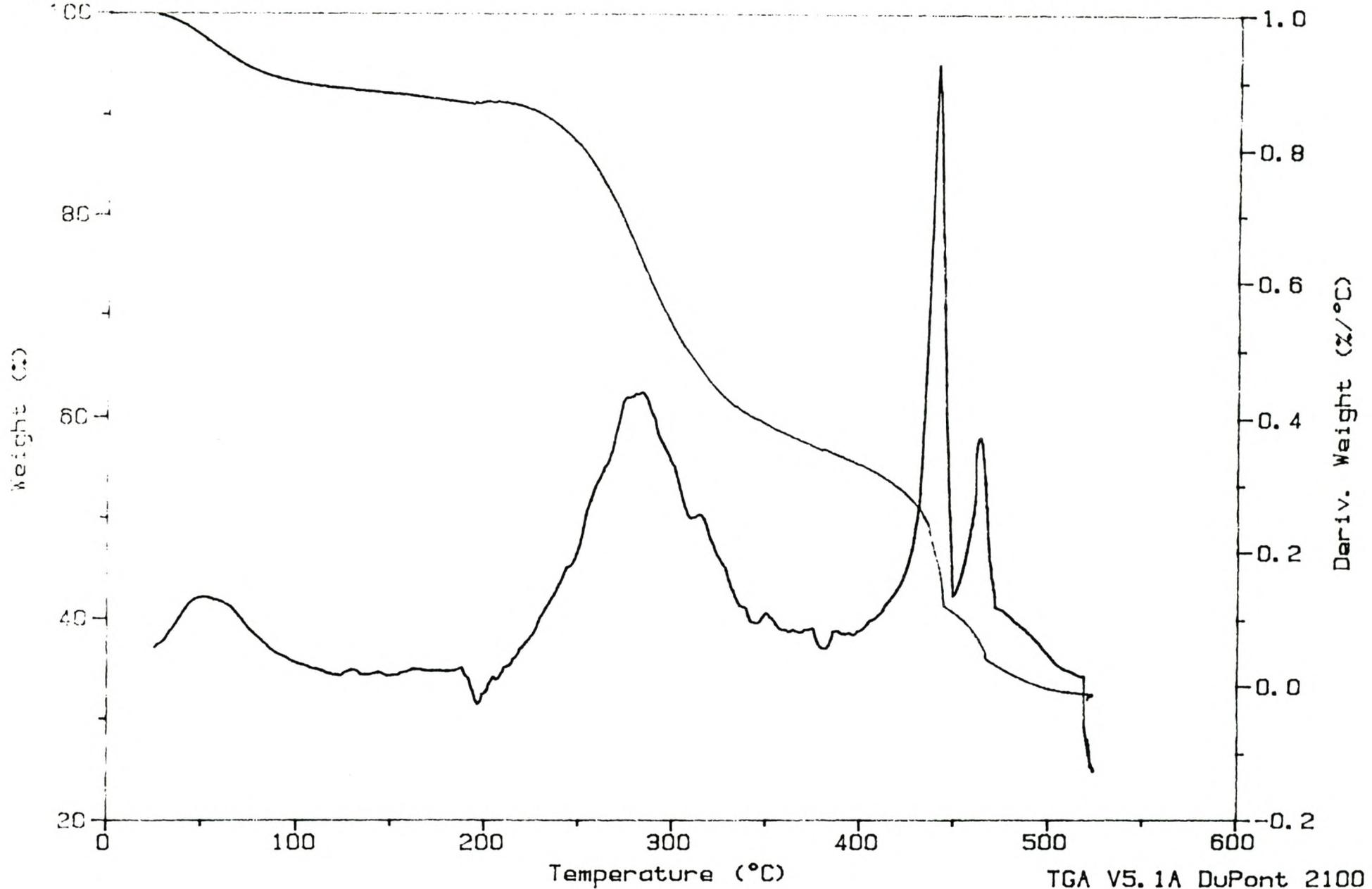
Sample: Rooibos Fresh
Size: 14.3780 mg
Method: Wian
Comment: 50ml/min N2

Operator: WA
Run Date: 16-Oct-00 12:17
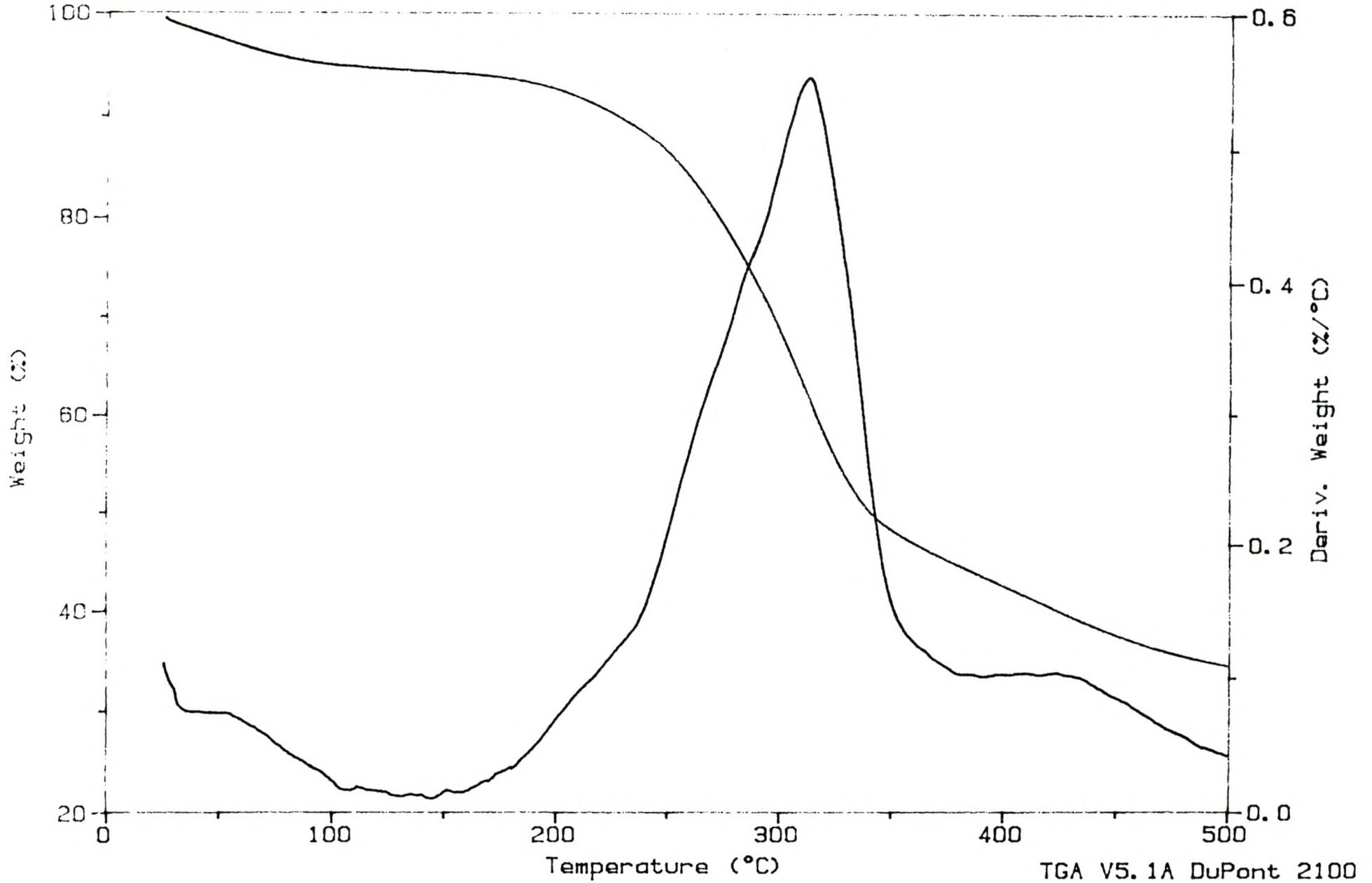
TGA V5.1A DuPont 2100

Appendix G

Sulphur contents of the different wood charcoals

Figure G1: Charcoal Sulphur Content
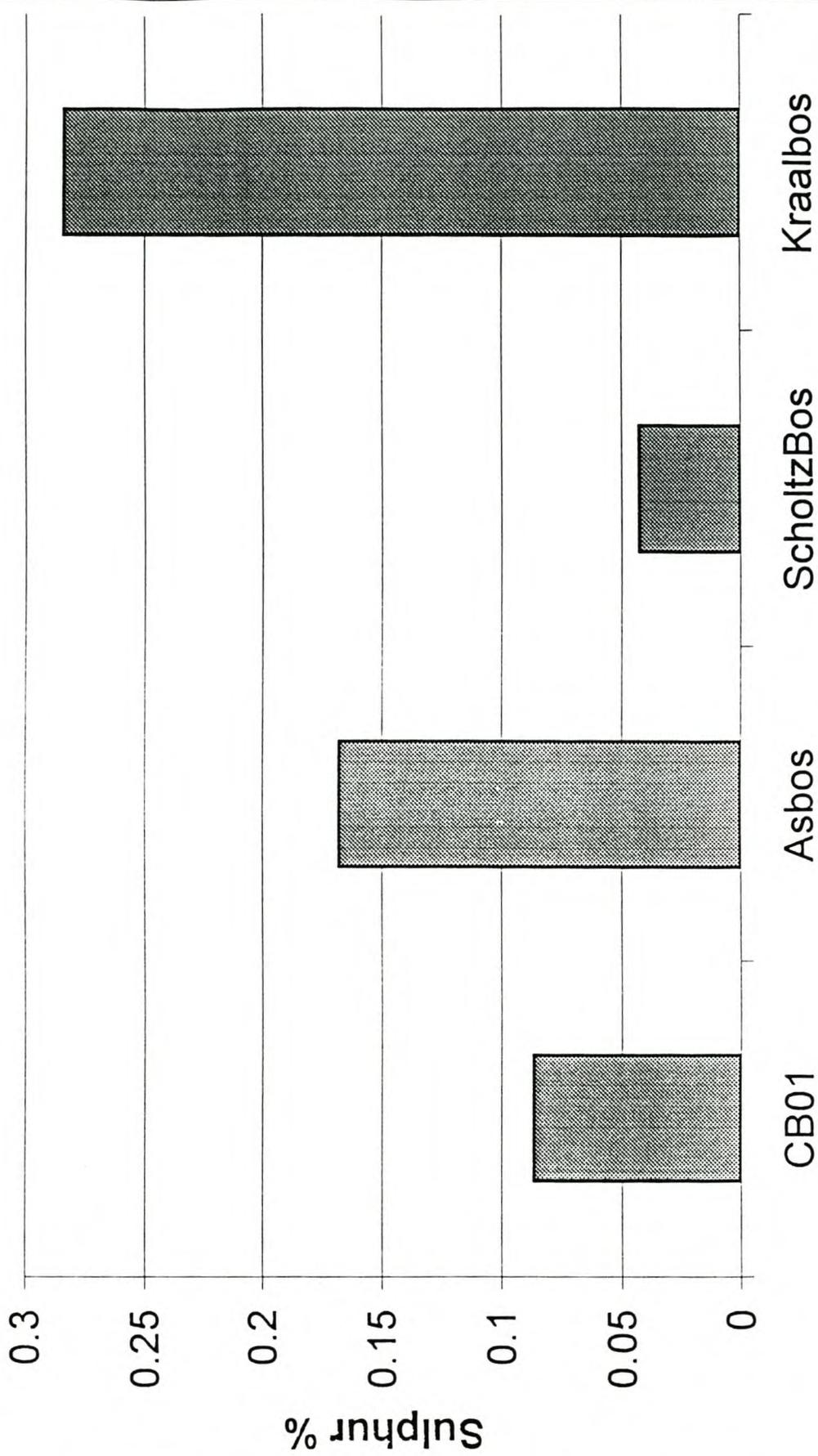
Appendix H

Example of the output file from the
thermodynamic equilibrium program (CEA)

```
*******************************************************************************

          NASA-GLENN CHEMICAL EQUILIBRIUM PROGRAM CEA, AUGUST 30, 1999
                   BY   BONNIE MCBRIDE AND SANFORD GORDON
          REFS: NASA RP-1311, PART I, 1994 AND NASA RP-1311, PART II, 1996

*******************************************************************************



 ! 'problem'  tp:
    problem case=bpnsonderdieseltp tp   p(atm)=0.15
 t(k)=1575.,793.,723.,693.,653.
 ,623.

 ! 'reactants' bpn sonder diesel tp:
    reac
       fuel=sel C 6.0 H 10.0 O 5.0 wt%=75. h,cal=-2. t(k)=298.15
       fuel= PVC C 2.0 H 3.0 CL 1.0  wt%=7.5 h,cal=-1. t(k)=298.15
       fuel= H2O H 2.0 O 1. wt%=8. h,cal=-1. t(k)=298.15
       fuel= Ash K 2.0 O 1. wt%=9.5 h,cal=-1. t(k)=298.15
 ! 'output'  tp:
    output   siunits massf trace=1.e-9  transport
 ! 'end'
    end

 OPTIONS: TP=T  HP=F  SP=F  TV=F  UV=F  SV=F  DETN=F  SHOCK=F  REFL=F  INCD=F
 RKT=F  FROZ=F  EQL=F  IONS=F  SIUNIT=T  DEBUGF=F  SHKDBG=F  DETDBG=F  TRNSPT=T


 T,K =  1575.0000    793.0000    723.0000    693.0000    653.0000    623.0000


 TRACE= 1.00E-09  S/R= 0.000000E+00   H/R= 0.000000E+00   U/R= 0.000000E+00


 P,BAR =        .151988


    REACTANT               WT.FRAC   (ENERGY/R),K   TEMP,K  DENSITY
        EXPLODED FORMULA
 F: sel                    .750000   -.100643E+01   298.15   .0000
         C  6.00000  H 10.00000  O  5.00000
 F: PVC                    .075000   -.503217E+00   298.15   .0000
         C  2.00000  H  3.00000  CL 1.00000
 F: H2O                    .080000   -.503217E+00   298.15   .0000
         H  2.00000  O  1.00000
 F: Ash                    .095000   -.503217E+00   298.15   .0000
         K  2.00000  O  1.00000


  SPECIES BEING CONSIDERED IN THIS SYSTEM
 (CONDENSED PHASE MAY HAVE NAME LISTED SEVERAL TIMES)
  LAST thermo.inp UPDATE:   11/08/99


  g 7/97  *C              g 8/99  CCL             g 8/99  CCL2
  x12/93  CCL3            tpis91  CCL4            tpis79  *CH
  g 9/99  CHCL            x12/93  CHCL2           g 7/99  CHCL3
  g 8/99  CH2             g 2/96  CH2CL           tpis91  CH2CL2
  g 8/99  CH3             tpis91  CH3CL           g12/92  CH2OH
  g10/92  CH3O            g 8/99  CH4             g 8/88  CH3OH
  tpis79  *CO             tpis91  COCL            tpis91  COCL2
```

tpis91	COHCL	g 9/99	*CO2	tpis91	COOH
tpis91	*C2	tpis91	C2CL	tpis91	C2CL2
tpis91	C2CL3	tpis91	C2CL4	tpis91	C2CL6
g 1/91	C2H	tpis91	C2HCL	tpis91	C2HCL3
g 6/89	CHCO,ketyl	g12/89	C2H2,vinylidene	g 1/91	C2H2,acetylene
tpis91	C2H2CL2	g 5/90	CH2CO,ketene	g 2/92	C2H3,vinyl
tpis91	C2H3CL	g 6/96	CH3CO,acetyl	g 1/91	C2H4
g 8/88	C2H4O,ethylen-o	g 8/88	CH3CHO,ethanal	g 8/88	CH3COOH
g12/92	C2H5	g 8/88	C2H6	g 8/88	C2H5OH
g12/92	CH3OCH3	g12/89	C2O	tpis79	*C3
x 4/98	C3H3,1-propynl	x 4/98	C3H3,2-propynl	g12/92	C3H4,allene
g12/92	C3H4,propyne	g 5/90	C3H4,cyclo-	bur 92	C3H5,allyl
g 2/95	C3H6,propylene	g 1/93	C3H6,cyclo-	g 6/90	C3H6O
g 6/90	C3H7,n-propyl	g 9/85	C3H7,i-propyl	g 6/90	C3H8
g 9/88	C3H8O,1propanol	g 9/88	C3H8O,2propanol	g 7/88	C3O2
g 7/88	C4	g 2/93	C4H2	g 5/90	C4H4,1,3-cyclo-
x10/92	C4H6,butadiene	x10/93	C4H6,1-butyne	x10/93	C4H6,2-butyne
g 5/90	C4H6,cyclo-	x 4/88	C4H8,1-butene	x 4/88	C4H8,cis2-buten
x 4/88	C4H8,tr2-butene	x 4/88	C4H8,isobutene	g 5/90	C4H8,cyclo-
g 6/90	(CH3COOH)2	x10/84	C4H9,n-butyl	x10/84	C4H9,i-butyl
g 1/93	C4H9,s-butyl	g 1/93	C4H9,t-butyl	g 6/90	C4H10,isobutane
g 6/90	C4H10,n-butane	g 7/88	C5	g 5/90	C5H6,1,3cyclo-
g 1/93	C5H8,cyclo-	x 4/87	C5H10,1-pentene	g 6/90	C5H10,cyclo-
x10/84	C5H11,pentyl	g 1/93	C5H11,t-pentyl	x10/85	C5H12,n-pentane
x10/85	C5H12,i-pentane	x10/85	CH3C(CH3)2CH3	g 2/93	C6H2
g 1/91	C6H5,phenyl	g 6/90	C6H5O,phenoxy	g 1/91	C6H6
g 6/90	C6H5OH,phenol	g 1/93	C6H10,cyclo-	x 4/87	C6H12,1-hexene
g 6/90	C6H12,cyclo-	x10/83	C6H13,n-hexyl	g 6/96	C6H14,n-hexane
g 1/93	C7H7,benzyl	g 1/93	C7H8	g 1/93	C7H8O,cresol-mx
x 4/87	C7H14,1-heptene	x10/83	C7H15,n-heptyl	x10/85	C7H16,2-methylh
x10/85	C7H16,n-heptane	x 4/89	C8H8,styrene	x10/86	C8H10,ethylbenz
x 4/87	C8H16,1-octene	x10/83	C8H17,n-octyl	x 4/85	C8H18,n-octane
x 4/85	C8H18,isooctane	x10/83	C9H19,n-nonyl	g 8/93	C10H8,naphthale
x10/83	C10H21,n-decyl	g12/84	C12H9,o-bipheny	g12/84	C12H10,biphenyl
g 7/97	*CL	tpis89	CLO	g 7/93	CLO2
tpis89	CL2	tpis89	CL2O	g 6/97	*H
g 9/96	HCO	tpis89	HCL	tpis89	HOCL
g 5/99	HO2	tpis78	*H2	g 8/88	HCHO,formaldehy
g 8/88	HCOOH	g 8/89	H2O	g 6/99	H2O2
g 8/88	(HCOOH)2	g 7/97	*K	J 3/66	KCL
J 3/63	KH	J12/67	KO	g 9/97	KOH
j12/83	K2	tpis82	K2CO3	tpis82	K2CL2
tpis82	K2O	tpis82	K2O2	g 9/97	K2O2H2
g 5/97	*O	tpis78	*OH	tpis89	*O2
tpis89	O3	x 4/83	C(gr)	x 4/83	C(gr)
x 4/83	C(gr)	g 8/89	H2O(s)	g 8/89	H2O(L)
coda89	K(cr)	coda89	K(L)	tpis82	KCL(cr)
tpis82	KCL(cr)	tpis82	KCL(L)	tpis82	KH(cr)
tpis82	KH(L)	g 8/97	KOH(a)	g 8/97	KOH(b)
g 8/97	KOH(c)	g 8/97	KOH(L)	tpis82	KO2(b)
tpis82	KO2(a)	tpis82	KO2(L)	tpis82	K2CO3(a)
tpis82	K2CO3(b)	tpis82	K2CO3(L)	tpis82	K2O(c)
tpis82	K2O(b)	tpis82	K2O(a)	tpis82	K2O(L)
tpis82	K2O2(cr)	tpis82	K2O2(L)		

SPECIES WITH TRANSPORT PROPERTIES

PURE SPECIES

C	CCL4	CHCL3	CH2CL2
CH3CL	CH4		

CH3OH	CO	CO2	C2H2,acetylene
C2H4˙	C2H6		
C2H5OH	CL2	H	HCL
H2	H2O		
O	OH	O2	

BINARY INTERACTIONS

C	O
CH4	O2
CO	CO2
CO	O2
CO2	H2
CO2	H2O
CO2	O2
H	H2
H	O
H2	H2O
H2	O2
H2O	O2
O	O2

O/F =   .000000

ENTHALPY	EFFECTIVE FUEL $h(2)/R$	EFFECTIVE OXIDANT $h(1)/R$	MIXTURE $h0/R$
(KG-MOL)(K)/KG	-.80013867E-02	.00000000E+00	-.80013867E-02

KG-FORM.WT./KG	bi(2)	bi(1)	b0i
*C	.30153770E-01	.00000000E+00	.30153770E-01
*H	.58737620E-01	.00000000E+00	.58737620E-01
*O	.28577285E-01	.00000000E+00	.28577285E-01
*CL	.12000399E-02	.00000000E+00	.12000399E-02
*K	.20170708E-02	.00000000E+00	.20170708E-02

POINT	ITN	T K	C	H	O	CL
1	18	1575.000	1.249	-10.687	-39.230	-33.992
		-20.798				
ADD	C(gr)					
1	5	1575.000	-2.282	-10.671	-35.701	-33.992
		-20.801				
2	15	793.000	-1.226	-9.831	-44.741	-52.030
		-20.504				
ADD	K2CO3(b)					
2	5	793.000	-1.226	-9.823	-44.744	-40.677
		-31.852				
ADD	KCL(cr)					
2	5	793.000	-1.226	-9.816	-44.736	-46.545
		-31.864				
3	5	723.000	-1.126	-9.865	-47.473	-48.699
		-35.751				
PHASE CHANGE, REPLACE K2CO3(b)			WITH K2CO3(a)			
4	5	693.000	-1.084	-9.920	-48.849	-49.800
		-37.632				
5	5	653.000	-1.028	-10.029	-50.897	-51.434
		-40.423				
6	5	623.000	-.987	-10.141	-52.614	-52.804
		-42.761				

THERMODYNAMIC EQUILIBRIUM PROPERTIES AT ASSIGNED

TEMPERATURE AND PRESSURE

CASE = bpnsonderdiesel

	REACTANT	WT FRACTION (SEE NOTE)	ENERGY KJ/KG-MOL	TEMP K
FUEL	sel	.7500000	-8.368	298.150
FUEL	PVC	.0750000	-4.184	298.150
FUEL	H2O	.0800000	-4.184	298.150
FUEL	Ash	.0950000	-4.184	298.150

O/F=   .00000 %FUEL=100.000000 R,EQ.RATIO= 3.108062 PHI,EQ.RATIO= .000000

THERMODYNAMIC PROPERTIES

P, BAR	.15199	.15199	.15199	.15199	.15199	.15199
T, K	1575.00	793.00	723.00	693.00	653.00	623.00
RHO, KG/CU M	1.9358-2	5.8661-2	7.2708-2	7.9312-2	8.8574-2	9.5773-2
H, KJ/KG	-901.01	-5657.92	-6327.95	-6542.91	-6777.88	-6921.74
U, KJ/KG	-1686.17	-5917.02	-6536.98	-6734.54	-6949.47	-7080.44
G, KJ/KG	-23553.1	-13266.6	-12627.5	-12370.7	-12041.5	-11803.2
S, KJ/(KG)(K)	14.3823	9.5949	8.7131	8.4096	8.0607	7.8353
M, (1/n)	16.679	25.448	28.757	30.068	31.641	32.641
MW, MOL WT	16.252	17.547	18.441	18.880	19.427	19.758
(dLV/dLP)t	-1.00019	-1.08451	-1.06746	-1.05820	-1.04416	-1.03352
(dLV/dLT)p	1.0025	2.5254	2.1333	1.9705	1.7461	1.5794
Cp, KJ/(KG)(K)	2.0972	11.6818	7.7559	6.5620	5.2291	4.3819
GAMMAs	1.3135	1.1036	1.1138	1.1179	1.1224	1.1255
SON VEL,M/SEC	1015.5	534.7	482.5	462.8	438.9	422.6

TRANSPORT PROPERTIES (GASES ONLY)
  CONDUCTIVITY IN UNITS OF MILLIWATTS/(CM)(K)

VISC,MILLIPOISE	.54939	.34991	.32303	.30839	.28746	.27147

  WITH EQUILIBRIUM REACTIONS

Cp, KJ/(KG)(K)	2.0983	14.1386	11.2104	9.5260	7.5010	6.1893
CONDUCTIVITY	2.5204	7.4980	6.9406	6.3333	5.3421	4.5010
PRANDTL NUMBER	.4574	.6598	.5217	.4639	.4036	.3733

  WITH FROZEN REACTIONS

Cp, KJ/(KG)(K)	2.0727	2.2320	2.1476	2.0956	2.0220	1.9681
CONDUCTIVITY	2.4760	1.5008	1.2024	1.0631	.8890	.7742
PRANDTL NUMBER	.4599	.5204	.5770	.6079	.6538	.6902

MASS FRACTIONS

CH3	1.860 -7	3.302-12	2.373-13	6.106-14	7.756-15	1.333-15
CH4	6.4571-5	2.9948-2	5.2111-2	6.2206-2	7.4185-2	8.1104-2
*CO	8.0035-1	1.1270-1	2.9516-2	1.5101-2	5.6287-3	2.4862-3
*CO2	3.2278-5	3.4197-1	3.3446-1	3.1809-1	2.9307-1	2.7438-1
C2H2,acetylene	1.618 -5	4.461-13	1.060-14	1.628-15	9.919-17	9.400-18
CH2CO,ketene	5.451 -9	8.389-12	6.868-13	1.884-13	2.665-14	5.078-15

199

C2H4	1.829 -7	5.972 -9	1.600 -9	7.631-10	2.350-10	8.303-11
C2H6	7.409-11	1.069 -7	1.725 -7	1.880 -7	1.865 -7	1.691 -7
*CL	9.765 -9	6.333-19	9.409-21	1.169-21	5.458-23	4.280-24
*H	4.513 -6	1.480-13	4.417-15	7.826-16	6.044-17	7.118-18
HCO	1.121 -8	1.850-14	4.593-16	7.205-17	4.576-18	4.541-19
HCL	8.3050-5	7.6087-8	2.3679-8	1.2706-8	5.0141-9	2.2912-9
*H2	5.9175-2	3.5980-2	2.3734-2	1.8660-2	1.2675-2	8.9983-3
HCHO,formaldehy	2.802 -8	5.486 -9	1.147 -9	4.976-10	1.384-10	4.624-11
HCOOH	3.489-12	1.434 -8	8.997 -9	6.531 -9	3.849 -9	2.403 -9
H2O	3.9379-5	1.4029-1	1.9995-1	2.2262-1	2.4920-1	2.6652-1
*K	3.201 -2	1.158-10	4.947-13	3.572-14	7.444-16	2.971-17
KCL	8.894 -2	3.531 -6	1.354 -7	2.757 -8	2.652 -9	3.781-10
KH	2.126 -5	5.836-15	1.318-17	6.786-19	8.387-21	2.131-22
KOH	4.461 -6	2.031 -8	4.831-10	7.680-11	4.964-12	4.994-13
K2	1.130 -6	1.721-21	8.041-26	6.538-28	5.388-31	1.447-33
K2CL2	3.573 -4	6.762 -7	1.640 -8	2.656 -9	1.813-10	1.935-11
C(gr)	1.8907-2	1.9318-1	2.1431-1	2.1740-1	2.1933-1	2.2059-1
KCL(cr)	.0000 0	8.9460-2	8.9464-2	8.9464-2	8.9464-2	8.9464-2
K2CO3(a)	.0000 0	.0000 0	.0000 0	5.6459-2	5.6459-2	5.6459-2
K2CO3(b)	.0000 0	5.6459-2	5.6459-2	.0000 0	.0000 0	.0000 0

* THERMODYNAMIC PROPERTIES FITTED TO 20000.K

PRODUCTS WHICH WERE CONSIDERED BUT WHOSE MASS FRACTIONS
WERE LESS THAN 1.000000E-09 FOR ALL ASSIGNED CONDITIONS

*C	CCL	CCL2	CCL3	CCL4
*CH	CHCL	CHCL2	CHCL3	CH2
CH2CL	CH2CL2	CH3CL	CH2OH	CH3O
CH3OH	COCL	COCL2	COHCL	COOH
*C2	C2CL	C2CL2	C2CL3	C2CL4
C2CL6	C2H	C2HCL	C2HCL3	CHCO,ketyl
C2H2,vinylidene	C2H2CL2	C2H3,vinyl	C2H3CL	CH3CO,acetyl
C2H4O,ethylen-o	CH3CHO,ethanal	CH3COOH	C2H5	C2H5OH
CH3OCH3	C2O	*C3	C3H3,1-propynl	C3H3,2-propynl
C3H4,allene	C3H4,propyne	C3H4,cyclo-	C3H5,allyl	C3H6,propylene
C3H6,cyclo-	C3H6O	C3H7,n-propyl	C3H7,i-propyl	C3H8
C3H8O,1propanol	C3H8O,2propanol	C3O2	C4	C4H2
C4H4,1,3-cyclo-	C4H6,butadiene	C4H6,1-butyne	C4H6,2-butyne	C4H6,cyclo-
C4H8,1-butene	C4H8,cis2-buten	C4H8,tr2-butene	C4H8,isobutene	C4H8,cyclo-
(CH3COOH)2	C4H9,n-butyl	C4H9,i-butyl	C4H9,s-butyl	C4H9,t-butyl
C4H10,isobutane	C4H10,n-butane	C5	C5H6,1,3cyclo-	C5H8,cyclo-
C5H10,1-pentene	C5H10,cyclo-	C5H11,pentyl	C5H11,t-pentyl	C5H12,n-pentane
C5H12,i-pentane	CH3C(CH3)2CH3	C6H2	C6H5,phenyl	C6H5O,phenoxy
C6H6	C6H5OH,phenol	C6H10,cyclo-	C6H12,1-hexene	C6H12,cyclo-
C6H13,n-hexyl	C6H14,n-hexane	C7H7,benzyl	C7H8	C7H8O,cresol-mx
C7H14,1-heptene	C7H15,n-heptyl	C7H16,2-methylh	C7H16,n-heptane	C8H8,styrene
C8H10,ethylbenz	C8H16,1-octene	C8H17,n-octyl	C8H18,n-octane	C8H18,isooctane
C9H19,n-nonyl	C10H8,naphthale	C10H21,n-decyl	C12H9,o-bipheny	C12H10,biphenyl
CLO	CLO2	CL2	CL2O	HOCL
HO2	H2O2	(HCOOH)2	KO	K2CO3
K2O	K2O2	K2O2H2	*O	*OH
*O2	O3	H2O(s)	H2O(L)	K(cr)
K(L)	KCL(L)	KH(cr)	KH(L)	KOH(a)
KOH(b)	KOH(c)	KOH(L)	KO2(b)	KO2(a)
KO2(L)	K2CO3(L)	K2O(c)	K2O(b)	K2O(a)
K2O(L)	K2O2(cr)	K2O2(L)		

NOTE. WEIGHT FRACTION OF FUEL IN TOTAL FUELS AND OF OXIDANT IN TOTAL OXIDANTS

Appendix I

Experimental Reproducibility

Experimental reproducibility

The reproducibility of the vacuum pyrolysis experiments are of cardinal importance. The batch operated tube furnace was designed and built because of the lack of reproducible result from the previous batch reactor. There are two main areas that had to yield accurate results, these where the charcoal and oil yields.

Table I.1 demonstrates the reproducibility of the reactor. The Asbos experiment redone with the purpose of ensuring accuracy, while the Scholtzbos experiment was done to see if a small heating rate difference had a significant effect. It can be seen that the charcoal yields of the Asbos experiments were within 2.5% of one another. It was consistently found throughout the experiments that the charcoal yield only exhibited deviations in the event of experimental error or feedstock variation. The Asbos oil yields were slightly more variable, with a difference of 4.7%. There were considerably more factors that influenced the oil yield and a reproducibility of close to 5% was expected. The Scholtzbos experiments were done to show the effect of changes in the heating rate and it can be seen that the charcoal yield were basically not affected, but that the oil yield became more inaccurate. It therefore appears that under normal operating conditions, where the heating rate are kept almost constant (as can be seen in the Asbos experiments) the reproducibility would be in the order of 2%-3% for the charcoal and 4%-5% for the oil. The charcoal variance might even be lower on average as will soon be seen from the experiments where errors occurred.

Table I. 1 Reproducibility of the Charcoal and Oil yields

Samples	Temp [C]	Heating Rate [C/min]	Pyro time [min]	Pressure kPa	Char %	oil total %	Difference Char [%]	Difference Oil [%]
Asbos	400	13.4	120	18	48.3	16.1	-2.5	4.7
	400	13.7	120	18	47.1	16.9		
Scholtzbos	450	12.6	60	18	43.2	18.0	0.6	8.1
	450	15.3	60	18	43.4	19.5		

The way the reactor was set up meant that because of experimental error the oil yield could be incorrect, but the charcoal yield might still be of use. The reason the charcoal yield could still be correct even if the oil yield were not, was that the experimental error could occur because of several different factors. Some of these factors would still allow for correct charcoal yields, while totally disrupting the oil yields. However, if the charcoal yield is incorrect the oil yield will always be incorrect as well.

There are several factors that can cause experimental errors, but most of them can be easily avoided. There are three main factors that can adversely influence the charcoal yield accuracy. The main error occurs when the sample is not placed correctly within the hot-zone. The sample cannot be placed too close to the access point of the reactor, because of the stainless steel tube that extends to the beginning of the hot-zone, but it can be placed too deep into the reactor. If this occurs, the charcoal yield will be higher and the oil yields lower than it should. This is because the entire sample is not heated to the same temperature and some of the sample therefore does not completely react to the extent that it should. This can be avoided by placing the sample close to the reactor access point and sliding the sample into the reactor with the stainless steel pipe connected to the brass end-cap. The second main error which could influence the charcoal yields accuracy is if air where to leak into the reactor. The chances of this happening are relatively slim since the reactor are sealed with o-rings, and unless the operator forgets to tighten the bolts after replacing the sample it should not happen. The entry points of the two thermocouples should be checked regularly to ensure that no air could leak in there. The last factor is if the feedstock character changes between runs because of aging, water content change or some other factor. This can be avoided by planning the sets of experiments in such a way that there will not be a significant (month or more) break between experiments.

The oil yields are more easily influenced as could be seen from table I.1. As was stated above, the oil yield will be incorrect if the charcoal yield is influenced by an unexpected external factor. There are two main factors which can seriously influence the oil yield, these are air leakage and incorrect cleaning of the process equipment. There are several connections between vacuum traps and between the reactor and the pipes where leaks can occur. The closer the leakage is to the reactor the greater the influence on the oil yields. Closer to the reactor the gases are still very hot and

therefore reacts with air. Further along the condensation train the air does not react to such a great extend with the gases, but it does cause water to condense in the traps. The water then increases the total liquid yield and skews the results. If the process equipment are not cleaned correctly the oil yield results and purity of the oil samples will be influenced.

Table I.2 shows the effects experimental error can have on the results. It can be seen that basically only the oil yields were influenced by the error for the Scholtzbos and coarse leather experiments. The sample was not placed correctly inside the reactor for the Kraalbos experiment and it can be seen that it cause a significant error in the charcoal yield and totally changed the oil yield. Luckily the air leaks mainly occurred if silicone grease was not applied or if the union connecting the reactor to the stainless steel pipe was not fastened. For the results presented in table I.2 the second value are the results from the experiment that was redone correctly.

Table I. 2 Effect of experimental errors on the product yields

Samples	Temp [C]	Heating Rate [C/min]	Pyro time [min]	Pressure kPa	Char oil %	total %	Difference Char [%]	Diffrence Oil [%]
Scholtzbos	450	11.4	30	18	42.3	16.2	2.7	30.0
	450	10.0	30	18	43.4	21.1		
Coarse	350	5.0	60	18	51.9	13.9	-4.9	49.0
Leather	350	5.0	60	18	49.4	20.6		
Kraalbos	380	12.3	60.0	18.0	21.5	5.1	15.0	144.8
	380	10.0	60	18	24.7	12.5		

The accuracy of the oil yield results can be improved by heating the pipes connecting the hot-zone of the reactor to the vacuum traps to over 160°C or 200°C. This would ensure that no condensation occurs in the pipes and would make the whole process much easier to operate and clean.

There is no reason why experimental errors should occur if the operator works carefully and ensures that all the connections are properly sealed. The seals can be made properly airtight by applying silicone grease. The charcoal yields are therefore

accurate to within at least 2%-3%, even with slight experimental errors, and the oil yield is accurate to within 4%-5%, if the reactor is operated correctly.

Appendix J

Differential pressure sensor calibration curve

Figure J1: Differentail Pressure Gauge Calibration Curve

$y = 22322x - 20672$
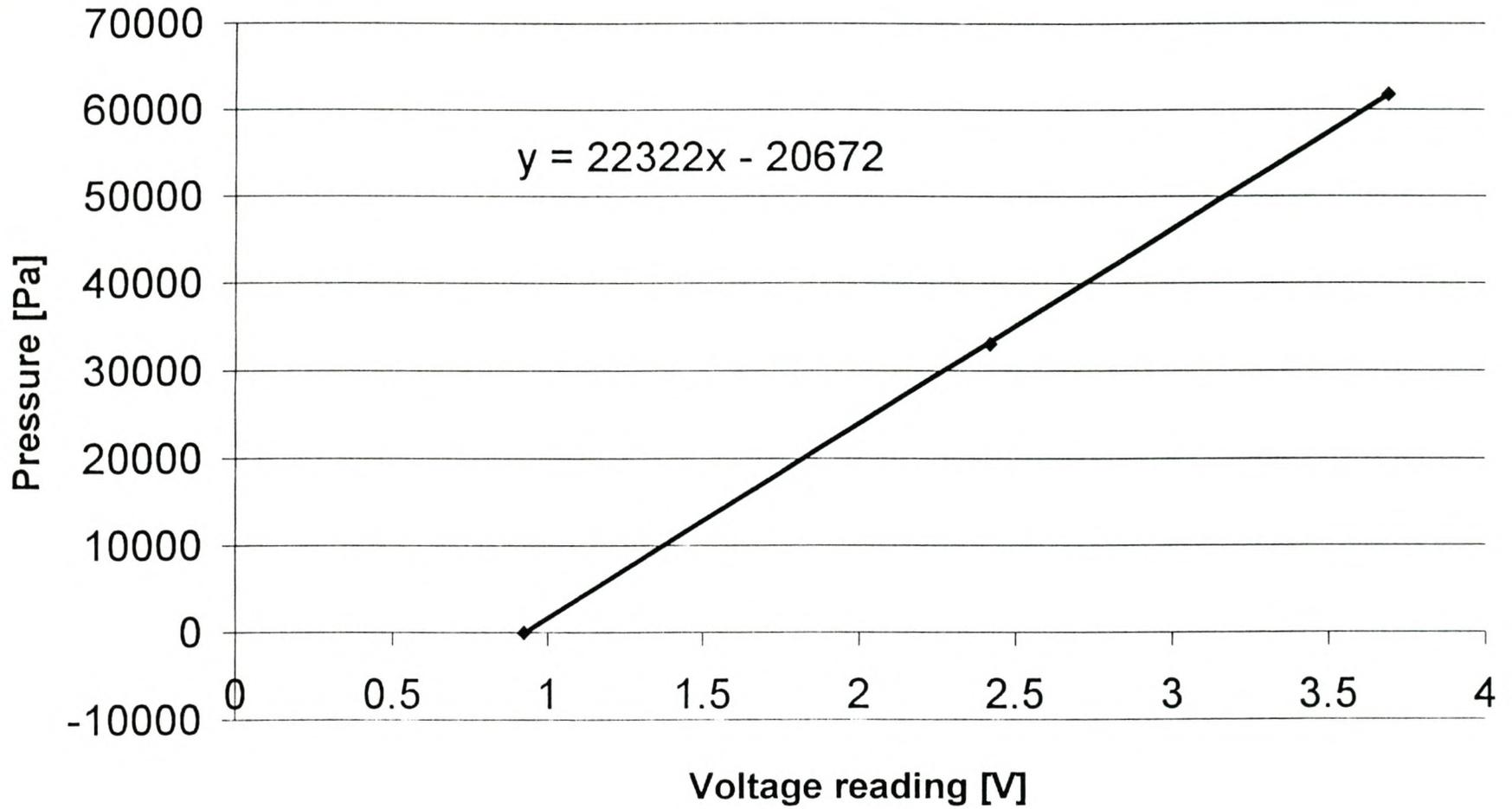
Appendix K

Reactor design

Brass sealing cap

90mm

61 ID
1mm thick

66φ

5φ

76

1 mm thick

49

27

67

9

5

90

9

61 ID

36

27

Tight fit in 61mm ID

90φ

1. Brass

Reactor design

1m long, 60mm ID, 3 mm thick Quartz tube

Viton o-ring