

Plasticization of Bagasse Residue

by

hih-Hsun
C.H. Hsieh



Thesis presented in partial fulfilment of the requirements for the degree

Master of Wood Science

at the

University of Stellenbosch

Date: March 1997

Study leader: Prof G.F.R. Gerischer

Internal Examiner: Dr T. Rypstra

External Examiner: Dr. R. Reimann

DECLARATION

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

11/12/1961

.....
Date

ACKNOWLEDGEMENTS

I express my sincere thanks and appreciation to:

1. Prof G.F.R. Gerischer (Dept of Wood Science) for his able help and constructive comments and advice as my study leader.
2. Dr T. Rypstra (Dept of Wood Science) for his continuous encouragement, able advice during this study.
3. Ms A. Lee for her help in correcting English grammar in my thesis.
4. Mrs S.L. Tseng, my wife, for her continuous encouragement and typing.
5. The University of Stellenbosch that made this study possible.

PLASTICIZATION OF BAGASSE RESIDUE

ABSTRACT

Auto-hydrolysis bagasse residue was used as a raw material for liquefaction with phenol to produce a novolac resin suitable for moulding applications. Sulphuric acid proved to be the most suitable catalyst. Using addition levels of 6%, a reaction time of 1 hour and a reaction temperature of 150°C, good liquefaction of the bagasse residue could be achieved. High-speed stirring accelerated the speed of liquefaction. Infrared spectra indicated that the chemical structure of the phenolated bagasse was complex. An increase in phenol content resulted in higher bending and tensile strength of moulded samples.

PLASTISERING VAN BAGASSE AFVALMATERIAAL

OPSOMMING

Auto-gehidroliseerde bagasse afvalmateriaal is as grondstof gebruik vir vervloeiing saam met fenolhars vir die produksie van 'n novolak hars wat geskik sal wees vir die maak van gevormde produkte. Dit is gevind dat swawelsuur die mees geskikte katalisator vir die proses was. Deur 6% swawelsuur, 'n reaksietyd van een uur en 'n temperatuur van 150°C te gebruik, is gevind dat uitstekende vervloeiing van die bagasse afvalmateriaal verkry kon word. Roering teen hoë spoed het die vervloeiing verhaas. Infra-rooi spektrogramme het aangedui dat die chemiese struktuur van die gefenoleerde bagasse baie kompleks is. 'n Toename in fenolinhoud het veroorsaak dat die buig- en treksterkte van gevormde monsters toegeneem het.

LIST OF CONTENTS

Objective	1
Chapter 1 Liquefaction of bagasse and other lignocellulosic residues:	
Literature review	2
1.1 Lignocellulose	2
1.1.1 Characteristics of lignocellulose	2
1.1.2 The conversion and uses of lignocellulosic residues	4
1.1.3 Utilisation of agricultural lignocellulosic residue	6
1.2 Liquefaction of lignocellulose	8
1.2.1 Influence of catalyst	8
1.2.2 Influence of temperature	8
1.2.3 Influence of liquefaction time	9
1.2.4 Influence of phenol/wood ratio	9
1.3 Liquefied lignocellulose in moulding applications	10
1.3.1 Moulding	10
1.3.2 Physical properties of mouldings made from novolacs	10
1.3.2.1 Effect of the amounts of reacted phenol	11
1.3.2.2 Effect of filler contents	11

1.3.2.3	Effect of curing time	11
Chapter 2	Experimental	13
2.1	Raw materials	13
2.1.1	Lignocellulosic residue	13
2.1.2	Phenol	13
2.1.3	Catalysts	14
2.1.4	Organic solvents	15
2.1.5	Novolac resin	15
2.1.6	Hexamine	16
2.2	Equipment for novolac preparation and moulding	16
2.2.1	Liquefaction of bagasse	16
2.2.1.1	Pressure bomb system	16
2.2.1.2	Pilot reactor system	17
2.2.2	Moulding	18
2.3	Experimental procedure of bagasse liquefaction (novolac preparation) and product moulding	19
2.3.1	Liquefaction	19
2.3.1.1	High liquefaction bagasse system	20
2.3.1.2	Low liquefaction bagasse system	21
2.3.1.3	Liquefaction temperatures	21
2.3.1.4	The effect of agitation during liquefaction	22

2.4	Degree of liquefaction	24
2.5	IR analysis	25
2.6	Evaluation of the phenolated bagasse as a moulding resin	25
2.6.1	Testing of novolac and moulded products	26
2.6.1.1	Bending strength and tensile strength	26
Chapter 3	Result and discussion	27
3.1	Liquefaction of bagasse	27
3.1.1	Catalyst	28
3.1.2	Liquefaction temperature	34
3.1.3	Acid catalyst addition level	37
3.1.4	Pilot reactor with stirring system	39
3.2	Infrared analysis	41
3.3	Physical properties of the moulded samples	46
3.4	Material cost comparison for replacing pure novolac moulding resin with phenolated bagasse	50
Chapter 4	Conclusion	51
Literature cited	53

LIST OF TABLES

Table 1.1: Utilisation of lignocellulosic residues	5
Table 1.2: Chemical conversion of the three major fractions of lignocellulosic materials into various by-products	6
Table 1.3: Composition of a typical moulding formulation	11
Table 2.1: Chemical composition and physical properties of the bagasse residue	13
Table 2.2: Phenol specification.....	14
Table 2.3: Specification of catalysts used for liquefaction	14
Table 2.4: Specification of organic solvents	15
Table 2.5: Novolac specification.....	15
Table 2.6: The dimensions of the pressure bomb.....	16
Table 2.7: Mould dimensions.....	19
Table 2.8: Reaction conditions for high liquefaction of bagasse.....	20
Table 2.9: Reaction conditions for low liquefaction of bagasse.....	21
Table 2.10: Reaction conditions during different liquefaction temperatures.....	22
Table 2.11: Reaction conditions for the pressure bomb in the oven.....	23
Table 2.12: Reaction conditions for the pilot reactor	23
Table 2.13: The composition of the moulded samples	25
Table 3.1: The relationship between catalyst and liquefaction technique	27
Table 3.2: Extractable material after HLC and LLC liquefaction with acidic catalyst.....	29

Table 3.3: Extractable material differences for the hydrochloric acid and sulphuric acid catalysts used in HLC and LLC.....	30
Table 3.4: Differences in extractable phenolated material in HLC and LLC using three acid catalysts	33
Table 3.5: The residual amount (%) and combined phenol (%) of phenolated wood using HCl catalyst.	34
Table 3.6: Extractable material after LLC at different liquefaction temperatures and 2% sulphuric acidic catalyst	35
Table 3.7: The effect of catalyst addition level on liquefaction under LLC.....	37
Table 3.8: Comparison of phenolation results of LLC liquefaction in pressure bomb and pilot reactor	39
Table 3.9: The relationship of Infrared spectral intensities of the OH-group, the -C-O-C- group and ortho-substitution benzene group at different (HCl and H ₂ SO ₄) levels	43
Table 3.10: The correlation of the bending strength and percentage of combined phenol at various catalyst addition levels.....	46
Table 3.11: The correlation of tensile strength and percentage of combined phenol for various levels of catalyst additions	48
Table 3.12: Moulding formulation of phenolated bagasse resin and commercial novolac	50

LIST OF FIGURES

Figure 1.1:	Microgel model of a high molecular mass ligno-sulphonate	4
Figure 1.2:	Effect of liquid/solids ratio on the amounts of combined phenol and unreacted wood residue (liquefaction time, 2 h; temperature, 160°C; catalyst content, 6.8%.)	9
Figure 1.3:	Effect of moulding time on the flexural strength of the moulding	12
Figure 2.1:	The pilot reactor and T 300A circulator heating unit	18
Figure 2.2:	Spiral mixer of pilot reactor.....	18
Figure 3.1:	Illustrating colour differences of phenolated materials for LLC.....	28
Figure 3.2:	Combined phenolated bagasse as a function of catalyst addition for the HLC reaction method	31
Figure 3.3:	Liquefaction % as a function of catalyst addition for the HLC reaction method	32
Figure 3.4:	Combined extractable material as a function of catalyst addition for the LLC reaction method	32
Figure 3.5:	Liquefaction % as a function of catalyst addition for the LLC reaction method.....	33
Figure 3.6:	The relationship of CP and residual amount (%) at different reaction temperatures	36

Figure 3.7: The relationship of liquefaction (%) and residual amount (%) at different reaction temperatures 36

Figure 3.8: Combined phenol and residual amount (%) at different catalyst addition levels 38

Figure 3.9: Liquefaction (%) and residual amount (%) at different catalyst addition levels 38

Figure 3.10: Residual amount (%) and CP of the extractable material during pilot reactor and pressure bomb phenolation 40

Figure 3.11: The relationship of residual amount (%) and liquefaction (%) of the extractable material during pilot reactor and pressure bomb phenolation..... 41

Figure 3.12: Infrared spectra of the hydrochloric acid catalyst at the 2, 4 and 6% concentration 44

Figure 3.13: Infrared spectra of the sulphuric acid catalyst at the of 2, 4 and 6% concentration 45

Figure 3.14: The relation between bending strength and combined phenol (%)..... 47

Figure 3.15: The relation between bending strength and liquefaction (%)..... 47

Figure 3.16: The effect of % of combined or reacted phenol on tensile strength 49

Figure 3.17: The effect of % liquefaction on tensile strength..... 49

Objective

The objective of this study was to investigate whether the liquefaction of bagasse with phenol and a suitable catalyst at an elevated temperature could result in novolac resin suitable as a low cost moulding adhesive.

Chapter 1

Liquefaction of Bagasse and other

Lignocellulosic Residues: Literature Review

Emerging technologies aimed at a more complete utilisation of agricultural lignocellulosic biomass, which at present can be regarded as an under-utilised raw material, have shown that such a resource could be turned into new products with expanding potential. One of the more recent areas of study is the plasticization of agriculture residue by using simple chemical modification techniques. Chemical modification, (i.e.: by an esterification or etherification reaction and some other derivatization reaction such as plasticization, followed by a dissolution stage in high powered solvent systems, such as polyhydric or phenol media), can convert all the main biomass components into a thermally flowable material (41). Useful end products, such as mouldable fibreboard, foams, various powder and liquid adhesives (phenolic resoles and novolacs) are foreseen. These can serve to form an alternative and sustainable industry in South Africa for supplying building components for activities such as building low-cost housing.

1.1 Lignocellulose

Lignocellulose, defined as a complex natural material comprising cellulose, hemicelluloses and lignin, is produced in vast quantities every year through photosynthesis in plants (1)(3)(4). It is a renewable resource and includes all of earth's vegetation, whether in a natural habitat or in a cultivated form as agricultural crops or forest plantations. New technologies for the utilisation of lignocellulosic residues such as using olive cake and grape by-products for animal nutrition, the fractionation of lignocellulose for the production of chemicals and rumen fermentations, are constantly being developed (1)(2).

1.1.1 Characteristics of lignocellulose

Cellulose, being the major polymeric component of bagasse (45%), consists of anhydroglucopyranose units which are joined β -(1 \rightarrow 4) -

glycosidic to form a linear molecule. The degree of polymerisation equals 5 000 - 10 000 glucose anhydride units. Hydrogen bonds hold neighbouring chains together to form a fibrous para-crystalline material which is insoluble in water and therefore more resistant to hydrolysis than other lignocellulosic polysaccharides (3).

Hemicelluloses differ from cellulose, because they are composed of various sugar units, with much shorter molecular chains which are branched. The sugar units (anhydro-sugars) making up the hemicelluloses, can be classified as pentoses, hexoses, hexuronic acids and deoxy-hexoses. Hemicelluloses are not crystalline and can therefore be easily hydrolysed (3).

Lignin, the third polymeric compound of lignocellulose, is a complex polyphenolic compound. The monomeric units are linked together by carbon-to-carbon as well as carbon-to-oxygen (ether) bonds. Lignin is quite stable and easy to isolate, but not in the undisturbed form. Isolation always results in modification, which makes the study of native lignin difficult. Lignin is made up by three basic structural units: p-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol. Lignin is a thermoplastic material (3). The molecular network of lignin extends throughout the lignocellulosic plant material. Lignin as it occurs in nature is insoluble in neutral solvents at room temperature. During pulping of wood chips, the lignin network is separated into fragments by the chemical action of the hot pulping liquor. Through the introduction of hydrophilic groups, the fragmented lignin sulphonate or alkali lignin is rendered soluble in water. Goring (5) proposed a microgel model for the lignosulphonate macromolecule in solution. Relatively short chains are cross-linked to give a gel-like structure, with ionizable compounds such as sodium chloride on or near to the surface (see Fig 1.1)(5).

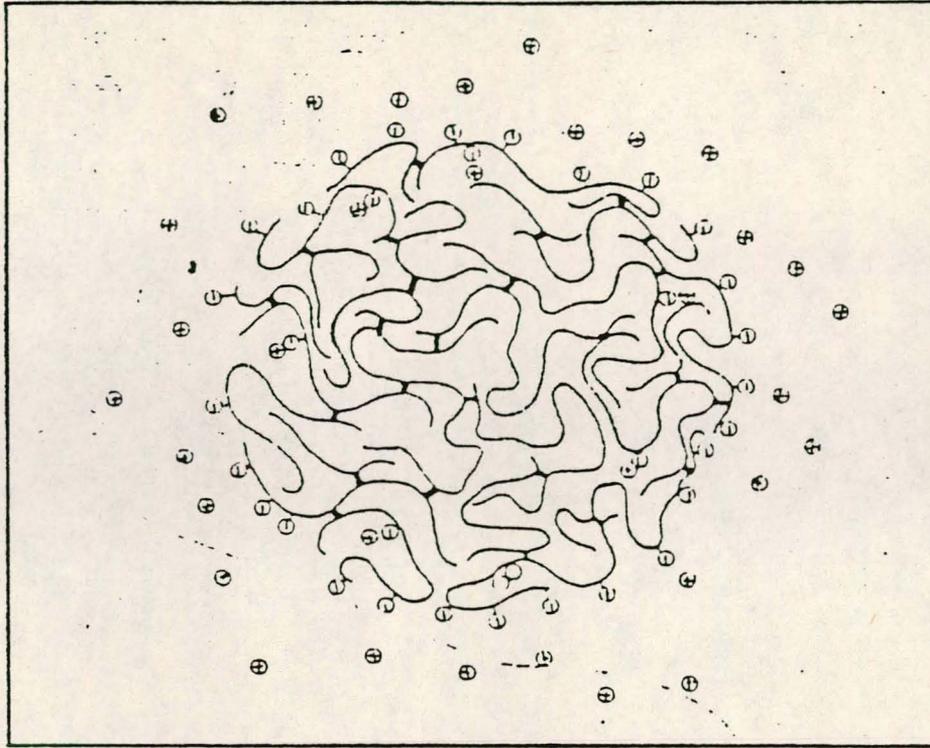


Fig. 1.1: Microgel model of a high molecular mass ligno-sulphonate (5).

1.1.2 The conversion and uses of lignocellulosic residues

Lignocellulosic residue can be converted into particles, fibres and chemical compounds (see Table 1.1).

Table 1.1 Utilisation of lignocellulose residues

Conversion process	Product
A. Reduction into particles	Particleboard
B. Fiberization Mechanical <ul style="list-style-type: none"> • Thermo-mechanical • Chemi-mechanical • Chemical 	Ground-wood pulp Thermo-mechanical pulp (TMP) Chemi-thermomechanical pulp (CTMP) Chemical pulp (bleached and unbleached) Dissolving Grade Pulp
C. Bio conversion <ul style="list-style-type: none"> • Fermentation 	Ethanol
D. Chemical modification <ul style="list-style-type: none"> • Liquefaction • Acid Hydrolysis 	Novolac, Resol Furfural

Particleboard manufacture and the various techniques of mechanical and chemical pulping have been well researched and enjoy a wide range of industrial applications. Bio-conversion of lignocellulose materials has also been investigated quite extensively. Enzymatic hydrolysis and digestibility of sugar cane bagasse has been reported by Rolz *et al.* (6), and Doran *et al.* (7). Dekker and Lindner (8) published a condensed review on bio-utilisation of lignocellulosic waste materials. The fungal degradation of bagasse has been studied by Rolz *et al.* (9)(10). Results on fermentation performance of bacteria and yeasts on bagasse residue have been published by Olsson *et al.* (11), Meyer *et al.* (12) and Ponce-Noyola *et al.* (13).

In a patent Shen (14) describes that lignocellulosic saw mill by-products originating from White Spruce and Jack Pine can be converted into a thermosetting, waterproof adhesive for the production of composite products. Mixed compounds having the well known characteristics of phenolic resin, and prepared from phenol homologs of lignite tar and furfural from agricultural wastes, have been described by Mikes (15). Leal (16) reported that phenolic compounds can be produced from lignin degradation products and by cleavage of ester linkages of lignin-xylans and/or lignin-glucans.

The three major constituents of lignocellulose can also be upgraded into various chemicals (see Table 1.2) (1).

Table 1.2 Chemical conversion of the three major fractions of lignocellulosic materials into various by-products (1)

Component	Process	End-product
Soluble sugars (mainly pentoses)	• heat and pressure treatment	furfural, furfuranic resins
	• catalytic hydrogenation	xylitol, polyols
Hemicelluloses	• fermentation	SCP (single cell protein), amino-acids
Cellulose	• defibrillation	pulp, paper, fluff
	• regeneration and derivatisation	regenerated cellulose
	• saccharification and fermentation	Carboxymethylcellulose (CMC), cellulose ethers and esters methyl-glucose, ethanol
Lignin	• hydrocracking	phenol, fuel oil
	• reaction with formaldehyde	phenolic resin
	• derivation	speciality polymers (pre-polymers, surfactants)

1.1.3 Utilisation of agricultural lignocellulosic residue

Lignocellulose is available in a variety of agricultural residues, from which cereal straw and bagasse (residues from sugar) can be singled out as the two most important ones. In 1993/4, South Africa produced over ten million tons of sugar cane (17).

World-wide, and also in South Africa, lignocellulosic residues from the sugar industry, apart from being used as fuel, additionally are used as an

inexpensive raw material for mechanical and chemical pulping (18)(19)(20)(21)(22)(23) and for composites manufacture (24)(25). Other uses for bagasse include furfural, which is produced by exposing pentoses to heat and acid such as sulphuric acid, extraction (1)(26), ethanol conversion (1), single cell protein production (1) and autohydrolysis lignin modification (1).

The chemical modification of lignocellulosic residues (which includes bagasse) has been described several times in literatures (1)(2)(27). The plastics made from such residues in the presence of phenol and suitable catalysts at elevated temperatures can produce a low cost Novolac type moulding resin. Bagasse is well suited for the manufacture of plastics because of its chemical composition and potential availability. The two types of plastics involved are those in which pith-free, very finely pulverised bagasse powder is used as a filler component, and true plastics, in which the bagasse lignin is utilised as the basic raw material. Dry bagasse contains from 13 to more than 22 percent of lignin, which reacts with plasticizers, whereby the softening point is lowered. Amongst these materials are aniline, phenol, and furfural produced by acid hydrolysis of the pentosans in the bagasse (27). The furfural and phenol, under acid condition can be polymerized as novolac resins (40). Novolac resin, which may be used directly or which is subjected to further treatment to make it either thermoplastic or thermosetting, has been described by Barnes (27).

Some unique properties of furfural-phenol novolac are described by Brown (28). Vega and Bao (29) described fractionation of the three main components of lignocellulosic material achieved by joint acid hydrolysis of cellulose and delignification with phenol.

Ysbrandy and Gerischer (30) investigated the substitution of phenolic novolac with various ratios of unmodified bagasse lignin for moulding applications. The lignin hindered the phenol novolac in the formation of a homogeneous cured resin network. The utilisation of lignocellulosic residues from furfural production for reactive extenders in phenolic formaldehyde resin is described by Ladomerski *et al.* (31).

Tonogai *et al.* (32) examined the degree of cure of novolac-hexamine systems with higher boiling point, polar solvents. The catalyst hexamine is an essential part of the curing reaction.

In a patent, Tsujimoto *et al.* (33) described the preparation of a lignocellulosic/phenolic containing composite. The conversion technique

which is described seems to be rather intricate, with medium strength properties of the final product being reported.

A powder type adhesive from bagasse residue for plywood manufacture, produced via the phenolation route has been described by Marcelo (34).

1.2 Liquefaction of lignocellulose

Most of the published research on liquefaction is based on milled wood powders. The liquefaction of wood can be carried out with phenol at elevated temperature under acid conditions. The phenolated wood product behaves as a thermoplastic material and can be melted at low temperatures. The wood matrix is cross-linked by phenol during the process of phenolation. The reaction is affected by the catalyst, temperature, reaction time and wood/phenol ratio (36)(37)(38).

1.2.1 Influence of catalyst

Liquefaction of milled wood powder in the presence of phenol and various types of catalysts have been reported by Alma *et al.* (35)(36) and Lin *et al.* (37)(39). The speed of liquefaction of wood is accelerated by the acid catalyst. It has been reported by Alma *et al.* (35)(36) that sulfuric acid will result in more liquefaction than phosphoric acid (37). No catalysts were used for liquefaction by Pu and Shiraish (38). They anticipated that some weak acid substances such as acetic acid would be formed by the decomposition of the wood components, and that these acids would act as catalysts in the liquefaction process. However, acetic acid did not significantly accelerate the wood liquefaction process. They also indicated that the presence of alkali, alkaline salt, and acid absorbers (such as calcium carbonate) appeared to consume some of the acid catalyst in the process of wood liquefaction and consequently wood liquefaction, was retarded. A high concentration of acid will accelerate the speed of liquefaction of wood and consequently higher levels of liquefaction will result (38).

1.2.2 Influence of temperature

There is a relationship between liquefaction efficiency and liquefaction temperature. Lin *et al.* (37) reports that as the liquefaction temperature

increased from 120° to 180°C, the amount increased from 45 to 83% and the percent residue decreased rapidly from 55 to 8%.

In a study by Alma (35), hydrochloric acid catalyst was used in wood phenolation. The study was performed at a liquefaction time of 150 minutes, a phenol/wood ratio of 4:1, an HCl catalyst addition level of 10%, and a range of reaction temperatures varying from 60°C to 180°C.

1.2.3 Influence of liquefaction time

With increasing liquefaction time, the combined phenol increases and the percent of residue decreases accordingly (37).

1.2.4 Influence of phenol/wood ratio

The liquid/wood ratio (phenol/wood) has a significant influence on both the amount of wood residue left over and the amount of phenol which reacted with the wood. Fig 1.2 shows a nearly linear increase in reacted phenol and nearly linear decrease in percent wood residue (37).

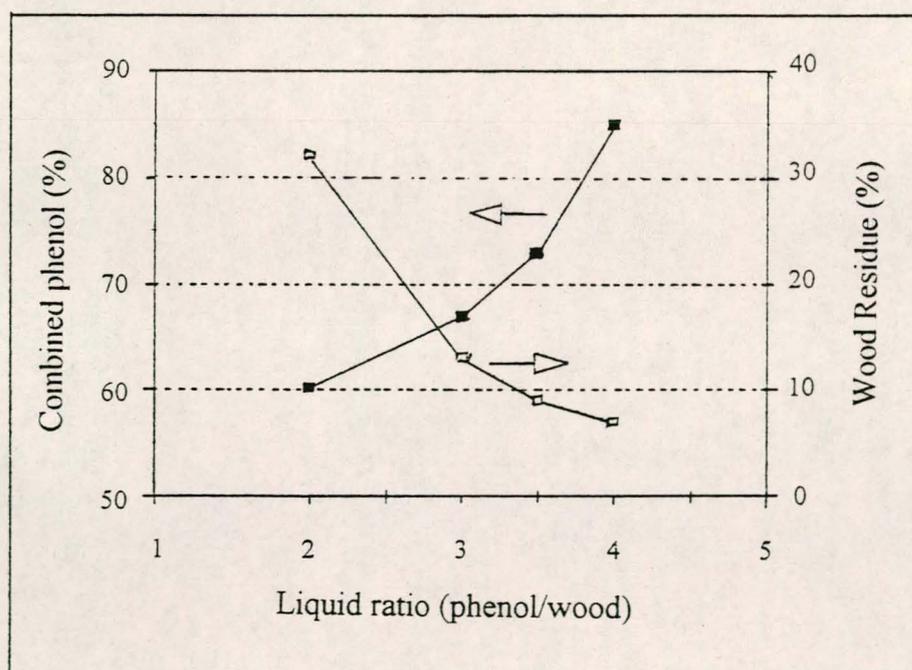


Fig 1.2: Effect of liquid/solids ratio on the amounts of combined phenol and unreacted wood residue (Liquefaction time, 2 h; temperature, 160°C; catalyst content, 6.8%.) (37)



1.3 Liquefied lignocellulose in moulding applications

Wood can be modified by liquefaction in the presence of the phenols (phenolation), with or without catalyst at elevated temperatures (35)(36)(37)(39). In this way, it is possible to produce novolac resins which can be employed for moulding applications.

1.3.1 Moulding

In the past, phenolic moulding compounds were produced and used in the production of parts ranging in mass from a few grams to several tons.

Four forms of phenolic materials are used for moulding applications, which are:

- granular powders which are putty-like when hot and uncured
- random-laid fibres coated with resin
- chopped fabric saturated with resin
- resin and fillers plasticized with solvents

Novolacs are most often used for moulding purposes as other phenol-formaldehyde substances have been found unstable in storage (40).

1.3.2 Physical properties of mouldings made from novolacs

Liquefaction of wood in the presence of phenol and the application of the resulting liquified material as novolac (such as thermosetting resins), has been studied by Alma *et al.*(35)(36) and Lin *et al.* (37)(39).

A typical molding composition as proposed by Lin (39) is shown in Table 1.3.

Table 1.3 Composition of a typical moulding formulation (39)

Ingredients	Mass Parts (g)
Liquefied wood resins or synthetic novolac resin	37.7
Wood powder	49.5-202.0
Hexamine	9.4
Calcium hydroxide	2.4
Zinc stearate	1.0

1.3.2.1 Effect of the Amounts of Reacted Phenol

The relationship between moulding composition, moulding conditions and the flexural properties of liquefied wood mouldings are largely dependent on the amount of reacted phenol. This relationship can be attributed to the fact that the liquefied wood resins with greater amounts of reacted phenol, have more cross-linking sites, therefore increasing the network density of the matrix (35)(39).

1.3.2.2 Effect of Filler Contents

The physical properties of the moulded products will also be determined by filler content. Results from Lin (39) suggest that with an increase in filler contents, all flexural properties increase linearly. This relation is applicable not only for different amounts of reacted phenol, but also for commercial novolac applications (39).

1.3.2.3 Effect of Curing Time

The flexural properties of moulded products also depend on curing time. Initially, the flexural strength of mouldings rises to a maximum with an increasing cure time. This is followed by a linear gradual decrease. The larger the amount of phenol reacted, the earlier this peak appears (See Fig 1.3). This result indicates that the inclusion of liquefied wood resin with larger amounts of combined phenol have shortened the curing time (39).

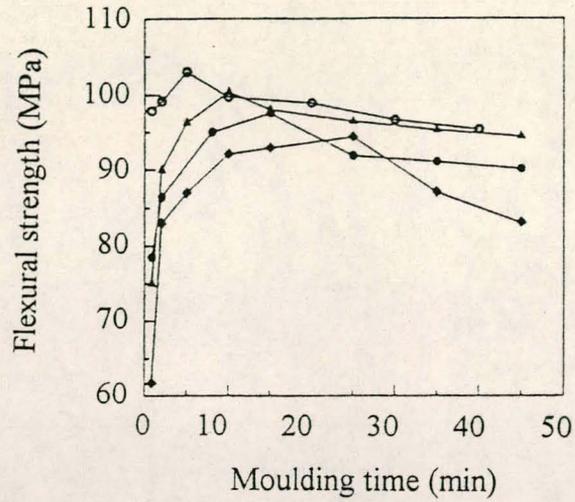


Fig 1.3: Effect of moulding time on the flexural strength of the moulding

Liquefied wood with combined phenol (◆) 60%, (●) 72%, and (▲) 81.6%, (○) commercial novolac resin. The filler content of all mouldings were 60% (39).

Chapter 2

Experimental

2.1 Raw materials

2.1.1 Lignocellulose residue

The bagasse was supplied by Illovo Sugar Ltd. from their Sezela furfural production plant near Durban. The properties of the bagasse are given in Table 2.1.

Table 2.1: Chemical composition and physical properties of the bagasse residue

Chemical composition (on dry basis)	%
Cellulose	50
Hemicelluloses	29
Lignin	20
Others	1
Ash content	3.17
Physical properties	%
Moisture content	40 - 50
Particle size distribution	%
> 2.36mm	45.56
> 1.40mm	18.74
> 1.00mm	12.68
< 0.7mm	10.47
> 0.7mm	1.56
Total > 1 mm	77.98
Total < 1 mm	15.81

* All data supplied by Illovo Sugar Ltd

2.1.2 Phenol

The phenol was supplied by SASOL Chemical Industries (Pty) Ltd, 2 Sturdee Avenue Rosebank, Johannesburg RSA. The specifications for the product are listed in Table 2.2.

Table 2.2: Phenol Specification

1. Description	
White crystalline solid	
2. Specification	mass %
Phenol	99.9
Total cresol	<0.1
Neutral oil	not detected
Pyridine base	not detected
Water content	0.05
Specific gravity at 20°C	1.07
Colour 5	APHA
Melting point	40.3 - 40.6 C
3. Uses	
In the manufacture of phenol-formaldehyde resins used in plywood, foundry mouldings and laminates, etc.	

2.1.3 Catalysts

Table 2.3: Specification of catalysts used for liquefaction

Sulphuric acid	98 %
MW	98.08
Specific gravity	1.84
Supplier	SAARCHEM HOLPRO ANALYTICAL
Phosphoric acid 85%	
MW	98.00
Supplier	N.T. LABORATORY (PTY) LTD
Hydrochloric acid	32 %
MW	36.46
Supplier	SAARCHEM HOLPRO ANALYTICAL

2.1.4 Organic Solvents

Table 2.4: Specification of organic solvents

Methanol	< 99.8 %
MW	32.04
Specific gravity	0.79
Supplier	MERCK
Acetone	> 99.5 %
MW	58.08
Supplier	BDH

2.1.5 Novolac resin

The novolac was supplied by NCP Resins. P.O. Box 2204, Durban 4000, RSA.

Table 2.5: Novolac specification

1. Type:	
Plyophen 602N, a fine, two-stage phenolic resin powder containing hexamethylenetetramine as a cross-linking agent.	
2. Suggested application:	
Plyophen 602N has been developed mainly for use in the manufacture of brake linings, brake blocks and other moulded products. It is also used for rubber compounding.	
3. Specification:	
Hexamine content	9.7-10.2 %
Sieve analysis on 200 mesh (% retention)	2.0 max. %
4. Typical properties:	
Hotplate gel time @ 150°C	65- 95 seconds

2.1.6 Hexamine

Hexamine was supplied by SAARCHEM (PTY) Ltd. The material used was 99.5% pure.

2.2 Equipment for novolac preparation and moulding

2.2.1 Liquefaction of bagasse

Two different liquefaction systems were used to prepare the novolac resin, namely a pressure bomb and a pilot reactor.

2.2.1.1 Pressure bomb system

Novolacs were made in a pressure bomb (a stainless steel container), which was fitted with a single-sided threaded lid. A Teflon spacer ring was placed inside each pressure bomb to prevent seepage of the resinous mixture from the container at high temperatures and elevated pressures. The dimensions of the pressure bomb are shown in Table 2.6.

Table 2.6: The dimensions of the pressure bomb

	Inside measurements (mm)	Outside measurements (mm)
Diameter	68.4	83.4
Height	136.0	170.0
Approx. volume	500 cm ³	

The content of the pressure bomb was heated in two ways, (i) by full immersion in heating oil and (ii) by placing it in an electrically heated oven.

(i) Heating oil

Silicone oil (SF 96 from General Electric Company) was used as a medium for thermal-transfer. The heating oil was kept at a constant 180°C by means of a computer controlled heating system.

(ii) Oven

The pressure bomb was placed in an oven and the temperature was maintained at 150°C.

2.2.1.2 Pilot reactor system

The double wall CrNiMo-steel pilot reactor used was a Buchi model BEP 280 laboratory cylindrical autoclave with magnetic drive and a stirring system fitted. It has a hemispherical bottom with 5 litres capacity and a maximum operating pressure and temperature of 40 bars and 250°C respectively.

The reaction vessel was coupled by means of a set of sensory steel hoses to a Brabender T 300A circulator heating unit with built-in electronic proportional temperature control. This unit had a maximum operating temperature of 260°C. Shell Thermia, grade B (paraffin based) thermostat oil was used.

The reaction temperature was measured by means of a PT100 probe. The probe was fitted on to the reactor lid and coupled to the external measurement sensor of the heating unit. In the pilot reactor, a spiral stirrer was used for the resinous materials during the reaction stage.

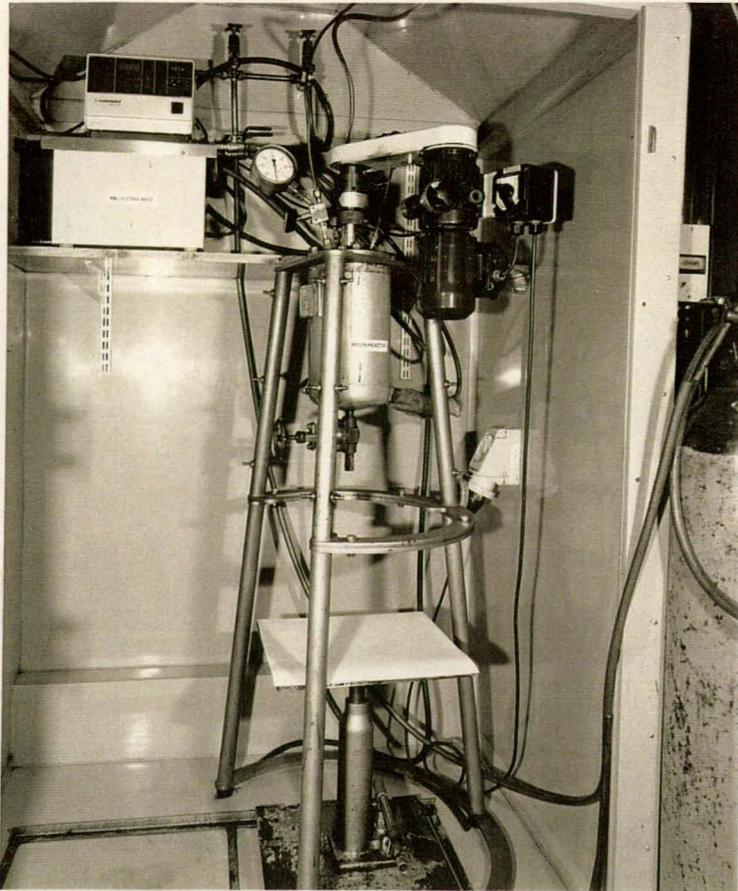


Fig 2.1: The pilot reactor and T 300A circulator heating unit



Fig 2.2: Spiral mixer of pilot reactor

2.2.2 Moulding

For the preparation of the moulded specimens a BURKLE hydraulic press was used. It was heated up to 250°C and the pressure applied was up to 31 MPa. The press was fitted with two thermocouples for temperature control.

The square-shaped mouldings had the following dimensions:

Table 2.7: Mould dimensions

	Inside dimension (mm)	Outside dimension (mm)
Length	135	150
The depth of the moulding was 13 mm.		

The thickness of the moulding was determined by placing spacers (or stoppers) between the female and male bi- sections.

2.3 Experimental procedure of bagasse liquefaction (novolac preparation) and product moulding

2.3.1 Liquefaction

The liquefaction of lignocellulose is dependant on temperature, catalyst type, concentration of catalyst, and liquefaction time. The bagasse liquefaction procedure was undertaken in three ways: (i) by using a pressure bomb in hot oil; (ii) use of a pressure bomb in an oven; (iii) use of a pilot reactor.

The pressure bomb method was employed evaluate the performance of three types of catalyst in a high and low liquefaction system. Method one consisted of a high liquefaction bagasse system and was carried out at a liquefaction temperature of 180°C, with a 3:1 ratio of phenol to bagasse, and a 2 hour liquefaction time. The low liquefaction bagasse system (method two) was carried out at a temperature of 150°C, a 2:1 ratio of phenol to bagasse, and a liquefaction time of 1 hour. In order to determine the most suitable catalyst as well as the best and most economical addition rate for the liquefaction of the bagasse residue, a series of preliminary pressure bomb tests were carried out.

The final stage of the liquefaction/phenolation reaction was repeated in a pilot reactor, using the best catalyst from the bomb reactor trials.

2.3.1.1 High liquefaction bagasse system

The pressure bomb in hot oil method (method one) was used for evaluating the high liquefaction bagasse system. Sulphuric acid, phosphoric acid and hydrochloric acid addition levels ranged from 0 to 6% based on the total mass of bagasse and phenol. The reaction conditions and the composition of the bagasse, phenol and catalyst, are listed in Table 2.8.

Table 2.8: Reaction conditions for high liquefaction of bagasse

Liquefaction time (hrs)	2		
Liquefaction temperature (°C)	180		
Phenol (g)	270		
Bagasse (g) dry mass	90		
Catalyst (%) mass	2	4	6
HCl (32%) (g)	23.1	46.9	71.9
H ₂ SO ₄ (98%) (g)	7.6	15.0	23.0
H ₃ PO ₄ (85%) (g)	8.7	17.6	27.1

The following procedure was followed:

The procedure followed here was:

- Each catalyst was added separately to 270 g phenol and homogenised by stirring.
- The solution of phenol and catalyst was added to 90 g bagasse and the mixture was stirred 5 minutes to ensure even mixing.
- 100g dry weight of the mixture was placed in the pressure bomb and tightly sealed.
- Oil was heated to 180°C and the pressure bomb was put in the hot oil bath for two hours.

2.3.1.2 Low liquefaction bagasse system

The low liquefaction of bagasse was carried out by placing the pressure bomb in an oven. The reaction conditions and the composition of the bagasse, phenol and catalyst are listed in Table 2.9.

Table 2.9: Reaction conditions for low liquefaction of bagasse

Liquefaction time (hr)	1		
Liquefaction temperature (°C)	150		
Phenol (g)	200		
Bagasse (g) dry mass	100		
Catalyst (%)	2	4	6
HCl (32%) (g)	19.1	39.1	59.8
H ₂ SO ₄ (98%) (g)	6.2	12.8	19.5
H ₃ PO ₄ (85%) (g)	7.2	14.7	22.5

The procedure followed here was:

- Each catalyst was added separately to 200 g phenol and homogenised by stirring.
- The solution of phenol plus catalyst was added to 100 g bagasse and the mixture was stirred for 5 minutes to ensure even mixing.
- 100g dry weight of the mixture was placed in the pressure bomb and tightly sealed.
- The oven was heated to 150°C and the pressure bomb was put in the oven for one hour.

2.3.1.3 Liquefaction temperatures

Liquefaction temperature is a very important parameter in the liquefaction process. According to Alma M.H. *et al.* (36) sulphuric acid can liquefy wood more effectively than hydrochloric acid. Sulphuric acid and hydrochloric acid were added and compared during a liquefaction process conducted at 120°, 150° and 180°C. This experiment was carried out with

the pressure bomb placed in the oven. The relative amounts of reactants and reaction conditions are listed in Table 2.10.

Table 2.10: Reaction conditions during different liquefaction temperatures

Liquefaction time (hrs)	1		
H ₂ SO ₄ (98%) (g)	6.2		
Phenol (g)	200		
Bagasse (g) dry mass	100		
Liquefaction temperature (°C)			
120°C	150°C	180°C	

The procedure followed was:

- The catalyst was added separately to 200 g phenol and homogenised by stirring.
- The solution of phenol plus catalyst was added to 100 g of bagasse and the mixture was stirred for 5 minutes to ensure even mixing.
- 100 g dry weight of the mixture was placed in the pressure bomb and tightly sealed.
- The oven was heated to 120°C, and the pressure bomb placed in the oven for one hour.
- The procedure was repeated with the oven at 150°C and 180°C.

2.3.1.4 The effect of agitation during liquefaction

The effect of agitation during liquefaction was evaluated in the pilot reactor and the liquefaction results were compared with those of the pressure bomb in the oven [method (ii)] (See Table 2.11). The pilot reactor vessel was able to take at least 900 grams of dry raw material (See Table 2.12).

The novolac (liquefied bagasse) produced in the pilot reactor was used as raw material for the manufacture of moulded samples.

Table 2.11: Reaction conditions for the pressure bomb in the oven

Liquefaction time (hrs)		1			
Liquefaction temperature (°C)		150			
Phenol (g)		200			
Bagasse (g) dry mass		100			
H ₂ SO ₄ (%)	2.0	4.0	6.0	8.0	10.0
g	6.2	12.8	19.5	26.6	34.0

Table 2.12: Reaction conditions for the pilot reactor*

Liquefaction time (hrs)		1		
Liquefaction temperature (°C)		150		
Phenol (g)		600		
Bagasse (g) dry mass		300		
H ₂ SO ₄ (%)	2.0	4.0	6.0	8.0
g	18.7	37.5	57.4	78.3

* The stirring speed is 500 r.p.m.

The liquefaction procedure with the oven heated pressure bomb was as follows:

- Each amount of catalyst (Table 2.11) was added separately to 200 g phenol and homogenised by stirring.
- The solution of phenol plus catalyst was added to 100 g bagasse and the mixture was stirred for 5 minutes to ensure even mixing.
- 100 g dry mass of the mixture was placed in the pressure bomb and tightly sealed.
- The oven was heated to 150°C, and the pressure bomb was put in the oven for one hour.

The liquefaction procedure for the pilot reactor was as follows:

- Each amount of catalyst (Table 2.12) was added separately to 600 g phenol and homogenised by stirring.
- The solution of phenol plus catalyst was added to 300 g bagasse and the mixture was stirred for 10 minutes to ensure even mixing. It was then placed in the vessel of the pilot reactor. The pilot reactor was sealed and heated to 150°C. A stirring speed of 500 rpm was maintained.

2.4 Degree of liquefaction

The efficiency of liquefaction was determined by extracting the phenolated material with a suitable solvent using the Soxhlet extraction method (41). For these extraction tests approximately 5 g of the sample material was taken using methanol as a solvent. Extraction time varied from 6 to 24 hours and extraction was considered to be complete when the extraction solvent in the Soxhlet appeared to be completely clear.

The extract was oven dried at 180°C to completely remove all the solvent and free phenol. The percentage of liquefied bagasse was calculated by means of the following equation:

$$\text{Percentage liquefaction} = \frac{W_1}{W_0} \cdot \frac{100}{1} \quad (\%)$$

$$\text{Percentage combined phenol} = \frac{W_1}{W_b} \cdot \frac{100}{1} \quad (\%)$$

Where: W_b : mass of bagasse

W_0 : mass of phenolated bagasse sample used for the extraction

W_b : extract mass after drying (phenolated bagasse)

The percentage of liquefaction is defined as the amount of phenolated bagasse that can be dissolved in methanol.

The percentage of combined phenol is that phenol which has reacted with the bagasse during the liquefaction process. During the extraction process,

not only the novolac resin (phenol reacted with acid hydrolysis bagasse), but also the unreacted phenol (portion not reacting with bagasse) were dissolved by the methanol. After drying at 180°C, the unreacted phenol was separated from the novolac resin. Therefore the extract after drying only represents the novolac resin.

2.5 IR analysis

Infra-red spectra of products were determined by using a Perkin Elmer Model 1600 infra-red (FTIR) spectrophotometer. Phenolated bagasse was dissolved in acetone. Two drops of the solution were placed on a clean NaCl window and dried over silica gel in a dessicator. The spectrum was recorded by scanning at 40 cm⁻¹ using a blank NaCl window as reference.

2.6 Evaluation of the phenolated bagasse as a moulding resin

Moulding samples were prepared to ascertain the bonding strength of the liquefied bagasse. The novolac was mixed with bagasse filler material and polymerized at elevated temperatures. The liquefied bagasse material was prepared using the pilot reactor. The composition of the moulded samples are listed in Table 2.13.

Table 2.13: The composition of the moulded samples

H₂SO₄ Catalyst %	Liquefied bagasse (g)	Filler (g)	Hexamine (g)	Wax (g)
	28.0% (dry)	62.9%	8.4%	0.7%
2	114.4	257.1	34.3	2.9
4	114.4	257.1	34.3	2.9
6	114.4	257.1	34.3	2.9
8	114.4	257.1	34.3	2.9

The procedure followed was:

- 90 cm³ methanol was used to dilute the liquefied bagasse. The mixture was stirred for half an hour using a magnetic stirrer. After homogenisation, 34.3 g hexamine and 2.9 g wax were added and mixed.
- This was added to 257.1 g filler (bagasse) and thoroughly mixed.
- 65 g (dry weight) of the above mixture was put in the mould.
- This material was pressed at 190°C with 1.96 MPa pressure for 10 minutes to obtain a product 5 mm thick. The moulded samples were pressed to a density of 0.7g/cm³.

After hot pressing, the mould was removed and cooled for 15 minutes. This cooling process prevented the moulded product from twisting during removal from the mould.

2.6.1 Testing of novolac and moulded products

2.6.1.1 Bending strength and tensile strength

An INSTRON universal strength testing machine was used to apply a bending and tensile load at a speed 0.2 cm/minute. A load cell with maximum capacity of 5 000 N was used but the full scale force was adjusted to 500 N. All specimens were conditioned at 23°C and 60% relative humidity (RH) before testing commenced.

The sample size for the bending tests was 135 mm length, 28 mm width and 5 mm thickness, whilst the sample size for the tensile tests was 135 mm length, 15 mm width and 10 mm thick.

Chapter 3

Result and Discussion

The literature review in Chapter One indicated that acidic catalysts are important in the liquefaction of lignocellulose (38). According to Sayyah *et al.* (40), the liquefaction of bagasse was initiated by furfural, which originated from the acid hydrolysis of the bagasse pentosanes. The furfural can condense with phenol and form a macromolecular chain. Phenol-furfural resins show enhanced flexibility using this process, with a low melting viscosity and a low viscosity index. Most scientific literature only refers to one or two liquefaction catalysts, ignoring the important effect that agitation has during the reaction period (35, 36, 37, 38). In the following discussion, the effectiveness of three types of acidic catalyst will be compared, in terms of amounts added, reaction time and temperature, as well as different liquefaction techniques as discussed in Chapter Two.

3.1 Liquefaction of bagasse

Table 3.1 explains the catalytic involvement in the various liquefaction techniques used.

Table 3.1: The relationship between catalyst and liquefaction technique

Acid catalyst	HLC ₁	LLC ₂	LT ₃	MA ₄
Sulphuric acid	Yes	Yes	Yes	Yes
Hydrochloric acid	Yes	Yes	No	No
Phosphoric acid	Yes	Yes	No	No

Yes or No meaning involved reaction, or not involved reaction.

1 HLC: high liquefaction condition.

2 LLC: low liquefaction condition.

3 LT: liquefaction temperature

4 MA: mechanical agitation

3.1.1 Catalyst

During the preliminary evaluation of the various catalysts using both HLC and LLC methods, both hydrochloric acid and phosphoric acid were eliminated on their low performance, also taking into consideration temperature and reaction time. The use of sulphuric and hydrochloric acid catalyst resulted in a liquefied product with a deep darkish colour and a sticky character. The higher the catalyst concentration used, the darker the colour and the more sticky the resulting material appeared. In general, the phosphoric acid produced a material of lighter colour.

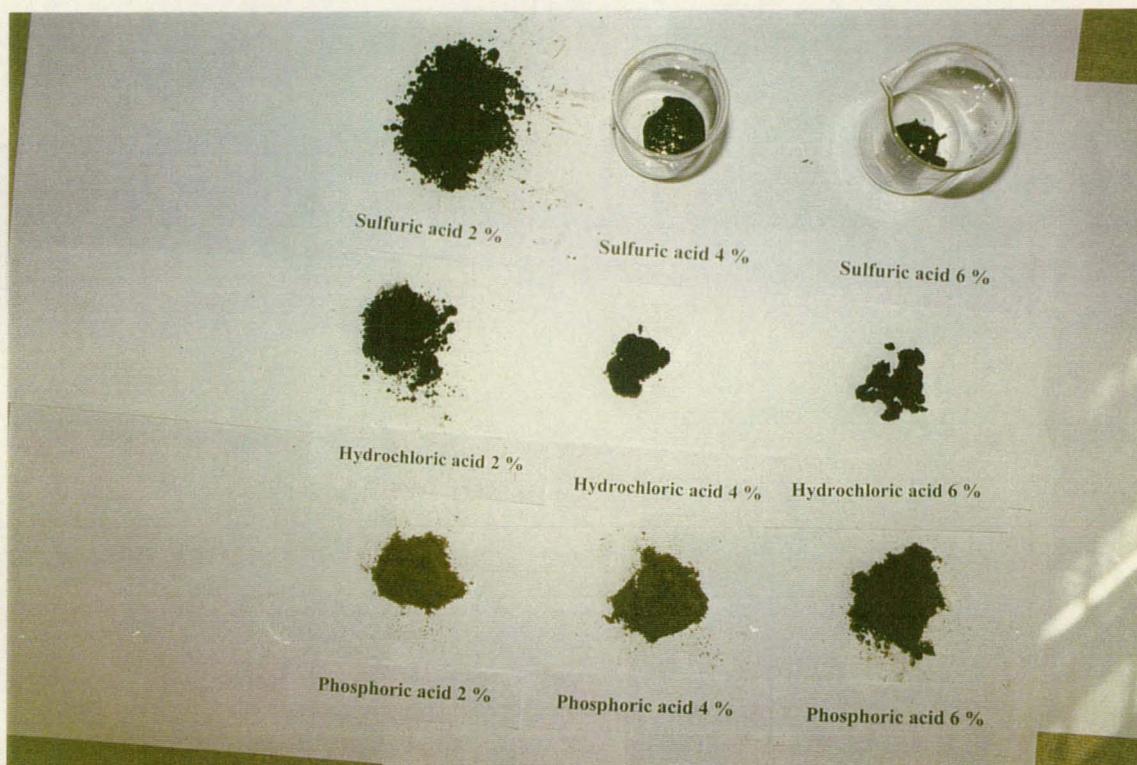


Fig 3.1: Illustrating colour differences of phenolated materials for LLC

The quantities of the Soxhlet extracted phenolated products are shown in Table 3.2. Each value represents the average of four measurements. The results in Table 3.2 are expressed in terms of mass of extractable material divided by the total mass of sample before extraction (liquefaction %), and mass of extractable material, divided by the original mass of bagasse residue used for phenolation (CP %).

Table 3.2: Extractable material after HLC and LLC liquefaction with acidic catalyst

		HLC				LLC			
Reaction conditions		Phenol/Bagasse Ratio 3 : 1 Liquefaction time: 2 hours Liquefaction temperature: 180°C				Phenol/Bagasse 2 : 1 Liquefaction time 1 hours Liquefaction temperature 150°C			
Catalyst	%	CP (%)	SQ	Liquefaction (%)	SQ	CP (%)	SQ	Liquefaction (%)	SQ
H ₂ SO ₄	0	10.7	0.9	3.0	0.3	3.7	1.3	1.3	0.5
	2	188.0	4.9	51.9	1.4	98.6	5.2	32.2	1.7
	4	221.1	5.5	59.7	1.5	186.4	8.7	61.0	2.8
	6	242.2	6.8	64.2	1.8	219.6	4.9	71.8	1.6
HCl	0	10.8	0.9	3.0	3.0	3.7	1.3	1.3	0.5
	2	182.1	6.7	48.2	1.8	89.4	10.0	26.9	3.0
	4	224.2	9.6	56.1	2.4	118.6	9.0	35.5	2.7
	6	261.9	8.5	63.5	3.8	159.0	9.2	48.0	2.8
H ₃ PO ₄	0	10.8	0.9	3.0	0.3	3.7	1.3	1.3	0.5
	2	59.0	6.0	16.2	1.7	10.4	3.1	3.5	1.0
	4	84.6	4.7	22.8	1.3	22.5	4.4	7.5	1.5
	6	104.1	3.9	27.3	1.0	37.9	6.9	12.7	2.3

* Liquefaction (%): the extract mass divided by the mass of the phenolated bagasse sample before extraction. The equation is $\frac{W_L}{W_0} \cdot \frac{100}{1}$.

* CP(%): the extract mass divided by the mass of the bagasse. The equation is $\frac{W_L}{W_B} \cdot \frac{100}{1}$.

* SQ: standard deviation

Table 3.2 shows that an increase in the % of catalyst increases the amount of material extracted. This applies for all three catalysts. The amount of substance extracted is an indication of the efficiency of the phenolation process. The extractable material was greatest using the HLC method. The HCl and H₂SO₄ catalysts resulted in similar amounts of extractable material produced for HLC. The H₂SO₄ catalyst was responsible for the largest amount of extractable material using the LLC method. The H₃PO₄

catalyst resulted in the smallest production of extractable material for the LLC and the HLC. It seems that the acid catalyst plays a very important role in the hydrolyzation of the bagasse into furfural. In this way the liquefaction of bagasse can be accelerated. The liquefaction process is initiated by the acid hydrolysis of the bagasse hemicelluloses and its chemical transformation of the saccharides into furfural. The available furfural reacts with phenol to produce high molecular mass compounds which tend to be more sticky. Higher liquefaction temperatures, longer liquefaction times and higher phenol/bagasse ratios all will increase the percentage liquefaction.

To overcome the sticky nature of the novolac resin, the molecular mass of the phenolated bagasse must be increased to transform it into a solid state. This could be achieved by either using longer liquefaction times and a high phenol/bagasse ratio.

The differences in CP % and liquefaction % between the hydrochloric and sulphuric acid catalysts are listed in Table 3.3. Differences were calculated by subtraction of results shown in Table 3.2.

Table 3.3: Extractable material differences for the hydrochloric acid and sulphuric acid catalysts used in HLC and LLC

Catalyst (%)	Difference in extractable material (H ₂ SO ₄ minus HCl)							
	CP (%)				Liquefaction (%)			
	H	P (%)*	LL	P (%)*	HLC	P (%)*	LL	P (%)*
2	5.9	3.2	9.2	10.3	3.7	7.6	5.3	19.7
4	-3.1	-1.4	67.8	57.2	3.6	6.4	25.5	71.8
6	-27.0	-10	60.6	38.1	0.7	1.1	23.8	49.6

* P(%): the difference in percentage of the $100 \times (H_2SO_4 - HCl) / HCl$

The % difference between the H₂SO₄ and the HCl catalysts for the HLC reaction method do not appear to be significant. This is also clearly illustrated in Figures 3.2 and 3.3. With regard to the amount of extractable material (CP %), the HCl catalyst seemed to perform best for the HLC at the higher addition levels. These results clearly show that two acid

catalysts resulted in large amounts of novolac product at the high reaction temperature and the higher phenol/bagasse ratio.

In the case of the LLC, the H_2SO_4 catalyst outperformed the HCl catalyst at all addition levels. It seems that at the low temperature and the low phenol/bagasse ratio, the sulphuric acid catalyst played a more important role in the hydrolysis of the bagasse. The strength of the acid used as a catalyst is therefore shown to be an important factor in obtaining a desirable product.

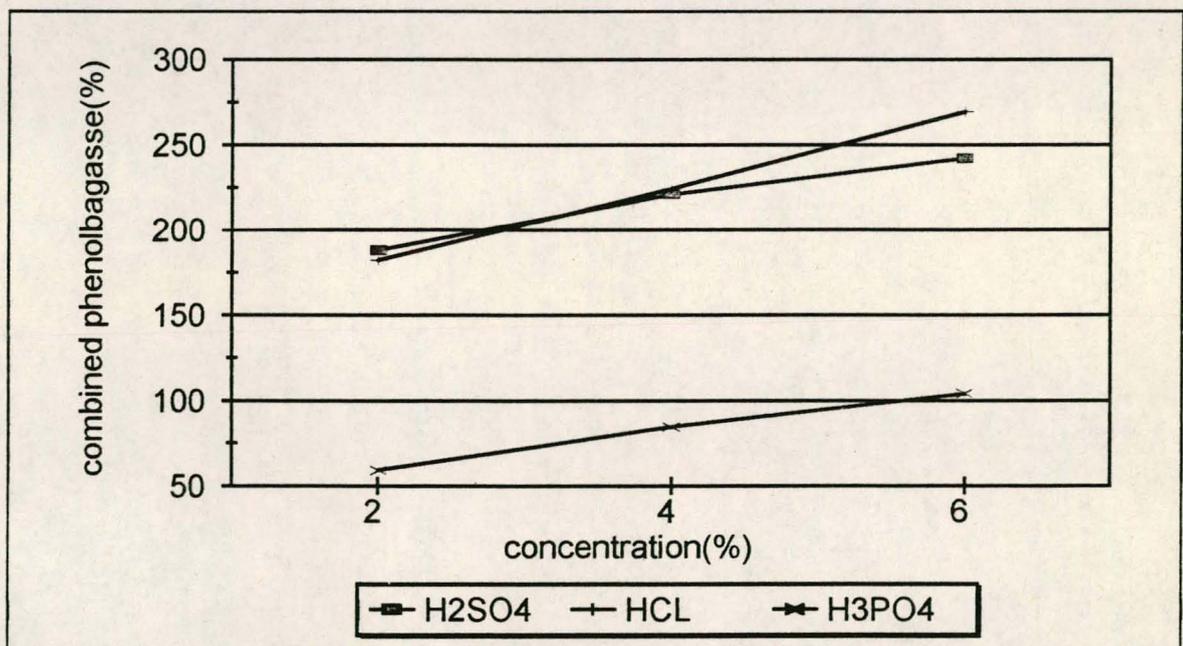


Fig 3.2: Combined phenolated bagasse as a function of catalyst addition for the HLC reaction method

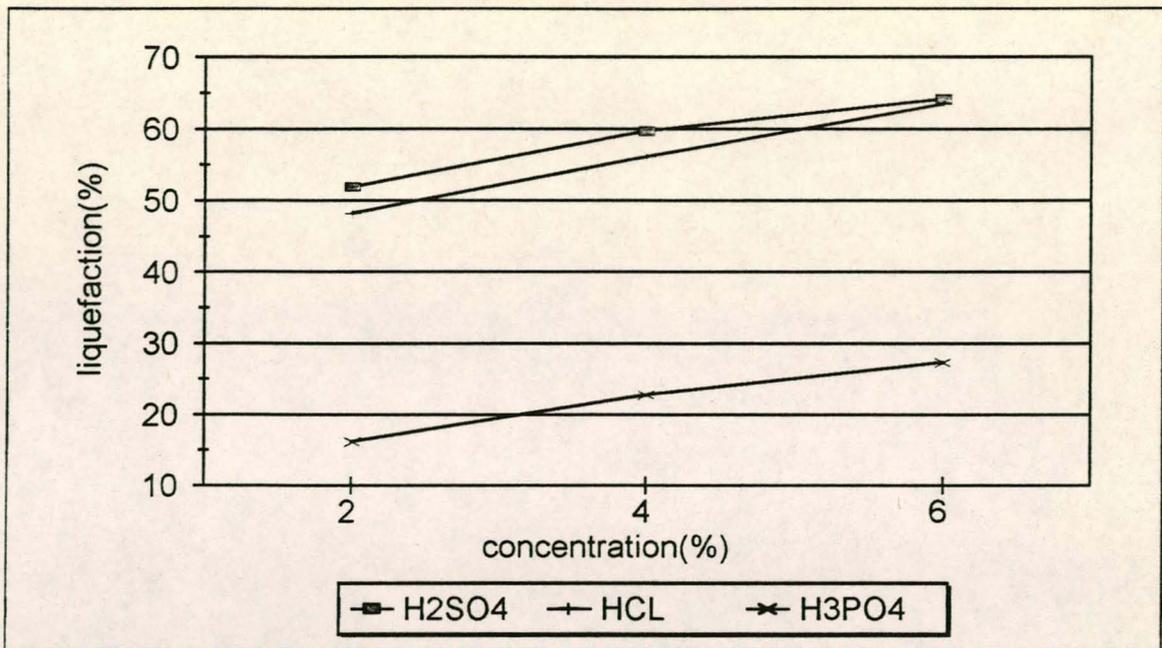


Fig 3.3: Liquefaction % as a function of catalyst addition for the HLC reaction method

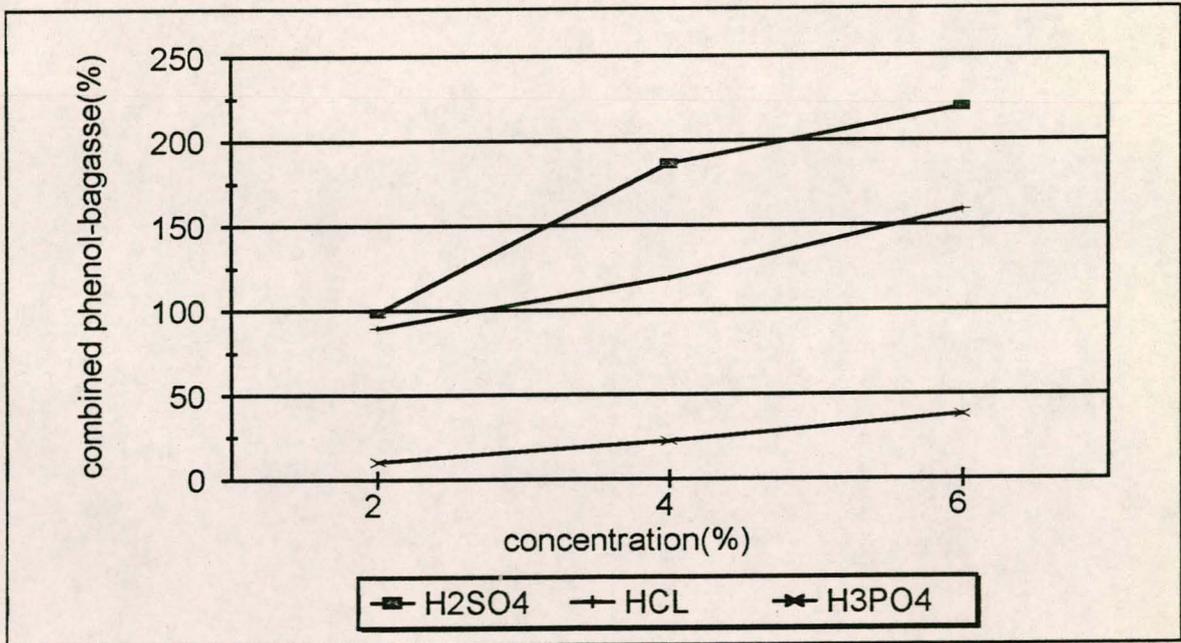


Fig 3.4: Combined extractable material as a function of catalyst addition for the LLC reaction method

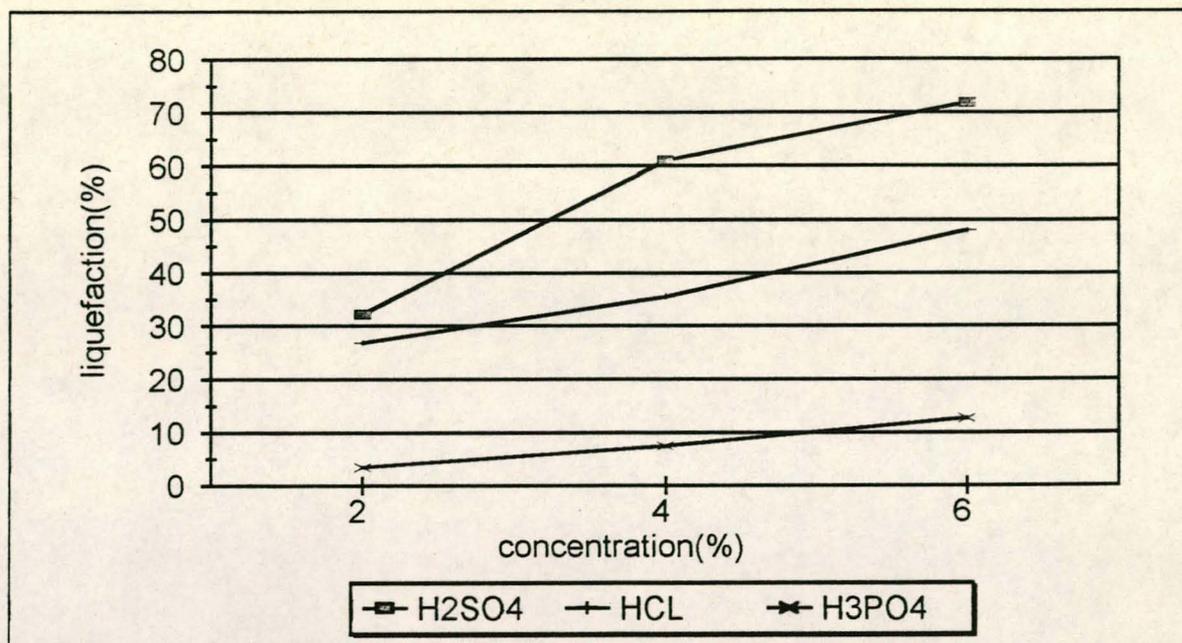


Fig 3.5: Liquefaction % as a function of catalyst addition for the LLC reaction method

The differences in CP % and liquefaction % between the HLC and LLC for all catalyst are listed in Table 3.4.

Table 3.4: Differences in extractable phenolated material in HLC and LLC using three acid catalysts

Catalyst	HLC - LLC											
	2				4				6			
	CP %		liquefaction %		CP %		liquefaction %		CP %		liquefaction %	
	C.P %	P (%)*	lique-faction %	P (%)*	C.P. %	P (%)*	lique-faction %	P (%)*	C.P. %	P (%)*	lique-faction %	P (%)*
H ₂ SO ₄	89.4	90.7	19.7	61.2	35.0	18.6	1.3	-2.0	23	10.3	-7.6	-10.6
HCl	92.7	103.7	21.3	79.2	106.0	89.0	20.6	58.0	110	69.3	15.5	32.3
H ₃ PO ₄	48.6	467.3	12.7	362.8	62.0	276	15.3	204.0	66	174.7	14.6	115.0

* P(%): the difference in percentage of the $100 \times (\text{HLC} - \text{LLC}) / \text{LLC}$

For the various levels of catalyst addition, hydrochloric and phosphoric acids resulted in a higher amount of extractable material under the HLC as compared to LLC (See Table 3.2). All data showed that the difference in extractive contents between the HLC and LLC methods decreased with increasing catalyst concentration. It can also be seen that increasing concentrations of catalyst can enlarge the amount of the extractable material from the liquefaction process. The HLC method, with a phosphoric acid catalyst, accelerated higher than other catalysts. At the higher H₂SO₄ levels, the difference in extractable material under HLC and LLC became small. When the acid catalyst was weak and at low concentrations, the reaction temperature and the phenol/bagasse ratio played an important role in the liquefaction of bagasse. In contrast, the stronger acid catalysts, such as sulphuric acid, more easily initiate the hydrolysis of bagasse to furfural under low reaction temperature and phenol/bagasse ratio.

As result of the above findings and taking into consideration that a chlorine containing acid catalyst would be less acceptable on the grounds of environmental considerations, it was decided to employ a H₂SO₄ catalyst for all of the pilot reactor studies which followed.

3.1.2 Liquefaction temperature

Research carried out by Lin *et al.* (37) indicated that a higher rate of liquefaction was achieved at a higher liquefaction temperature.

The results of this study are listed in Table 3.5.

Table 3.5: The residual amount (%) and combined phenol (%) of phenolated wood using HCl catalyst

Temperature (°C)	Residual Amount (%)*	Combined phenol (%)
60	51.36	34.0
90	31.74	117.0
120	7.31	161.5
150	2.42	200.0
180	1.12	125.0

* Residual amount means the residual extract mass divided by the mass of the bagasse. The equation is $\frac{W_r}{W_b} \cdot \frac{100}{1}$ (35).

Similar results were obtained by using a liquefaction temperature of 150°C, a phenol/bagasse ratio of 2:1, a liquefaction time of only one hour, with only 4% H₂SO₄ catalyst addition. This indicated that under less demanding reaction conditions good liquefaction of the bagasse residue could be achieved, which would contribute towards the economic viability of such a by-product utilisation.

From the preliminary work, it became evident that with a LLC an acceptable bagasse liquefaction could be obtained at the higher H₂SO₄ catalyst addition levels (see Table 3.2). It was therefore decided to further evaluate the LLC phenolation performance employing different temperature levels. A low catalyst addition was selected in order to prevent that a higher catalyst addition level would not override the temperature effect.

Table 3.6: Extractable material after LLC at different liquefaction temperatures and 2% sulphuric acidic catalyst

LLC		H ₂ SO ₄ (2% catalyst)		
Temperature		120°C	150°C	180°C
C.P.	%	76.7	114.1	125.7
	s _Q	15.6	9.1	13.2
Liquefaction	%	22.8	33.9	37.3
	s _Q	4.6	2.7	3.9
Residual Amount	%	31.9	26.3	22.8
	s _Q	3.7	4.7	0.6

From Table 3.6 it can be seen that the highest CP(%) and liquefaction (%) was achieved at the highest liquefaction temperature. The residual amount (%) was decreased with the rise in temperature (See Figures 3.6 and 3.7). By raising the temperature from 150°C to 180°C, for both CP (%) and liquefaction (%), an improvement of only 9% in the liquefaction process was obtained. A CP ratio of only 0.39 was calculated. An appreciable gain in extractive material of almost 33% and a CP ratio of 1.25 was recorded when the temperature was raised from 120°C to 150°C. It therefore seems unlikely that the additional cost incurred in raising the liquefaction temperature from 150°C to 180°C would be compensated by the small gain in extractable material obtained. When the temperature was raised to 180°C, the phenol changed from a liquid to a vapour state. The reaction

speed between phenol and furfural was not accelerated by the higher temperature. It was therefore decided to carry out all further liquefaction reactions at 150°C.

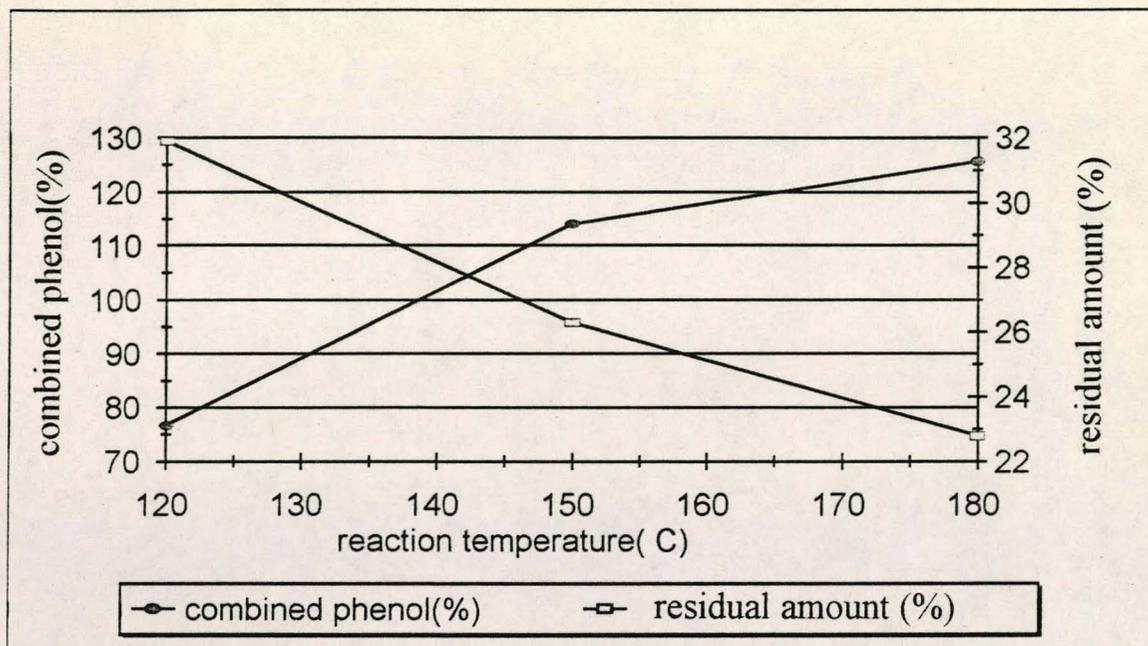


Fig 3.6: The relationship of CP and residual amount (%) at different reaction temperatures

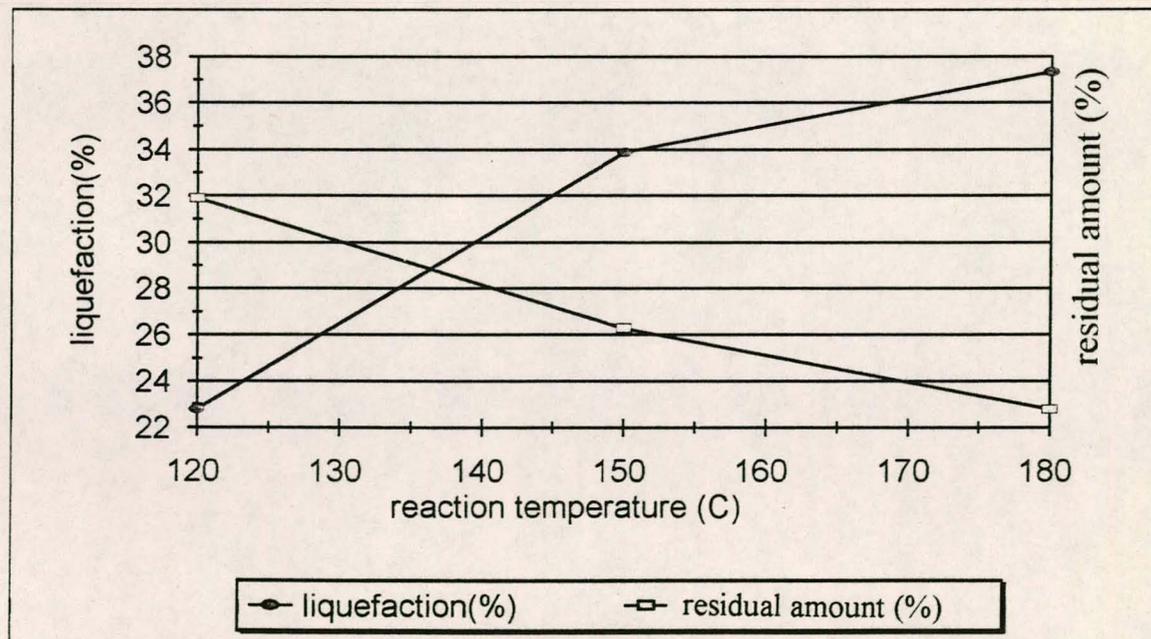


Fig 3.7: The relationship of liquefaction (%) and residual amount (%) at different reaction temperatures

3.1.3 Acid catalyst addition level

The results from the preliminary liquefaction trials (Table 3.2) indicated that the largest quantity of the extractable material was obtained at the 6% catalyst addition level. Higher H₂SO₄ catalyst addition levels and its effect on liquefaction were established. These results are listed in Table 3.7. Figures 3.8 and 3.9 indicate that the effect of higher catalyst addition levels produces negligible improvements in phenolated bagasse liquefaction and residual amounts. Also, the CP % gradients, which are high initially, became smaller with the higher catalyst addition levels. This confirms that the costs involved with higher catalyst addition levels are not justifiable. It is assumed that hemicelluloses of the bagasse are completely hydrolysed into furfural. Cellulose, however, is very difficult to convert into furfural due to its crystalline nature. Therefore, the amount of furfural produced can not be increased by adding more acid catalyst. The results obtained confirm this.

Result from experiments by Alma *et al.* (36) on phenolated wood using hydrochloric acid as a catalyst, indicated that liquefaction is enhanced by increasing the concentration of the acid catalyst up to 12%. Own results shown in Table 3.7 confirm that with H₂SO₄ as catalyst, high liquefaction rates can be obtained at much lower catalyst addition levels.

Table 3.7: The effect of catalyst addition level on liquefaction under LLC

Reaction condition		Phenol/Bagasse 2 to 1 Liquefaction time 1 hours				
		Liquefaction temperature 150°C				
H ₂ SO ₄ Catalyst %		2%	4%	6%	8%	10
Combined phenol-bagasse	%	98.6	186.5	219.6	221.8	235.1
	s _Q	5.2	8.7	4.9	4.6	8.2
Liquefaction bagasse	%	32.2	61.0	71.8	72.5	75.9
	s _Q	1.7	2.8	1.6	1.5	2.7
Residual Amount	%	21.7	14.2	13.2	12.8	12.6
	s _Q	1.4	1.4	1.9	1.5	1.9

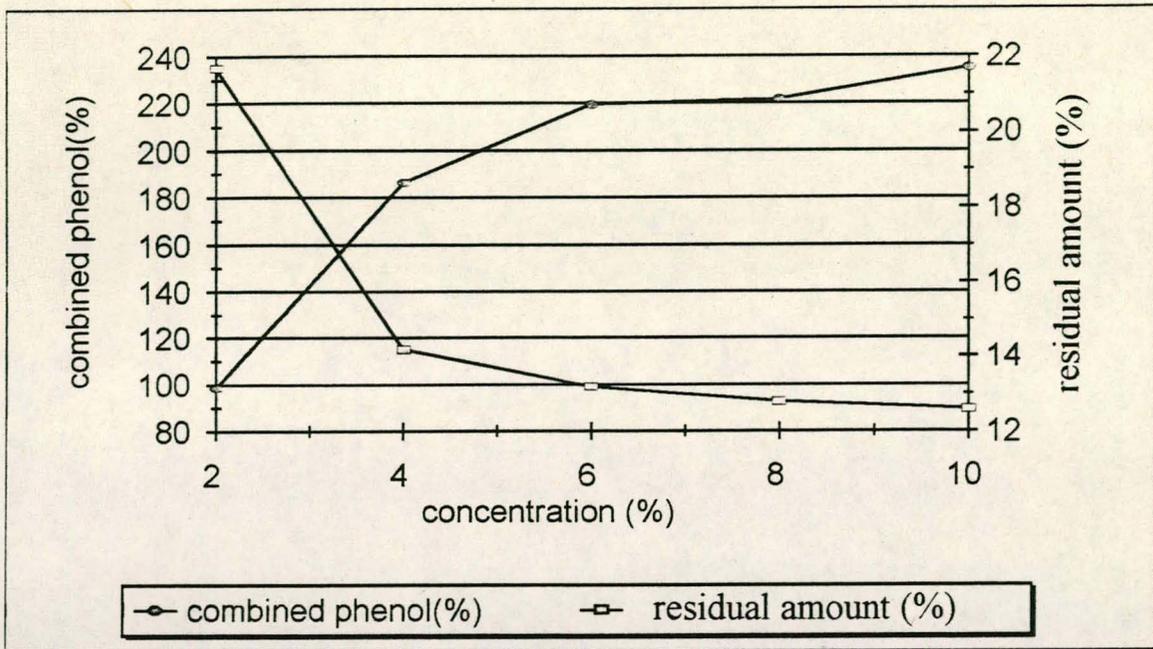


Fig 3.8: Combined phenol and residual amount (%) at different catalysts addition levels

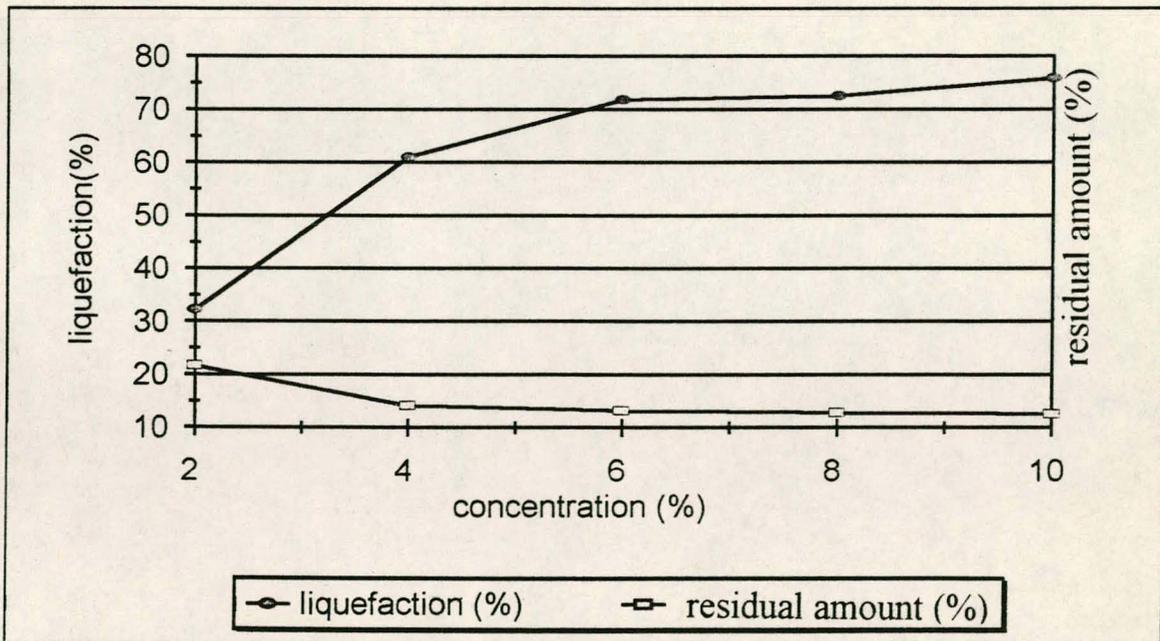


Fig 3.9: Liquefaction (%) and residual amount (%) at different catalyst addition levels

3.1.4 Pilot reactor with stirring system

The literature reviewed, dealing with liquefaction, mostly refers to the importance of physical factors such as temperature and its effect on wood phenolation (36, 37, 38, 39). The effect of physical factors such as high speed stirring is not however dealt with in these reports. In this study, it was noticed that the liquefaction reaction initially is heterogeneous, especially in the absence of a stirring mechanism. The liquefaction reaction does not proceed smoothly during this period. This is due to a poor transfer of heat through the mixture. The transformation of the reactant into an apparently homogeneous state is therefore largely dependent on efficient stirring. In the pilot reactor phenolation studies, the effect of stirring on liquefaction was investigated under conditions as shown in Table 3.8. The effect of stirring during the pilot LLC studies greatly increased the liquefaction/ phenolation rates and decreased the residual amount.

Table 3.8: Comparison of phenolation results of LLC liquefaction in pressure bomb and pilot reactor

Reaction condition		Phenol/Bagasse 2 to 1, Liquefaction temperature 150°C			
Sulphuric acid %		2	4	6	8
Pressure bomb					
C.P	%	98.6	186.4	219.6	221.8
	s _Q	5.2	8.7	4.9	4.6
liquefaction	%	32.2	61.0	71.8	72.8
	s _Q	1.7	2.8	1.6	1.5
residual amount	%	21.7	14.2	12.8	12.6
	s _Q	1.4	1.4	1.9	1.5
Pilot reactor					
C.P.	%	139.5	249.2	285.4	295.7
	s _Q	9.0	9.5	16.7	9.5
liquefaction	%	41.4	74.3	84.7	87.8
	s _Q	2.7	2.8	4.9	2.8
residual amount	%	20.1	11.2	1.5	0.2
	s _Q	4.2	5.7	0.4	0.1
Pilot - Pressure bomb					
C.P. (%)		40.9	62.8	65.8	73.9
liquefaction (%)		9.2	13.3	12.9	15.3
residual amount (%)		-1.6	-3.0	-11.3	-12.4

The bagasse liquefaction process carried out in the pilot reactor greatly increased the amount of phenol produced at all three catalyst addition levels. The differences in phenolated material obtained by the pressure bomb method and the pilot reactor method are given in Table 3.8. It can be seen that the differences level off toward the higher catalyst addition levels, which is also clearly reflected in Figures 3.10 and 3.11. The results shown in Table 3.8 suggest that a 6% catalyst addition level would be optimum for achieving satisfactory liquefaction rates.

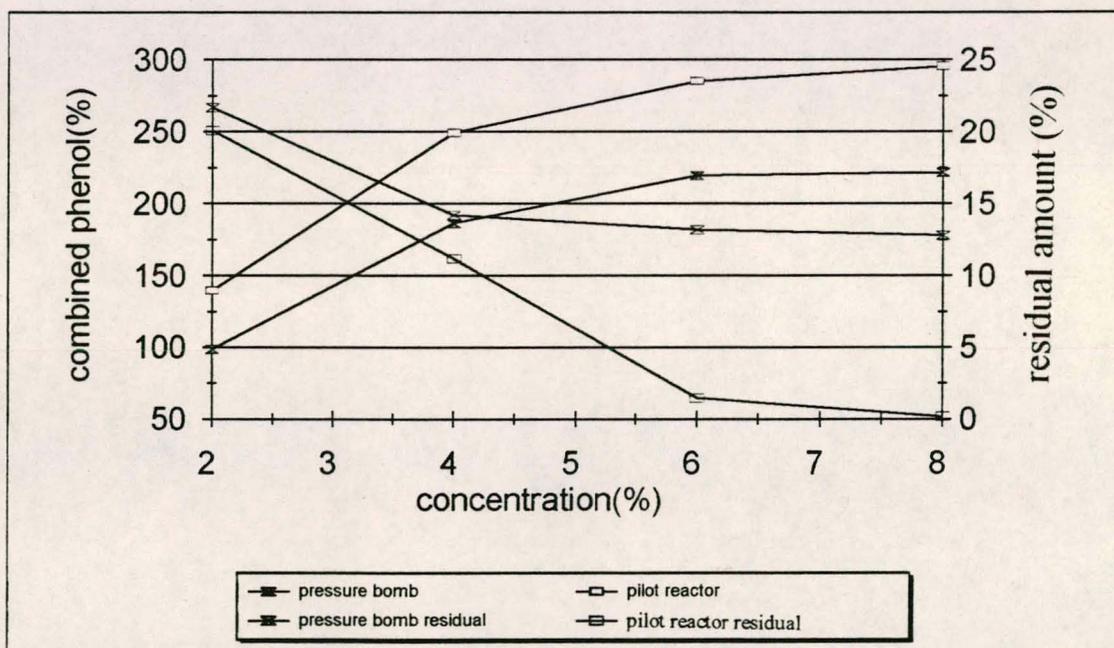


Fig 3.10: Residual amount (%) and CP (%) of the extractable material during pilot reactor and pressure bomb phenolation

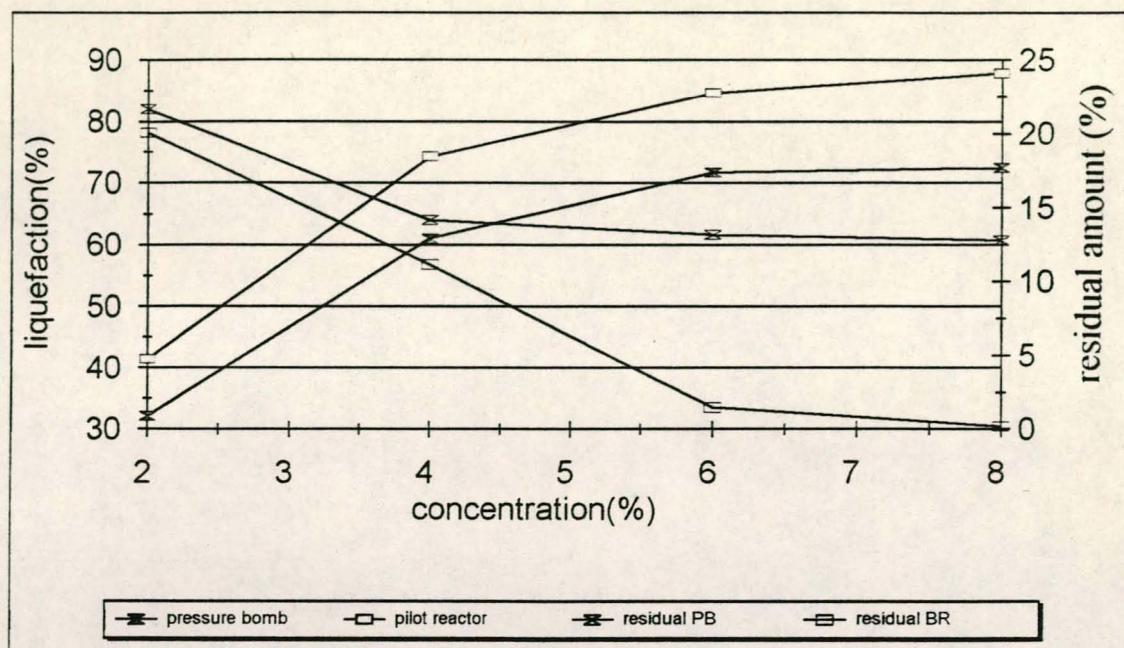
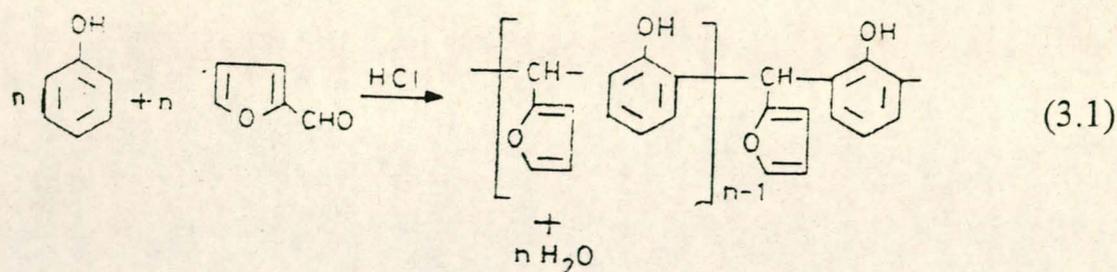


Fig 3.11: The relationship of residual amount (%) and liquefaction (%) of the extractable material during pilot reactor and pressure bomb phenolation

3.2 Infrared analysis

In an infrared spectroscopy study by Sayyah *et al.* (40), the reaction of bagasse pith with phenol was analysed and characteristic peaks of the C-O-C- group were observed at $1\ 100 - 1\ 020\ \text{cm}^{-1}$ and $1\ 230\ \text{cm}^{-1}$ bands. The polymeric OH group was found at $3\ 400\ \text{cm}^{-1}$; the C-H of the furan ring was seen at $2\ 930\ \text{cm}^{-1}$; C=C was detected from stretching at $1\ 520 - 1\ 450\ \text{cm}^{-1}$, and ortho-substitution in the benzene ring was discovered at $750\ \text{cm}^{-1}$ bands. This author (40) suggested that the novolac condensation reaction between phenol and furfural produced by the acid hydrolysis of bagasse pith in the presence of concentrated HCl, lead to the formation of a macromolecular chain, according to the following reaction (Eq. 3.1):



(The magnitude of "n" depends upon on reaction conditions.)

According the above reaction, the higher amount of furfural was produced under higher catalyst addition levels. It condensated with phenol and polymerised as a novolac with larger molecular mass.

According the above information, the OH group originated from the phenol, the -C-O-C- group from the furfural, and the ortho-substitution in the benzene ring groups from the reaction between phenol and furfural produced by the acid hydrolysis of the bagasse pith in the presence of concentrated HCl. These groups produced independent and characteristic infra-red transmission frequencies.

Infrared spectra of hydrochloric and sulphuric acids using the LLC method are shown in Figures 3.12 and 3.13. The intensities of the transmission peaks of the OH group and the ortho-substitution in the benzene ring are listed in Table 3.9. According to the reaction as suggested by Sayyah (40), the phenol/furfural/ortho-substitution benzene ratio of the polymer should be constant. As seen from Table 3.9, the ratios of the -OH/ ortho-substitution group, and -OH/furfural group both decreased with increasing catalyst concentration. It appears that both the ortho-substitution group and furfural group are increased by increasing concentration of catalyst. It seems that the higher number of -OH groups may get involved in the polymerisation at higher addition levels of catalyst. Knop *et al.* (42) indicated that the mechanism for the furfural and phenol reactions was not fully understood. Furan ring scission and reaction with another phenol nucleus might occur, leading to a relatively wide range of products.

Table 3.9: Infrared spectral intensities of the OH-group, the -C-O-C-group and ortho-substitution benzene group at different catalyst (HCl and H₂SO₄) levels

%	-OH group	-C-O-C-group	Ratio1*	ortho subst. benzene	Ratio2**
HCl					
2	6.5	4.8	1.35	2.6	2.5
4	6.5	5.7	1.14	2.8	2.32
6	6.7	6	1.12	3.5	1.91
H ₂ SO ₄					
2	8.8	7.4	1.19	3.6	2.44
4	6.2	5.3	1.17	2.8	2.21
6	7.6	7.3	1.04	4.1	1.85

* Ratio1 means the intensity of the -OH group/ the intensity of the -C-O-C- group

** Ratio2 means the intensity of the -OH group/ the intensity of the ortho subst. benzene group

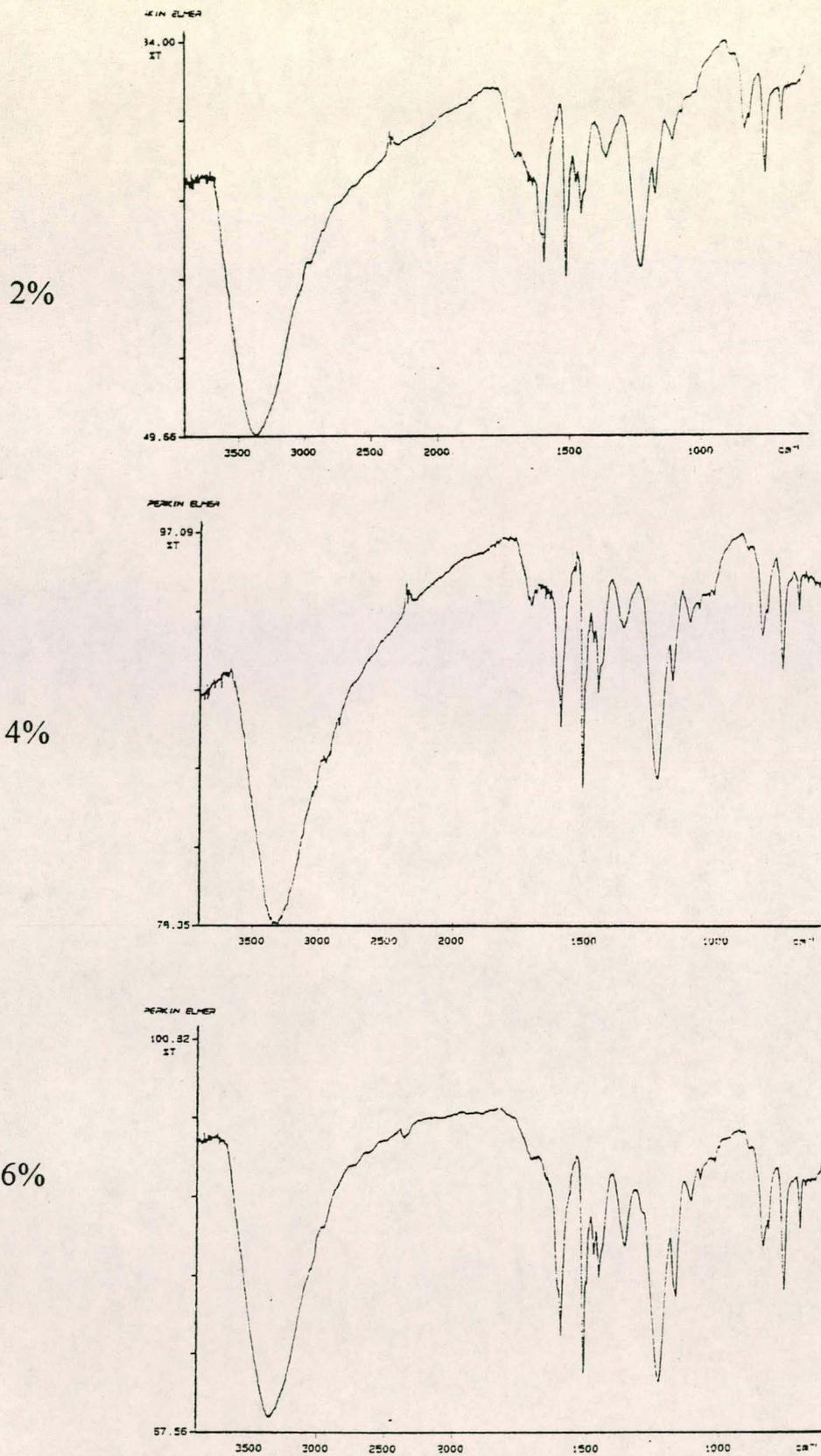


Fig 3.12: Infrared spectra of hydrochloric acid catalyst at 2, 4 and 6% concentration

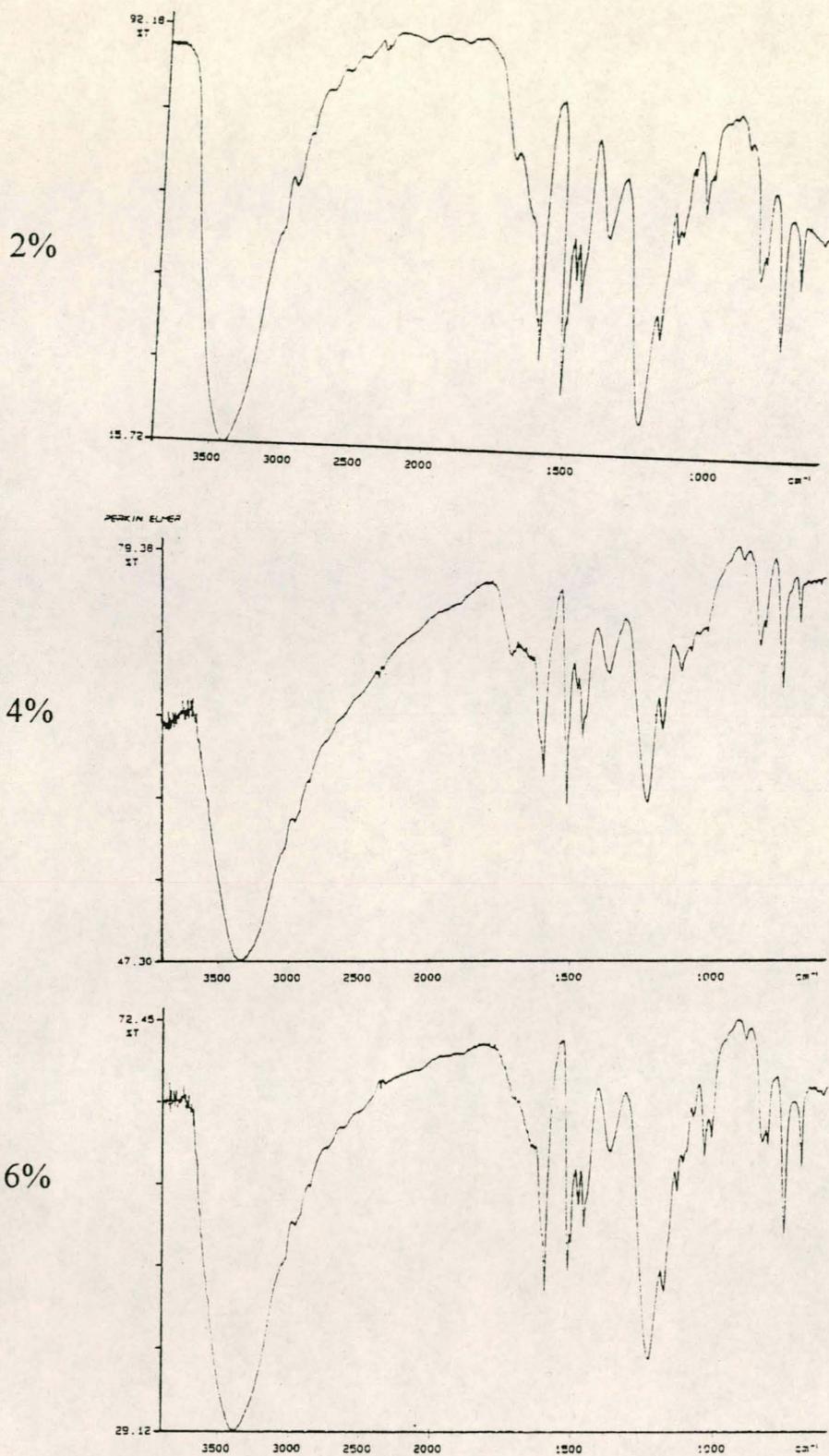


Fig 3.13: Infrared spectra of sulphuric acid catalyst at 2, 4 and 6% concentration

3.3 Physical properties of the moulded samples

From the pilot reactor study as previously described, it can be seen that higher addition levels of catalyst resulted in a larger amount of the combined phenol, leading to a higher molecular mass (see Table 3.8).

Results from the bending tests using 2, 4, 6 and 8 percent sulphuric acid catalyst for the pilot reactor liquefaction are listed in Table 3.10. Each value represents the average on ten measurements from each five mouldings. Fig 3.14 graphically shows the relationship between bending strength and the combined phenol (%), and Fig 3.15 shows the relationship between the bending strength and the amount of liquefaction (%). From the above results it can be seen that the higher combined phenol ratio results in higher bending strength. This relationship can be attributed to the fact that the liquefied bagasse resin (with the larger amount of combined phenol) has more cross-linking sites represented by the larger molecular mass; therefore, the network density of the matrix (e.g. liquefied bagasse resin) increases. An alternative explanation may be that an increase in the combined phenol enhances the interaction between liquefied bagasse resin and bagasse filler. The commercial novolac had the highest bending strength of all the samples tested. This indicates that a stronger molecular bond, with more cross-links does produce a better product.

Table 3.10: The correlation of bending strength and percentage combined phenol at various catalyst addition levels (refer to Table 2.13)

Catalyst (%)		2	4	6	8	Novolac
C.P.	%	139.5	249.2	285.4	295.7	
	s _Q	9.0	9.5	16.7	9.5	
Liquefaction	%	41.4	74.3	84.7	87.8	
	s _Q	2.7	2.8	4.9	2.8	
Bending	MPa	3.5	6.1	7.5	8.6	10.5
	s _Q	1.6	1.8	2.0	2.3	2.0

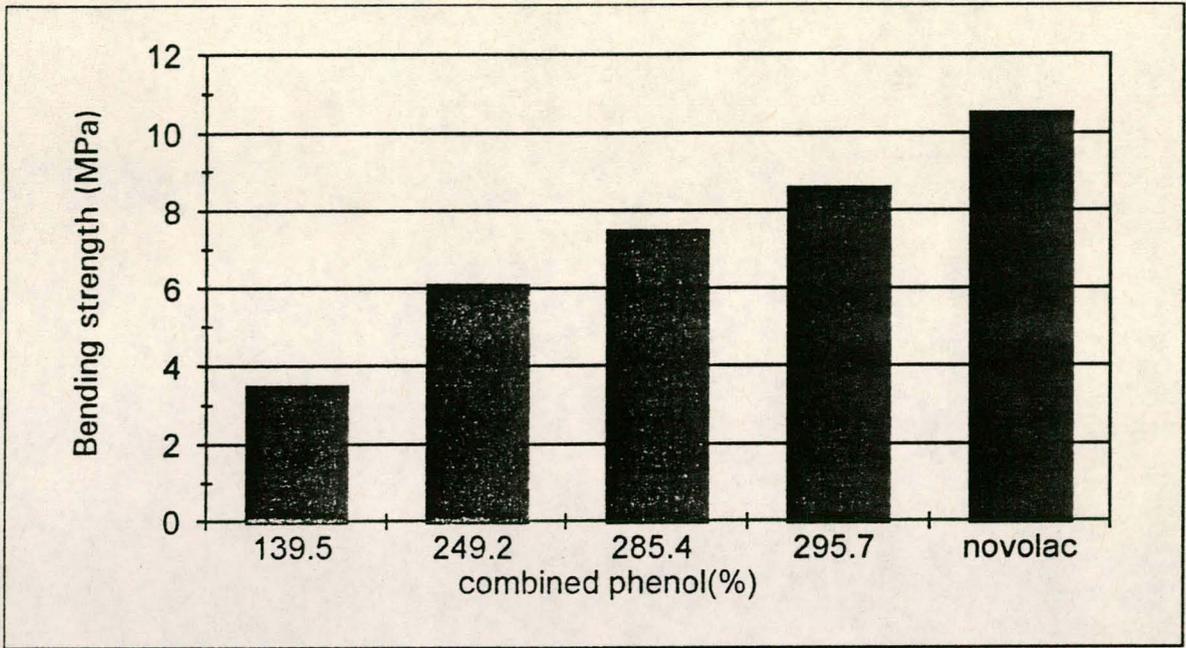


Fig 3.14: The relation between bending strength and combined phenol (%)

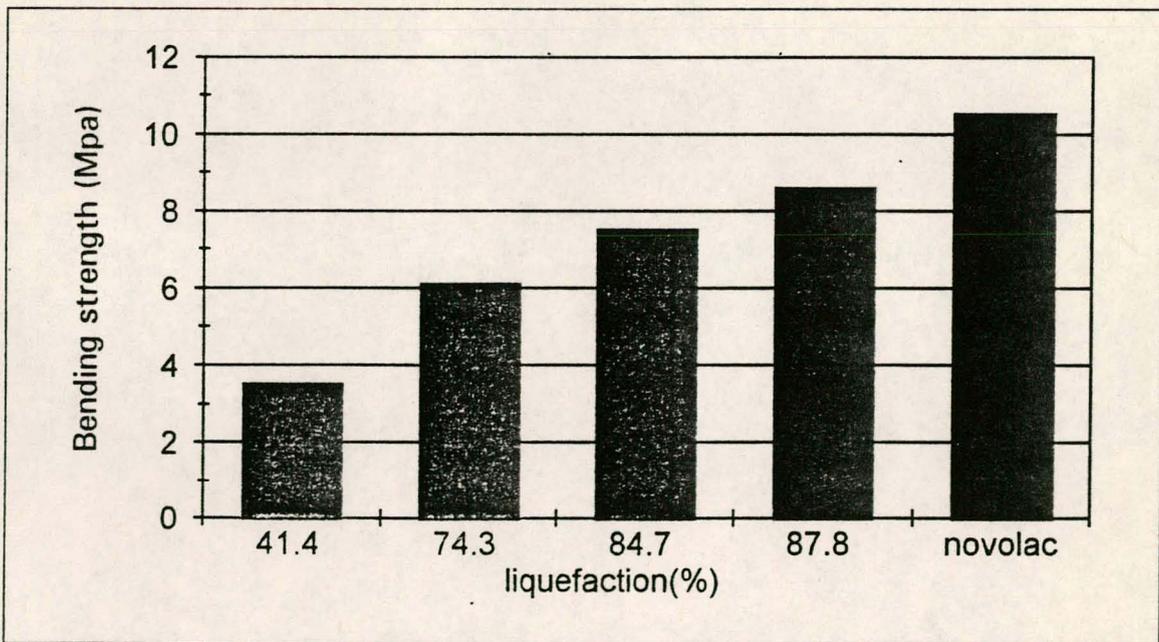


Fig 3.15: The relation between bending strength and liquefaction (%)

Results for the tensile tests are listed in Table 3.11. Each value represents the average of ten measurements on each of five mouldings. Figures 3.16 and 3.17 respectively show how the combined phenol % and the liquefaction % influence the tensile strength of the moulded samples.

From the above results it can be seen that a higher tensile strength is obtained for the samples with the bagasse novolac prepared at the 6% catalyst addition level. The tensile strength of the commercial novolac samples did not match the results obtained with phenolated bagasse at the 6 and 8 % catalyst addition levels. It seems that the amount of combined phenol which in turn is dependent on the amount of catalyst addition, will provide more crosslinking sites, thereby increasing the network density of the matrix, which seems to be an important consideration for obtaining higher flexural strength. The matrix reinforcing effect of the bagasse filler particles in pure tension is becoming less effective when the novolac shows more brittleness. This in turn is dependent on the conversion of the liquefied bagasse into combined phenol.

This again is dependent on the amount of acid catalyst added which was shown to be best around 6% addition for bagasse residue. The presence of furfural alcohol under acidic catalyst conditions, most likely reacted with bagasse to form a wide range of polymer chain lengths due to homo and co-polymerisation.

Table 3.11: The correlation of tensile strength and percentage of combined phenol for various levels of catalyst additions (refer to Table 2.13)

Catalyst (%)		2	4	6	8	Novolac
C.P.	%	139.5	249.2	285.4	295.7	
	s _Q	9.0	9.5	16.7	9.5	
Liquefaction	%	41.4	74.3	84.7	87.8	
	s _Q	2.7	2.8	4.9	2.8	
Tensile stress	MPa	2.2	3.5	5.1	4.8	4.7
	s _Q	0.5	0.8	0.7	1.7	1.2

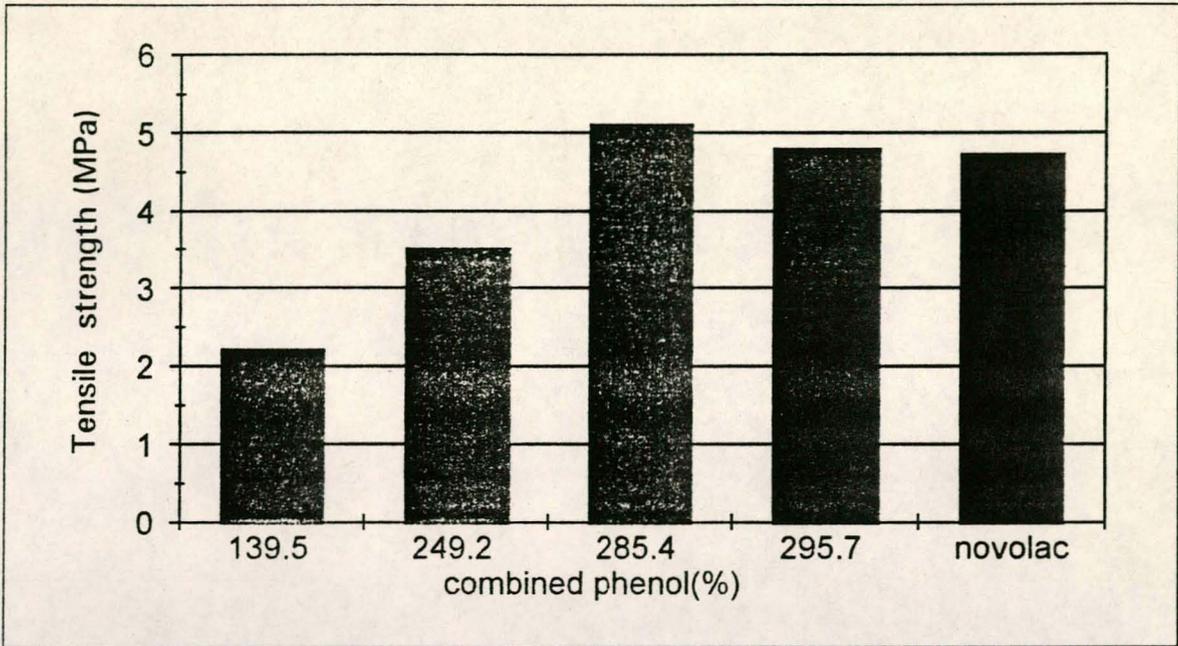


Fig 3.16: The effect of % combined or reacted phenol on tensile strength

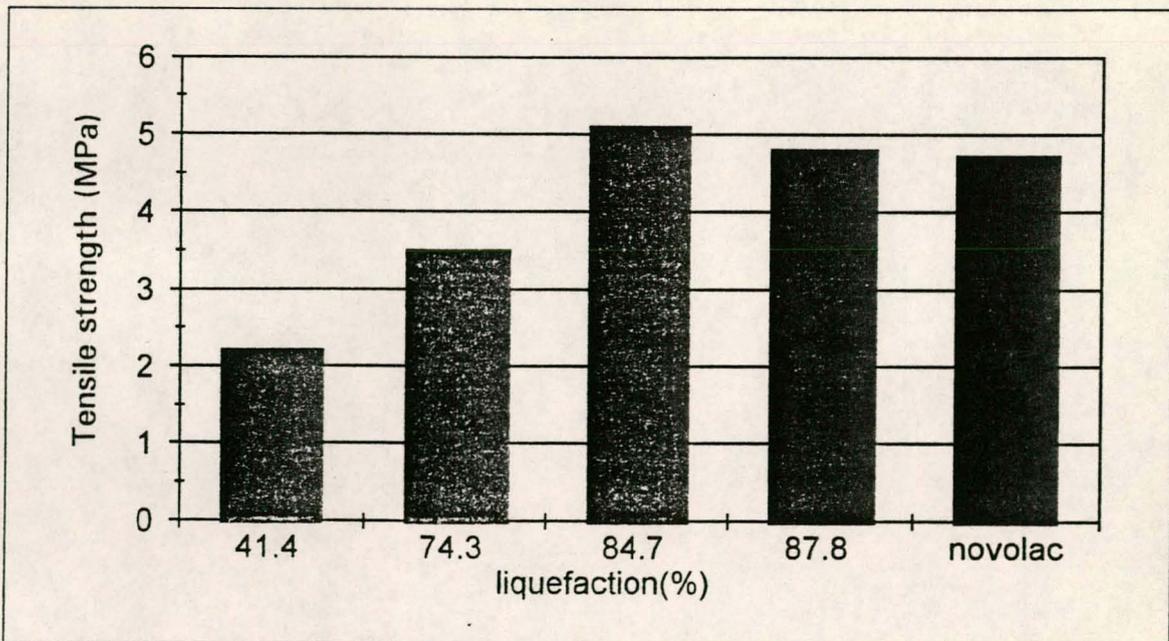


Fig 3.17: The effect of % liquefaction on tensile strength

3.4 Material cost comparison for replacing pure Novolac moulding resin with the phenolated bagasse resin

Serious market competition makes the cost of product manufacturing a very important factor in the market promotion of a new product. A competitively priced quality product will obviously replace a more expensive one.

The material costs of moulding formulations using commercial novolac and phenolated bagasse resin are listed in Table 3.12. According to Table 3.12, the cost of raw materials for moulding applications is 22,2% cheaper using phenolated bagasse resin.

Table 3.12: Moulding formulation of phenolated bagasse resin and commercial novolac

Raw material costs: Phenolated bagasse			
		Moulding (kg) formula	Cost (Rand)
Phenolated Bagasse (Novolac)	R4.5 / kg	28.0	126.00
Bagasse, phenol and sulphuric acid	R10.0/kg	0.7	7.00
Wax	R0.1/ kg	62.9	6.29
Filler	R15.0/kg	0.3	4.50
Solvent	R37.0/kg	8.4	310.80
Hexamine			
Total cost:	R 449.80		
Moulding cost per kg:	R 4.48		
Raw material costs: Commercial novolac			
		Moulding (kg) formula	Cost (Rand)
Novolac	R9.0/kg	28.0	252.00
Wax	R10.0/kg	0.7	7.00
Filler	R0.1/ kg	62.9	6.29
Hexamine	R37.0/kg	8.4	310.80
Total cost:	R576.09		
Moulding cost per kg:	R5.76		

Chapter 4

Conclusion

The liquefaction of bagasse with phenol under acidic catalytic conditions to form a novolac product is a two step reaction. Initially, furfural is produced through the acid hydrolysis of bagasse using a concentrated acid. The second step consists of condensing phenol under acid conditions to produce the novolac resin.

Furfural is a very important reagent in the process of bagasse liquefaction. It is influenced by temperature, type and concentration level of the catalyst used. The mechanical stirring system also plays an important role. To produce the largest amount of phenolated bagasse at the lowest possible cost, the following four conditions must be met:

1. concentrated sulphuric acid must be used;
2. the catalyst concentration must be 6%;
3. the temperature for liquefaction must be around 150°C;
4. mechanical stirring must be used.

By meeting these conditions, a low amount of the residual extraction mass and a high amount of combined phenolated material is obtained.

The performance of the sulphuric acid catalyst used for bagasse liquefaction proved to be satisfactory under low liquefaction conditions in order to achieve good combined phenol bagasse yields.

Using infra-red spectra analysis, it could be shown that the polymerisation of phenol and the furfural formed from the acid hydrolysis of the bagasse at a high level of catalyst addition, resulted in a structurally more complex novolac product.

addition obtained the highest strength. The 6% sulphuric acid catalyst addition obtained resulted in a novolac with the highest tensile strength for moulding purposes. The tensile strength values obtained were somewhat higher as compared to the commercial novolac moulded samples.

The economic consequences of replacing pure novolac phenolic resin with the new product are as following:

1. The cost of raw materials for moulded products using liquefied bagasse will be somewhat cheaper than commercial novolac system.
2. The new product is sticky and more difficult to handle.

Literature Cited

1. Paterson-Jones J.C., "The biological utilization of bagasse, a lignocellulose waste", 1989, published by Claire McKinnon, FRD, CSIR.
2. Van Meer J.M., Rijkens B.A., Ferranti M.P., "Degradation of lignocellulosics in ruminants and in industrial process", 1987 Elsevier Applied Science Publisher Ltd.
3. Haygreen J.G., Bowyer J.L., "Forest production and wood science", 1982, published by The Iowa State University Press.
4. Fengel D., Wegener G.B., "Wood chemistry ultrastructure", 1984, published by Walter de Gruyter & Co.
5. Goring D.A.I., "Lignin", Summer 1964 Trend No. 3.
6. Rolz C., De Arriola M.C., Valladares J., De Cabrera S., "Effects of some physical and chemical pretreatments on the composition, enzymatic hydrolysis and digestibility of lignocellulosic sugar cane residue", Process Biochemistry, February 1987, pp 17-23.
7. Doran J.B., Aldrich H.C., Ingram L.O., "Saccharification and fermentation of sugar cane bagasse by *Klebsiella oxytoca* P2 containing chromosomally integrated genes encoding the zymomonas mobilis ethanol pathway", Biotechnology and Bioengineering, 1994 **44**, pp. 240-247.
8. Dekker R.F.H., Lindner W.A., "Bio-utilization of lignocellulosic waste materials: a review", South African Journal of Science., 1979, **75**, pp. 65-71.
9. Rolz C., De Leon R., De Arriola M.C., De Cabrera S., "Biodelignification of lemon grass and citronella bagasse by white-rot fungi", Applied and Environmental Microbiology, 1986 **52(4)**, pp. 607-611.
10. Rolz C., De Leon R., De Arriola M.C., De Cabrera S., "White-rot fungal growth on sugarcane lignocellulosic residue", Applied Microbiology and Biotechnology, 1987, **25**, pp. 535-541.

11. Olsson L., Hahn-Hagerdal B., "Fermentative performance of bacteria and yeasts in lignocellulose hydrolysates", *Process Biochemistry*. 1993, **28**, pp. 249-257.
12. Meyer P.S., Du Preez J.C., Kilian S.G., "Chemostat cultivation of *candida blankii* on sugar cane bagasse hemicellulose hydrolysate", *Biotechnology and Bio-engineering*, 1992 **40**, pp. 353-358.
13. Ponce-Noyola T., De la Torre M., "Interactions in a mixed culture composed of *Cellulomonas flavigena* and *Xanthomonas* sp. growing in continuous culture on sugar cane bagasse", *Applied Microbiology and Biotechnology*, 1993, **40**, pp. 531-534.
14. Shen, Kuo Chen.: 1990 European Patent application, Application No: 90314424.4.
15. Mikes J.A., "On the behavior of mixed furfural-formaldehyde phenoplasts", *Journal of Polymer Science*, 1961, **53**, pp. 1-8.
16. Leal E.R., Rodriguez-Vazquez R. and Galindo T., "Separation of Phenolic compounds from sugarcane bagasse pith and their determination by HPLC", *Journal of Wood Chemistry and Technology*, 1994, **14**(3), pp. 369-382.
17. South Africa Yearbook 1995.
18. Helmy S.A. and Abou-State M.A., "Viscose pulps from Egyptian bagasse with high chemical reactivity", *Holzforschung*, 1991, **45**(6), pp. 433-436.
19. Zhan H., Yue B., Chen G., Liu B. and Xu J., "Study on the characteristics of potassium-based and sodium-based sulfite pulping of bagasse", *Cellulose Chemistry and Technology*., 1995 **29**, pp. 173-180.
20. Yu J.L. Ma Y.W. and Chen J.X., "Studies of bagasse neutral sodium sulfite pulping with lower permanganate number and higher yield", *Cellulose Chemistry and Technology*, 1994, **28**, pp. 649-655.
21. Helmy S.A. and Abou-State M., "Viscose pulps from Egyptian bagasse by alkaline solvent pulping", *Cellulose Chemistry and Technology*, 1994, **28**, pp. 29-33.

22. Atchison J.E., "Making the right choices for successful bagasse newsprint production: part 2", *Tappi Journal.*, 1993, **76**(1), pp. 187-193.
23. De Groote R.A.M.C., Curvelo A.A.S., Alaburda J. and Botaro V.R., "Acetosolv pulping of sugar cane bagasse. II", *Cellulose Chemistry and Technology*, 1993, **27**, pp. 555-563.
24. Wiecke P.H., "KK MDF, the first bagasse MDF board plant", *Nonwood Plant Fiber Pulping progress report No. 17*, pp. 59-61, Tappi Press.
25. Anosour O.Y., "Lignocellulose-polymer composite. III", *Journal of Applied Polymer Science*, 1993, **47**, pp. 839-846.
26. Bawagan B.O., "Wood Wastes and Agricultural Residues as Source of Furfural", *Forpridecom Technical Note*, October 1978, Number 194.
27. Barnes A.C., "The Sugar Cane", published by Interscience Publisher Inc. 1964.
28. Brown L.H., "Resin forming reactions of furfural and phenol", *Industrial and Engineering Chemistry*, 1952, **44**(11) pp. 2673-2675.
29. Vega A., Bao M., "Fractionation of lignocellulose materials with phenol and dilute HCl", *Wood Science and Technology*, 1991, **25**, pp. 459-466.
30. Ysbrandy R.E., Gerischer G.F.R., Sanderson R.D., "Preparation of moulding resins from inexpensive by-products: substitution of phenol novolac with unmodified lignin in moulding resin and its effect on physical properties of mouldings", *South African Forestry Journal*, 1994, **170**, pp. 27-29.
31. Ladomerski J., Wienhaus O., Pecina H., "Zur Nutzung von Lignocellulose-Rückständen (LCR) aus der Furfuralerzeugung für die Herstellung von Phenolharzklebstoffen", *Holz als Roh- und Werkstoff* 1989, **47**, pp. 47-52.
32. Tonogai S., Sakaguchi Y., Seto S., "Curing behavior of two-step phenolics by solvent extraction", *Journal of Applied Polymer Science*, 1978, **22**, pp. 3225-3234.

33. Tsujimoto N., Yamakoshi M., Kudo T., Horiuchi Y., Shimizu J., "Manufacture of lignocellulosic material-phenolic compound composites", Can. Pat. Appl. CA 2,026,406.
34. Marcelo G., "Preparation of phenolic-type adhesive from bagasse for plywood", Braz. Pedido PI BR 90 00,456.
35. Alma M.H., Yoshioka M. and Shiraish N., "New novolac-resin type molding materials from phenolated wood using hydrochloric acid catalyst", Holz als Roh- und Werkstoff, 1994, **52**, p. 38.
36. Alma M., Yoshioka M., and Shiraishi N., "Preparation and characterization of the phenolated wood using hydrochloric acid (HCl) as a catalyst", Wood Science and Technology, 1995, **30**(1), pp. 39-47.
37. Lin L., Yoshioka M., Yao Y. and Shiraishi N., "Liquefaction of wood in the presence of phenol using phosphoric acid as a catalyst and the flow properties of the liquefied wood", Journal of Applied Polymer Science, 1994, **52**, pp. 1629-1636.
38. Pu S. and Shiraishi N., "Liquefaction of wood without a catalyst IV. Effect of additives, such as acid, salt, and neutral organic solvent", Mokuzai Gakkaishi 1994, **40**(8) pp. 824-829.
39. Lin L., Yoshioka M., Yao Y. and Shiraishi N., "Physical properties of moldings from liquefied wood resins", Journal of Applied Polymer Science, 1995, **55**, pp. 1563-1571.
40. Sayyah S.M., Gawish N.M., Mourad A. & Moustafa A.B., "Preparation and characterization of some phenol-modified moulding resins from Egyptian bagasse pith", Indian Journal of Technology, 1985, **23**, pp. 348-354.
41. Rusan V., Popa V.I., "Interferences between chemical components of wood and synthetic copolymers", Cellulose Chemistry and Technology, 1992, **26**, pp. 591-606.
42. Knop A., Pilato L.A., "Phenolic Resins", published by Springer-Verlag, Berlin, Heidelberg 1985.

