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Degradation of phenethoxybenzene in sodium hydroxide

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Simple lignin model compounds containing β -O-4 aryl ether linkages have been utilized as a means to understand lignin depolymerisation. The effects of reaction temperature, time, catalyst concentration, and initial phenethoxybenzene (PEB) concentration on the degradation of PEB in NaOH were investigated. Operating at 300 °C for 1 h resulted in the highest combined yield of the primary products, phenol and styrene, and also resulted in a reduced amount of degradation products formed. The proportion of oligomeric and polymeric materials formed depended on the NaOH concentration, but not on the initial PEB concentration for equal reaction time. The results were used to suggest probable reaction pathways for PEB degradation.

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1. Introduction

Lignin is a complex, amorphous and non-linear biopolymer, the molecular mass of which is determined by the random crosslinked polymerisation of three different phenolic moieties. The approximate structure of lignin was first proposed in 1977,¹ and is known to include many hydroxyl, ether and phenolic functional groups. As a result, this material has the potential to be used as a feedstock for the production of phenol and other closely related derivatives; such as benzene, toluene and xylene (BTX), vanillin, guaiacol and eugenol.^{2,3}

Studies into the structure of lignin indicate that the monomer units are interconnected *via* ether and C–C bonds, in a ratio of 2 : 1.⁴ The most predominant linkage, the β -O-4 bond, occurs within the guaiacylglycerol β -aryl ether substructure with a prevalence of 40–60%⁵ (Fig. 1). The prevalence of the various types of inter-monomer linkages, as well as the three monomer units themselves, vary with the type of lignocellulosic material source.⁶ Not only is the β -O-4 bond present at significantly higher quantities than any other monomer linkage, it is also the most easily chemically cleaved with the exception of the α -O-4 bonds.⁷ The other types of linkages present, both ether and C–C, are more resilient to thermal and thermochemical disruption.

Many studies have been conducted by pyrolysis on lignin and its model compounds.^{8–11} A complex set of radical, rearrangement and elimination reaction occur, which are influenced by processing conditions and lignin origin. However, when lignin is heated in the presence of water it undergoes hydrolysis. This

process can be catalysed by the presence of either acid or base, which also tends to reduce the range of products obtained.12,13 Under ambient basic conditions ethers will generally not undergo hydrolysis, so the depolymerisation of lignin is generally performed under moderate temperature (250-333 °C) and high pressure (1-240 bar), in a process known as hydrothermal liquefaction (HTL).14 The significant reaction pathways involved are, (a) hydrolysis and cleavage of the ether and C-C bonds, (b) alkylation, (c) demethoxylation, and (d) condensation. Demirbas et al.15 suggested that when lignin is exposed to temperatures in excess of 250 °C, free phenoxyl radicals are formed via thermal decomposition and that these radical species tend to elicit condensation and repolymerisation reactions, resulting in the formation of solid char material. This char product is undesirable as it is very difficult to break-down or utilise in any economically advantageous manner. Roberts et al.¹⁶ demonstrated that, under basic conditions, the primary products obtained in lignin depolymerisation are in fact phenolic monomers, and that the oligomers observed result from subsequent condensation reactions of the (highly reactive) monomer intermediates.

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It is thought that the problematic repolymerisation reactions associated with lignin depolymerisation, are initiated by radical formation. Therefore, preventing or limiting these radical reaction pathways is pertinent to increasing the yield of the desirable low molecular weight hydrolysis products. Radical reactions (as opposed to ionic reactions), become less prevalent as solvent density increases, since the radical species have less space to diffuse and propagate the chain reaction and instead are more likely to recombine with their composite reactant species.¹⁷ Previous studies have shown that this can be aided by the addition of an alkali salt,^{18,19} which increases the ionic properties of the water and results in an increase in monomer

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product yield. Miller *et al.*²⁰ concluded that the more alkaline salts were most effective not only in enhancing lignin depolymerisation, but in preventing repolymerisation reactions and the subsequent formation of polymeric solids.

Despite NaOH catalysis system been widely studied with lignin model compounds, such as phenethoxybenzene, PEB (Fig. 2) and benzyl phenyl ether (BPE), the physico-chemical reactions in these systems with lignin are still difficult to predict, and how to limit the multiplicity of products formed is still a big challenge. This has implication in product recovery and purification. As such, the approach the authors have adopted in the present study is to specifically focus on the optimization of the reaction conditions of PEB in NaOH. This will provide pointers for the HTL of black liquor, which is of particular interest to our group. This is achieved by investigating the influence of reaction conditions, such as reaction time and reactant concentration on the product range obtained from PEB using HTL. It is acknowledged that PEB is one of the simplest lignin model compounds as it does not contain phenyl hydroxyl groups besides the β -O-4 bond. Of particular interest in the present study is the molecular weight distribution of the products obtained. If the reaction conditions can be optimised in such a way so as prevent or limit the polymerisation of primary products, similar conditions may prove effective in the depolymerisation of lignin (in black liquor) without subsequent



Fig. 2 Lignin model compound phenethoxybenzene (PEB) with β -O-4 linkage labelled.

condensation reactions and the resultant formation of char and other low-value materials.

Materials and method

Phenethoxybenzene (>95%) was obtained from Ark Pharm. For the processing of analytical results, phenol (Sigma-Aldrich, >99%) and styrene (Fluka, >99%) were used as standards for product quantification. Acetone (Sigma-Aldrich, >99%) was used as the GC-MS solvent and 4-ethylphenol (Fluka, >98%) as an internal standard. Organic extractions were performed using diethyl ether (Sigma-Aldrich, >99%). All chemicals were used as received.

2.1 Experimental

The HTL experiments were conducted in 316-stainless steel tube reactors of 6.3 mm internal diameter and length 16 cm (volume of 5 mL). An additional reference reactor was designed with an internal thermocouple and pressure transducer attachment, to allow for the real-time monitoring of the internal reaction temperature and pressure. Experiments were conducted within a fluidised sand bath (SBL-2D, Techne Inc., Burlington, NJ) over a temperature range of 250-350 °C and reaction time of 30-120 min. This temperature range was selected based on numerous previous studies on lignin depolymerisation, wherein the temperature for effective hydrothermal cleavage of the β -O-4 bond was determined to be approximately 280 °C.²¹⁻²³ The concentration of NaOH catalyst solution was varied between 0 and 5 wt%. This range was utilised due to both the approximate compositional similarity to black liquor,²⁴ and previous similar work performed in the area.12 The concentration of PEB in solution was varied between 2.4 and 9.0 wt%. Experiments were conducted in duplicate, though for the molecular weight measurements experiments were in triplicate to provide errors for the data reported in the figures.

A standard work-up method for analysing the reactant mixture obtained in the HTL of PEB was developed. After the

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reaction was performed the reactors were removed from the heated sand bath and immediately guenched in roomtemperature water. The contents of the reactors were then washed with 3×3 mL volumes of diethyl-ether. The biphasic mixture obtained was vigorously agitated and then centrifuged, before collecting the organic phase. In order to remove the small quantity of solid material present the aqueous phase was filtered through a pre-weighed sintered crucible. Once filtered, the pH of the aqueous phase was adjusted to 2.5 with the use of 2 M H₂SO₄. A second organic extraction was then performed using 3×3 mL portions of diethyl ether. Once again the solution was vigorously agitated and centrifuged, and the organic phase obtained was combined with the first. The bulk of the diethyl ether was removed from the organic phase via mild vacuum distillation at 35 °C. In order to remove any residual ether, the oil was air-dried overnight and the final dry mass recorded. For the experiments performed with no catalyst the pH of the aqueous phase was not adjusted, as the pH was already slightly acidic (as opposed to highly basic), and as such a one-step organic extraction procedure was performed. Initial testing indicated the importance of removing the solvent under mild conditions, due to the relative volatility of styrene. A flowchart of this workup procedure is illustrated in Fig. 3.

2.2 Analysis of products

The organic/oil phase samples were analysed by GC-MS using an Agilent 6890 Series Gas Chromatograph and a HP 5973 mass spectrometer detector, employing helium as the carrier gas. The installed column was an Agilent CP-wax 52 CB, 30 m \times 0.25 mm \times 0.25 μm . Samples were injected with a split ratio of 10 : 1 into the injection port set at 230 °C. The temperature program



Fig. 3 Flowchart describing the work-up method used for preparing and characterising the organic, aqueous and solid phases for the HTL of PEB.

commenced at 90 °C and heated at a rate of 3 °C min⁻¹ to a temperature of 230 °C. Once the temperature was reached the column was then held for another 5 min. Compounds were identified by means of the Wiley library-HP G1035A and NIST library of mass spectra and subsets-HP G1033A (a criteria quality value >80% was used). Acetone was used as the solvent with approximately 15 mg of oil dissolved in 1.0 mL of acetone. ¹H-NMR spectra of the organic phase samples were obtained using a Varian VNMRS 400 NMR and analysed using the ACD/ NMR Processor Academic software package. FT-IR spectra of the samples were collected using a Nicolet 870 FT-IR spectrometer equipped with a Smart Endurance single bounce diamond ATR accessory (Nicolet Instrument Corp., Madison, WI). Spectra were collected in the spectral range 4000–525 cm⁻¹, using 64 scans and 4 cm⁻¹ resolution.

Size exclusion chromatographic (SEC) analysis for molecular weight measurement incorporated a GPC Water Breeze system model 151 with an isocratic HPLC pump. Eluted fractions were detected with UV and refractive index Water model 2414 detector. Three Phenomenex phenogel columns (500, 104 and 106 Å porosity; 5 μ m bead size) were used for size exclusive separation. The mobile phase was tetrahydrofuran (THF) with 1 mL min⁻¹ flow rate at 30 °C. A 100 μ L sample having a concentration of 5 mg mL⁻¹ in THF was injected into the SEC instrument after filtration with a 0.4 μ m Teflon syringe type filter.

3. Results and discussion

3.1 Influence of reaction temperature

A series of HTL experiments were performed in 5 wt% NaOH solutions at 250, 300 and 350 $^{\circ}$ C for 120 min, and at PEB concentrations of 2.4–9.0 wt%. The yields of phenol, styrene and residual PEB obtained by quantitative GC-MS analysis of the oil phase are presented in Table 1. Qualitative FT-IR and ¹H-NMR analysis were conducted on the oil phase samples to support the results obtained by GC-MS.

The results indicate that at 250 °C the majority of the PEB does not degrade, and so the yields of styrene and phenol are low. At 300 °C (except at PEB concentration of 6.8 and 9.0 wt%) and 350 °C no residual PEB remain. It is at these temperatures that the phenol yields are highest, and reached \sim 48%. The styrene yields are highest at 300 °C, and were hardly detected at 350 °C. In the study by Eom et al.²⁵ with use of 0.25% Na₂CO₃, PEB conversion reached 100% at 300 °C with a reaction time of 2 h, and maximum yield of phenol (40%) was obtained at 400 °C. Although the processing conditions between the present study and those of Eom et al.25 are slightly different, the general trends are similar in terms of PEB degradation and the increase in phenol yield with temperature, as well as phenol being the major product. The reduction in styrene concentration with increasing temperature was obtained in both studies. However, no ethyl benzene was obtained in the present study as the gas used was air instead of hydrogen. Eom et al.25 observed the presence of ethyl benzene when the gas present in the reactor was hydrogen instead of helium, as the compound is produced from the hydrogenation of styrene.

Table 1 shows that at 250 °C as the initial PEB concentration increases the amount of phenol dropped, while at 350 °C the reverse is true. The styrene yield remains constant at 250 °C and the yield is 0% at 350 °C. At the lower temperature, as shown in Table 1, with increasing initial PEB concentration the amount of unconverted PEB increases. This does not fully account for the reduced amount of phenol obtained; indicating that perhaps some of the phenol is undergoing some side reactions. At 350 °C any styrene formed *in situ* would have participated in some side reactions either on its own or with phenol.

Table 1 also shows that with increasing reaction temperature, the cumulative yield of styrene, phenol and residual PEB drops significantly, indicating the formation of products other than styrene and phenol. At 350 °C there is little impact on phenol yields, but a significant effect on styrene is observed as yield reduces to 0%. Fig. 4 shows the continuous conversion of PEB to phenol and styrene, as well as increasing peak intensities

Table 1 Products of PEB conversion (in 5 wt% NaOH) with temperature at 120 min^a

Reaction temperature (°C)	PEB conc. (wt%)	Styrene yield (wt% of PEB mass)	Phenol yield (wt% of PEB mass)	Residual PEB (wt% of PEB mass)	Amount of styrene, phenol & PEB (wt% of PEB mass)	Oil phase accounted for by styrene, phenol & PEB (wt%)
250	2.4	3.4	20.9	37.3	61.7	82.3
	4.7	4.2	9.1	60.7	73.9	84.1
	6.8	3.6	6.6	63.8	74.0	83.1
	9.0	3.4	4.3	70.2	77.9	84.3
300	2.4	13.4	41.9	0.0	43.6	55.3
	4.7	9.6	48.3	0.0	33.4	57.9
	6.8	10.3	40.9	6.5	43.5	57.7
	9.0	7.9	28.7	4.0	34.3	40.6
350	2.4	0.0	43.2	0.0	43.2	48.2
	4.7	0.0	35.0	0.0	35.0	47.5
	6.8	0.0	47.6	0.0	47.6	45.4
	9.0	0.0	48.1	0.0	48.1	57.6

^{*a*} Error of $\pm 4\%$.



Fig. 4 GC-MS chromatograms of oil samples produced at 120 min and 5 wt% NaOH for PEB concentration of 4.7 wt% at (a) 250 °C, (b) 300 °C, (c) 350 °C and (d) styrene concentration of 4.7 wt% at 350 °C.

with temperature associated with other compounds (Table 2). It is noted that not all polymeric (high molecular weight, HMWM) material may be volatile and identified by GC-MS.

In an attempt to elucidate the origin of these other compounds, several HTL experiments were conducted in which PEB was substituted with styrene. The GC-MS analyses indicate that the additional compounds present are formed as a result of reactions between styrene molecules which occurred at 350 $^{\circ}$ C, but not 300 $^{\circ}$ C. Fig. 4(d) compares the GC-MS chromatograms obtained for the styrene and PEB HTL experiments at 350 $^{\circ}$ C.

A previous study on the HTL of PEB reported a lower than expected yield of styrene, which was explained by the strong reactivity of this species and its propensity towards oligomerisation.²⁶ A similar work by Roberts *et al.*¹⁸ investigated the

Table 2 Identified compounds from GC-MS analysis

	Retention	
Peak	(min)	Name
1	3.46	Styrene
2	4.30	α-Methylstyrene
3	4.69	2-Pentanon-4-hydroxy-4-methyl
4	5.43	1-Propenyl-benzene
5	6.74	1-Methyl-2-(2-propenyl)-benzene
6	11.06	Acetophenone
7	15.88	α-Methyl-benzenemethanol
8	18.89	Phenylethyl alcohol
9	19.01	Butylated hydroxytoluene
10	21.89	Diphenylmethane
11	22.04	Phenol
12	24.12	1,1-(1,2-Dimethyl-1,2-ethanediyl)bis-benzene
13	27.28	1,4-Benzenediol-2,5-bis-(1,1-dimethylethyl)
14	28.57	1,1'-(1-Butene-1,3-diyl)dibenzene
15	28.82	1,3-Diphenylpropane
16	29.29	(E)-But-1-ene-1,3-diyldibenzene
17	29.56	Unidentified compound
18	30.74	1-Phenyl-2-(2-vinylphenyl)ethanone
19	31.07	Dihydro-5H-dibenzo cycloheptene
20	32.01	3-Phenethylbenzoic acid
21	33.14	2-Methyl-9,10-dihydroanthracene
22	33.15	Phenethoxybenzene (PEB)
23	33.34	1,2,3,4-Tetrahydro-1-1-phenyl napthalene
24	33.72	3-Phenyl-2H-chromene
25	34.16	Unidentified compound
26	34.86	1,2-Diphenylcyclopropane
27	34.98	1,1'-(3-methyl-1-propene-1,3-diyl)bis benzene
28	35.67	1,1'-(1,2-dimethyl-1,2-ethenediyl)bis(E)benzene
29	36.76	4-Phenyl-1,2-dihydronaphthalene
30	36.99	1,1'-(1-butene-1,4-diyl)bis(Z)benzene
31	40.61	1-Phenyl-napthalene
32	44.50	9-(2-Propenyl)-anthracene
33	46.41	2-Phenyl-naphthalene
34	46.82	2-(1-Phenylethyl)-phenol

hydrolysis of benzyl phenyl ether (BPE) in water and several metal carbonate bases. It was reported that with increasing reaction severity (increased reaction temperature and reaction time), there was an increase in the degree of secondary reactions of the primary products (phenol and benzyl alcohol), resulting in the production of HMWM. The authors were surprised to observe that upon exposing a 5 wt% aqueous solution of BPE to a temperature of 300 °C for 1 h, that more than 20% of the material was converted to compounds too large to be detected by GC-MS. On this basis of the work of Roberts and co-workers, a proportion of the phenol generated in the present studies would have been involved in secondary reactions producing HMWM.

The oil phase samples obtained when a reaction temperature of 300 °C and 350 °C was applied, have a cumulative composition of styrene, phenol and residual PEB of only around 50% (based on GC-MS analysis, see Table 1). It appeared likely that the oil phase samples contained a significant proportion of material too large and non-volatile to be observed *via* GC-MS. The oil phase samples were analysed *via* SEC in order to determine the relative amount of material present that was likely not to have been detected *via* GC-MS. **3.1.1 High molecular weight material (HMWM).** The molecular weight distribution of the oil samples was determined by SEC. The intention was to identify the prevalence of any aromatic oligomers and larger polymeric material which may have been formed in the HTL of PEB.

In addition to styrene, phenol and PEB, several polystyrene standards (PSS) were also analysed in an attempt to calibrate various elution periods to approximate molecular weight ranges. It is important to bear in mind that SEC does not provide a true measurement of molecular weight. The results are determined by the hydrodynamic volume of the eluted species, which does not necessarily correlate with molecular weight but is useful for comparative analysis.

The general profile of the SEC chromatograms obtained through analysis of the organic phase samples is shown in Fig. 5. This figure is divided into peaks observed as a result of those species of hydrodynamic volume less than or equal to PEB, and those larger than PEB. The first peak (from right to left), is caused by styrene, residual solvents and other small compounds, the second is due to phenol and the third by PEB (and any similar sized compounds present at low concentration). *Via* the analysis of the polystyrene standards, the maximum molecular weight material present in the organic phase samples is approximately 5000 g mol⁻¹. This indicates that the HTL reaction produces not only small aromatic oligomers, but also significant amounts of large chain polymeric materials.

In order to determine the influence of reaction temperature on the amount of HMWM produced, the SEC chromatograms of each of the organic phase samples were compared. This involved integrating the plots and determining the relative percentage of area in each region relating to materials of hydrodynamic volume greater than PEB. The results of this analysis are presented graphically in Fig. 6.

The data indicates that for a reaction temperature of $250 \,^{\circ}\text{C}$ very little of the organic phase produced has a hydrodynamic volume greater than that of PEB. This is not surprising, as the vast majority of the PEB sample is not actually broken down at this reaction temperature. When the temperature is increased to 300 °C, the percentage of higher molecular weight material increases to approximately 33% irrespective of the starting PEB concentration. Surprisingly, when the reaction temperature is further increased to 350 °C the amount of HMWM reduces. Given that this is an increase in reaction severity, it is expected that this value would increase.¹⁸

This observation can be explained by reviewing the GC-MS chromatograms of the oil phase and styrene test samples produced at 300 $^{\circ}$ C and 350 $^{\circ}$ C. Numerous products were observed in the chromatograms of the 350 $^{\circ}$ C tests that were not present at 300 $^{\circ}$ C. What appears to be causing this result is that at 350 $^{\circ}$ C the entirety of the styrene produced not only undergoes polymerisation, but is then subsequently thermally degraded to smaller volatile species. At 300 $^{\circ}$ C a portion of the styrene is polymerised, but this material does not appear to then experience thermal degradation. This observation correlates with that previously reported in the literature, in that



Fig. 5 General appearance of the SEC chromatograms of oil phase samples obtained via HTL of PEB.



Fig. 6 Percentage of HMWM in PEB HTL oil phase samples (based on integration of respective SEC chromatograms) for reactions performed at 250 °C, 300 °C and 350 °C (120 min reaction time and 5 wt% NaOH solvent).

polystyrene begins to experience significant thermal degradation at approximately 350 $^{\circ}\mathrm{C.^{27}}$

3.1.2 Reaction pathways. In their recent publication, Eom et al.25 proposed reaction mechanisms for the hydrolysis of PEB to phenol and styrene, both in the presence and absence of Na_2CO_3 (Fig. 7). It is the opinion of the authors of the present work that the mechanisms suggested could be viewed as an unlikely explanation for the results obtained. Each of the mechanisms described involves the coordination of the sodium cation with the oxygen atom of PEB. Sodium is a highly ionic species and as such is considered incapable of coordinating in this manner. Furthermore, these species have not previously been shown to exist in free solution. They are observed in the electrospray plasma of MS sources where droplet evaporation forces sodium ions to form such complexes. Softer metals like magnesium and transition metals such as iron and cobalt frequently exhibit this kind of behaviour, but not hard bases like sodium. It is likely that the reaction is actually much

simpler, since the most reactive species involved is the hydroxide ion, and is therefore most likely the attacking species (Fig. 8). The reaction produces styrene and the phenoxide ion (later acidified to phenol), which provides a driving force for the process due to the resonance stabilization this species experiences. As these hydrothermal conditions favour radical reactions, homolytic cleavage and hydrogen abstraction dominates. The proposed mechanism is catalytic and so would not require a mole of NaOH to produce a mole of the primary products as stated in standard organic chemistry text books.

The two major aryl dimer species observed in the GC-MS results can be explained mechanistically as the product of two styrene molecules. Two mechanisms have been proposed for dimerization of styrene: the Flory mechanism;28 and the Mayo mechanism.29 However, these relate to self-polymerisation under low temperatures. Under hydrothermal and radical conditions we propose that styrene is likely to dimerise in one of two ways (Fig. 9), the more stable of which being the formation of a head to tail linkage (H-T) with the tertiary radical. The second process involves the less stable primary radical and the formation of a tail to tail linkage (T-T). Both dimer species will exhibit cis/trans isomerism. Given that the reaction mechanisms described are competing, the relative proportion of each species produced will be highly dependent upon reaction kinetics and thermodynamics. These species (but-1-ene-1,3divldibenzene and but-1-ene-1,4-divldibenzene), would be likely to undergo cyclisation (Fig. 10) and produce their respective tetrahydrophenol naphthalene isomers (1,2,3,4tetrahydro-2-phenyl-napthalene and 1,2,3,4-tetrahydro-1phenyl-napthalene, respectively), both of which have been identified in the GC-MS chromatograms as the two most prevalent cyclic aryl dimers. Rather than terminate at the point of dimerization, these radical mechanisms could potentially propagate to form oligomers and solid polymeric materials. It is likely that this is a significant contributor to the HMWM produced in the HTL of PEB. It should be noted that these proposed reaction pathways are tentative though based on sound organic chemistry knowledge, as high temperature





Fig. 7 Proposed reaction mechanisms of PEB pathways in the presence and absence of Na₂CO₃.²⁵



Fig. 8 Probable mechanism proposed for the base-catalysed hydrolysis of PEB.

electron paramagnetic resonance spectroscopy and isotopic labelling will be required to confirm the depolymerisation and repolymerisation processes.

3.2 Influence of NaOH catalyst concentration

Given that PEB was found to remain predominantly intact when exposed to a reaction temperature of 250 °C, this temperature was concluded to be insufficient for further experimentation. Both 350 °C and 300 °C were effective at converting the various concentrations of PEB material within 120 min of reaction time. However, at 350 °C the styrene was completely consumed and converted to HMWM, which then underwent partial thermal degradation. At 300 °C the styrene product did experience a reduction in yield due to self-polymerisation, however this was significantly less pronounced than when reacted at 350 °C. As a result all further experiments were conducted at 300 °C. A second series of HTL experiments were performed for 120 min at 300 °C, utilising a NaOH solution of concentration 0.0-5.0 wt%, as solvent. These tests were performed in an attempt to determine the influence of NaOH concentration on product selectivity. Based on the quantitative GC-MS analysis of the oil phase obtained in each experiment, the relative yields of phenol, styrene and residual PEB were determined and are presented in Table 3. The GC-MS chromatograms also showed the same minor compounds were produced for each of the different NaOH catalyst concentrations tested.

With the addition of only 0.25 wt% NaOH to the reaction solvent, the PEB is completely consumed. The phenol yield tends to experience a slight increase with increasing NaOH concentration above 0.25 wt%, however the styrene yield experiences a positive influence. The most significant of these occurs at a PEB concentration of 2.4 wt%, where the styrene yield increased from 0.0 to 21.0%, for the 0.25 and 1.0 wt% NaOH tests, respectively.



Fig. 9 Probable mechanisms for the production of styrene dimers via radical polymerisation.



Fig. 10 Mechanisms for the cyclisation of styrene dimers.

Table 3	Styrene, phenol & residual PEB yields for PEB HTL experiments of varying NaOH solvent and PEB concentration (120 min reaction time &
300 °C	C reaction temperature) ^{a}

NaOH conc. (wt%)	PEB conc. (wt%)	Styrene yield (wt% of PEB mass)	Phenol yield (wt% of PEB mass)	Residual PEB (wt% of PEB mass)	Yield of styrene, phenol & PEB (wt% of PEB mass)	Oil phase accounted for by styrene, phenol & PEB (wt%)
0.00	2.4	13	13	98.6	101.2	74.0
	4.7	1.3	1.8	92.6	95.7	80.7
	6.8	1.4	1.8	87.3	90.5	79.7
	9.0	0.5	1.7	92.5	94.7	83.4
0.25	2.4	0.0	32.4	0.0	32.4	58.5
	4.7	1.7	36.3	0.0	38.0	52.9
	6.8	2.2	36.7	0.0	38.9	56.1
	9.0	3.5	38.4	0.0	41.9	50.5
1.00	2.4	21.0	42.1	0.0	63.1	39.8
	4.7	15.7	50.2	0.0	65.9	39.1
	6.8	8.8	35.5	0.0	44.3	38.7
	9.0	9.6	41.4	0.0	51.0	41.0
5.00 ^{<i>b</i>}	2.4	13.4	41.9	0.0	55.3	43.6
	4.7	9.6	48.3	0.0	57.9	33.4
	6.8	10.3	40.9	6.5	57.7	43.5
	9.0	7.9	28.7	4.0	40.6	34.3
^a Associated e	rror range of \pm	=4%. ^{<i>b</i>} Data previously r	eported in Table 1.			

It is clear from these data that PEB does not experience significant degradation when reacted in water (no catalyst) at 300 $^\circ$ C for 120 min. Further increasing the reaction temperature

to 350 °C is unlikely to have a highly significant influence on the reaction rate observed, given that 300 °C is already in excess of the 280 °C β -O-4 degradation temperature.²¹⁻²³ A second test was

performed, this time increasing the reaction time to 10 h. Two PEB concentrations were trialled, 2.4 and 4.7 wt%, and the amounts of PEB remaining were 84 and 85%, respectively. Both tests yielded approximately 1 wt% styrene and 7 wt% phenol. The conversion of PEB with no catalyst (~15%) is slightly lower than the ~30% conversion achieved under hydrogen atmosphere at 290 °C and 10 h reaction.²⁶ This confirms that radical mechanisms are involved in PEB conversion as the hydrogen will quench radicals and stop them from reforming into PEB.

3.2.1 High molecular weight material (HMWM). The SEC chromatograms of each of the organic phase samples were obtained and the amount of HMWM for each determined. These data were grouped so as to elucidate any influence of NaOH catalyst concentration on the amount of HMWM produced (Fig. 11). The results indicate that the amount of HMWM produced was lowest when utilising a 1 wt% NaOH solution and a PEB concentration of 2.4 wt%. A PEB concentration of 4.7 wt% also produced a significantly lower amount of HMWM at this catalyst concentration (1 wt% NaOH). For the conditions tested, HMWM was not significantly influenced by the concentration of NaOH catalyst solution.

What is most surprising about these data is that a NaOH concentration of 0.25 wt% did not produce a significantly greater amount of HMWM, as expected. Considering the significantly reduced yield of styrene obtained in these experiments it was expected that this material had undergone self-polymerisation to produce HMWM. As previous stated, phenol will also participate in the formation of these products.

3.2.2 Selected NaOH concentration. The results of this area of work are inconclusive in determining which NaOH concentration is most effective in producing monomeric products from PEB. What is clear however is that NaOH is very effective at catalysing the degradation of PEB in solution at 300 $^{\circ}$ C. The lower limit of efficacy for NaOH concentration has not been determined; however it has been shown to be less than 0.25 wt%. An additional experiment was performed using 0.04 wt% (0.001 M) NaOH solution, however the degree of PEB



Fig. 11 Percentage of HMWM in PEB HTL oil phase samples (based on integration of respective SEC chromatograms) for reactions performed using 0.25, 1 and 5 wt% NaOH (120 min reaction time & 300 °C reaction temperature).

degradation achieved was comparable to that of water, indicating that the catalytic threshold is between 0.04 and 0.25 wt%.

The NaOH concentration utilised in the remainder of this study is 5 wt%. This value has been selected due to the fact that it is similar to the previously reported concentration of NaOH in black liquor, produced *via* the NaOH pulping process.²⁴

3.3 Influence of PEB concentration & reaction time

A final series of HTL experiments were performed at 300 °C, utilising a 5 wt% NaOH catalyst solution and reaction times of 30, 60 or 90 min and the results are presented in Table 4. For all experiments performed in water, the PEB concentration had no significant effect on its conversion rate (see Table 3). It appears therefore that the thermal degradation of PEB in water is a zero order reaction. It is likely however that the rate constant for this non-catalysed degradation causes the reaction to proceed so slowly that the rate order cannot be determined over the time period tested. PEB concentration probably does influence the reaction rate, however it may require a reaction time of several days to properly observe this influence. In a study on the similar diaryl ether (BPE) it was determined that this compound degrades much faster in water than PEB, and that the reaction is first order with regards to BPE concentration.³⁰

For the experiments which utilised NaOH as a catalyst, both the reaction time and the starting concentration of PEB had a significant influence on the percentage of material left unconverted. Upon analysing the interrelationship of these three factors, it is apparent that the NaOH catalysed reaction is pseudo-first order.

Over the range of experimental conditions tested, the maximum yield of primary products (phenol and styrene), was obtained at both the lowest concentration of PEB (2.4 wt%) and the shortest reaction time (60 min). Increasing reaction time above 60 min did not generally increase the yield of phenol, and tended to negatively influence the yield of styrene. This is despite the fact that a significant quantity of PEB often remained after 60 min (up to 34 wt%). When the reaction time was increased the cumulative quantity of styrene, PEB and phenol in the organic phase dropped significantly. This effect is explained by a coinciding increase in the amount of polymeric material observed in the oil, most likely caused by the self-polymerisation of styrene.

3.3.1 High molecular weight material (HMWM). The SEC chromatograms of each of the organic phase samples were obtained and compared. On analysis of these data several trends are evident. Firstly (and as predicted), for each different PEB concentration analysed, there is an increase in the production of HMWM with increasing reaction time.

The data also suggests that the initial concentration of PEB in the reactant mixture does not influence the production of higher molecular weight material for equal reaction times. The proportion of such material produced appears to be equal across each of the four PEB loading concentrations, for each distinct reaction time tested. The only time when this is not the case is for experiments where the combination of PEB and reaction time results in little of the PEB material being **Table 4** Styrene, phenol & residual PEB yields for PEB HTL experiments of varying reaction time and PEB concentration (5 wt% NaOH solvent & 300 °C reaction temperature)^{*a*}

Reaction time (min)	PEB conc. (wt%)	Styrene yield (wt% of PEB mass)	Phenol yield (wt% of PEB mass)	Residual PEB (wt% of PEB mass)	Yield of styrene, phenol & PEB (wt% of PEB mass)	Oil phase accounted for by styrene, phenol & PEB (wt%)
30	2.4	1.1	33.4	0.0	34.5	69.3
	4.7	5.8	28.3	14.0	48.1	71.5
	6.8	8.3	27.0	18.6	53.9	70.4
	9.0	8.0	15.0	49.0	72.1	85.3
60	2.4	18.6	55.3	0.0	73.8	69.4
	4.7	18.2	44.0	5.6	67.8	67.1
	6.8	20.9	38.3	22.3	81.6	73.4
	9.0	17.4	30.1	33.8	81.3	79.1
90	2.4	10.3	29.2	0.2	39.7	34.3
	4.7	13.3	43.3	0.9	57.5	54.4
	6.8	10.5	25.6	11.6	47.7	58.4
	9.0	10.9	28.5	16.4	55.7	52.4
120 ^b	2.4	13.4	41.9	0.0	55.3	43.6
	4.7	9.6	48.3	0.0	57.9	33.4
	6.8	10.3	40.9	6.5	57.7	43.5
	9.0	7.9	28.7	4.0	40.6	34.3

converted (such as when a 9.0 wt% PEB solution was reacted for 30 min).

3.4 Analysis of aqueous phase

The aqueous phase samples from these experiments, as well as standard solutions of PEB, phenol, styrene and diethyl ether were analysed *via* HPLC. The intention of this work was to determine the identity and prevalence of any observable species which remained in the aqueous phase after organic extraction. It was determined that the immiscibility of styrene and PEB in water prevented the retention of any detectable quantity of these materials. Phenol and diethyl ether were clearly detected in the samples and the quantity of phenol present was determined through the analysis of calibration standards. The results indicated that the aqueous phase samples contain between 0 and 3 wt% of the initial mass of PEB detected.

In addition to phenol and diethyl ether, two unidentified peaks were observed. It was determined in the GC-MS analysis of the organic phase samples that the aromatic alcohols 2-(1phenylethyl)-phenol and phenylethyl alcohol were always present to some degree. It is likely that one of these chemical species is responsible for one of the unknown HPLC chromatogram peaks. The second peak resembles a solvent peak, in that it is intense and broad in nature and eluted early in the run. This peak was only present for those HTL experiments where significant breakdown of the PEB occurred (*i.e.* not for those experiments performed in water). Given the unexpected position and shape of this peak it is possible that it is caused by small quantities of polymeric material in solution.

3.5 Analysis of solid and gaseous phases

The solid phase of the reactant mixture was obtained upon filtering the aqueous phase. This material was found to be insoluble in all solvents tested (including; diethyl ether, tetrahydrofuran, acetone and hexane) and is highly likely to be comprised of polymeric solids, as has been reported previously.²⁵ Due to the very low density and quantity of this material produced (generally <1 mg), the experimental error involved made it difficult to accurately quantify the yield. It is approximated that up to 4 wt% was produced with NaOH catalyst, and a negligible amount for the control (water) tests.

4. Conclusions

To limit the proportion of HMWM formed (without the use of capping agents) in lignin depolymerisation, the ratio of feed to catalyst concentration as well as reaction time (preferably 1 h) must be taken into consideration. Solvent density and ionic strength should also be considered as these aspects will also influence the reaction mechanism. A reaction temperature around 300 $^{\circ}$ C gives high product yield, and reduces the multitude of side products formed. The information obtained from this study will be used in the investigation of the conversion of black liquor to chemicals.

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