

## **Kraft lignin depolymerisation in sub- and supercritical water using ultrafast continuous reactors. Optimization and Reaction Kinetics.**

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### **Abstract.**

Kraft lignin was rapidly depolymerised in a continuous reactor using sub- and supercritical water. The reaction yielded an aromatic oil rich in high value aromatic monomers such as guaiacol, vanillin, acetovanillone and homovanillic acid. Different temperatures between 300 and 400°C and reaction times from 60 ms were studied. An increment in reaction time at every temperature studied promoted secondary reactions of repolymerisation of the lignin products. Those undesired reactions were more relevant as

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### **List of abbreviations:**

SEMR: Sudden Expansion Micro Reactor

SF: Solid Fraction

LO: Light Oil

AR: Aqueous Residue

temperature increased. An optimal temperature of 386 °C at a reaction time of 170 ms was found, with a maximum yield in phenolic compounds obtained. At those conditions, a bio-oil containing low molecular weight compounds was obtained with a yield of 44.6%. A selectivity to the four cited monomers of 9.9% was achieved, with little formation of solid residue (3.5%). A simple kinetic model was proposed to describe the yield for the different fractions and fitted to experimental data.

## 1. Introduction

Lignin is an aromatic biopolymer that constitutes 25-35 % of woody biomass[1]. It is composed by randomly connected monolignols (sinapyl, coniferyl and p-coumaryl alcohols) with varying proportions. Lignin is a low-value substance generated mainly in pulp and paper processes and more recently in biorefineries. In most cases, it is mostly consumed as low-grade fuel in the same industry where it is produced[2]. Its low cost and wide availability is one of the main reasons why there is a growing interest in upgrading lignin by converting it into useful products or by depolymerisation to recover its constituent monomers. Nevertheless, lignin is the only renewable source of aromatic moieties.

Recently, many studies have been focused on the hydrothermal decomposition of lignin[3-10]. In those studies, high temperature pressurized water has proven to be effective on the depolymerisation of lignin to high value-added products (i.e. phenolic compounds). However, the main drawback is the high yields of hydrochar obtained due to repolymerisation reactions.

At conditions close to the critical point (22.1 MPa, 374°C), water can dissolve organic compounds thanks to its low dielectric constant. Moreover the high temperatures greatly increase reaction kinetics allowing intensified processes[11]. Additionally, the adjustable

properties of supercritical water allow controlling the performance of the reaction. Dielectric constant and ionic product of high-temperature water are key parameters that depend greatly on pressure and temperature. In this way, reactions in sub- and supercritical water (SCW) are dominated mainly by ionic or radical mechanisms respectively[12-15]. Ionic reactions are more favoured in the subcritical than in the supercritical region because of the higher dielectric constant. Also, higher concentration of  $H^+$  and  $OH^-$  ions from the water dissociation promote acid or basic-catalysed reactions. On the other hand, radical reactions favourably occur under supercritical conditions.

Depolymerisation of lignin under supercritical conditions occur mainly because of the cleavage of ether bonds from the abundant  $\beta$ -aryl ether ( $\beta$ -O-4) linkages in softwood lignin[16,17]. Faravelli et al.[18] reported that this is the weakest bond inside the lignin structure and it can be homolytically cleaved to initiate the radical reaction. However, although supercritical conditions enhance decomposition of lignin into monomers, rapid interaction of these highly reactive radicals to form higher molecular weight fragments occurs. It has been proposed that the low dielectric constant of SCW promotes the dissolution of lignin and the reaction of soluble lignin fragments with low molecular weight soluble compounds to form polymers and cross-linked phenolic fragments[19]. Also, repolymerisation reactions are promoted by increasing temperature[4]. This was also noticed in other study, where heavier products were formed during hydrothermal reactions leading to condensed compounds and, when high temperatures and/or long residence times were reached, to cross-linked phenolic fragments[20].

It was recently demonstrated in a previous work[3], that depolymerisation of lignin in supercritical water can be optimized by controlling reaction times in the order of milliseconds and adding NaOH as catalyst. At 386 °C and 240 ms the yield of aromatics is maximized and that of char is minimized. At 300 ms the yield of monoaromatics

reached 10.5 %. NaOH helps the depolymerisation while preventing monomer and oligomer condensation. According to this report, depolymerisation starts with a very rapid step of dehydration, where most of the aliphatic –OH moieties are lost followed by cleavage of ether and C-C bonds. Depolymerisation proceeds to the optimum point while at longer reaction times repolymerisation reactions take place. At the reaction times explored 0 – 500 ms the different stages of the process could be distinguished.

In this paper, we present a more detailed study about the stages of depolymerisation and repolymerisation of Kraft lignin in high-temperature water. Particularly the effect of temperature and catalyst addition on the reaction kinetics, exploring the range of sub- and supercritical conditions. The yield of the different fractions (aromatic oil and char) obtained is determined and the major monomeric compounds are quantified. A simple reaction model is proposed and the kinetic constants fitted to experimental data.

## **2. Experimental**

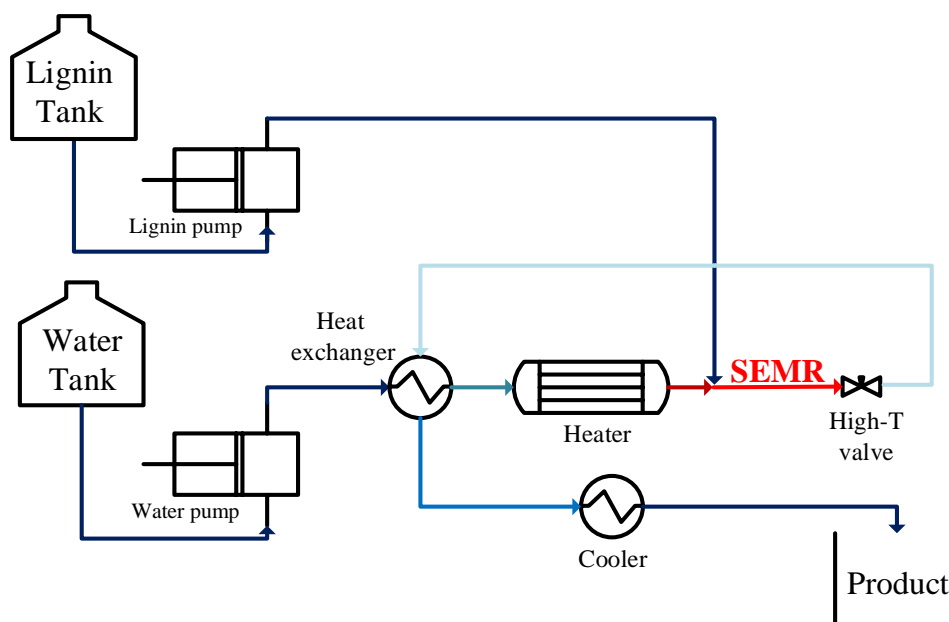
All the chemicals were purchased from Sigma-Aldrich. Kraft lignin with low sulphur content (4%) was used as starting material. Ethyl acetate (>99%) was employed to extract the lower molecular weight aromatic compounds from the liquid products. The calibration standards used in the GC-MS analysis were: guaiacol ( $\geq 99\%$ ), vanillin (99%), acetovanillone ( $\geq 98\%$ ), homovanillic acid ( $\geq 97\%$ ), as well as the internal standard 2-phenyl ethanol ( $\geq 99\%$ ).

Experimental equipment and procedures as well as analytical protocol were similar than those described in reference [3]. All the reactions were conducted in continuous fashion using the so-called Sudden Expansion Micro-Reactor (SEMR) developed in our laboratory[21,22] to achieve reaction times below 1 second. A simplified scheme of the plant is shown in Figure 1. Stainless steel pipes were used to build the micro-reactors. An

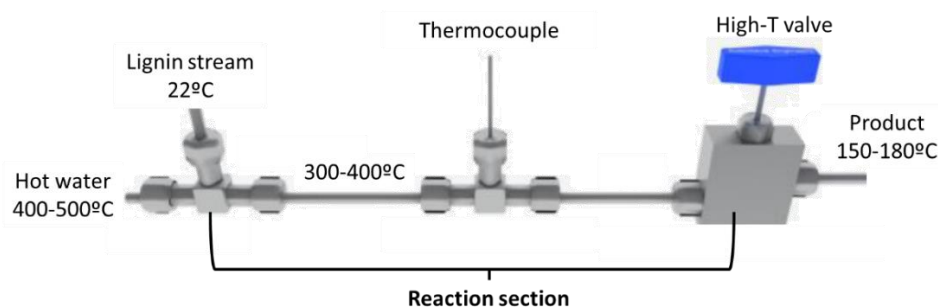
illustration of a micro-reactor can be seen in Figure 2. Heating was achieved by mixing the compressed room temperature lignin solution with a stream of hot pressurized water in a “T” junction so that the target temperature (300-400 °C) is instantaneously achieved. A thermocouple located in the middle point of the reactor monitored the reaction temperature. Instantaneous cooling to 150-180 °C was achieved by sudden decompression using a high-temperature valve, model Autoclave 30VRMM4812-HT, stopping rapidly the reaction. This cooling method is more effective than the conventional heat transfer methods because the temperature change is instantaneous (0.01-1 ms), allowing an accurate control of the reaction time and avoiding sample dilution. After the decompression, a jacket cooler was set up in order to further cool the sample down to room temperature.

The reactions were carried out at four different temperatures, two of them at subcritical conditions (300 and 370 ± 2 °C), while other two at supercritical conditions (386 and 400 ± 2 °C). The pressure in the reactor was fixed at 260 ± 8 bar for all the experiments. Reactions close to the critical point (370, 386 and 400 °C) were performed at reaction times below 360 ms. However, reactions at subcritical conditions away from the critical point of water (300 °C) were carried out in a broader range of reaction times, up to 4.6 s. The reaction time was controlled by changing the total flow and the reactor volume. At 300 °C, the minimum reaction time reached using the smallest reactor and the maximum flow rate was 170 ms, because of the high density of water. The lignin concentration at the inlet of the reactor was 1000 ppm (0.1% w/w) in all experiments. This low initial concentration was chosen to avoid blockages at the decompression valve. The lignin solution was fed to the reactor by a Lewa EK1 pump at a flow rates within 1.6-2.5 L·h<sup>-1</sup>, and water was pumped by a Milton Roy pump at flow rate within 3.5-5.1 L·h<sup>-1</sup>. Micro-reactors were built with reaction volumes between 0.5 and 12.3 cm<sup>3</sup>. The short time

needed to start and stop the reaction, along with the small reactor volume, allowed the micro-reactor to be considered as isothermal, having a constant and homogenous reaction rate through the whole reactor. A summary of all the experiments performed in this study is presented in Table S2



**Figure 1.** Simplified schema of the pilot plant used for depolymerising lignin using sub- and supercritical water.



**Figure 2.** Sudden-expansion micro-reactor (SEMR). Instantaneous heating of lignin solution is achieved by mixing it with hot water. Instantaneous cooling is achieved by sudden decompression using a high-temperature valve.

Once the reaction finished, the reaction mixture was fractionated following a procedure similar to that described in references [3,9]. Firstly, the solid was separated from the liquid by centrifugation and the liquid was recovered by carefully pipetting it. Then, the wet solid was washed with milli-Q water and dried in an oven at 45°C, obtaining the *solid fraction* (SF). The liquid fraction was subjected to a liquid-liquid extraction process with ethyl acetate (1:2 vol/vol). The solvent was evaporated from the aqueous extract using a rotary evaporator and the extract was then dried in a vacuum oven at 40°C yielding a fraction, weighed and labelled as *light oil* (LO). The remaining water was removed from the aqueous raffinate in a freeze-dryer and labelled as *aqueous residue* (AR). All the fractions were carefully weighed. The yield of a fraction, %  $Y_i$  is calculated as:

$$\%Y_i = \frac{C_i}{C_{Lg}} \times 100 \quad (1)$$

Where  $C_i$  is the concentration ( $\text{g L}^{-1}$ ) of the fraction ‘ $i$ ’ in the product mixture and  $C_{Lg}$  the corresponding concentration of feed lignin taking dilution into account.

Phenolic monomers contained in the *aromatic oil* were detected and quantified by a gas chromatograph equipped with a capillary column HP-5ms, 30 m x 0.25 mm x 0.25  $\mu\text{m}$  (Agilent Technologies, USA). Data of the chromatographic separations were acquired using a quadrupole mass spectrometer detector (5977A-Agilent Technologies, USA). Validation of compound identification was carried out by comparison of their MS spectra and their retention times with standards. Quantification was carried out employing the internal standard method[23].

Analogously, the yield in the monomer ‘ $x$ ’, % $Y_x$ , present in the product mixture, is referred to the total amount of lignin and calculated as equation 2. It was assumed that all the monomers are concentrated in the aromatic oil fraction:

$$\%Y_x = \frac{C_x}{C_{Lg}} \times 100 = \frac{\%X_x^{oil} C_{oil}}{C_{Lg}} = \frac{\%X_x^{oil} \cdot \%Y_{oil}}{100} \quad (2)$$

Where  $C_x$  is the concentration of the monomer 'x' in the product mixture and  $C_{oil}$  is the concentration of the aromatic oil in the product mixture ( $\text{g} \cdot \text{L}^{-1}$ ).  $\%X_x^{oil}$  ( $\text{g} \cdot \text{g}^{-1}$ ) is the mass fraction (or selectivity) of the monomer 'x' in the aromatic oil.

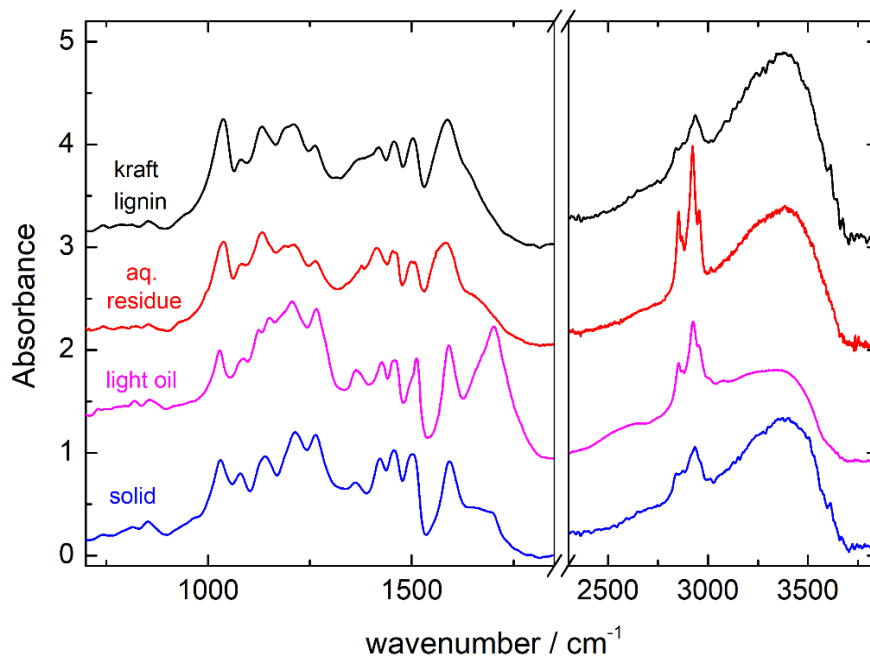
The different fractions obtained were analysed by FT-IR with a Bruker Tensor 27 equipment. Further details of the analytical procedures can be found in reference [3].

### 3. Results ad discussion

#### 3.1. Characterization of the fractions

Fractionation according to the solubility in water and ethyl acetate has been used in other reports and the nature of the different fractions defined [3,9,10]. In literature, aromatic oil fraction contains low molecular fragments of lignin as well as most of the monoaromatics produced. Thus LO was considered as a desired crude depolymerisation product. SF is composed of molecules of high molecular weight which have lost enough functionality (-OH moieties) to lose its solubility in water. Components of the solid fractions are usually undesired repolymerisation products obtained at the lasts stages of the reaction[9] but in some cases they are modified forms of the starting lignin obtained at very early stages.[3] Finally AR has been proposed to contain lignin or partially depolymerised lignin.





**Figure 3.** FTIR spectra for kraft lignin and the different fractions obtained in this work.

The identity of the fractions has been confirmed by FT-IR as it provides information about chemical functionalities present. Figure 3 shows the spectra of Kraft lignin, and the three fractions obtained after the fractionation. As can be observed, the FT-IR spectra of lignin and AR were very similar, which indicated that they have a similar structure and functional group types. Thus it is possible to confirm that AR fraction is practically unconverted or partially depolymerised soluble lignin as stated in literature [9]. Small differences could only be observed in the 3000-2800 cm<sup>-1</sup> region corresponding to the stretching of C-H bonds typical of aliphatic hydrocarbons, which is more intense in the case of the aqueous fraction. It has also been observed that this fraction tends to concentrate aliphatic moieties.

On the other hand, the spectra for solid fraction presents essential differences such as in the bands 1710-1665 cm<sup>-1</sup>, typical of the bond C=O in aldehydes and ketones and the bands corresponding to C-O stretching in the region 1300-1000 cm<sup>-1</sup>, which indicates that

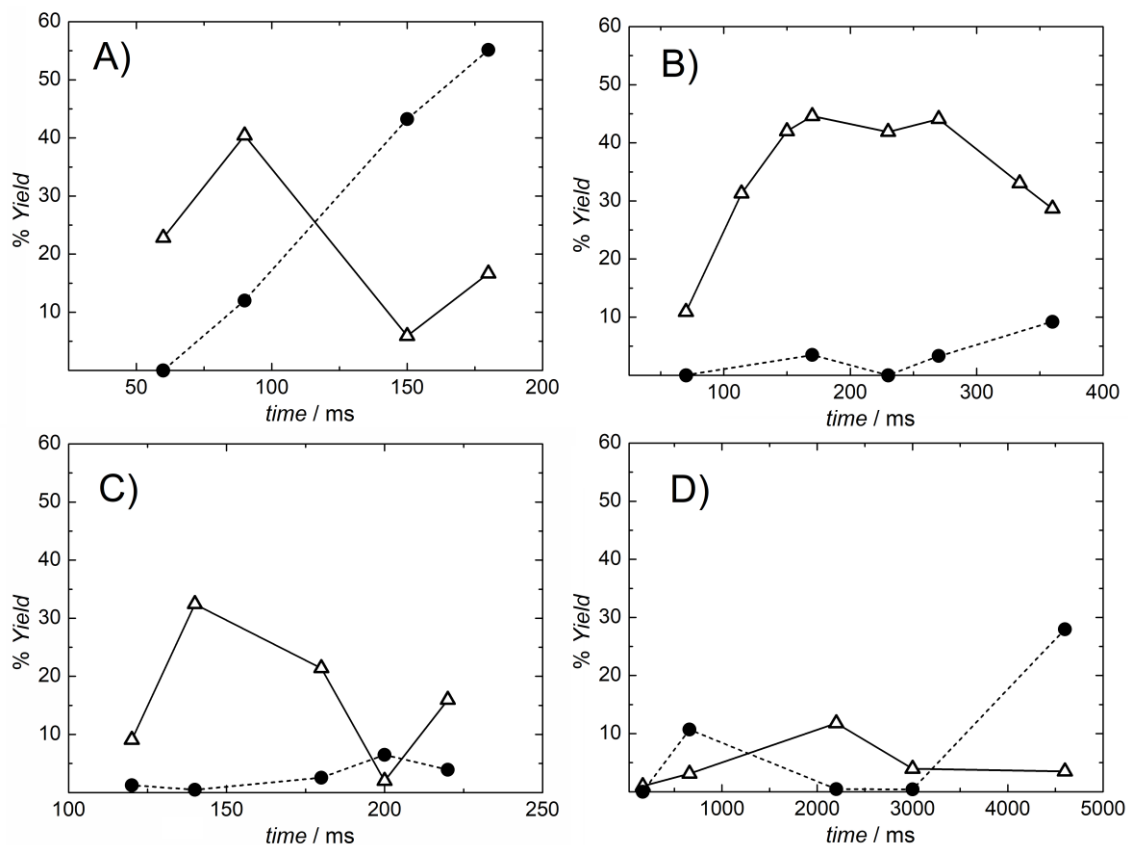
the structure of lignin has been altered mainly in the aliphatic C-O bonds, unlike the aromatic structure, which has changed very little because the region between 1400 and 1650  $\text{cm}^{-1}$  does not change significantly in any of the fractions. Some smaller differences can also be found in the regions 1400-1300  $\text{cm}^{-1}$  and 900-700  $\text{cm}^{-1}$  corresponding to the C-H bending typical of saturated and unsaturated hydrocarbons, respectively. The light oil seems to contain an even higher proportion of C=O groups than the solid and both solid and light oil fractions seem to have lost -OH moieties since the broad band within 3000 – 3500  $\text{cm}^{-1}$  reduced its relative intensity compared to the starting lignin. These results agree with the depolymerisation mechanisms proposed in previous reports [3,9]. The main feature of the reaction is the removal of aliphatic -OH from starting lignin and the increment of unsaturated moieties such as carbonyl and double bonds. Upon depolymerisation, smaller fragments constituting the light oil would become more soluble in water but with a chemical structure that make them preferentially soluble in ethyl acetate (a similar behaviour than the detected monomers such as vanillin, acetovanillone, guaiacol, etc, which are concentrated in the light oil). Moreover, it has been reported that the light oil has a molecular weight significantly lower than the rest of the fractions [3,9,10].

### **3.2. Effect of temperature and reaction time in the depolymerisation products.**

Yield of the main products (aromatic oil and solid fraction) obtained at different temperatures and reaction times is presented in Figure 4. Higher conversion of lignin to an aromatic oil containing low molecular weight phenolic compounds was observed under supercritical conditions (400 and 386 °C, Figures 4A and 4B) at low reaction times, reaching maxima in the aromatic oil yield of 40.4 and 44.6 % at 90 ms and 170 ms respectively at the conditions studied. At subcritical conditions close to the critical point of water (370 °C, Figure 4C), the reaction is also fast but the yield of aromatic oil is lower

(32. 4% at 140 ms). On the other hand, under subcritical conditions at a temperature far from the critical point (300 °C, Figure 4D), lignin depolymerised much slower and less efficiently, reaching a maximum oil yield of only 11.8% at much higher reaction times (2.2 s). Thus, at higher temperatures, lower reaction times are required for reaching higher yields as expected from the kinetic point of view. The fact that the behaviour of the reaction is so sensitive to temperature (Figures 4A-C) is likely due to the conditions are very close to the critical point (374 °C) and it is known that properties of substances, like expansion coefficient, diverge most around this point, thus, small changes in temperature lead to large changes in density and then to reaction performance.

In addition to the decomposition of lignin into soluble products, it was also observed that insoluble products were formed at all temperatures, but never in concentrations high enough to block the pipes at the conditions studied. In most of the cases, the maxima in aromatic oil appears at reaction times close to minima in solid products (except at 400 °C that the minima could not be confirmed at the timescale explored). This phenomena has been observed in the previous report using NaOH as catalyst[3]. Plots for solid products yield vs time suggest that a similar mechanism operates in the case of experiments without catalyst at every temperature. i.e. After the yield of aromatic oil has reached a maximum, it starts to decrease with reaction time at the same time as the yield of char increases, formed by repolymerisation reactions via radical coupling and/or via ionic reactions (condensation). The solid formation was more significant at higher temperatures. At 400°C the solid yield increased drastically with the reaction time. However, at 300°C higher reaction times of seconds were required to observe a minor formation of non-soluble products.



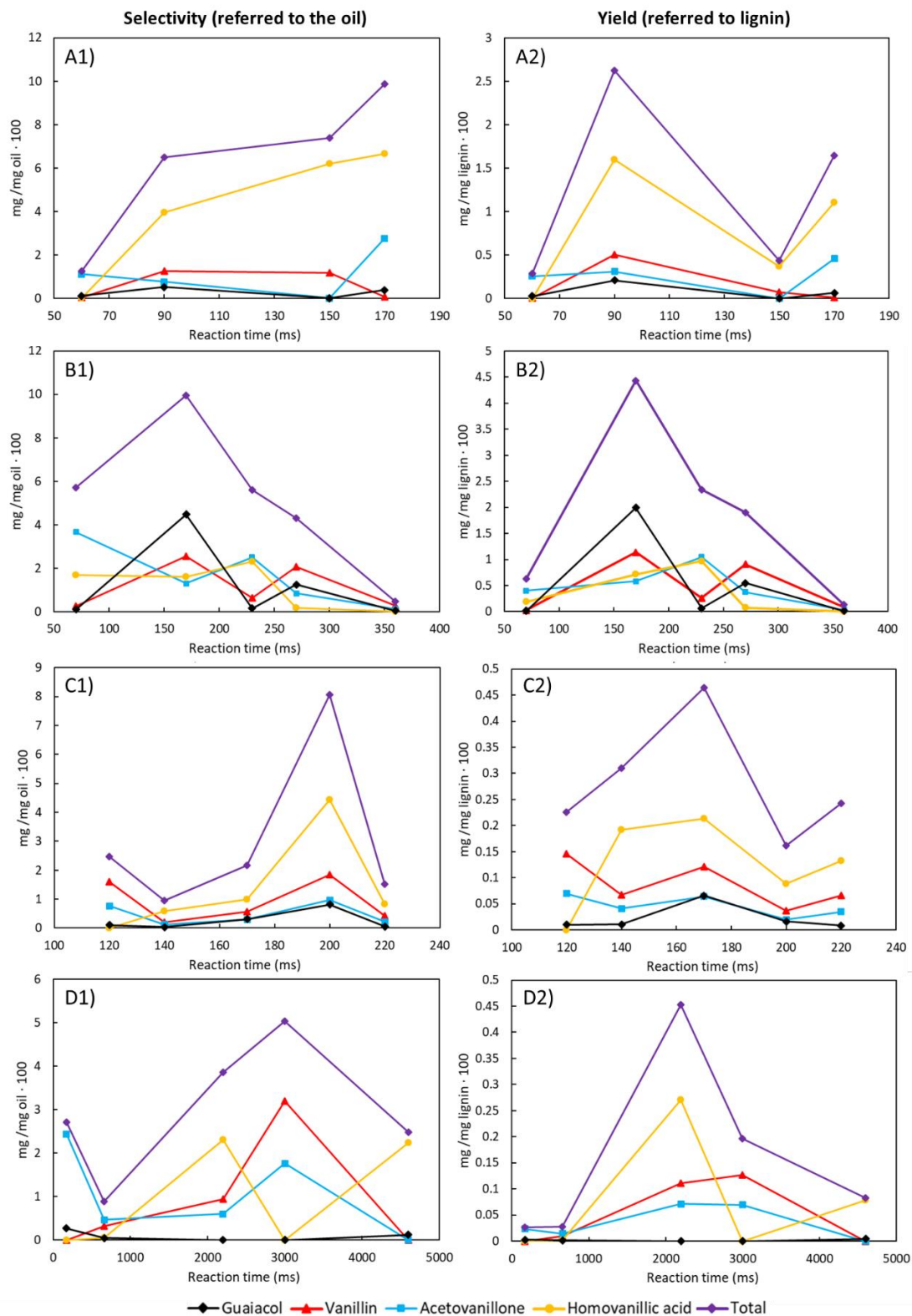
**Figure 4.** Yield of aromatic oil (continuous line) and solid fractions (dotted line) vs reaction time at A) 400 °C, B) 386°C, C) 370°C and D) 300°C. Fractionation yields calculated as in equation 1.

Mass balance closure is difficult to achieve in these experiments. Total Organic Carbon for some samples of the experiment at 386 °C with NaOH (Table S4) revealed a high variability (Total Carbon =  $98 \pm 7.5$  %). Out of this, about 4% was inorganic carbon from  $\text{CO}_2$  released by decarboxylation of lignin. Mass volatilized in form of other gases was not determined. For the experiments without NaOH, mass of aqueous residue obtained from freeze-drying was utilized for balance closure. The precision using this method was lower, an average mass closure balance of  $90 \pm 33$  % was obtained.

### 3.3. Yield and selectivity of monomers

During hydrothermal degradation, various aromatic monomers were formed. Table S3 and Figure S4 show the results of the qualitative examination of the aromatic oils using GC-MS, and a sample chromatogram. The major compounds identified in the aromatic oils were guaiacol, vanillin, acetovanillone and homovanillic acid; all of them are derived from coniferyl alcohol, which is the main monomer of softwood lignins. Other analytes were also detected in small amounts. Indeed, a total of 17 compounds have been identified, showing the complexity of the degradation pathway. In Kraft lignin, the amount of aliphatic –OH and the  $\beta$ -O-4 linkages is reduced because the Kraft pulping process promotes recondensation reactions[24,25] and the formation of Ar-Ar and Ar-O-Ar bonds, which are more resilient to cleave[26]. For this reason, the theoretical maximum yield of monomers may be lower than 100%. However, for this lignin, as the yield of vanillin and acetovanillone are significant there must be a certain proportion of linkages that can be cleaved by SCW.

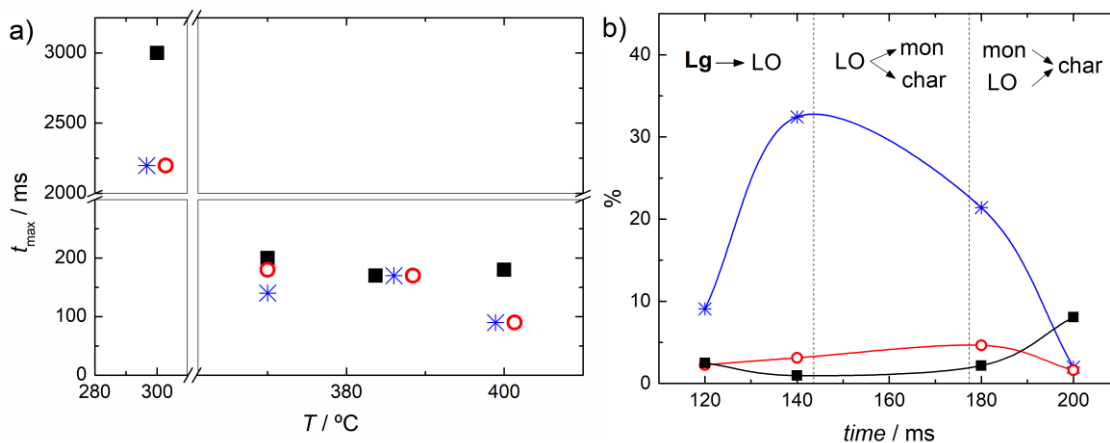
Figure 5 shows the selectivity of the major monomers vs time,  $\%X_x^{oil}$  defined as the mass fraction of the monomer in the aromatic oil. However, it was important for determining the optimal reaction time for each temperature to consider not only the selectivity, but also the yield of this fraction referred to the loaded lignin ( $\%Y_x$ , calculated with equation 2).



**Figure 5.** Composition (selectivity,  $\%X_x^{oil}$ ) of the aromatic oil (1) and yield of monomers,  $\%Y_x$  (2) calculated with equation 3 obtained at A) 400 °C, B) 386 °C, C) 370 °C and D) 300 °C.

At 386 °C maxima for both selectivity and yield appear at  $t = 170$  ms. The aromatic oil fraction was very selective, with a total composition in high value monomers of 10%. Moreover, the yield is also maximum reaching a total of 4.7% (2.2% to guaiacol, 1.1% to vanillin, 0.7% to homovanillic acid and 0.7% to acetovanillone).

At 400°C, the curve of the selectivity of monomers in the oil (Figure 5-A1) followed an increasing trend. However, the plot for the total yield present a maximum at  $t = 90$  ms. This trend suggests that soluble lignin fragments repolymerise preferentially than monomers. A similar behaviour is observed at other temperatures: Figure 6a shows the reaction time at which maxima in aromatic oil yield, monomer yield and monomer selectivity appear. In general, maxima in aromatic oil tends to appear first or together to the maxima in monomer yield and the maxima in selectivity appears at longer reaction times. This behaviour suggests that there are three types of mechanisms acting simultaneously but with different predominance at different stages of the reaction. Figure 6b compares the curves for oil, solid fraction and monomer yield and selectivity at different times for the reaction at 370 °C up to 200 ms. Three stages can be distinguished: 1) Lignin depolymerises into oligomers, forming the light oil. 2) Part of the oligomers keep splitting to monomers, but the rest start to repolymerise to char. 3) Both monomers and oligomers degrade to char but the latter react preferentially and as consequence the selectivity to monomers increase.



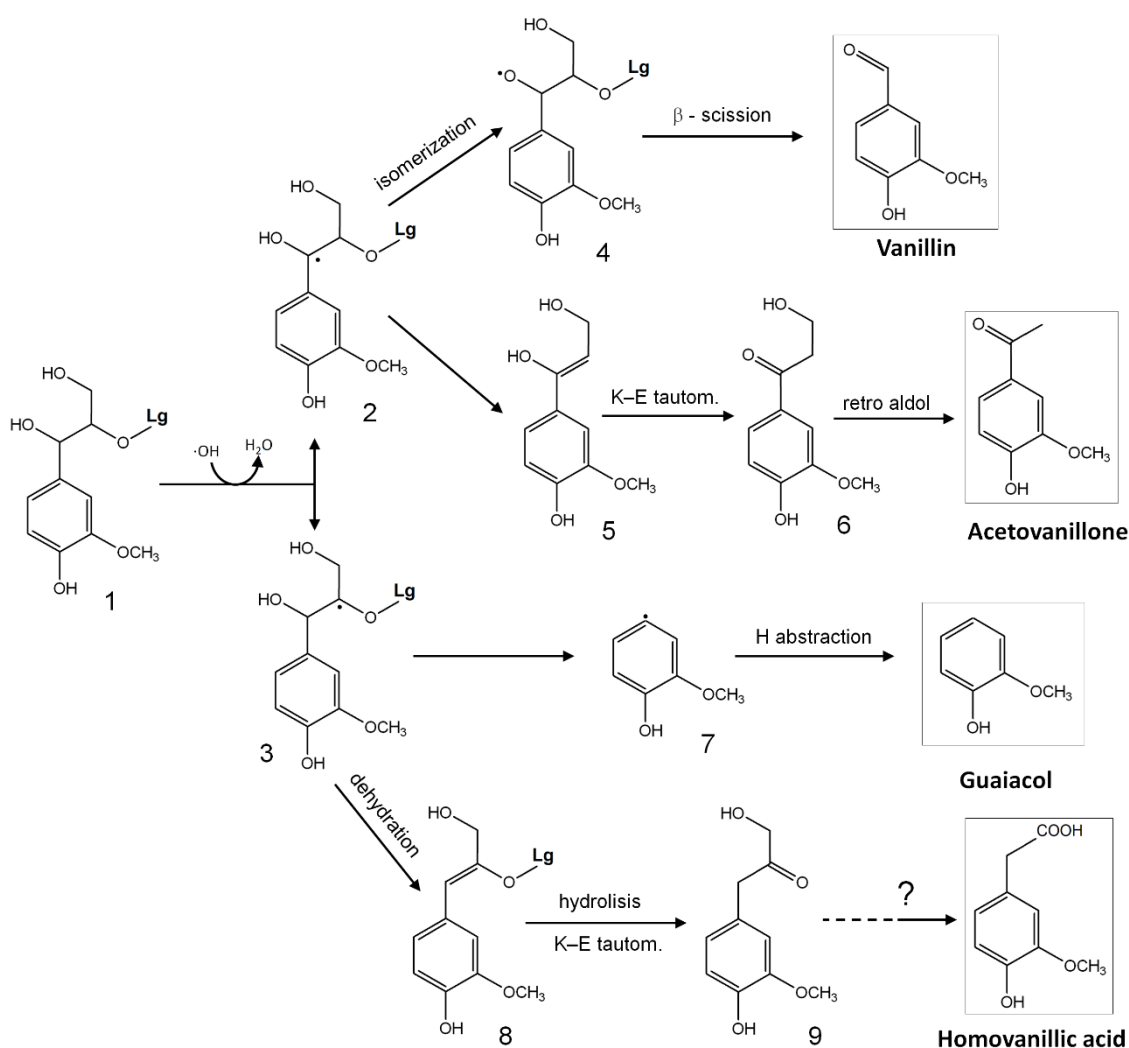
**Figure 6.** Behaviour for the different reaction trends for the depolymerisation of Kraft lignin. (\*): Light oil yield. (○): Monomer yield. (■): Monomer selectivity. a) Time at which the trend reached a maximum for different temperatures. b) Trends vs reaction time at 370 °C.

Regarding the yield of individual monomers, changing the reaction conditions from sub- to supercritical influenced the behaviour of lignin depolymerization. Vanillin, acetovanillone and homovanillic acid are produced at any temperature but, to a much lower extent at lower temperatures. However, formation of guaiacol is almost completely inhibited at 300 °C. These differences could be related to different mechanisms operating preferentially in media with different properties (radicalary Ar-C cleavage to form guaiacol) as discussed above.

The mechanisms of lignin depolymerisation in supercritical water are still open to debate. Some mechanisms based in the cleavage of  $\beta$ -O-4 bond in subcritical water have been proposed in literature, for example, via nucleophilic attack of an adjacent methoxy group[27] or heterolytically via a six-membered transition state[28]. Those mechanisms convert hydroxyl groups in position  $\alpha$  to carbonyl moieties. The monomers thus obtained are vanillin and acetovanillone from guaiacyl units and their counterpart syringaldehyde and acetosyringone from syringyl units. At supercritical conditions, however, radicalary



mechanisms are dominant and must also be considered [3,12,13]. In the present work, along with guaiacol and homovanillic acid, those  $\alpha$ -carbonyl monomers are also obtained and it is observed in FTIR that new C=O groups are formed on the structure of oil and char, likely from conversion of hydroxyl groups. Possible mechanisms for formation of these monomers from  $\beta$ -O-4 bonds via radicalary reactions can be proposed, analogously to mechanisms described upon treatment of glycerol[14], and also taking into account lignin pyrolysis mechanisms[29] (Figure 7).



**Figure 7.** Proposed radical mechanisms for the production of the major monomers from a  $\beta$ -O-4 linkage in kraft lignin by depolymerisation in SCW.

Monomers would be formed from a terminal structure such as that represented in 1. Then, by an H-metathesis step the radicalary reaction is propagated to form either 2 (more stable) or 3. By mechanisms of isomerization and  $\beta$ -scission, the  $C_{\alpha}$ - $C_{\beta}$  bond would be cleaved to form vanillin. The  $-OH$  in  $\alpha$  position would be converted into the carbonyl of vanillin. The route for acetovanillone would occur if from 2, the  $\beta$ -O bond is cleaved as proposed by Faravelli et al.[18] 5 will immediately proceed to a keto-enol tautomerization to form an analogous to acetovanillone substituted by a  $CH_2OH$ , this latter compound could suffer a rapid retro aldol reaction to form acetovanillone plus formaldehyde.

A structure with a radical in position  $\beta$  can be obtained by H-abstraction to give 3 or by homolytic cleavage of the ether bond (not represented). In any case, the reaction to 7 requires higher activation energy so it would be only possible at higher temperatures[18], which is consistent with the low amount of guaiacol obtained at 300 °C (Figure 5D)

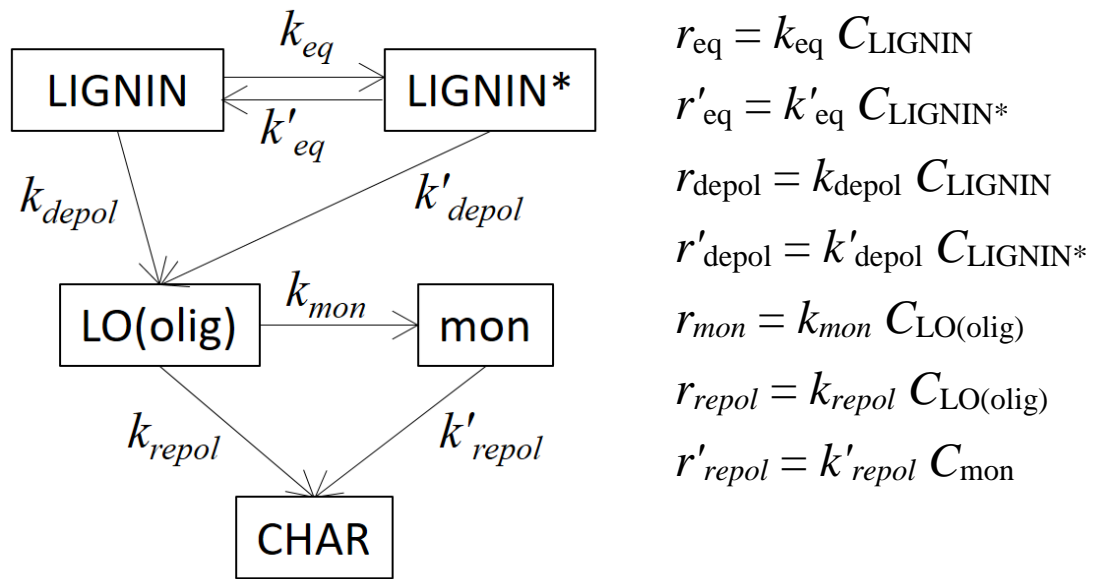
Acidic moieties have rarely been detected in lignin depolymerisation. Vanillic acid has been generated during oxidative cleavage of lignosulfonate but they rapidly decarboxylates to guaiacol [9]. Homovanillic acid has been detected in a previous report[3]. The fact is that formation of organic acids such as lactic or acetic acid is very common in upon hydrothermal treatment of organic compounds[30-32]. It would be plausible that an analogous guaiacyl-substituted (such as homovanillic acid) is synthesized by similar mechanisms. It has been proposed that lignin rapidly dehydrate in hydrothermal alkaline medium[3]. this dehydration could proceed via the intermediate 3 (thus competing with guaiacol). A further hydrolysis and keto-enol tautomerization would generate a  $\beta$ -ketone. This structure could rearrange to homovanillic acid but further studies would be necessary to confirm this hypothesis.

### 3.4. Globalized kinetic model

One of the main problems when proposing a kinetic model for lignin depolymerisation is the lack of knowledge of the mechanism. Mainly because the structure of most lignins is highly random and not fully determined. Moreover, in high-temperature water, reactions tend to be uncontrolled leading to a complex mixture of compounds.

A robust kinetic model, must be verified with a sufficient number of significant experimental observations, and it is obvious that the more complex the model is, the more data requires for its validation. In this work, it has been preferred to propose a simpler model based on the lumped parameter approach[33], Due to the complex structure of lignin and the variety of scissions that can happen during its depolymerisation, the mechanism proposed is not based in individual reactions between individual molecules but in groups of compounds with the same characteristics (corresponding to the fractions described in this work) that are transformed by similar kind of reactions. Also, they will be quantified in mass instead of in mol. This approach does not intend to describe all the individual reactions occurring but a set of globalized reactions. For this reason, it must rather be called *globalized kinetic model*, which is an approach that can be a good starting point to study this process for practical purposes.

This model can be derived from a lumped parameter [33] model taking into account the following approximations: a) the concentration of water can be considered constant; b) the empirical formula of the fractions do not change a lot upon reaction; c) the proportion of gas products formed is low and they do not react significantly with other products. The transformation/reactions taking place between fractions were chosen according to the observations previously reported. A scheme of the reaction pathway is shown in figure 8.



**Figure 8.** Simplified mechanism for Kraft lignin depolymerisation. **LIGNIN\*** is a non-soluble dehydrated form of lignin, **LO(olig)** is the fraction of light oil excluding monomers. **mon** are the amount of all the identified monomers and **CHAR** is the repolymerisation products. *C* is the concentration in mass for each fraction related to the total mass of lignin loaded.

The very first step of this reaction is a fast transformation of lignin into a dehydrated form of it, insoluble in water which would accumulate in the SF. This assumption has been done in basis of previous observations[3,18,34] . Subsequently, lignin is depolymerised into a mixture of lower molecular weight compounds, smaller enough to be soluble in water and ethyl acetate, thus forming part of LO. In the following step, this oligomeric mixture would further depolymerise to monomers. Finally, monomers and oligomers will degrade into a non-soluble char via repolymerisation reactions.

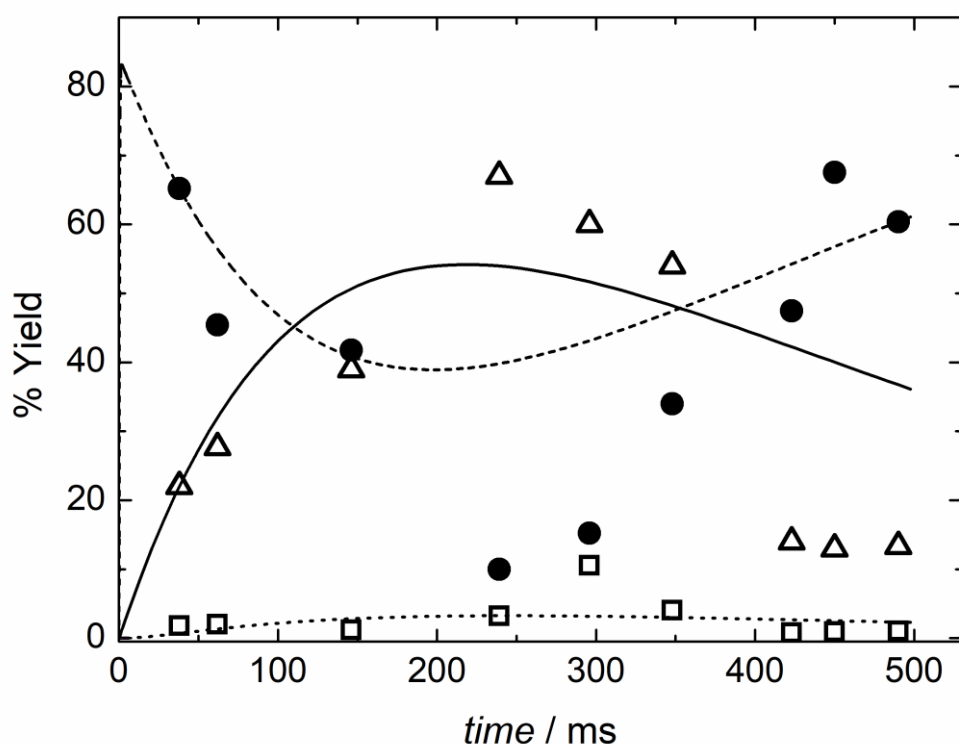
This globalized kinetic model is fitted to the experimental data reported, that is, the concentration in mass obtained, taking into account the following mass balance:

$$LO = LO(olig) + mon$$

Solid = LIGNIN\* + CHAR

The fitting was carried out by minimization of the absolute error between experimental and calculated yields, i.e. by minimization of the difference between experimental and calculated yield. Using the objective function  $OF = \sum | \% Y_{exp} - \% Y_{calc} |$ . The minimization was carried out using the 'fminsearch', function implemented on Matlab, which uses a simplex search method.

Data of this reaction at 386 °C using NaOH as catalyst[3] were also fitted using this model. The results are shown in Figure 9. As it can be appreciated, despite its simplicity, the model can reproduce satisfactorily the main features of the experimental set of data. That is the minimum in the solid fraction and the maximum in aromatic light oil monomers yield. We have calculated an average deviation of 78% between the experimental and calculated yields. Such relatively high differences are expectable, as the actual reaction mechanism is likely to be much more complex.



**Figure 9.** Yield for the different fractions from Kraft lignin ultra-fast depolymerisation at 386 °C using NaOH as catalyst (obtained from reference [3]) and fittings of the kinetic model in Figure 8. (—△—): LO. (---●---): SF. (···□···): mon.

This model was next fitted to the experimental data obtained in this work at the temperatures of 370 °C, 386 °C and 400 °C without any catalyst. Results are represented in Figure S5. As in Figure 9, the model can describe the model semi-quantitatively which is a good starting point for future research. It must be noted that this is a concept that has not been studied before and it can be useful if the fractions are intended to be used as a whole. More improvements are needed to the model, for example, consider a wider variety of compounds, the variation in composition of the fractions or gas products, however these improvements need to be backed by further experimental observations and new data, otherwise they would remain speculative.

Table 1 shows the fitted pseudo-kinetic constants for the mechanism represented in Figure 8. All the constants for the reaction without NaOH increase with temperature and they follow the Arrhenius' law (Table S5) suggesting that the mechanisms governing these reactions are the same within the studied range (370-400 °C). The significantly high values for most of the  $E_a/R$  values indicate a high dependence of the reaction kinetics with temperature. In this case, the model does not describe any minimum for the solid fraction. Since  $k'_{eq} \gg k_{eq}$ , the equilibrium is displaced towards the original form of lignin, unlike when NaOH is used as catalyst. The increment of solid fraction is faster at the highest temperatures, which is expected as repolymerisation is favoured by temperature[8,9].

The model, however cannot describe well the repolymerisation reactions. According to Table 1, they proceed mainly from monomeric species, since  $k'_{repol} \gg k_{repol}$ . Unlike what

is deduced from Figure 6. These inaccuracies may be because of the simplicity of the model, which is unable to describe all the features. For example, the condensed bonds in Kraft lignin that limit the theoretical maximum yield of monomers. It is also possible that repolymerisation starts occurring at earlier stages of the reaction, between lignin and reactive fragments, as demonstrated in acid-catalysed depolymerisation of lignin [34]

Table 1 also shows that for the reactions with NaOH, most of the kinetic constants associated to depolymerisation are significantly larger than in neutral medium, which is consistent with the catalytic activity of the former. However, repolymerisation reactions are also faster. NaOH also displaces the equilibrium  $\text{LIGNIN} \leftrightarrow \text{LIGNIN}^*$  to the right, as  $k'_{\text{eq}} < k_{\text{eq}}$  so the minimum in SF can be appreciated.

**Table 1.** Fitted pseudo-kinetic constants for the depolymerisation of lignin according the model in Figure 8.

	$k_{\text{eq}}$	$k'_{\text{eq}}$	$k_{\text{depol}}$	$k'_{\text{depol}}$	$k_{\text{mon}}$	$k_{\text{repol}}$	$k'_{\text{repol}}$
386 °C, NaOH	2430	229.7	107.3	10.0	3.312	0.1215	115.5
370 °C	0.0172	286	0.0100	7.41	0.236	$2.15 \times 10^{-8}$	46.5
386 °C	0.0473	349	2.63	20.9	0.461	$1.24 \times 10^{-6}$	72.1
400 °C	0.110	512	6.67	42.1	0.832	$1.98 \times 10^{-5}$	167.9

All constants are given in  $\text{s}^{-1}$

#### 4. Conclusions

The hydrothermal decomposition of kraft lignin was performed in sub- and supercritical water. This lignin was successfully depolymerised into a low-molecular-weight aromatic oil containing monomeric compounds such as guaiacol, vanillin, acetovanillone and

homovanillic acid. Optimal operating conditions were 386 °C and 170 ms. At this temperature and reaction time, a yield of aromatic oil yield of 44.6% was obtained, with a total of the four selected monomers of 9.9%, suppressing almost totally the solid formation. The solid fraction consisted of repolymerised products, reaction more favoured at higher temperatures and reaction times.

Results also suggest a sequential depolymerisation/repolymerisation mechanism in which lignin degrades into a light oil first and monomers after and these last two degrade to hydrochar by recondensation reactions. A simple kinetic mechanism is proposed, which can describe qualitatively the main features of the reaction.



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