



Hydrothermal liquefaction of lignin in near-critical water in a new batch reactor: Influence of phenol and temperature



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ABSTRACT

The hydrothermal conversion of Kraft lignin (6 wt.%) in the presence of K_2CO_3 (1.7 wt.%) was studied as a function of temperature ($T=280\text{--}350\text{ }^\circ\text{C}$) and phenol mass fraction ($w_{Ph}=0.0\text{--}9.7\text{ wt.}\%$). The process was carried out in a new batch reactor with injection of lignin slurry enabling fast heating of the biomass, effective control of reaction pressure, and withdrawal/quenching of the products. An aqueous phase and biocrude were obtained, both containing a broad spectrum of aromatic monomers and dimers. The former group consisted mostly of methoxybenzenes, guaiacols, catechols, and alkylphenols, while the latter included anisolic/phenolic dimers. For a given w_{Ph} (3.4 wt.%), the total yield of monomeric aromatics (Y_T) was maximized at $320\text{ }^\circ\text{C}$. At $T=300\text{ }^\circ\text{C}$ and without phenol, Y_T was low, whereas it increased steeply up to $w_{Ph}=6.5\text{ wt.}\%$.

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1. Introduction

Lignin is the second most common terrestrial biopolymer on Earth, and the most significant naturally occurring source of aromatics in nature. It accounts for 15–40% of the biomass (on a dry mass basis) and approx. 40% of its energy content [1–3]. The largest manufacturer of lignin is the pulp industry, with the Kraft process being the dominating technology. The amount of lignin extracted in the pulping process in the western hemisphere is estimated to be in the order of 50 million tons per year. Currently, more than 98% of the extracted lignin is utilized at the pulp mills as a low value fuel for production of steam and power [1,2]. The remaining amount, accounting for approx. 1 million tons per year, is made available for a number of low-value commercial uses, such as dispersant in cement, binder for animal feed pellets, additive for drilling fluids in the oil industry, or dust suppressing agent for roads [1]. Since the energy efficiency of pulp mills has been increasing in recent years, it is anticipated that growing amounts of lignin will be available for external uses in the years to come [4]. In addition, lignin-rich residue streams are also obtained in the production of bioethanol

from lignocellulosic feedstock, with a number of industrial plants already operational, under construction, or at demonstration stage. Therefore, valorization of the excess lignin is deemed a major factor in maximizing sustainability and profitability of lignocellulosic biorefinery units [3].

In recent years numerous chemical process routes for conversion of lignin into valuable products, e.g. drop-in biocrude and chemical feedstocks, have been studied on laboratory scale [5–9]. One of the most promising technologies for converting lignin is hydrothermal liquefaction (HTL) performed in near-critical water ($T=240\text{--}370\text{ }^\circ\text{C}$ and $p=10\text{--}30\text{ MPa}$), which has been reported in the literature in a number of variants [10–16]. The properties of near-critical water (NCW) as a reaction medium are appealing for a number of reasons: NCW exhibits an increased solvent power towards low-polarity compounds, while still being a good solvent for polar compounds and salts; the ionic product is higher than at lower temperatures, which leads to catalytic effects towards many ionic reactions; the density of the reaction medium is adjustable, with relatively small variations of temperature and pressure [17–21]. Moreover, application of NCW as reaction medium renders the energy intensive process step of drying the biomass obsolete. In addition, the relatively mild temperatures of NCW allow the integrity of aromatic rings to be retained, thus favoring process routes leading to aromatic monomeric compounds.

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The addition of K_2CO_3 to the NCW reaction medium was shown to increase the yields of liquid products and to decrease char formation during conversion of lignocellulosic biomass, with higher yields of liquid products compared to additions of other alkali salts (Na_2CO_3) and strong bases (KOH, NaOH) [22–24]. In the case of hydrothermal conversion of lignin, the beneficial effect of K_2CO_3 was observed to increase the yields of monomeric aromatic compounds [14,25]. Moreover, the use of organic co-solvents in hydrothermal liquefaction led to a reduction in char formation during conversion of lignocellulosic biomass. This effect was explained with the increase of biomass solubility in the reaction medium and with the action of the co-solvent as capping agent or scavenger of the unstable fragments produced in the depolymerization of biomass [26–29]. In the case of lignin conversion, phenol was clearly associated with lower char formation due to its role as capping agent [26–28]. The role of phenol as capping agent was described extensively in studies on hydrothermal conversion of a lignin model compound by Lin et al. [30–32]. In addition, Fang et al. [28] also observed that the use of phenol as co-solvent favor the solubilization of lignin in the reaction medium. The combined use of K_2CO_3 and phenol in the NCW reaction medium gave promising results in the conversion of Kraft lignin to bio-oil and water-soluble aromatic chemicals [14,15,25]. While the presence of phenol in NCW conversion of lignin showed favorable results, the effect of its amount in the reacting system has not been investigated yet.

Laboratory experiments on NCW conversion of biomass are often performed in batch mode on small scale reactors (<100 mL). These systems have the advantage of minimizing practical problems common for the continuous systems (e.g. clogging of flow control valves), and are therefore to be preferred in the initial screening of an innovative process. However, typical laboratory batch equipment for NCW conversion suffers from a number of limitations, which makes the interpretation of the results somewhat uncertain. More specifically, laboratory batch systems often require the biomass to be charged in the reactor before the heating and pressurization and they lack the means for reaction products quenching, thus leading to uncertainties in the interpretation of the reaction time and temperature. Product quenching is typically only possible in micro-reactors, which can be heated and cooled in thermostatic baths. However, in these cases, the reactor volume is typically extremely small (few mL) and does not allow accurate yield calculations of different product fractions. In addition, batch laboratory reactors used for conversion by NCW are often not equipped with means for controlling reaction pressure, thus leading to non-negligible density variations of the reaction medium due to the relatively high compressibility of NCW.

Among these factors, the slow heating time of hydrothermal batch reactors is one of the major drawbacks when operating on lignocellulosic materials, leading to results very different from those obtained in continuous stirred tank reactors (CSTR) or plug flow reactors (PFR) with product recycle, where a fast heating of the feed is achieved. As a consequence, results obtained in laboratory scale batch reactors often do not provide an accurate basis for developing continuous flow processes. For example, Kruse et al. [33] found “completely different results” when comparing hydrothermal gasification of lignocellulosic biomass in supercritical water in a batch reactor and in a CSTR. A possible way to overcome this drawback is to preliminarily fill the batch reactor with water (or water + additives), heat and pressurize the reactor and then inject the biomass. This solution, together with the relative technical details, was described by Modell [34]. A batch system with biomass injection was also reported by Schmieder et al. [35], even though without details on the operating procedure. A more detailed description of the advantages that can be obtained with a batch reactor equipped with an injection system was provided by Barbier et al. [36], who tested a new reactor on glucose decomposition

in supercritical water. However, not many details on the specific issues that can be encountered when injecting a biomass slurry were provided in a subsequent publication which comprised lignin conversion [37].

The aim of the present work is demonstration of a new laboratory batch reactor encompassing fast biomass heating, pressure control, and product quenching. Fast biomass heating is achieved through feed injection into the pre-heated and pre-pressurized reactor. Pressure control during reaction is obtained by injecting/withdrawing small and finely regulated amounts of water into/from the system. Additionally, sampling ports for immediate withdrawal and quenching of the products make it possible to stop the hydrothermal conversion at the desired reaction time. In this work, this new batch reactor was applied to the conversion of Kraft lignin in NCW, in the presence of K_2CO_3 and phenol. The effect of reaction temperature and phenol mass fraction in the feed was studied.

2. Materials and methods

2.1. Materials

The biomass used in this study was Kraft pine lignin Indulin[®] AT (Specialty Chemicals Division, Mead-Westvaco Corporation South Carolina, USA). The biomass was in the form of a free flowing brown powder with no insolubles in warm aqueous solution of 5% NaOH. The moisture content of the lignin powder was 3.6 wt.%, the ash content was 1.9 wt.%. The average molar mass stated by the supplier was 8000 g/mol. The elemental composition of dry lignin on an ash-free basis was as follows: 64.4% carbon, 6.7% hydrogen, 1.8% sulfur, and 27.1% oxygen.

The organic solvents were purchased from Sigma-Aldrich: tetrahydrofuran (THF, anhydrous, $\geq 99.9\%$, inhibitor-free), acetone (used for cleaning purposes, ACS reagent, $\geq 99.5\%$), diethyl ether (DEE, Laboratory Reagent, $\geq 99.5\%$, GC). K_2CO_3 (anhydrous, free-flowing, Redi-DriTM, ACS reagent, $\geq 99\%$) was used as catalyst. Additional chemicals were used: liquefied phenol ($\geq 89\%$, water approx. 10%) as co-solvent, N_2 ($\geq 99.998\%$) for purging the reactor of oxygen before heating up, and syringol (2,6-dimethoxyphenol, 99%) as internal standard (IS). Distilled water was used in all experiments as the primary reaction solvent.

2.2. Experimental apparatus

The new experimental set-up presented in this work (Fig. 1), built by SITEC-Sieber Engineering AG, was specifically conceived and designed for biomass hydrothermal conversion studies. The core part of the set-up is the reactor (R1, 99 mL, wetted parts in Inconel 625), which can operate up to 400 °C and 300 bar. The reactor is heated with four electrical heating cartridges immersed in the reactor shell (500 W each). The inner temperature is measured with a thermocouple type K (class 1, accuracy $\pm 0.5\%$) and it is controlled by a mixed cascade/slave PID controller. The reactor pressure is measured at a top connection by a pressure gauge with an accuracy of $\pm 1\%$. The reactor is equipped with a magnetic stirring system, coupled with a heating plate providing supplementary heat to the reactor. Heat dispersion is limited by a high-temperature insulation jacket wrapped around the reactor. The reactor is connected with two high-pressure precision hand pumps (P1 and P2; stroke capacity: 100 mL; capacity per revolution: 2 mL; maximum operating pressure: 300 bar). The pump P1 can be used for injecting/withdrawing water in/from the system for the purpose of precise pressure control. P1 is protected by a filter (F1) to avoid contact with slurry particles. P2 was specifically designed with a protecting sealing part for enabling it to pump slurry in and out

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