Effect of Water – Carbon Dioxide Ratio on the Selectivity of Phenolic Compounds Produced from Alkali Lignin in Sub- and Supercritical Fluid Mixtures

Abu M. Numan-Al-Mobin^{1}, Praveen Kolla¹, David Dixon¹, and Alevtina Smirnova^{1*}*

¹South Dakota School of Mines and Technology, Rapid City, South Dakota, United States

ABSTRACT: Lignin is considered as the most abundant renewable carbon source after cellulose and non-commercialized waste product with constantly growing annual production exceeding 50 million tons per year. This article is focused on a newly developed selective synthesis of high-value phenolic products from lignin in presence of supercritical carbon dioxide (scCO₂) known as sustainable, non-flammable, naturally abundant, and catalytically active solvent. Depending on the synthesis conditions, such as temperature (250, 300, and 350°C) and water-to-scCO₂ ratio (1:5, 1:2, 1:1, and 2:1), high yield of the specific phenolic compounds such as phenol, guaiacols, and vanillin has been achieved. The GCMS analysis reveals the trend of the increased total phenolic yield with temperature and strong dependence of the selectivity on the water-to-scCO₂ ratio. The maximum selectivity toward formation of the specific phenolic products, such as guaiacol and vanillin was observed at the highest H₂O:scCO₂=1:5 ratio. At 350 °C the relative yield of guaiacol was ~39% whereas at 250 °C vanillin was a dominant phenolic monomer with a relative yield of ~33%. Moreover, at the intermediate temperature of 300 °C both guaiacol and

vanillin were produced with relative yields of ~28% and ~13%, respectively. The highest amounts of scCO₂ resulted in the highest total relative phenolic yields of ~79%, ~71%, and ~73% at 250, 300, and 350 °C, respectively. Demonstrated for the first time, the effect of water-to-scCO₂ ratio in the process of alkali lignin liquefaction will have significant impact on selective synthesis of phenolic compounds, their use in synthesis of “green” polymers with desirable properties, and sustainable utilization of both carbon dioxide and lignin waste.

KEYWORDS: *Lignin, Liquefaction, Selectivity, Phenolic product, Supercritical carbon dioxide*

INTRODUCTION

More than 50 million tons of lignin waste are produced annually by the paper industry alone and only ~2% are used for power generation with low (<30%) energy efficiency. Furthermore, the amount of produced lignin increases every year as a result of the biorefinery efforts aimed at biofuel production from biomass [1]. In this regard the recently proposed hydrothermal lignin liquefaction in presence of supercritical carbon dioxide [2] opens a new venue in sustainable lignin waste utilization.

As a natural biopolymer, lignin consists of three phenyl-propanoid monomers, specifically p-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol coupled via C–O and C–C bonds that create branched and high molecular weight rigid structure highly resistive toward chemical or biochemical degradation. Among other bonds, the most common bond in lignin is aryl-ether β–O–4 bond, which often comprises ~50% of all linkages and can be cleaved in presence of homogeneous or heterogeneous catalysts [3, 4].

The earlier approaches for lignin depolymerization include enzymatic, electrochemical, and photocatalytic degradation, pyrolysis, degradation in presence of ionic liquids, and microwave oxidative irradiation. Moreover, the hydrothermal conversion of lignin has been extensively studied [5], though without significant progress in selective synthesis of high-value phenolic compounds.

Supercritical water (scH₂O), subcritical water (scbrH₂O), or scCO₂ have been used separately in the past for biomass or lignin reforming [6], however their combination has not been considered yet. The process of lignin conversion in scH₂O with addition of phenol (60 min; 673 K) demonstrated the maximum tetrahydrofuran soluble (TS) total yield of 19.02% at a phenol/lignin ratio of 10, residence time 64 min, and water density of 0.5 g/cm³. It was concluded that supercritical water promotes lignin conversion not only to lower molecular weight, but also to higher molecular weight products by crosslinking. The proposed mechanism [6] involves two steps. At first, decomposition of the lignin by hydrolysis and dealkylation yields low molecular weight fragments that have reactive functional groups and compounds such as syringols, guaiacols, and catechols. Then, a cross-linking reaction among these fragments and residual lignin give higher molecular weight fragments.

In comparison to the properties in liquid state, supercritical fluids, such as water or carbon dioxide, possess high diffusivity and absence of mass transport limitations within the pores of lignin. Furthermore, the water viscosity, hydrogen bonding between water molecules, and the dielectric constant decrease [7], as well as water density that define the rate of chemical reactions. For example, at a constant pressure of 40 MPa and the temperatures of 250, 380, and 400°C, the decomposition rates of lignin in sub- and supercritical water are 8.3×10^{-4} , 1.1×10^{-3} and $1.5 \times 10^{-3} \text{ min}^{-1}$, respectively [8].

As a homogeneous catalyst, scCO₂ has been used in isomerization experiments [9]. Furthermore, hydrogenation of carbon dioxide to formic acid from scCO₂ in presence of H₂ and ruthenium phosphine catalyst was reported [10]. The use of scCO₂, in which hydrogen is highly miscible with water, significantly increased the rate of reaction (up to 1,400 moles of formic acid per mole of catalyst per hour) which was much slower in liquid organic solvents [10].

A synergistic effect of the scCO₂ and sub-supercritical water [2] toward alkali lignin selective liquefaction has been recently demonstrated. In comparison to the reaction performed in nitrogen,

carbon dioxide in its supercritical state significantly enhanced reaction selectivity toward specific phenolic compounds. In comparison to the reaction performed in nitrogen, carbon dioxide in its supercritical state significantly increases reaction selectivity toward specific phenolic compounds.

In continuation to our previous study [2], the current effort is focused on optimization of the alkali lignin liquefaction in presence of sbcrH₂O-scCO₂ mixtures at the specific reaction conditions, such as different sbcrH₂O to scCO₂ ratios (1:5, 1:2, 1:1, and 2:1), temperatures (250, 300, 350 °C) and lignin loadings (0.1, 0.25, 0.5g). The advantages of the scCO₂-assisted hydrothermal lignin reforming are discussed in terms of a synergistic effect of sbcrH₂O and scCO₂ for selective formation of the phenolic compounds at different residence times, temperatures, and lignin loadings.

EXPERIMENTAL SECTION

Materials. Alkali lignin and 4-chloroacetophenone were purchased from Sigma Aldrich. Deionized water was obtained from a Milli-Q® Integral Water Purification System (EMD Millipore Corp. Billerica, MA, USA). For the LLE, acetic acid and dichloromethane (DCM) of GC quality were obtained from Sigma Aldrich (Atlanta, GA, USA). The reactor, tubing and fittings were purchased from High Pressure Equipment Company (Erie, PA, USA) and Swagelok (Solon, Ohio, USA).

Hydrothermal treatment of lignin. The treatment of alkali lignin at sub- and supercritical conditions in a temperature range of 250–350 °C was carried out in a stainless steel high-pressure vessel (316 SS) having a capacity of 12 mL with a pressure tolerance of up to 103 MPa. A type K thermocouple was inserted through the bottom of the vessel to measure the temperature inside the vessel by an AMProbe temperature meter. The internal pressure was controlled by the pressure sensor connected to the monitor. To achieve reproducible synthesis conditions, the temperature ramp was adjusted in each experiment. The batch reactor for the hydrothermal procedure is shown in Figure 1.

Figure 1. The batch reactor for the lignin hydrothermal treatment in a mixture of sbcH_2O and scCO_2 .

In these experiments, 0.10, 0.25, and 0.50 g of lignin were placed inside the vessel, followed by addition of the varying amounts (2, 4, 6, or 8 mL) of deionized water. The vessel with the inserted thermocouple was sealed and placed into the split Carbolyte furnace for hydrothermal treatment. In order to reach the targeted temperature within the shortest period of time, the initial set-up temperature of the Carbolyte temperature controller was adjusted to 700 °C with a ramp rate of 100 °C/min. Depending on the synthesis conditions, after 5-10 min (Figure 2) the temperature was adjusted to the required value. The pressure inside the vessel (22.063 MPa) was maintained by a Teledyne syringe pump 260D pressurized with liquid CO_2 . When the pressure and temperature requirements were met, a stopwatch was used to record the residence time. During this time period, the temperature and pressure inside the vessel were continuously monitored by an AMProbe temperature controller and a pressure sensor, respectively (Figure 2). After 10 min, the furnace was turned off and the pressure was released. The reaction vessel was then cooled down by the immersion it into cold water. The liquid that

came out through the pressure valve during the pressure adjustment was collected and combined with the liquid phase from the pressure vessel to measure the final weight.

Figure 2. The plot of temperature (a) and pressure (b) for 10 min of residence time at 250, 300, and 350 °C.

Characterization of the liquid organic phase. After the lignin treatment in a mixture of subcrH₂O and scCO₂, the liquid organic phase was separated from the solid phase by centrifugation. The weight of the solid phase before and after hydrothermal reforming in scCO₂ was measured gravimetrically. In the experimental temperature range of 250-350 °C the alkali lignin consumption was ~50% [2].

Separation of the liquid organic phase from aqueous phase was performed by liquid-liquid extraction (LLE) using dichloromethane (DCM). In the first step of extraction, 10 µL of acetic acid were added to every 1.0 mL of a liquid sample for adjustment of the pH value to ~2.0. Then the recovery standard (4-chloro-acetophenone) was added enabling to monitor and correct for losses during the extraction. The sample was then extracted three times with 1.0 mL of DCM with vigorous shaking. After the DCM (bottom layer) and the water (top layer) phases were separated, the bottom layers were collected and combined, and then the 4-chloroacetophenone was added to the sample for quantitative analysis.

The GC-MS analysis of the liquid organic samples was performed using GCMS-QP2010 Ultra Gas Chromatograph/Mass Spectrometer (GCMS) from Shimadzu. All injections (1.0 μL) were conducted in a split mode with sampling time of 1 min. A 30 m Rxi®-5Sil MS fused silica column (Restek Corporation, Bellefonte, PA, USA) with a 0.25 mm I.D. and a 0.25 μm film thickness was used for all separations. Ultra-pure helium (99.999%) was used as a carrier gas with a constant flow rate of 5.8 $\text{mL} \cdot \text{min}^{-1}$. The initial oven temperature was set up to 50 $^{\circ}\text{C}$ and held up for 1.0 min, then ramped to 280 $^{\circ}\text{C}$ with a rate of 10 $^{\circ}\text{C}/\text{min}$. This step was followed by a ramp to 320 $^{\circ}\text{C}$ with a rate of 20 $^{\circ}\text{C}$ and 5 min dwell time. The injector and the transfer line temperatures were set up to 250 and 300 $^{\circ}\text{C}$, respectively. All the MS data were acquired in a total ion current (TIC) mode with a mass range of 45–500 m/z . The relative yield (R.Y.) of the phenolic products was defined as:

$$R.Y. = \frac{\text{Area under the GCMS peak}}{\text{Total area of the GCMS peaks}} \times 100\%$$

In terms of the total yield and mass balance, only solid and liquid phases were taken into consideration. The mass of the gases, such as CH_4 , CO , CO_2 , or H_2 that are usually produced at the temperatures above the experimental temperature range (250–350 $^{\circ}\text{C}$) [11] was considered negligible in comparison to the weight of the solid and liquid products. To confirm the reproducibility of the results, the experiments were repeated three times for the same sample and the standard deviation was estimated in the range of 0.5–2.6%.

A Total Organic carbon (TOC) analyzer TOC-L_{CPN} from Shimadzu was used for characterization of the total organic carbon in the sample. The TOC-L was calibrated using potassium hydrogen phthalate (KHP) from 0 mg/L to 1000 mg/L. In order to obtain the results in the calibration range, the samples were diluted 30 times prior to the measurement.

RESULTS AND DISCUSSION

In the experimental temperature range of 250–350 $^{\circ}\text{C}$ (Figure 2) and constant pressure of 22.063 MPa carbon dioxide forms a supercritical fluid and water is present in a subcritical state. Complex interactions

between two fluids and the properties of the supercritical carbon dioxide in sub- or supercritical water affect the mutual solubility of the reagents [12], chemical reactions, and kinetics of the catalytic processes that take place on the lignin surface and within its porous structure. Furthermore, the phenolic species produced during hydrothermal treatment are known to catalyze lignin polymerization [6], which makes the analysis of lignin liquefaction even more complicated.

Effect of the sbcrH₂O:scCO₂ ratio. The comparative GC-MS results for the lignin decomposition products formed in sbcrH₂O and scCO₂ fluid mixtures within a temperature range of 250-350 °C and 10 min residence time (Figure 3) provide an evidence for selective production of specific phenolic compounds. The yield of four/five major phenolic products is considered in regard to the lignin liquefaction at sbcrH₂O and scCO₂ ratios (1:5, 1:2, 1:1, and 2:1) and different temperatures, such as 250, 300, and 350 °C. At the lowest temperature of 250 °C (Figure 3a) and the highest amount of scCO₂ (sbcrH₂O:scCO₂ = 1:5), vanillin is found as the major reaction product with the relative yield of ~33%. The yields of two other phenolic products, specifically guaiacol and methyl-(2-hydroxy-3-ethoxy-benzyl) ether are up to 19% and 21%, respectively. Vanillin and methyl-(2-hydroxy-3-ethoxy-benzyl)ether show the decreasing trend when the amount of scCO₂ decreases (except at sbcrH₂O:scCO₂ = 2:1 which could be due to the catalytic effect of scCO₂). The highest yields of the major phenolic products are found at sbcrH₂O:scCO₂ = 1:5 ratio (Figure 3a).

At 300 °C (Figure 3b), for sbcrH₂O-scCO₂ = 1:5 ratio, guaiacol has the highest yield of ~28%. Compared to the scCO₂ hydrothermal treatment of lignin at 250 °C, the temperature increase to 300 °C causes a significant increase in guaiacol concentration (~47%). In addition, a new product, *p*-ethylguaiacol, is observed at this temperature. Furthermore, an increase in the amount of scCO₂ (two and five times higher than sbcrH₂O) yields a higher amount of phenols (~40%). Interestingly, at 300 °C, compared to

250 °C, the relative yield of vanillin decreases by 63% indicating the change in selectivity from vanillin to guaiacol.

At 350 °C, the highest relative yield of guaiacol (~39%) is obtained at sbcrH₂O-scCO₂=1:5 ratio. A further increase in the guaiacol relative yield at 350 °C by 38% and 104% was observed when compared to the yield at 300 °C and 250 °C, respectively (Figure 3d). It is worth mentioning, that at 350 °C, when the amount of sbcrH₂O is higher, the yield of guaiacol becomes higher (~36%), however, it does not exceed the yield (~39%) found at sbcrH₂O:scCO₂=1:5 ratio.

Considering the selectivity, each temperature results in a specific phenolic compound. For example, at 250 °C (Figure 3a) vanillin has the yield of ~33%, whereas, at 300 °C (Figure 3b), guaiacol has the highest relative abundance (~28%). However, at 350 °C (Figure 3c), the amount of guaiacol is significantly higher (~39%) when a large amount of scCO₂ at the volume ratio of sbcrH₂O:scCO₂=1:5 is used.

The observed difference at sbcrH₂O:scCO₂ ratios at all temperatures with respect to a higher selectivity toward guaiacols can be explained by the presence of carbon dioxide as an acidic homogeneous catalyst that affects the kinetic pathways of lignin depolymerization [13] and prevents the corresponding phenolic products from repolymerization [14-16].

(a)

(b)

(c)

Figure 3. GC-MS analysis data of the products formed after lignin hydrothermal treatment with scCO₂-sbcrH₂O ratios (1:5, 1:2, 1:1, and 2:1) at (a) 250 °C, (b) 300 °C, and (c) 350 °C.

Effect of the residence time on sbcrH₂O:scCO₂. Evaluation of the selectivity toward formation of the specific phenolic products at various residence times (1, 10, and 20 min) was performed at 300 °C 0.1 g lignin loading. At 1 min residence time the relative yield of vanillin is the highest (~21%). However, when the residence time increases to 10 and then to 20 min (Figure 4), the relative yield of guaiacol becomes higher resulting in ~18%, and ~22%, respectively. However, only vanillin shows an exception demonstrating a higher relative yield at 1 min residence time, indicating the change in selectivity.

Figure 4. GC-MS analysis data of the products formed after lignin hydrothermal treatment for different residence times at 300 °C and lignin loading of 0.10g at a constant scCO₂:sbcrH₂O = 1:1 volume ratio.

Effect of the lignin loading on sbcrH₂O:scCO₂. The results of the alkali lignin decomposition in scCO₂-assisted hydrothermal environment studied for different lignin loadings (0.10, 0.25, and 0.50g), while maintaining constant temperature (300 °C), residence time (10 min), and sbcrH₂O-scCO₂=1:1 ratio are presented in Figure 5. As expected, the produced amounts of guaiacol, vanillin and methyl-(2-hydroxy-3-ethoxy-benzyl)ether increase with lignin loadings. However, the guaiacol demonstrated a different trend indicating that significant increase in relative yield (from 17% to 25%) is observed while changing the lignin loading from 0.1 to 0.25g. Further increase in lignin loading to 0.5g does not increase the relative yield of guaiacol. A different outcome is detected for *p*-propylguaiacol which is produced in the highest amount of ~12% at the medium lignin loading of 0.25g. Regarding the total yield of the phenolic compounds, the variation of the lignin loading results in formation of ~44%, ~63%, and ~65% at 0.10, 0.25, and 0.50g loadings of lignin, respectively, which is an expected outcome considering that formation of phenolic monomers is proportional to the total amount of lignin in the reaction mixture.

Figure 5. GC-MS analysis data of the products identified after the scCO₂ hydrothermal treatment for different lignin loadings (0.10, 0.25, and 0.50 g) at 300 °C, 10 min residence time, and constant sbcrH₂O – scCO₂=1:1 ratio.

Total organic carbon (TOC) analysis. The results of the TOC evaluation for different sbcrH₂O-scCO₂ ratios (Figure 6) demonstrate that the concentration of the total organic carbon increases with temperature. At 350 °C (Figure 6a), the highest amount of carbon (58.25 mg/L) is detected which indicates that the maximum conversion of lignin takes place compared to 250 °C and 300 °C. However, the 10 min residence time results in the highest amount of total organic carbon (Figure 6b). On the other hand, less amount of organic carbon produced at larger residence time (20 min) can be attributed to the repolymerization of the monomeric phenols [15]. Furthermore, the higher amount of lignin in the reaction mixture generates higher amounts of the organic carbon during the scCO₂ hydrothermal treatment (Figure 6c). Overall, the TOC results obtained by fixing all the parameters of the reaction mixture except one (Figures 6a,b,c) are in good correlation with the GC-MS results and demonstrate the

importance of parameters optimization providing a reasonable comparison of the TOC amounts in the liquid phase in regard to the scCO_2 - assisted hydrothermal process.

Figure 6. The total organic carbon (TOC) concentration for different: (a) Treatment temperatures at constant $\text{sbcrH}_2\text{O}:\text{scCO}_2=1:1$ ratio, lignin loading (0.10g) and residence time (10 min), (b) Residence times at constant temperature (300 °C), $\text{sbcrH}_2\text{O}:\text{scCO}_2 = 1:1$ ratio, and lignin loading (0.10 g), and (c)

Lignin loading at constant temperature (300 °C), sbcrH₂O:scCO₂ = 1:1 ratio, and residence time (10 min).

Pathways for the scCO₂ –Assisted Selective Catalysis. The properties of sub- or supercritical water as a strong oxidizing agent are well known [5, 18]. However, these properties do not allow to achieve selective synthesis of phenolic products from lignin due to strong repolymerization [6] that results in formation of higher molecular weight products and decreases the reaction selectivity. In presence of scCO₂ performing as an acidic catalyst without mass-transport limitations, the repolymerization process is eliminated, which is also confirmed by the absence of tar or char in the experimental temperature range of 250-300°C. The presence of supercritical carbon dioxide as a homogeneous catalyst [2] increases the acidity of the reaction media, promoting the β-O-4 bond scission. During this process lignin as an aromatic heteropolymer forms various phenols and methoxy phenols through the hydrolysis of the ether β-O-4 bond. Degradation of lignin can proceed further through hydrolysis of methoxy groups, without compromising the stability of the benzene ring itself. The efficiency of this reaction is enhanced due to the properties of the supercritical CO₂ fluid that can penetrate small pores of lignin (< 250nm) [17] without mass transport limitations.

The absolute values of the alkali lignin decomposition in the scCO₂-assisted hydrothermal process. The amount of solid phase left over after decomposition of the alkali lignin in scCO₂-assisted hydrothermal process was evaluated by the gravimetric analysis. The results indicate that the amount of lignin left over in the reactor is about 75% at 250 °C and gradually decreases with temperature reaching ~62% and ~50% at 300 °C and 350 °C, respectively. These values are supported by comparing the SEM images of the untreated raw lignin and the lignin after the scCO₂-assisted hydrothermal treatment (Figure 7) at 250 °C, 10 min residence time, and sbcrH₂O:scCO₂=1:1 ratio. In comparison to the untreated lignin

(Figure 7a) that does not show any porosity, the structure of lignin after treatment at 250 °C has different morphology and demonstrates significant effect of scCO_2 in combination with sbcH_2O . At 300 °C, lignin starts to melt and the surface porosity is not visible anymore.

Figure 7. SEM images of raw lignin and decomposed lignin in presence of scCO_2 - sbcH_2O : (a) raw lignin, (b) 250 °C, (c) 300 °C, and (d) 350 °C at $\text{sbcH}_2\text{O}:\text{scCO}_2 = 1:1$ ratio, and 10 min residence time.

This process continues at 350 °C, demonstrating a rigid structure of the solid phase leftover from lignin. Despite previous publications [18] where the tar or char formation was detected at these temperatures, no evidence of tar or char was found at 250 or 300 °C. At 350 °C a small amount of char has been found in the lignin sample, which is in correlation with the previous study emphasizing that the char formation is promoted at higher temperatures. In order to minimize or eliminate the amount of the solid lignin phase in the process of scCO_2 hydrothermal reforming, a circulation type of the reactor with continuous flow of the lignin-water mixtures should be considered in future along with the detailed

analysis of the selectivity mechanisms toward formation of specific phenolic compounds within a continuous flow reactor system.

CONCLUSIONS

The effect of temperature, residence time, and amount of lignin on the selectivity and the yield of the phenolic products from the scCO₂-assisted hydrothermal reforming was investigated in a mixture of sbcrH₂O and scCO₂. The GC-MS analysis demonstrates the dependence of the organic phase composition and selectivity on sbcr H₂O-scCO₂ ratio and the reaction temperature. At higher temperature (350 °C), the reaction selectivity is the highest demonstrating the relative yield of ~39% toward guaiacol for sbcrH₂O-scCO₂=1:5 ratio, whereas, at 250 °C, for the same ratio, vanillin is found as a dominant phenolic monomer (~33%). At 300 °C, when the amount of scCO₂ is five times higher than subcrH₂O, the highest yield was observed for guaiacol (~28%). The total relative phenolic yield was higher (79, 71, and 73% at 250, 300 and 350 °C, respectively) when the lower amount of water, and correspondingly the higher amount of scCO₂ was used.

Besides reaction temperature and sbcrH₂O-scCO₂ ratio,, the residence time and the lignin loading both have strong effect on the reaction selectivity. For example, at the shortest residence time of 1 min vanillin is the dominant product, whereas at higher residence times, guaiacol has the largest relative yield. The experiments performed for the evaluation of the reproducibility of the results confirm the above conclusions and emphasize the sensitivity and selectivity of the lignin decomposition in regard to the four main reaction parameters, such as reaction temperature, lignin loading, residence time, and scCO₂ - subcrH₂O ratio.

As a result of using scCO₂ in combination with subcrH₂O an energy-efficient “green” approach for selective synthesis of specific phenolic products from alkali lignin has been introduced for the first time. Furthermore, considering that both lignin and carbon dioxide as a

“greenhouse gas” can be efficiently consumed in the reaction, the development of the scCO₂ - assisted hydrothermal selective synthesis of phenolic products from lignin or biomass can be envisioned as an important step toward environmental protection.

AUTHOR INFORMATION

Corresponding Authors

* A.M. Numan-Al-Mobin. E-mail: abu.numan-al-mobin@mines.sdsmt.edu.

* A. Smirnova. E-mail: Alevtina.smirnova@sdsmt.edu

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