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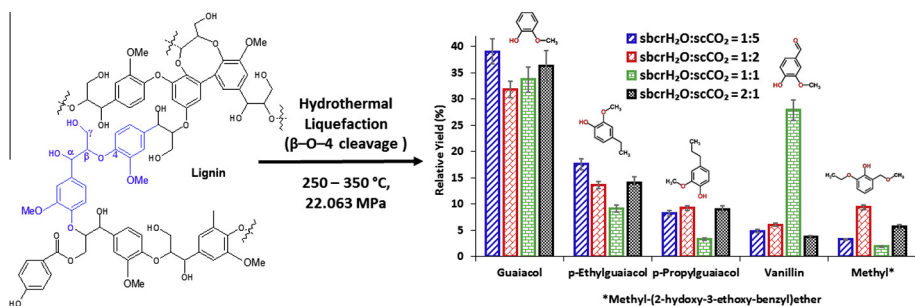
Effect of water–carbon dioxide ratio on the selectivity of phenolic compounds produced from alkali lignin in sub- and supercritical fluid mixtures



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GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 14 April 2016

Received in revised form 7 July 2016

Accepted 12 July 2016

Keywords:

Lignin

Liquefaction

Selectivity

Phenolic product

Supercritical carbon dioxide

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.

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1. 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 phenylpropanoid 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 (schrH₂O), or scCO₂ has 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 gives higher molecular weight fragments.

In comparison with 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 defines 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 1.5×10^{-3} 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 1400 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 with the reaction performed in nitrogen, carbon dioxide in its supercritical state significantly enhanced reaction selectivity toward specific phenolic compounds. In comparison with the reaction performed in nitrogen, carbon dioxide

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In continuation to our previous study [2], the current effort is focused on optimization of the alkali lignin liquefaction in presence of sbrH₂O–scCO₂ mixtures at the specific reaction conditions, such as different sbrH₂O to scCO₂ ratios (1:5, 1:2, 1:1, and 2:1), temperatures (250, 300, 350 °C) and lignin loadings (0.1, 0.25, 0.5 g). The advantages of the scCO₂-assisted hydrothermal lignin reforming are discussed in terms of a synergistic effect of sbrH₂O and scCO₂ for selective formation of the phenolic compounds at different residence times, temperatures, and lignin loadings.

2. Experimental section

2.1. 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).

2.2. 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 Fig. 1.

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

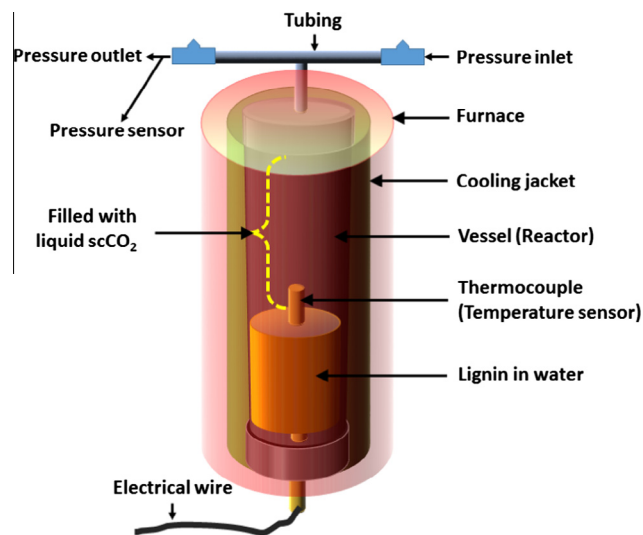


Fig. 1. The batch reactor for the lignin hydrothermal treatment in a mixture of sbrH₂O and scCO₂.

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