Effects of Process Parameters on Conversion of Rice Straw-Lignin into Bio-Oil by Hydrothermal Liquefaction

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Lignin derived from rice straw, an abundant renewable feedstock in nature, has the potential to be utilized as a substitute for fossil fuels in the production of value-added aromatic derivatives. However, depolymerization becomes one of the most difficult obstacles in the lignin-to-valuable products conversions due to the structural complexity and recalcitrance of lignin. In this work, rice straw-derived lignin was depolymerized to aromatics by using the hydrothermal liquefaction method in the ethanol-water solvent under hydrogen pressure. Effects of various process parameters on yields such as reaction time, ethanol concentration, reaction temperature, initial hydrogen pressure, and solvent-to-lignin ratio, were investigated. The suitable conditions for the highest yield of oil products (~ 75 %) were determined to be 65 vol. % ethanol, 250 °C, 60 min, 20 bar of hydrogen, and the solvent-to-lignin ratio of 35 mL/g. The obtained oil products were characterized by gas chromatography-mass spectrometry (GC-MS) and Fourier transform infrared (FT-IR). The bio-oil was mainly aromatics such as phenol, 3-ethylphenol, guaiacol and had a heating value of 22.2 MJ/kg. Hydrothermal liquefaction was demonstrated as an appropriate method for lignin depolymerization into aromatic compounds with high production yields.

1. Introduction

Phenols sourced from fossil fuels are a major supplier of raw materials for the production of numerous consumer goods and the main source of energy for manufacturing and transportation processes (Hernandez et al., 2018). However, the long-term depletion of fossil resources, coupled with concerns about the sustainability of their use, has necessitated research into new alternatives for chemicals or fuel production (Ahlbom et al., 2021). For this purpose, lignin has emerged as a potential candidate due to its one-of-a-kind aromatic structure. Lignin is a natural polymer made essentially from three phenol-based building blocks, p-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol, linked randomly by C–C or C–O–C bonds (Besse et al., 2015). Lignin can be found in a wide range of agricultural waste products, including maize, rice straw, corn stover, sugarcane bagasse, and so on (Do et al., 2020). Rice straw is a rich source of lignin, but due to the difficulties of extracting lignin, it is not widely used in Vietnam for purposes other than burning. Recently, Do et al. (2020) completed a study on the lignin recovery process from rice straw, in which the silica concentration in lignin is effectively and selectively reduced. Le et al. (2020) developed a pilot-scale procedure for recovering lignin from the black liquor of rice straw bioethanol production based on the previous lab-scale lignin recovery method. A paddy-based biorefinery is also developed from the recovery bioethanol system and the conversion of lignin into value-added products (Le et al., 2022a). Lignin recovered at a pilot scale from bioethanol production includes little silica but has a relatively low purity (about 77 %). It could not be used for the production of pharmaceuticals or biomedical applications but is a great source of material to convert into energy. In addition, the processing of lignin into more value-added materials is expected to add economic value to the bioethanol production process from lignocellulosic materials which ultimately can lower the cost of bioethanol production. Instead of using actual lignin, conversion of lignin has primarily been carried out on model compounds that share at least one structural similarity characteristic with lignin (Jiang and Wu, 2019). There are now only very few studies on converting rice straw lignin into phenolic-rich bio-oil. This necessarily requires thorough research on rice straw lignin conversion.

Thermochemical conversion is the typical approach for converting lignin to low-molecular-weight compounds. Within that, hydrothermal liquefaction (HTL) is an outstanding method to produce lignin-based products under mild conditions compared to others (Erdocia et al., 2017). The roles of solvent in liquefaction of lignocellulose biomass including lignin were investigated, indicating that water/ethanol mixture results in higher yields of bio-crude and much lower solid residue yield than using pure water (Feng et al., 2018). In addition, the hydrogen pressure in the lignin depolymerization was demonstrated when helping to reduce the yield of biochar, which was attributed to the suppression of condensation reactions induced by unstable lignin-derived oligomers under the reductive atmosphere (Liu et al., 2020). Studies on hydrothermal degradation of lignin alone are not as common as studies on cellulose. Although hydrothermal depolymerization has been performed on most lignin model molecules, the depolymerization of actual lignin with low purity has not been reported elsewhere due to its fewer applications. In this work, rice straw-derived lignin with low purity was firstly depolymerized by using the hydrothermal liquefaction method. This process was carried out under mild conditions in the ethanol-water solvent in the presence of initial hydrogen. The goal of this study was to investigate the effects of the ethanol-water concentration, temperature, reaction time, initial hydrogen pressure, and solvent-to-lignin ratio. Based on it, the appropriate conditions could be explored to obtain the maximum oil yield. The depolymerized oil product was further analysed by gas chromatography-mass spectrometry (GC-MS). The properties of initial lignin, residual solids, and oil products were characterized by Fourier transform infrared (FT-IR) spectroscopy.

2. Materials and methods

2.1. Materials

The lignin used was a brown powder obtained by alkaline extraction from rice straw black liquor (Le et al., 2022b). This rice straw lignin has the following composition: 78.91 % lignin, 15.52 % carbohydrates, and 5.57 % ash. All reagents were purchased from commercial suppliers with the pure grade, including ethanol and ethyl acetate; hydrogen, and nitrogen with a purity of 99.9 %. All aqueous solutions were prepared with distilled water.

2.2. The typical process for hydrothermal depolymerization of lignin, separation, and characterization

The hydrothermal depolymerization reactions of the lignin were conducted in a 600 mL batch reactor (series 4540, Parr Instrument Company, USA) with a 4848 PID controller. The flow chart of the experiment was shown in Figure 1.
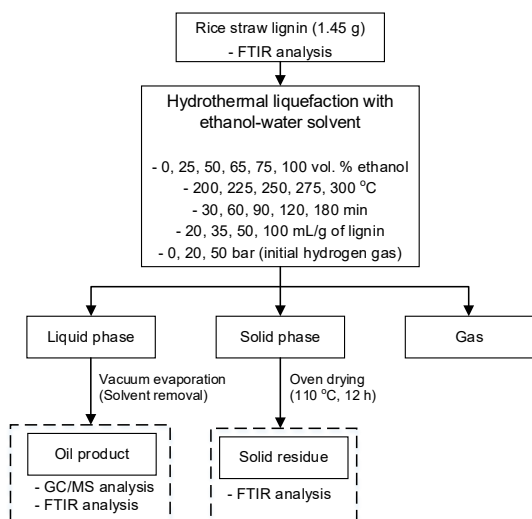

Figure 1: The flow chart of the experiments

Initially, 1.45 g of rice straw lignin and 50 mL of aqueous ethanol solution in various concentrations were loaded into the reactor. After the reactor was sealed, it was purged with sufficient hydrogen. Hydrogen was injected into the reactor three times to remove the air and pressurize. The reaction time was measured when the reactor reached the designed temperature. After the reaction, the mixture was cooled to room temperature by a water batch. The mixture of products and solvent was vacuum filtered to separate into two distinct phases: solid phase and liquid phase. The solid phase was oven-dried at 110 °C for 12 h to recover solid residue (SR). The solvent removal from the liquid phase to obtain the oil product (OP) was carried out using a rotary vacuum evaporator. The conversion rate and yields of SR and OP were calculated using the following equations:

$$OP \ yield \ (wt.\%) = \frac{weight \ of \ oil \ fraction \ (g)}{weight \ of \ initial \ lignin \ (g)} \times 100 \ \% \tag{1}$$

$$SR \ yield \ (wt.\%) = \frac{weight \ of \ solid \ residue \ (g)}{weight \ of \ initial \ lignin \ (g)} \times 100 \ \% \tag{2}$$

$$Conversion \ rate \ (\%) = \frac{weight \ of \ initial \ lignin \ (g) - weight \ of \ solid \ residue \ (g)}{weight \ of \ initial \ lignin \ (g)} \times 100 \ \% \tag{3}$$

The qualitative analysis of the oil products was characterized by GC-MS (6890N) equipped with a DB-5 column (30 m x 0.32 m x 0.25 µm). The temperature procedure was as follows: initial oven temperature was 60 °C for 2 min, and then heated to 140 °C at 10 °C/min and held for 5 min, followed by 280 °C at 20 °C/min and held for 9 min. Identification of the compounds was carried out by comparing the mass spectra obtained with those contained in the NIST 14 MS database. FTIR spectra were recorded using a Frontier MIR/NIR spectrometer (Perkin Elmer, Waltham, MA, USA). The transmittance was measured over the range of 4,000-400 cm^{-1} with a resolution of 4 cm^{-1}. All analyses were done at least in triplicate, and the data are expressed as mean values ± standard deviation (S.D.) for each measurement.

3. Results and discussion

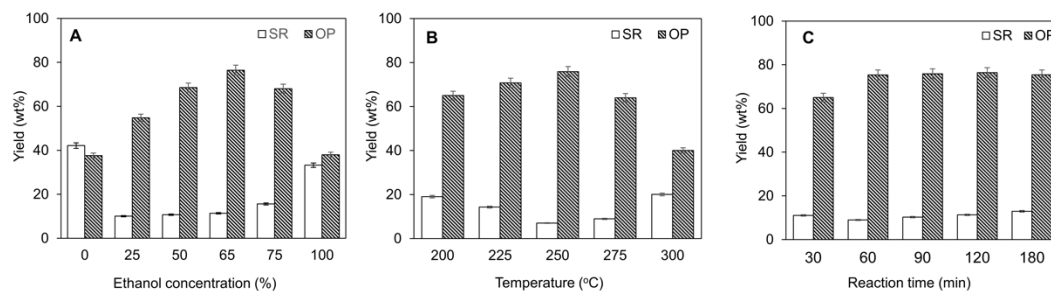### 3.1. Effects of parameters on the hydrothermal depolymerization of lignin

Figure 2: Effect of process parameters of ethanol concentration (A), temperature (B), and reaction time (C)

3.1.1. Effect of ethanol concentration

Ethanol is one of the popular solvents for HTL of lignin because it leads to higher conversion and lower char yields (Patil et al., 2020). The results of the effects of ethanol concentration on the yields of OP and SR (Figure 2A) indicated that using a co-solvent system showed improved lignin degradation, specifically, water-ethanol co-solvent degradation was much more effective as compared to individual mono-solvent systems (Cheng et al., 2012). As can be seen, the ethanol concentration of 65 % gives the low SR yield of 11.36 % and the highest OP yield of 76.43 %, which is consistent with the results of Ye et al. (2012). The addition of ethanol to generate a co-solvent system outperforms the use of mere water as a solvent. Lignin and lignin-related compounds (low molecular weight) dissolve well in ethanol-water co-solvent systems, which can significantly impede their repolymerization. This inhibitory ability is thought to be owing to the activity of ethanol as a capping agent of aromatics, a formaldehyde scavenger, and a hydrogen donor source (Patil et al., 2020). However, too much ethanol may result in little or no hydrolysis, resulting in a drop in OP yield (Cheng et al., 2012).

3.1.2. Effect of temperature

Temperature influences the product slate and yields by causing fragmentation and depolymerization of lignin (Patil et al., 2020). The depolymerization of lignin occurs when the temperature is sufficiently larger than the activation energy barriers kinetically for the break of the bonds in the lignin structure (Yuan et al., 2010). The effects of reaction temperature on the yields of OP and SR are displayed in Figure 2B. The results illustrate that the OP yield is greatest at 250 °C, while the SR yield is lowest. The OP yield gradually rises with the increase of temperature from 200 to 250 °C while the SR falls. The results demonstrated that at low temperatures, hydrothermal depolymerization is thermodynamically endothermic, but at high temperatures, it is exothermic. As a result, lignin depolymerization is the dominant reaction during the early phases, and repolymerization becomes active later in the hydrothermal process, resulting in char formation (or SR) (Akhtar and Amin, 2011).

3.1.3. Effect of reaction time

Reaction time is the time the reactants are held at the temperature setpoint that determines the extent of lignin depolymerization (Patil et al., 2020). The influence of reaction time on products of lignin depolymerization is presented in Figure 2C. Prolonging the reaction time beyond 60 min, the OP yield did not change significantly (less than 2 %), and at 60 min, the OP yield was significantly higher than at 30 min, and the SR was also the lowest (8.97 %). The results indicated that a long reaction time is required to ensure complete severance of all ether bonds in the structure of lignin and a gradual cleavage of stable C-C bonds thereafter (Yuan et al., 2010). Linkage cleavage occurs at shorter times (less than 60 min), as evidenced by an increase in OP and a decrease in SR. When the reaction duration is extended, however, side reactions embark on occurring and gradually dominate, increasing the amount of SR. Extending the reaction time after nearly all ether linkages have been severed does not improve the oil product yield.
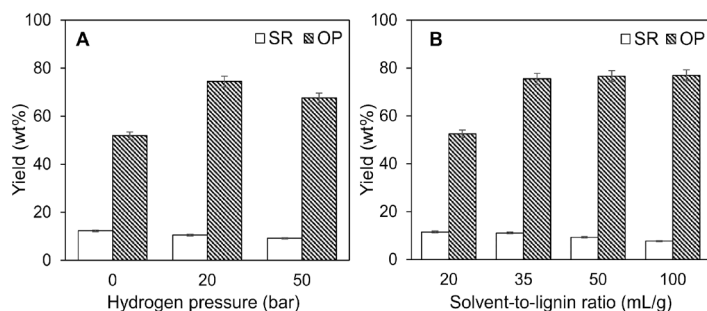

Figure 3: Effect of process parameters of initial hydrogen pressure (A), and solvent-to-lignin ratio (B)

3.1.4. Effect of initial hydrogen pressure

The use of hydrogen sources can achieve improved monomer yields, and especially the presence of hydrogen in a gaseous or radical form enhances product selectivity (Patil et al., 2020). Figure 3A depicts the yields of lignin-degraded products including OP and SR as a function of initial hydrogen gas pressure. As can be seen, when the initial hydrogen pressure is 20 bar, the OP yield is highest and the SR obtained is relatively low. Hydrogen is known as a recondensation reaction inhibitor because it can limit free radical reaction formation from cleavage of inter-unit linkage during the depolymerization process of lignin (Kim et al., 2013). Indeed, the study reveals that when the initial hydrogen pressure increases, the quantity of SR falls continuously. Relative hydrogen pressure ensures the safety of the equipment when performing the process at the lab scale. An initial hydrogen pressure of 20 bar is suitable for the depolymerization of lignin at 250 °C in an ethanol-water solvent system (65 vol.% ethanol).

3.1.5. Effect of solvent-to-lignin ratio

The effects of solvent-to-lignin ratios on the lignin depolymerization were demonstrated in Figure 3B. The OP yield increased considerably when the solvent-to-lignin ratio was adjusted from 20 to 35 mL/g. However, when this ratio continued to increase up to 100 mL/g, a slight increase (less than 3 %) was witnessed in the yield of OP. As the ratio of solvent to lignin increases, the amount of SR decreases. This result is consistent with the previous finding of Kim et al. (2013), showing that increasing the solvent ratio reduces char formation.

3.2. Fourier transform infrared (FT-IR) spectroscopy analysis

The differences between the FT-IR spectra of lignin and SR obtained at 250 and 300 °C (Figure 4A) were demonstrated by the gradual weakening in the intensity of most of the peaks assigned to the characterized absorbance of linkages or functional groups in lignin, indicating that lignin was depolymerized into oligomers and monomers. The absorbance of linkages or functional groups in lignin indicates that lignin was depolymerized into oligomers and monomers. The absorbance intensity of the peak at 3,350 cm^{-1} decreased, implying that the efficient dehydration at high temperatures also contributed to the –OH reduction (Long et al., 2014a). The reduced absorption intensity of S units (1,126 cm^{-1}) and G units (1,262 and 1,030 cm^{-1}) further confirmed that these units in the structure of lignin were converted to related aromatic products. In addition, a significant decrease in the peaks in the SR spectrum was observed as the temperature increased from 250 to 300 °C while the quantity of oil product obtained decreased, suggesting that the process of decomposition and carbonization of intermediate compounds to generate char occurs mostly at high temperatures. Based on the FT-IR spectroscopy results of oil products when using solvents in various ethanol concentrations (Figure 4B), these spectra all include the characteristic peaks for functional groups and linkages in the structure of lignin. A

significant difference was experienced in the peaks at 1,713 cm^{-1} and 1,664 cm^{-1} due to C=O and C=C stretching, proving that dehydration to form alkenes occurs less efficiently with increasing ethanol concentration.
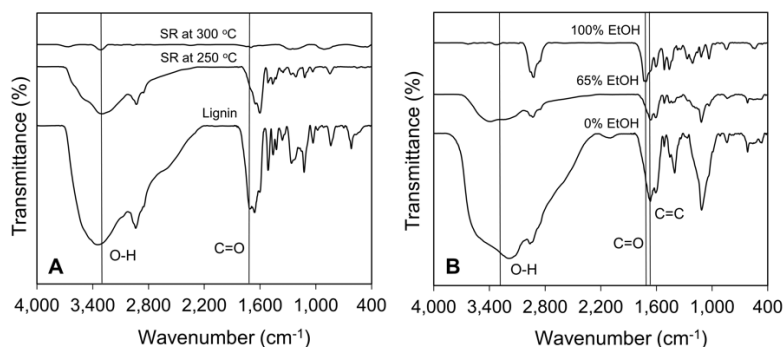

Figure 4: FT-IR spectra of lignin and solid residues (SRs) (A), and oil products (B)

3.3. Main aromatic compounds of liquefied lignin

The GC-MS analysis method was used to identify the composition of lignin hydrothermal liquefaction oil products and some detected aromatic compounds in the obtained oil products were listed in Table 1.

Table 1. Main aromatic compounds from lignin hydrothermal liquefaction

No.	Compounds	Ret. time (min)	Area (%) *
1	Phenol	6.745	8.00
2	Formic acid phenyl ester	6.780	4.43
3	Ethoxy-Benzene	6.814	4.06
4	2,5-Dihydroxyacetophenone	6.888	3.14
5	Guaiacol	8.920	4.18
6	2,4,6-trimethyl-Phenol	9.412	2.53
7	2,3-Dihydroxybenzoic acid	9.789	3.81
8	2,5-Dihydroxybenzoic acid	9.824	2.80
9	3-ethyl-Phenol	10.264	5.39
10	Methyl-Benzenemethanol	10.293	6.00
11	2,4-Dimethoxytoluene	11.414	2.50
12	Carvacrol	31.167	4.38

*Based on the integration of 12 major peaks, without including the small peaks with area < 1 %

The results indicate that the oil product was mainly constituted by aromatic compounds belonging to H-type compounds including phenol, 3-ethylphenol, carvacrol, ethoxybenzene, derivatives of p-hydroxyphenyl, formic acid phenyl ester. This shows that of the three structural units of lignin, the H unit is the most susceptible to hydrolysis, followed by the G unit (represented by guaiacol) while the S unit is the most difficult to hydrolyse under hydrothermal conditions. This result is consistent with the study of Long et al. on the hydrothermal process of lignin (Long et al., 2014b). In addition, the presence of other compounds was detected such as epinephrine, norepinephrine, 2,5-dihydroxyacetophenone, benzoic acid, gentisic acid, 2-2-propenyl-furan, 5-ethyl-2-furaldehyde, and methyl-benzenemethanol. The derived-lignin oil product was also measured at heating value and compared with some other oils. The calorific value of this oil product is 22.2 MJ/kg, which is higher than that of bio-oil from pyrolysis (13–18 MJ/kg) but lower than that of fuel oil (40.3 MJ/kg).

4. Conclusions

This study was successful in depolymerization of rice straw-derived lignin into various aromatic compounds of lower molecular weights by using the hydrothermal liquefaction method. The role of process parameters including ethanol concentration, temperature, reaction time, the ratio of solvent to lignin, and initial hydrogen pressure is clarified. The temperature and composition of the co-solvent have a significant effect on the yield and quality of the bio-oil. Low temperatures cannot provide enough energy to break the lignin ether bond. High temperature leads to coal recovery and formation. The ratio of co-solvent between ethanol and water greatly determines the efficiency of the process. Conditions of 250 °C, 60 min, the solvent-to-lignin ratio of 35 mL/g, 20 bar of initial hydrogen, and 65 vol.% ethanol-water led to the highest yield of lignin-derived oil products. The

bio-oil consists mainly of value-added phenolic compounds such as ethylphenol, carvacrol, phenol, and guaiacol with a heating value of 22.2 MJ/kg. The obtained lignin liquefaction oil products show the potential to replace phenols sourced from fossil fuels for various industrial applications such as phenolic resin synthesis, chemicals, and even further biofuels.

Acknowledgements

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