Conversion of Loblolly pine biomass residues to bio-oil in a two-step process: Fast pyrolysis in the presence of zeolite and catalytic hydrogenation

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Abstract: In the present study, Loblolly pine biomass residue was converted to bio-oil in a two-step process, consisting of 1) fast pyrolysis in the presence of zeolite ZSM-5 as a catalyst to produce pyrolysis oil, 2) hydrogenation of pyrolysis oil using formic acid as the hydrogen source in presence of Ru/activated carbon catalyst. Pyrolysis oils were analyzed by ^{13}C, ^{31}P and HSQC-NMR and the results revealed that the zeolite-induced catalytic fast pyrolysis process led to effective demethoxylation, producing more catechol and p-hydroxy-phenyl hydroxyl groups in the bio-oils, resulting in a decrease in the methoxyl group content by about 85 % and rich aromatic structures in the pyrolysis oils. The properties of pyrolysis oil with and without zeolite were in the bio-oil range. Hydrogenated pyrolysis oil showed that 79 % of the aromatic protons are eliminated and 87 % of protons are aliphatic in nature, with no oxygen attached to the α-carbon.

1. Introduction

Forestry and agricultural waste are significant biomass sources. Globally, every year vast quantities of forestry and agricultural waste are underutilized. The effective usage of agriculture waste can lead towards covering the current and future demands for fuels; also it can minimize local dependency on fossil fuels, such as natural gas (AlNouss et al., 2019). Pyrolysis of agricultural waste and industrial residue (Mondal et al., 2020a) to produce bio-oils is one potential option, not only for appropriate utilization of waste, but also as a good contribution to the economy in fuel sectors (Sipra et al., 2018). Furthermore, one of the great advantages, biomass based fuel is carbon neutral, as compared to fossil fuel (Linger et al., 2014). Integrated forest biorefinery for manufacturing bio-fuels, materials and chemicals is promising (Demirbas, 2009a).

A two-step process consisting of pyrolysis, followed by catalytic hydrogenation, is attractive for converting biomass to biofuel: in the first step, biomass is transformed to pyrolysis oil, gas and char, and these products are upgraded in the next step (de Miguel Mercader et al., 2011; Wildschut et al., 2010). Due to unwanted properties of bio-oils such as poor volatility, thermal instability, corrosiveness, high viscosity, lower heating value and cold flow problems (Kan et al., 2016; Mostafazadeh et al., 2018), upgrading prior to their use would be necessary, to allow them as substitutes for diesel, gasoline, etc.

ZSM-5 zeolite has been investigated in biomass fast pyrolysis (Atutxa et al., 2005; Che et al., 2019; Engtrakul et al., 2016; Nishu Liu et al., 2020; Zhang et al., 2014, 2015). Due to good pore structure, high thermal stability and tunable acidity, ZSM-5 zeolite is a leading choice for upgrading catalysts (Engtrakul et al., 2016; Wang et al., 2017). By decreasing the quantity of oxygenated species through deoxygenation reactions and at the same time enhancing the aromatic compounds in bio-oils, ZSM-5 zeolite is able to induce substantial changes in bio-oil composition (Iliopoulou et al., 2019). For upgrading the bio-oil via catalytic hydrogenation, many catalysts such as Pt, Pd, Ru, Rh are often used (Dwiatmoko et al., 2016; Yati et al., 2016; Yoon et al., 2013, 2015). Metal impregnated, (especially transition and rare earth metal) ZSM-5 is better for reducing oxygenated compounds conducting to higher capacities of hydrocarbons and reducing the cost of catalysts (Foster et al., 2012; Olcese et al., 2012; Qi et al., 2017; Yung et al., 2016; Zhu et al., 2010).

De Wild et al., studied a two-step process, pyrolysis of lignin followed by catalytic hydrogenation of resultant pyrolysis oil. They found that 15 wt% of monomeric aromatics were formed, of which 11 wt% were alkylphenols, with minimum solid residue (De Wild et al., 2017). Vispute et al., studied a two-step process process for hydrogenation of biomass pyrolysis oil produced from pinewood and the water soluble part of the oil was transformed to gasoline type compounds (Vispute et al., 2010). They used different temperatures (125 o C, 250 o C) and different catalysts (Ru/C and Pt/C) in every step but the H2 gas pressure was the same. Horacek et al., used a zeolite beta supported platinum catalyst for hydrogenation and deoxygenation processes. They used pyrolysis oil model compounds such as, phenol, o-, m- and p-cresols, guaiacol, eugenol and found that phenol was suitable for both processes. They reported that cresol and methyl substituted phenol were less reactive towards hydrogenation because the methoxy group was proven to hamper both processes (Horáček et al., 2013). The two-step hydrogenation process of biomass pyrolysis oil produced from ethanol organosolv lignin (extracted from pine wood) for the purpose of producing gasoline range oil was reported (Ben et al., 2013). In both hydrogenation steps, Ru/C catalyst was used, with the results showing that ether bonds and methoxyl groups were extensively cleaved in the 1st step, leading to the production of simple aromatic molecules. The yields of carbon for the 1st and 2nd step were 35 % and 33 %, respectively (Ben et al., 2013). Recently, we studied the two-step process for the conversion of Loblolly pine residue to bio-oil via slow pyrolysis with zeolite followed by catalytic hydrogenation (Mondal et al., 2020b). We found that the zeolite effectively induced decarboxylation reactions, resulting in the content of aliphatic hydroxyl groups in heavy oil decreasing by 57 % (Mondal et al., 2020b).

In the present study, we carried out a systematic study on the pyrolysis of Loblolly pine residue, a biomass waste. We used formic acid (instead of hydrogen gas) as the hydrogen source for the hydrogenation of pyrolysis heavy oil. We studied fast pyrolysis in the presence and absence of ZSM-5 zeolite, and the subsequent pyrolysis heavy oils were characterized by ^{13}C, ^{31}P, HSQC and ^{19}F-NMR and Gel Permeation Chromatography (GPC). Typical properties of heavy oils were tested, and hydrogenated oils were analyzed by 1 H-NMR.

2. Materials and methods

2.1. Materials

All chemicals and reagents were bought from VWR International or Sigma-Aldrich (St. Louis, MO) and, in this study they are used without any purification. The Loblolly pine residue sample was collected from a University of Georgia research pilot in Macon, GA. Zeolites (CBV 3020E) were purchased from Zeolyst, Inc. Prior to the use for pyrolysis, the Loblolly pine residue was milled through a Wiley mill to pass a 2 mm screen based on Tappi method T257 cm-02.

2.2. Chemical composition analysis of Loblolly pine residue

Basic chemical compositions including α-cellulose, hemicellulose, lignin, dichloromethane (DCM) extractives, tannins and ash content were analyzed on the Loblolly pine residue samples. The analysis procedures were based on literature methods (Huang et al., 2011). It should be noted that the sugar components (arabian, galactan, glucan, xylan, mannan) in the hemicellulose were also analyzed in this research. The lignin analysis included the acid insoluble lignin (Klason lignin) and the acid soluble lignin.

2.3. Preparation of pyrolysis sample

The pyrolysis samples were prepared using mechanically stirred pine residue and zeolites with 1:1 wt ratio. The zeolite used in this study was activated in the pyrolysis tube at 500 °C in the presence of nitrogen for 6 h. A blank pine residue sample (R) was prepared for pyrolysis comparison. Detailed information of zeolite used in this study is given in Table 1.

2.4. Pyrolysis experiment of Loblolly pine residue

The pyrolysis experiment was carried out by following the literature method (Ben and Ragauskas, 2011a). In brief, for this fast pyrolysis process, about 100 mg of the sample was fed into a small (r =1.5 cm, h =15 cm) fast stirred pyrolysis reactor. The reactor was plunged in the pre-heated sand bath and the reactor was flushed with pre-heated N_2 gas maintaining 500 $mL \cdot min^{-1}$ flow rate. The sample was heated up to 600 °C and, at the bottom of the reactor the heating rate was more than ~2000 °C/s. Two condensers were plunged in liquid N_2 and, during pyrolysis, the outflow directly passed through it. When pyrolysis was complete, the tube was taken out from the sand bath and allowed to cool at a normal temperature under passing constant

N_2 flow. Pyrolysis products were collected by taking out the condensers from liquid N_2 and, subsequent analysis was done.

2.5. Hydrogenation of pyrolysis oil

Hydrogenation of pyrolysis heavy oil was performed by following the published method (Ben, 2012). A 300 mL Parr 4520 Micro Stirred Reactor was used for the hydrogenation process. In the process, 150 mg heavy oil, 50 mL DI water and 0.5 g formic acid were loaded in a glass liner with 15 mg 5 wt% Ru/activated carbon catalyst (Alfa Aesar, Product No. 7440-18-8). Air from the inside of the reactor was moved out by passing N_2 gas and, stirring rate of the reactor was adjusted ~200 rpm. Reactor pressure and temperature were maintained at 10 MPa and 250 ± 3 °C, respectively. After 4 h reaction, the reactor was plunged in an ice bath to cool off and release pressure. 0.45 μm syringe filter was used to take out the catalyst from the heavy oil solution. The water solution of the hydrogenation products (50 mL) was extracted by 2.0 mL CDCl3. The CDCl3 was evaporated from the hydrogenated bio-oil under reduced pressure. The obtained bio-oil was collected for further analysis.

2.6. GPC analysis of pyrolysis oil

The weight average molecular weights (Mw) of the heavy oil after getting each step of pyrolysis was determined by Gel Permeation Chromatography (GPC) analysis following the published method (Ben and Ragauskas, 2011a). Before injecting the sample to the detector, the heavy oil was dissolved in tetrahydrofuran (1 mg mL−1) and the solution was filtered via a syringe filter (0.45 μm). Polymer Standards Service (PSS) WinGPC Unity software data analysis was used to analyze the results. The calibration curve was plotted, and Mw was calibrated against this calibration curve.

2.7. Pyrolysis heavy oil characterization by using different NMR

2.7.1. Quantitative ^{13}C-NMR

Bruker Avance/DMX400 MHz NMR spectrometer was used to perform all NMR spectra in this study. For performing quantitative ^{13}CNMR, about 100.0 mg oil was dissolved in 450 µL dimethyl sulfoxide-d6 (DMSO-d6) and a reverse gated decoupling pulse sequence was applied in this technique (Ben and Ragauskas, 2011b). Approximately 1 mg mL−1 chromium acetyl acetonate, a relaxation reagent, was added into the solutions so that the measurement time was reduced.

2.7.2. Quantitative ^{31}P-NMR

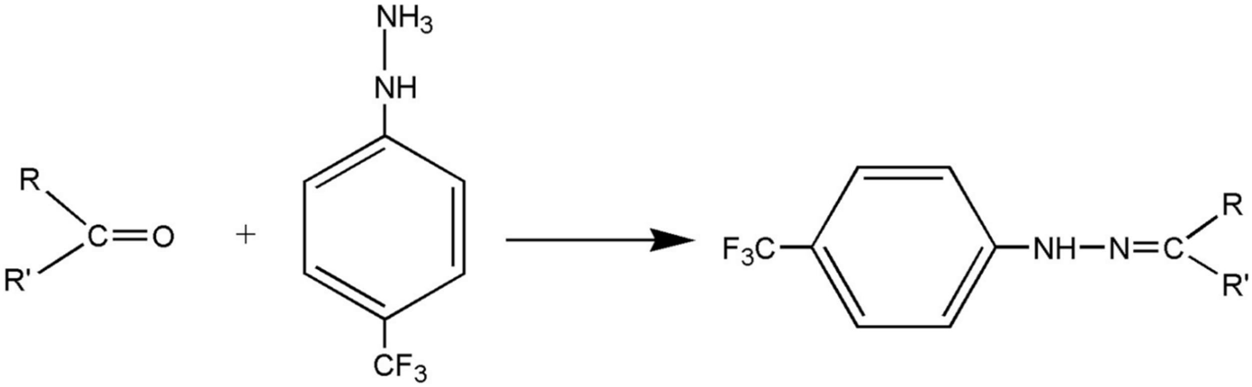
^{31}P-NMR analysis samples were prepared according to published literature (Ben and Ragauskas, 2011a). 10 mg heavy oil sample was taken for in situ derivatization with phosphating reagents. ^{31}P-NMR spectra data was acquired by applying decoupling pulse.

2.7.3. HSQC-NMR

For HSQC-NMR analysis, the same type of sample was used as ^{13}CNMR. HSQC-NMR was acquired applying a standard Bruker pulse sequence “hsqcetgpsi.2″, well described in the published literature (Ben and Ragauskas, 2011c). About 70.0 mg heavy oil sample was used for the experiment. Central solvent peak was used for calibration of chemical shift. Then, MestReNova v7.1.0 software was used for data processing.

2.7.4. ^{19}F-NMR

For the analysis of ^{19}F-NMR, about 60.0 mg of pyrolysis oil was taken and the carbonyl-containing compounds in pyrolysis oil, can react with trifluoromethylphenylhydrazine in accordance with the following reaction:



^{19}F-NMR spectroscopy was applied directly for analyzing the derivatives. To do that, the published method was followed (Huang et al., 2014) and the integration result was accomplished by using MestReNova v7.1.0 software.

2.7.5. Quantitative ^{1}H-NMR

Quantitative ^{1}H-NMR was acquired with 16 transients and 1 s pulse delay. (Note: the longest T1 was determined to be 0.16 s). The sampling of ^{1}H-NMR was the same as Quantitative ^{13}C-NMR.

2.8. Physical properties determination of pyrolysis oil

Pour points and cloud points of pyrolysis heavy oil were measured by 70Xi cloud, pour and freeze point lab analyzer manufactured by Phase Technology. All the tests used manufactory default analysis methods and, the data was processed by the analyzer. Cetane number of the pyrolysis oil was measured by ZX-101XL portable octane/cetane analyzer (Zeltex, Inc. USA). The pH value of the pyrolysis oil was determined by the pH meter (Mettler Toledo FE28-Meter).

The pyrolysis oil liquid relative density was measured through a pycnometer by following ASTM standard (ASTM, 1988). The elements "C, H, O and N" were analyzed by a PerkinElmer Optima 7300 DV Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES). The flash point of bio-oil was determined by the small scale closed cup method according to ASTM D3828 (Products, A.C.D.-o.P., Lubricants (2009)). Bio-oil viscosity was measured by using a viscometer (Brookfield, DV-3TTJC).

The Higher Heating Value (HHV) of bio-oil was measured by the oxygen-bomb colorimeter (Parr 6400, USA) based on a literature method (Demirbas, 2009b).

3. Results and discussion

3.1. Chemical composition analysis

The chemical composition analysis of Loblolly pine residue is listed in Table 2. The α-cellulose and hemicellulose contents in Loblolly pine residue are close to the data of Loblolly pine stem wood mentioned in the literature (Huang et al., 2011). However, the residue contains 4.7 % of tannins, which does not exist in stem wood. This is due to the presence of small amounts of bark in the samples.

3.2. Pyrolysis yields analysis

Pyrolysis yields of different products obtained from pine residue with and without zeolite are presented in Fig. 1. The pyrolysis of Loblolly pine produces different products, including gas, light oil, heavy oil and char. The gas products are mainly comprised of H_2, CO, CO_2, and CH_4 and the char is mainly carbon material. In addition, the light oil contains 80 % water and small amounts of methanol, catechol and acetic acid. However, the heavy oil contains a large number of various aromatic chemicals, which are regarded as the most important product of pyrolysis

(Ben, 2012; Ben and Ragauskas, 2012). Results show that the heavy oil yield (26 %) produced from the pine residue pyrolysis was higher than the yield (22 %) from slow pyrolysis of pine (Ben and Ragauskas, 2011c). This might be due to the fact that pine residue contains more lignin than the stem wood of pine (Huang et al., 2011). Similarly, the yield of heavy oil, exceeded the slow pyrolysis of pine residue, with (16 %) and without (22 %) zeolite ZSM-5 (Mondal et al., 2020b). This is due to the fact that a higher heating rate promotes more C-C breakages and demethoxylations of the lignin than the slow pyrolysis (Ben and Ragauskas, 2013). In addition, the results show that ZSM-5 assisted pyrolysis process produced more light oil and char but less gas and heavy oil, than the non-zeolite assisted pyrolysis. These results support the conclusion that zeolites enhance the secondary reaction of pyrolysis heavy oil to char and light oil (Ben and Ragauskas, 2011b). Similar results have been reported (Özbay, 2015) for pine wood sawdust in the presence of catalysts, showing that in the presence of catalysts, the yield of oil decreased while the yield of char increased. These results imply that the dehydration and condensation of carbon matrix reactions will lead to more char formation (Rutkowski, 2012).

3.3. Quantitative 31P-NMR analysis of pyrolysis heavy oil

To find out hydroxyl functional groups in heavy oils, quantitative ^{31}P-NMR is one of the best processes (David et al., 2012; Kosa et al., 2011). The integration results are summarized in Fig. 2. As shown in Fig. 2, addition of zeolite led to a decrease in the aliphatic hydroxyl groups in the oils by 50 %. The results show that the zeolites assisted pyrolysis oils were dehydrated significantly, while the quantity of acidOH also significantly decreased. Therefore, the addition of zeolites efficiently induces the decarboxylation reactions. Zeolite assisted pyrolysis of heavy oil contains less guaiacyl and, catechol type hydroxyl groups and more p-hydroxy-phenyl hydroxyl groups which indicates that the transformation of ether bonds to the p-hydroxy-phenyl hydroxyl groups was enhanced during the fast pyrolysis of pine residue in presence of zeolite. Similar finding was reported in the published literature (Ben and Ragauskas, 2011b). Due to decomposition of ether bonds in lignin structure (Ben and Ragauskas, 2011a) during fast pyrolysis of pine residue in presence of ZSM-5, the aliphatic hydroxyl and acid hydroxyl groups were significantly removed.

3.4. Quantitative ^{13}C-NMR analysis of pyrolysis oil

The quantitative results of ^{13}C-NMR of pyrolysis heavy oil are shown in Fig. 3. Results show that the quantity of methoxyl group reduced by 85 %, indicating that the fast pyrolysis process with zeolite is effective for the cleavage of methoxyl groups. Content of carbonyl groups was also reduced by 99 %, indicating a low acidity in the pine residue fast pyrolysis heavy oil. Interestingly, the percentages of aromatic CeC bonds in the pyrolysis oils are higher than the aliphatic CeC bonds, which can be explained by the increased production of polyaromatic hydrocarbons or biphenyl structures in the process. Zeolite can lead to a decrease in the percentage of aromatic ether substitute and an increase in the aromatic CeC bond in the heavy oil, which indicates that zeolite enhances the cleavage of ether bonds (Ben and Ragauskas, 2011b) in lignin structure of pine residue. These results support the conclusion that the addition of zeolite enhances deoxygenation reactions such as aliphatic hydroxyl groups, carboxyl groups, methoxyl groups and the ether bonds in lignin structure during pyrolysis.

3.5. HSQC-NMR analysis of pyrolysis oil

HSQC-NMR (2D NMR) analysis was performed on the pyrolysis oil samples, so that different CeH bonds could be obtained (Anika et al., 2010; Ben and Ragauskas, 2011c; Samuel et al., 2010). The assignments of the HSQC analysis were based on our previous work on pyrolysis of

Kraft lignin and cellulose, as shown in Figs. S1 and S2, respectively. The HSQC-NMR spectra for the pyrolysis oils with and without zeolite are shown in Figs. S3-S6. Results express that, the main component in pyrolysis oil is levoglucosan (compound I in Fig. S2), which was also the main product from the pyrolysis of cellulose and hemicellulose (Ben, 2012). The assignments of each carbon present in levoglucosan and HSQC-NMR spectra are presented in Fig. S3. It shows that the quantity of levoglucosan decreased in the zeolite assisted pyrolysis oil. HSQCNMR spectra of aromatic CeH bonds for pyrolysis heavy oil are presented in Fig. S4. It indicates that the major aromatic components in the pine residue pyrolysis oils contain A1, A2, A3, B1 and B2 (compounds in Fig. S1) type of aromatic CeH bonds, which is comparable with lignin pyrolysis oils. In addition, the contents of E3 and B1 (compounds in Fig. S1) type aromatic CeH bonds increased significantly in zeolite assisted pyrolysis. Fig. S5 indicates that the methoxyl groups (C1 and C2) decrease significantly in the zeolites upgraded samples. Fig. S6 shows that the content of aliphatic CeH bonds is not significantly different in the zeolite-assisted and non-zeolite assisted pyrolysis samples.

3.6. Molecular weight analysis of pyrolysis oil

The M_w for pyrolysis heavy oil of Loblolly pine residue is presented in Fig. 4. Results show the M_w of heavy oil produced from pine residue (575 g/mol) is higher than the raw pine bark (411 g/mol), pine bark (430 g/mol) (Ben et al., 2019) and pine wood (430 g/mol) (Hassan et al., 2009). This result indicates that the lignin content of pine residue is higher than raw pine bark, pine bark and pine wood, respectively. Resulting pine residue produced higher M_w oil (Fahmi et al., 2008; Ren et al., 2017). Zeolite assisted pyrolysis oil led to a decrease in the M_w by 47 %, which is attributed to the zeolite induced catalytic degradation, producing lower molecular weight bio-oil. Similar results were reported (Williams and Nugranad, 2000), after the use of ZSM-5 zeolite, Mw of pyrolysis oil decreased.

3.7. 19F-NMR analysis of pyrolysis oil

Table 3 represents the ^{19}F-NMR analysis of the carbonyl group in the pyrolysis oils. After the use of zeolite with pine residue, carbonyl group content and quinone content in heavy oil decreased by 10 % and 25 %, respectively. These results show good agreement with the observation of 13C-NMR measurements (Fig. 3).

3.8. Typical properties of pyrolysis oil

Typical properties of pyrolysis oil are shown in Table 4. Zeolite assisted pyrolysis oil exhibited lower pour point than the non-zeolite assisted oil. This is because zeolite enhances the degradation of aliphatic hydroxyl groups and methoxyl groups (Fig. 3). It is noted that the cloud points for pyrolysis oils were difficult to obtain, due to the dark color of the oil making observation difficult (Lu et al., 2009). Results show that cetane number of the pyrolysis oils is lower than the biodiesels range, this is due to the fact that they contain a significant amount of aromatic compounds (Santana et al., 2006). Furthermore, the addition of zeolite enhances the decomposition of methoxyl groups, resulting in a higher centane number in the bio-oils, in comparison to the non-zeolite assisted pyrolysis oils. After purification of pyrolysis oil, the cetane number must be in the range of bio diesel. Other properties of pyrolysis oil are in-between the bio-oil range and show good consistency with reference values.

3.9. Hydrogenation analysis of pyrolysis oil

Fig. S7 shows that the ^{1} H-NMR spectrum for the Loblolly pine residue pyrolysis oil and hydrogenated Loblolly pine residue pyrolysis oil. The integration results are summarized in

Table 5. After hydrogenation, 79 % of the aromatic structures/protons disappear, while 87 % of protons are aliphatic, with no oxygen attached to the α-carbon. These results indicate that the majority of carbons in the hydrogenated pyrolysis oils are aliphatic in nature and the hydrogenated oils have relatively low oxygen content. In addition, after hydrogenation, the heavy oil contains fewer aromatic protons and more aliphatic protons that indicate during the process of hydrogenation, the benzene ring can also be hydrogenated. Fig. S8 shows the 1 H NMR spectrum for the ZSM-5 assisted Loblolly pine residue pyrolysis oil and hydrogenated Loblolly pine residue pyrolysis oil. The integration results are shown in Table 6, which confirms that the hydrogenation process significantly increases the aliphatic carbons and decreases the aromatic carbons. Table 7 compares the ^{1} H- NMR results obtained before and after hydrogenation. Table 7 shows that after hydrogenation of pine residue, the decreasing rate of aromatic protons and increasing rate of aliphatic protons is 79 % and 83 %, respectively, which is much higher than previous reported results (Ben et al., 2013). Ben et al. used pine wood ethanol organosolv lignin and Ru/C as the catalyst (Ben et al., 2013). From that result, it might be said that the quality of hydrogenated oil produced from the pyrolysis of pine residue is much better than for the pine wood ethanol organosolv lignin.

4. Conclusion

In the present study, Loblolly pine biomass residue was converted to bio-oil in a two-step process: 1) fast pyrolysis with or without ZSM-5, 2) hydrogenation of pyrolysis oil using formic acid as the hydrogen source. NMR analyses of pyrolysis oil supported the conclusion that the use of zeolites as a catalyst decreased the aliphatic hydroxyl groups in the heavy oils by 50 % and induced demethoxylation reactions. In the process, methoxyl groups cleaved effectively and were lowered by 85 %. Moreover, the zeolite catalyzed pyrolysis process led to a decrease in the carbonyl group of oil by 99 %, with the Mw decreasing by 47 %. Typical properties of pyrolysis oil were in the bio-oil range and the addition of zeolites does not significantly affect the physical properties of pyrolysis oil. The hydrogenation process removes 79 % of the aromatic structures/protons of the pyrolysis oils, with the vast majority of carbon (87 %) of hydrogenated oils being aliphatic.

Credit authorship contribution statement: Ajoy Kanti Mondal: Writing - original draft, Methodology. Chengrong Qin: Methodology, Data curation. Arthur J. Ragauskas: Conceptualization, Investigation. Yonghao Ni: Validation, Supervision. Fang Huang: Writing - review & editing.

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Appendix A. Supplementary data Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.indcrop.2020.112318.

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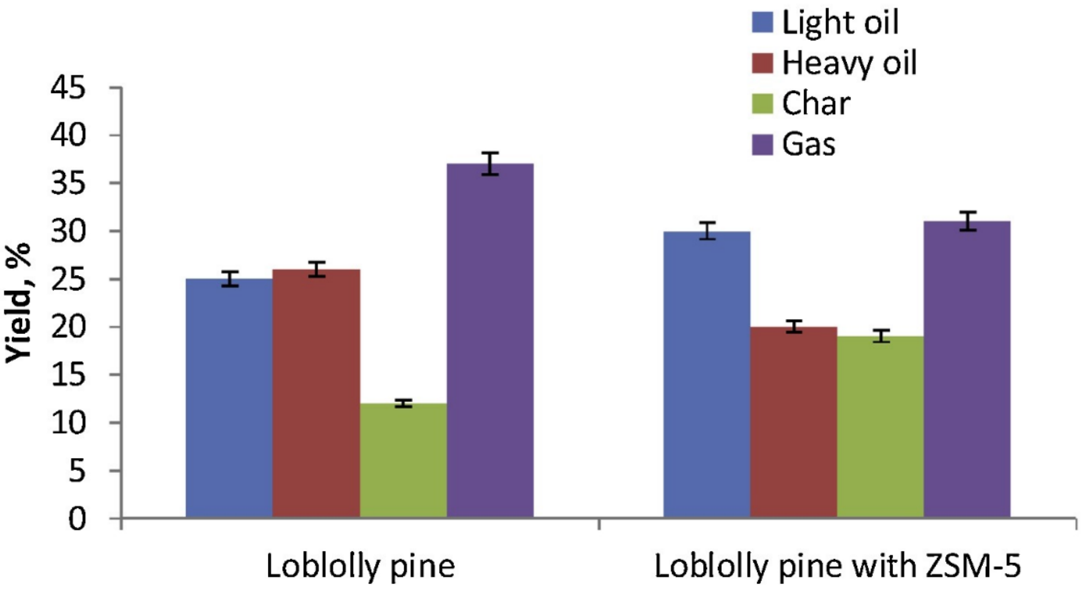

Figure 1. Yields (wt%) of light oil, heavy oil, char (excluding the weight of zeolite) and gas for the fast pyrolysis of Loblolly residue (R) with 1.0/1.0 ($W_{additive}/W_{residue}$) of ZSM-5 zeolite.

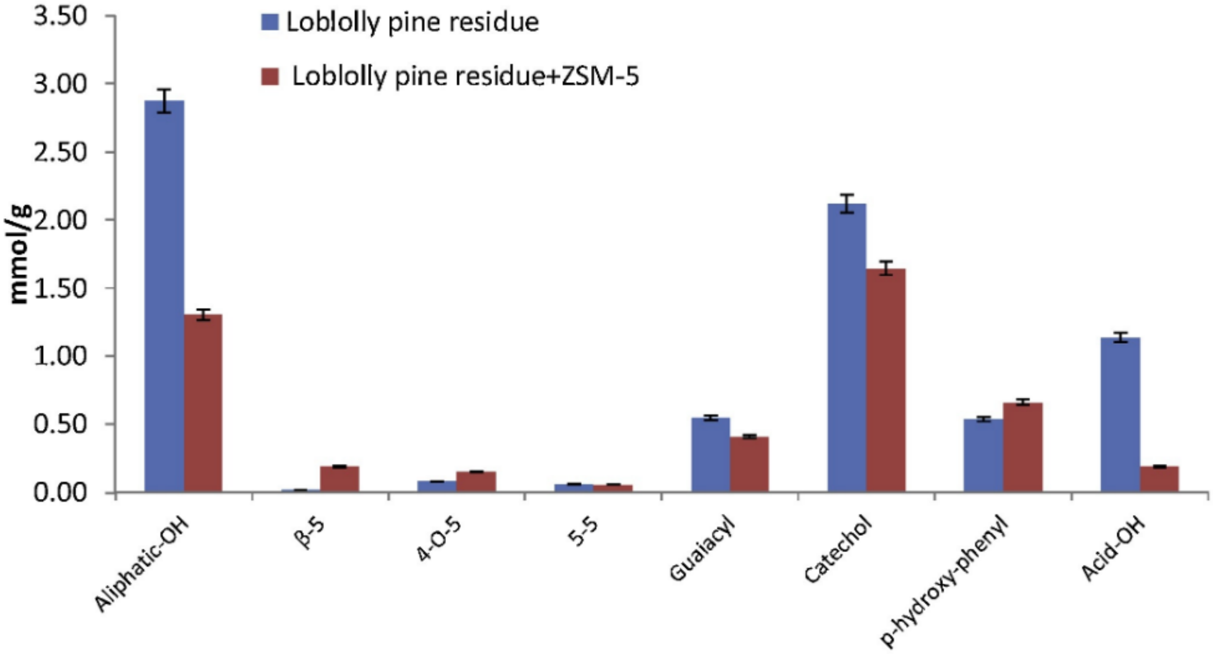

Figure 2. Hydroxyl group contents of heavy oils produced by pyrolysis of Loblolly pine residue.

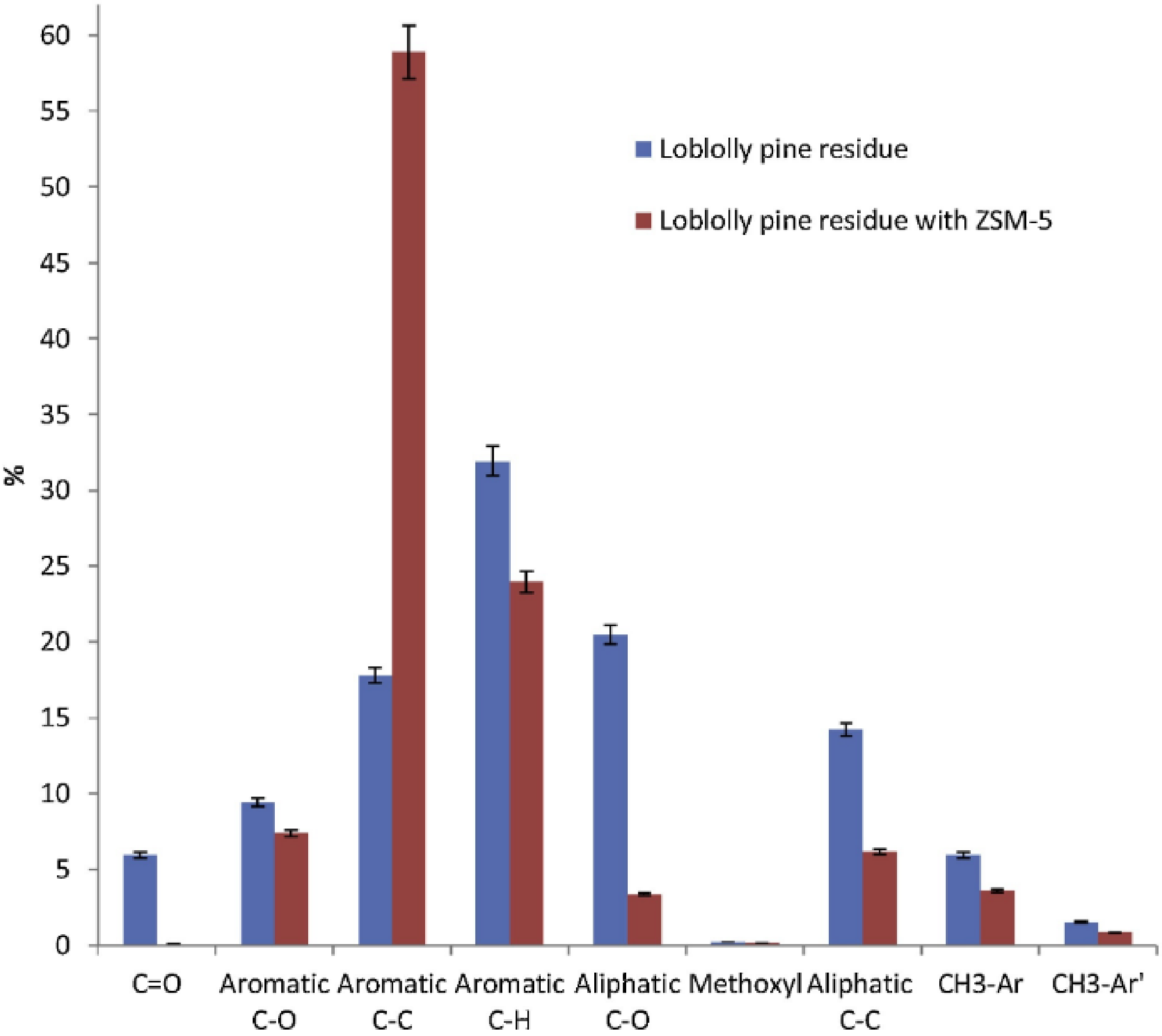

Figure 3. Quantitative ^{13}C-NMR results for heavy oils produced from Loblolly pine (Shown are the percentage of different carbon based in the total carbon).

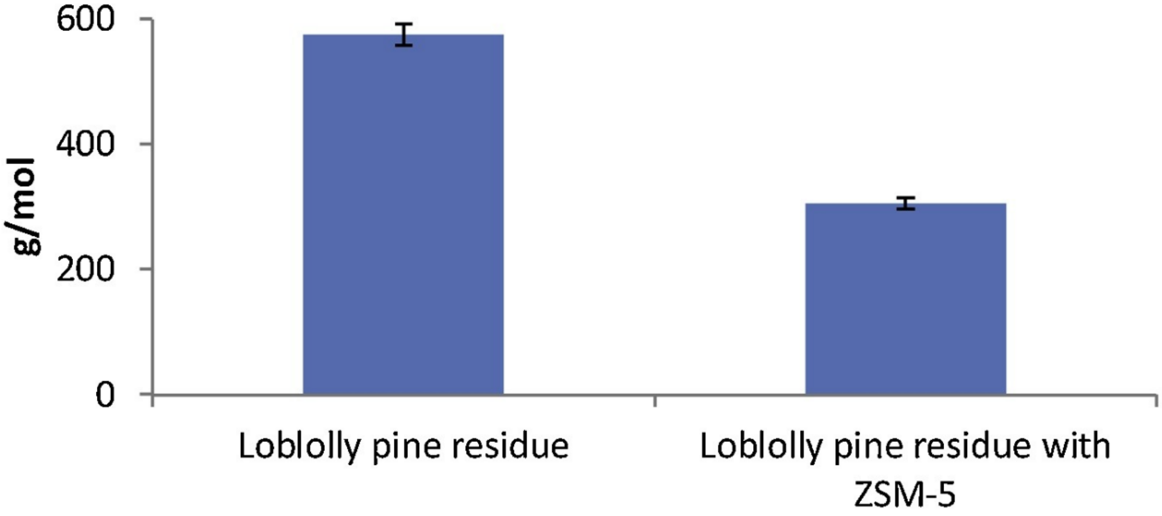

Figure 4. Molecular weight distributions (M_w) of heavy oils produced by pyrolysis of Loblolly pine residue.

Table 1. Detailed description of zeolite (CBV 3020E) used in this work.

	CBV 3020E
SiO_2/Al_2O_3 mole ratio	30
Framework	MFI
Code name	Z
Pore dimension	3
Pore size (Å)	5.1 × 5.5, 5.3 × 5.6

Table 2. Chemical composition analysis of the Loblolly pine residue (wt% on the o.d. sample).

α-cellulose	hemicellulose					Lignin		DCM extractive	tannins	ash
1	arabinan	galactan	glucan	xylan	mannan	acid-insoluble (Klason lignin)	acid soluble			
44.5	1.3	2.0	2.2	6.3	8.6	25.7	1.1	2.5	4.7	0.8

Table 3. ^{19}F-NMR analysis of the carbonyl groups in the pyrolysis oils.

Sample ID	^{19}F-NMR analysis	
	Carbonyl (aldehyde and ketone) (mmol/g)	Quinone (mmol/g)
Loblolly pine residue pyrolysis oil	4.65	0.95
ZSM-5 assisted Loblolly pine residue pyrolysis oil	4.11	0.74

Table 4. Physical properties of bio-oil and pyrolysis oil produced from Loblolly pine residue with and without ZSM-5.

	Bio-oil from Loblolly pine residue		Bio-oil	Reference
	Pyrolysis without ZSM-5	Pyrolysis with ZSM-5		
Pour point (℃)	−27	−23	−36 to -9	(Oasmaa and Czernik, 1999)
Relative Density	1.3	1.3	1.1-1.3	(Oasmaa and Czernik, 1999)
Flash point (℃)	85	83	50-100	(Oasmaa and Czernik, 1999)
Cloud point (℃)	n. d[a]	n. d[a]	–	–
Cetane number	18.5	20.6	49-62	(Mishra et al., 2016)
pH	2.5	2.4	2.0-4.0	(Lu et al., 2009)
C (%)	56.4	56.7	54-58	(Zhang et al., 2007)
H (%)	6.2	6.4	5.5-7.0	(Zhang et al., 2007)
O (%)	35.8	36.0	35-40	(Zhang et al., 2007)
N (%)	0.1	0.1	0.0-0.2	(Zhang et al., 2007)
Viscosity (at 50℃), mPa·s	110	102	40-100	(Zhang et al., 2007)
HHV, MJ/kg	17.0	17.2	16-19	(Zhang et al., 2007)

[a] Not detectable.

Table 5. Chemical shift assignment ranges of ^{1}H-NMR and functional group contributions of different types of protons before and after of hydrogenation of pyrolysis oils produced from Loblolly pine residue.

Type of protons	Range (ppm)a	Loblolly pine residue pyrolysis oil	Hydrogenated Loblolly pine residue pyrolysis oil
-CHO, -COOH	10-9.6	0.53[b]	0.04
ArH, HC=C-	8.2-6.0	13.27	2.80
$-CH_n-O-$, CH_n-O-	6.0-3.0	38.60	10.06
$-CH_3$, $-CH_n-$	3.0-0.5	47.60	87.10

Table 6. Chemical shift assignment ranges of ^{1}H-NMR and functional group contributions of different types of protons before and after of hydrogenation of pyrolysis oils produced from Loblolly pine residue with ZSM-5.

Type of protons	Range (ppm)	ZSM-5 assisted Loblolly pine residue pyrolysis oil	ZSM-5 assisted Hydrogenated Loblolly pine pyrolysis oil
-CHO, -COOH	10-9.6	0.28	0
ArH, HC=C-	8.2-6.0	22.17	11.43
$-CH_n-O-$, CH_n-O-	6.0-3.0	26.94	14.74
$-CH_3$, $-CH_n-$	3.0-0.5	50.61	73.84

Table 7. Comparison between the ^{1}H-NMR results before and after hydrogenation of pine residue with and without ZSM-5 zeolite and previous reported literature (Ben et al., 2013) (decreasing percentage rate of -CHO, -COOH; ArH, HC=C-; -CH_n-O-, CH_n-O- and the increasing percentage rate of -CH−CH_3, −CH_n- after hydrogenation).

Type of protons	Loblolly pine residue pyrolysis oil	ZSM-5 assisted Loblolly pine residue pyrolysis oil	Pine wood ethanol organosolv lignin pyrolysis oil (after 1st step hydrogenation) (Ben et al., 2013)
-CHO, -COOH	92	100	100
ArH, HC=C-	79	48	32
-CH_n-O-, CH_n-O-	74	45	33
-CH_3, -CH_n-	83	45	45