Hydrogenation of Pyrolysis Oil from Loblolly Pine Residue

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Abstract

Loblolly pine residue prepared with and without zeolite ZSM-5 was pyrolyzed at 600℃ and the pyrolysis oil was hydrogenated using formic acid as a hydrogen source, in the presence of a Ru/activated carbon catalyst. As indicated by the pyrolysis yield, addition of the zeolite ZSM-5 increased the yield of light oil but decreased the yield of heavy oil. The pyrolysis oils were analyzed by ^{13}C, ^{31}P, ^{19}F, and heteronuclear single quantum coherence or heteronuclear single quantum correlation nuclear magnetic resonance (HSQC-NMR), demonstrating that the zeolite ZSM-5 could efficiently induce decarboxylation reactions and decreased the content of aliphatic hydroxyl groups in the heavy oil by 57%. After hydrogenation of the bio-oil, the aromatic carbon content decreased by 78%, with a significant increase in the aliphatic carbon content.

Keywords: hydrogenation; pyrolysis oil; Loblolly pine residue; zeolite ZSM-5

1 Introduction

To cope with the increasing global energy consumption and limited petroleum resources, new processes for the production of renewable fuels and chemicals must be developed[1-2]. One logical choice is to convert renewable biomass sources to fuels that can be used to replace oil. Biomass fuels are not like fossil fuels as the former derive carbon from the atmosphere during growth, which is then returned to the atmosphere during combustion. This process maintains the carbon cycle with no net rise in the atmospheric CO_2 levels[3].

The pyrolysis of Loblolly pine residue to produce bio-oil is not only an efficient means of utilizing forestry residue, but also provides a source of renewable fuel. Some unexpected properties of bio-oil such as thermal instability, corrosiveness, cold flow problems, high viscosity, and poor volatility are the main obstructions to its use as a substitute fuel[4]. Thus, bio-oils must be upgraded prior to use as replacement fuels. The fuel properties of pyrolysis oil can be improved by hydrogenation using H_2 gas in the presence of a catalyst. However, H_2 gas is flammable upon contact with air, its production and compression costs are very high, and storage and transportation are difficult, all of which hinder the use of H_2 gas[5]. Unearthing hydrogen donor molecules as non-H_2-gas hydrogen sources to reduce various unsaturated compounds and produce value-added chemicals is a major research challenge[6-10]. Various hydrogen donors such as sodium formate[11], formic acid[12], and alcohols[13-14] have been applied to the transfer-hydrogenation of compounds such as ketones[12], esters[12], phenols[15], and aldehydes[11, 16].

Vispute et al[17] applied a two-step hydrogenation process to pine wood pyrolysis oil to produce gasoline-type compounds. They used hydrogen gas as the hydrogen source and applied different catalysts, temperatures, and hydrogen pressures in different steps. Wild et al[18] studied the pyrolysis of five lignin samples, with subsequent catalytic hydrogenation of the resulting pyrolysis oils, and achieved 15 wt% of monomeric aromatics with minimum solid formation during the hydrogenation process. Recently, Shafaghat et al[5] examined the feasibility of different types of primary and secondary alcohols as hydrogen donors to replace H_2 gas in the hydrogenation of pyrolysis oil. They used Pd/C as a catalyst in the hydrogenation of guaiacol and found that only the secondary alcohols can act as H-donors for guaiacol transformation over Pd/C[5]. Horáček et al[19] used a *β*-zeolite-supported platinum catalyst for the hydrogenation and deoxygenation of pyrolysis oil model compounds such as, phenol, *o*-, *m*- and *p*-cresols, guaiacol, and eugenol and found that phenol is suitable for hydrogenation and deoxygenation. They also reported that cresol and methyl-substituted phenol were less reactive towards hydrogenation because the methoxy group was proven to hamper hydrogenation and deoxygenation.

Our group successfully produced gasoline-range oil from the hydrogenation of pyrolysis oil made from pine wood ethanol organosolv lignin. A two-step hydrogenation process was conducted in presence of a Ru/C catalyst. It was found that the ether bonds and methoxy groups of the heavy oil were broken in the first step to produce simple aromatic molecules. The carbon yield was 35% and 33% for the 1st- and 2nd-step hydrogenation processes[20].

Based on prior study, herein we investigated the pyrolysis of Loblolly pine residue, instead of Loblolly pine, to optimize the utilization of waste biomass. Formic acid was used as a hydrogen donor for the hydrogenation of pyrolysis heavy oil, instead of hydrogen gas, as the former is safe, easy to handle, and inexpensive. Pyrolysis was performed in the presence and absence of a ZSM-5 zeolite catalyst, and the subsequent pyrolysis heavy oil was analyzed by ^{13}C, ^{31}P, ^{19}F, HSQC-NMR, and gel permeation chromatography for determination of its molecular weight. The physical properties of the pyrolysis oil were also examined, and the hydrogenated oil was characterized by ^{1}H-NMR.

2 Materials and methods

2.1 Materials

All chemicals and reagents were purchased from VWR International or Sigma-Aldrich (St. Louis, MO, USA) and used in this study without further purification. The Loblolly pine residue sample was collected from a plantation in Macon (Georgia, USA). The sample was milled through a Wiley mill to pass through a 2-mm screen based on TAPPI method T257 cm-02. The zeolite ZSM-5 (CBV 3020E) was purchased from Zeolyst International (USA). Ru/activated carbon catalyst (Product No. 7440-18-8) was purchased from Alfa Aesar (Ward Hill, USA).

2.2 Preparation of pyrolysis sample

The pyrolysis samples were prepared by mechanically stirring the pine residue and zeolites in a 1:1 ratio (*w*/*w*). The zeolites were activated in the pyrolysis tube at 500°C under nitrogen for 6 h. A blank pine sample (R) was also prepared for comparison. A detailed description of the zeolites used in this study is given in Table 1.

Table 1 Detailed description of zeolites used in this work

Physical properties	CBV 3020E
SiO_2/Al_2O_3 mole ratio	30
Framework	MFI
Code name	Z
Pore dimension	3
Pore size/nm	0.54

2.3 Pyrolysis of Loblolly pine residue

The pyrolysis experiments were performed in a quartz pyrolysis tube that was heated in a split tube furnace[21]. In general, 6.0 g of sample was used for pyrolysis. The sample was kept in a quartz sample boat, which centered in a pre-heated pyrolysis tube. During pyrolysis, a thermocouple was immersed in the powder sample to measure the heating rate. The furnace was pre-heated at 600°C and the pyrolysis tube was inserted into the furnace after flushing with N_2 gas at a flow rate of 500 mL/min. After completion of pyrolysis, the pyrolysis tube was removed from the furnace and allowed to cool down to room temperature under constant N_2 flow. The condensers were then removed from the liquid N_2 and the pyrolysis products (oil and char) were collected for subsequent chemical analysis. Generally, the liquid fraction comprised heavy and light oil and formed two immiscible phases. The light oil was collected by decantation of the upper portion and the reactor was washed thoroughly with acetone, followed by evaporation under reduced pressure to recover the heavy oil. The char yield and gas formation was calculated gravimetrically and from the mass difference, respectively.

2.4 Hydrogenation of pyrolysis oil

The hydrogenation of pyrolysis heavy oil was carried out as reported[22]. In brief, the hydrogenation reaction was carried out in a 300 mL Parr 4520 Micro Stirred Reactor.

In this process, 150 mg of heavy oil, 50 mL of DI water, and 0.5 g of formic acid were loaded into a glass liner with 15 mg of 5 wt% Ru/activated carbon catalyst. Formic acid dissociates in the presence of DI water to exhibit acidic behavior. The stirring rate in the reactor was adjusted to approximately 200 r/min. To remove the air present in the reaction vessel, the reactor was purged five times with N_2 gas. The reactor was heated to 250±3°C and the temperature was maintained for 4 h; the pressure in the vessel was ~10 MPa. Once the reaction time was reached, the reactor was cooled in an ice-water bath to release the pressure in the vessel. After the hydrogenation process, a 0.45-μm syringe filter was used to remove the catalyst from the heavy oil solution. The aqueous phase of the hydrogenation products (50 mL) was extracted with 2.0 mL $CDCl_3$. The $CDCl_3$ phase was dried with $MgSO_4$ and filtered through a 0.45-μm syringe filter. The relaxation reagent chromium(III) acetylacetonate (0.01 mol/L) was added to the $CDCl_3$ filtrate to provide complete relaxation of all nuclei, and the $CDCl_3$ solution was used as the NMR sample for the hydrogenation product.

2.5 Characterization of pyrolysis oil by gel permeation chromatography (GPC)

The weight average molecular weight (M_w) of the heavy oils after each pyrolysis step was determined by GPC according to literature methods[9]. Before the GPC analysis, a solution of the sample was prepared by dissolving the oil in THF (1 mg/mL) and filtering the solution through a syringe filter (0.45 μm). The sample solution was then injected into a Polymer Standards Service (PSS) Security 1200 system with an Agilent High-Performance Liquid Chromatography (HPLC) vacuum degasser, isocratic pump, refractive index (RI) detector, and UV detector (270 nm). Separation was carried out with four different Waters Styragel columns (HR0.5, HR2, HR4, HR6); tetrahydrofuran (THF) was used as the mobile phase (1.0 mL/min) with an injection volume of 30 μL. Data analysis was performed with PSS WinGPC Unity software. A calibration curve was constructed and the molecular weight (M_w) was calibrated using this curve. The calibration curve was fitted to a third-order polynomial equation and the retention volumes obtained from a series of narrow molecular weight distribution polystyrene standards (i.e., 7.21×10^3, 4.43×10^3, 1.39×10^3, 5.80×10^2 Da), dioctyl phthalate (M_w=390 g/mol), 2,29-dihydroxy-4,49-dimethoxyl-benzophenone (M_w=274 g/mol), 2-phenylhydroquinone (M_w=186 g/mol), phenol (M_w=94 g/mol), and acetone (M_w=58 g/mol). The R^2 value for the curve fit was 0.998.

2.6 Characterization of pyrolysis oil by NMR

2.6.1 Quantitative ^{31}P-NMR

Before the quantitative ^{31}P-NMR analysis, the samples were prepared in the following manner: 10.0 mg of heavy oil was derivatized *in situ* with 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane (TMDP) in a solution of (1.6:1 *V/V*) pyridine/$CDCl_3$, chromium acetylacetonate (relaxation agent), and endo-*N*-hydroxy-5-norbornene-2,3-dicarboximide (NHND, internal standard). ^{31}P-NMR spectral data were acquired at room temperature by applying an inverse-gated decoupling pulse sequence with a pulse angle of 90° and a 25 s pulse cycle; 128 scans were used and the LB was 4.0 Hz.

2.6.2 Quantitative ^{13}C-NMR

A Bruker Avance/DMX 400 MHz NMR spectrometer was used to perform all NMR spectral studies. Quantitative ^{13}C-NMR was performed by dissolving 100.0 mg of heavy oil in 450 μL of dimethyl sulfoxide-d_6 (DMSO-d_6) and applying a reverse-gated decoupling pulse sequence with a 90° pulse angle, a pulse delay of 20 s, and 6000 scans, at room temperature, with a line-broadening (LB) of 5.0 Hz. Chromium acetylacetonate (1 mg/mL, a relaxation reagent) was added to the solutions to reduce the measurement time.

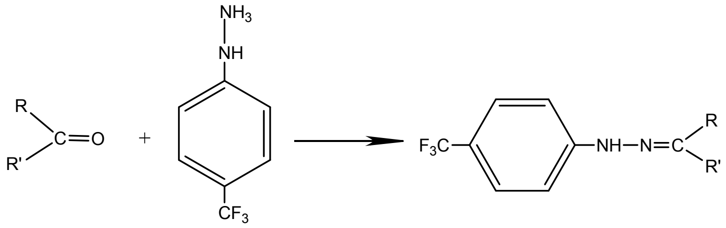
2.6.3 HSQC-NMR

HSQC-NMR analysis was performed with the same sample preparation used for the ^{13}C-NMR analysis. The HSQC-NMR data were acquired by applying a standard Bruker pulse sequence ‘‘hsqcetgpsi.2’’ with a pulse angle of 90°, 1.5 s pulse cycle, 0.11 s acquisition time, $^1J_{\mathrm{C-H}}$ of 145 Hz, 48 scans, and acquisition of 1024 data points (for ^{1}H), and 256 increments (for ^{13}C). The pulse widths and spectral widths of ^{1}H and

^{13}C were p1=11.30 μs, p3=10.00 μs, and 13.02 ppm and 220.00 ppm, respectively. The chemical shift was calibrated relative to the central solvent peak. MestReNova v7.1.0 software was used with a default processing template and automatic phase and baseline correction; HSQC-NMR data processing and plots were implemented using the same software.

2.6.4 ^{19}F-NMR

Carbonyl-containing compounds, i.e., pyrolysis oil, can react with trifluoromethylphenylhydrazine as follows (Scheme 1):



Scheme 1 Reaction between pyrolysis oil and trifluoromethylphenylhydrazine

The derivatives were directly analyzed by ^{19}F-NMR spectroscopy. The ^{19}F-NMR was used to quantitatively analyze the carbonyl content in the aldehyde and ketone compounds within the pyrolysis oil. The pyrolysis oil was derivatized as follows: the pyrolysis oil (~60 mg) was dissolved in 500 μL DMF; 1 mL of 50/50 DMF/water (*V/V*) containing 110 mg of 4-trifluoromethylphenylhydrazine was then added. To complete the reaction, the mixture was kept in the dark with continuous stirring at room temperature for 24 h. Thereafter, the derivatized pyrolysis oil sample was precipitated by adding ~20 mL dilute hydrochloric acid (pH value=2.0) and then frozen. Upon melting of the frozen sample at room temperature, the aqueous layer was discarded and the precipitate was vacuum-dried. The dried precipitate was dissolved in 450 μL of DMSO-d_6 containing 3-trifluoromethoxybenzoic acid (10 mg /mL, Lancaster Synthesis Incorporated) as an internal standard for the ^{19}F-NMR analysis. A 90° pulse without proton decoupling, 10 s pulse delay, and ~400 acquisitions were used for the quantitative ^{19}F-NMR analysis. Integration was accomplished by using MestReNova v7.1.0 software.

2.6.5 Quantitative ^{1}H-NMR

The quantitative ^{1}H-NMR data were acquired with 16 transients and 1 s pulse delay. The sampling procedure used for ^{1}H-NMR was the same as that used for the quantitative ^{13}C-NMR.

2.7 Determination of physical properties of bio-oils

The pour-points and cloud-points of the pyrolysis heavy oils were measured with a 70Xi cloud-, pour-, and freeze-point lab analyzer manufactured by Phase Technology. All the tests were performed with the manufacturer's default methods and the data were processed by the analyzer. The cetane number of the pyrolysis oil was measured with a ZX-101XL portable octane/cetane analyzer (Zeltex, Inc., USA). The pH value of the pyrolysis oil was determined with a pH meter (Mettler Toledo FE28-Meter, Zurich, Switzerland). The specific gravity of the liquid pyrolysis oil was determined by pycnometry according to ASTM standards[23]. C, H, O, and N analysis was performed with a PerkinElmer Optima 7300 DV inductively coupled plasma-optical emission spectrometer (ICP-OES). The flash-point of the bio-oil was determined by the small-scale closed cup method according to ASTM D3828[24]. The viscosity of the bio-oil was measured with a viscometer (Brookfield, DV-3TTJC, Middleboro, USA). The higher heating value (HHV) of the bio-oil was determined by using an oxygen-bomb colorimeter (Parr 6400, USA) based on a literature method[25].

3 Results and discussion

3.1 Pyrolysis yield

The yields from the zeolite-assisted pyrolysis of Loblolly pine residue are summarized in Fig.1. The results show that addition of the zeolite increased the production of light oil and char, but decreased the yield of heavy oil and gas. This is because the zeolite induces secondary reaction of the heavy oil to generate light oil and char[26]. Thus, the production of heavy oil decreased and the fraction of light oil and gas increased after using the zeolite. A similar observation was reported[27] for the catalytic pyrolysis of pinewood sawdust.

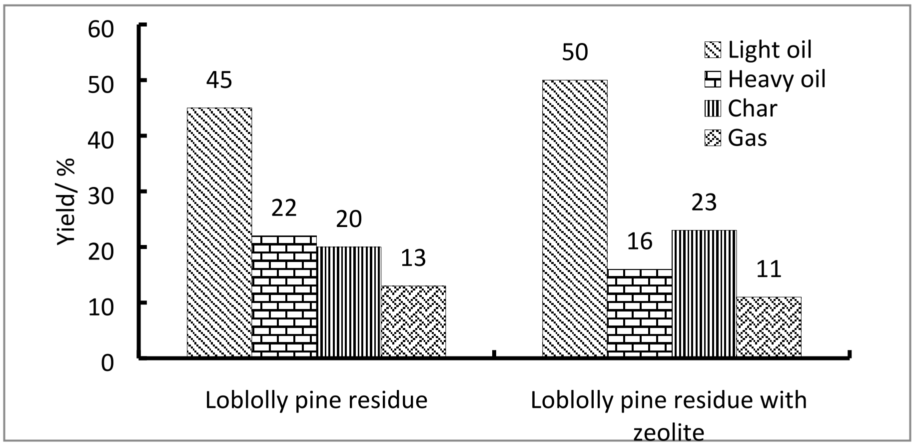


Fig.1 Yields (wt%) of light oil, heavy oil, char (excludes the weight of zeolite), and gas for the pyrolysis of Loblolly pine residue (R) with 1.0/1.0 ($W_{\mathrm{additive}}/W_{\mathrm{lignin}}$) of zeolite

3.2 Quantitative ^{31}P-NMR analysis of pyrolysis oil

Quantitative ^{31}P-NMR is one of the best processes for assay of the hydroxyl functional groups in heavy oils[28-29]. The integrated ^{31}P-NMR data for the heavy oils are summarized in Fig.2. As shown in Fig.2, the zeolite could decrease the aliphatic hydroxyl group content of the heavy oils by 57%. The results show that the pyrolysis oils formed by the zeolite-assisted process contained very little water. After use of the zeolites, the carboxylic acid content also decreased slightly. This result indicates that the zeolites could induce decarboxylation reactions to a small extent.

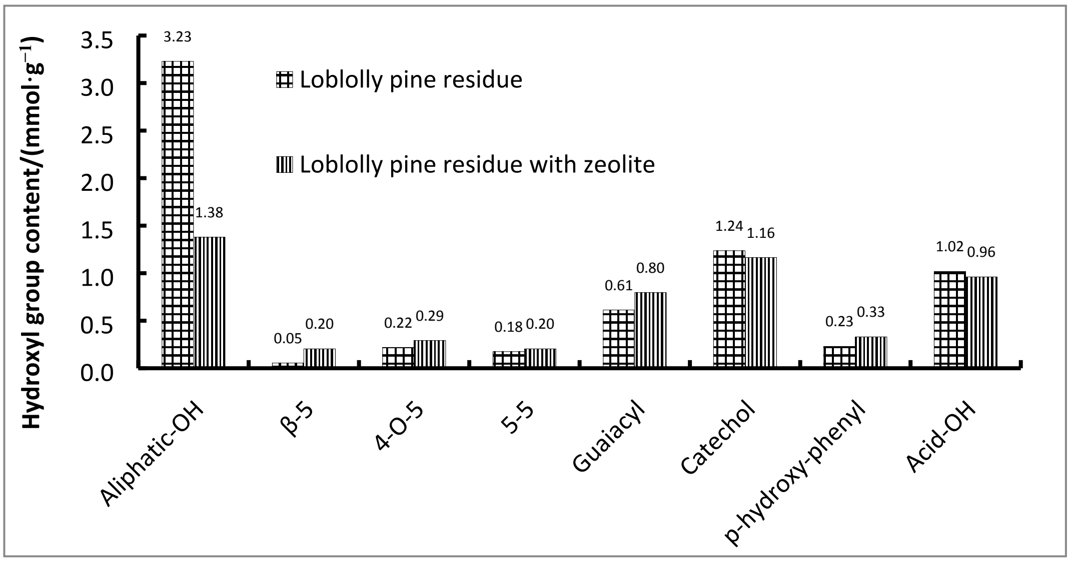


Fig.2 Hydroxyl group content of different heavy oils produced by pyrolysis of Loblolly pine residue

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

To fully characterize the functional groups in the heavy oils, detailed analysis was accomplished by using ^{13}C-NMR. Fig.3 shows the quantitative integrated ^{13}C-NMR data for the pyrolysis heavy oil. The content of carbonyl groups decreased by 29%, indicative of lower acidity of the pine residue pyrolysis oil. Another trend observed from ^{13}C-NMR data is that the pyrolysis oils from zeolite-assisted process contained remarkably more aromatic C—C bonds compared to the pyrolysis oils from the non-assisted zeolite process. In addition, the content of aliphatic C—C bonds in the bio-oils from zeolite-assisted pyrolysis was lower than that in the bio-oil from non-zeolite assisted pyrolysis, which indicates that the zeolite could improve cleavage of the aliphatic C—C bonds. Interestingly, the percentage of aromatic C—C bonds in the oils from the zeolite-assisted process was much higher than the aliphatic C—C bonds, which indicates that the increase in the aromatic C—C bonds arises primarily from polyaromatic hydrocarbons or biphenyl structures. Addition of the zeolite diminishes the number of carbonyl groups in the bio-oils, but increases the number of aromatic C—C bonds.

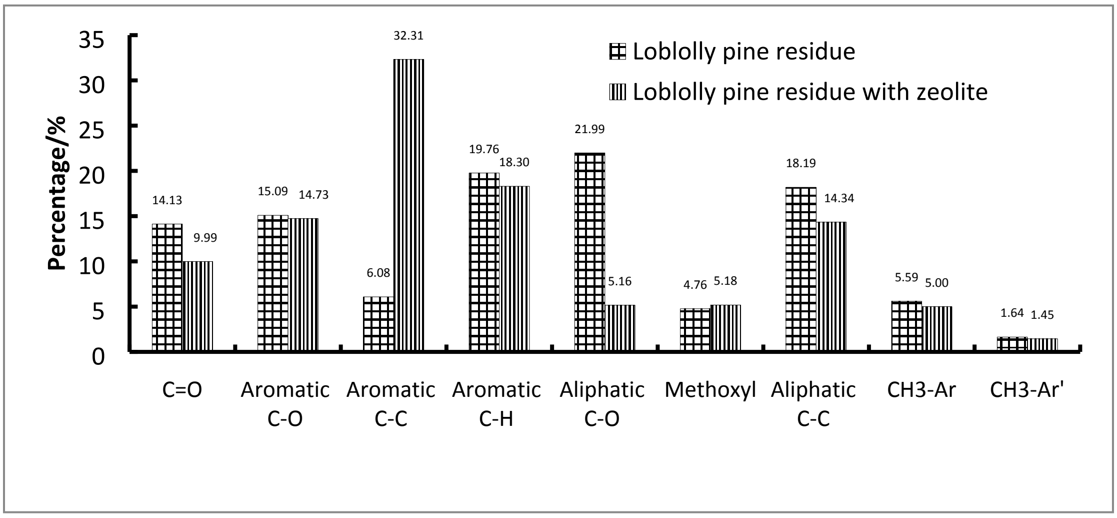


Fig.3 Quantitative ^{13}C-NMR integration data for heavy oils produced from Loblolly pine residue (the results are shown as the percentage of total carbon)

3.4 HSQC-NMR analysis of pyrolysis oil

HSQC-NMR (2D NMR) is a modern technique that can be applied to the semi-quantitative analysis of more than thirty different C—H bonds[30-32], and was applied herein to the analysis of the different C—H bonds in pyrolysis oil. Analysis of the different C—H bonds in pyrolysis oil using HSQC-NMR is a well-studied technique, and some limitations of ^{13}C-NMR can be overcome using this method. The Loblolly pine residue contains significant amount of lignin and cellulose[33], therefore, it is necessary to understand the pyrolysis compounds from these wood fractions. Based on the ^{1}H- and ^{13}C-NMR chemical shifts of the compounds in the pyrolysis oils[30], the detailed HSQC-NMR assignments for the compounds in the pyrolysis oil produced from Loblolly pine residue Kraft lignin and cellulose are summarized in Fig.4 and Fig.5, respectively. The HSQC-NMR spectra of the pyrolysis oils formed in the presence of the zeolites are shown in Fig.6~ Fig.9. Levoglucosan (Compound I in Fig. 5) is one of the major components present in the Loblolly pine residue pyrolysis oil, and was mainly derived from the pyrolysis of cellulose and hemicellulose in the Loblolly pine residue. Fig.6 shows the HSQC-NMR spectra and the assignments of each carbon for levoglucosan in the Loblolly pine residue pyrolysis oils. The content of levoglucosan decreased after zeolite-assisted pyrolysis. These results indicate that the zeolite could significantly promote the decomposition of cellulose and hemicellulose during the pyrolysis process, which is consistent with previous reports[22]. Fig.7 shows the signals of the aromatic C—H bonds in the HSQC-NMR spectra of the Loblolly pine residue pyrolysis oils. The data indicate that the major aromatic components in the Loblolly pine residue pyrolysis oils contained A1, A2, A3, B1, and B2 types (shown in Fig.4) of aromatic C—H bonds, similar to lignin pyrolysis oils. In addition, the content of E2 and B1 type (shown in Fig.4 and Fig.5) aromatic C—H bonds decreased significantly during zeolite-assisted pyrolysis, which is mainly attributed to the decomposition of lignin[21]. Fig.8 indicates that the methoxyl groups (compounds C1 and C2 in Fig.4) increased in the zeolite-upgraded samples, which is consistent with the results shown in Fig.3. Fig.9 shows that the content of aliphatic C—H bonds was not significantly different in the samples from the zeolite-assisted and non-zeolite-assisted pyrolysis processes.

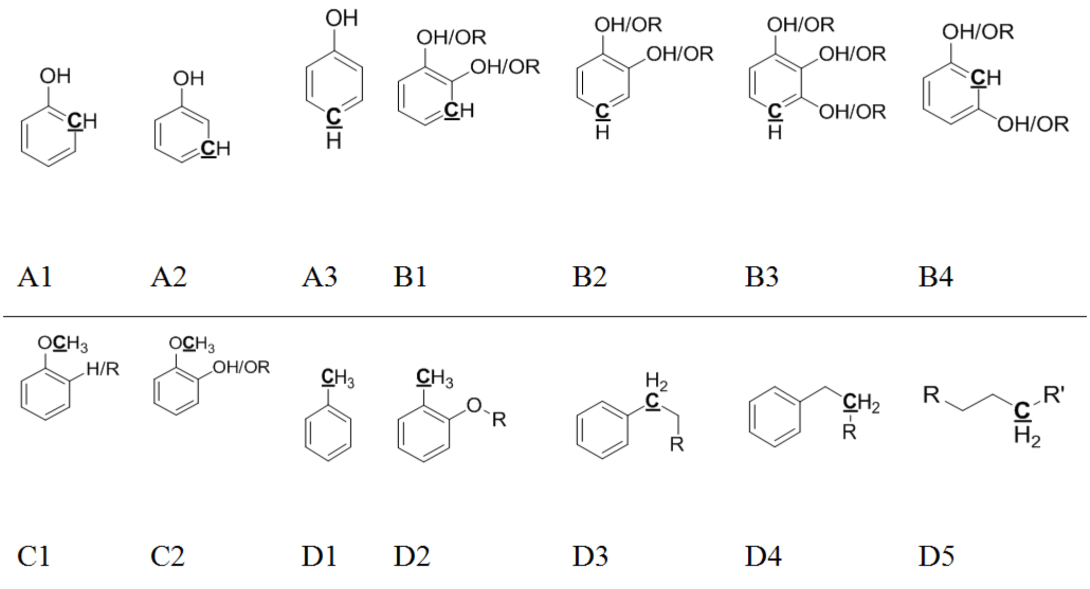


Fig.4 Detailed structures and assignments from HSQC-NMR analysis of pyrolysis oil produced from Loblolly pine residue Kraft lignin

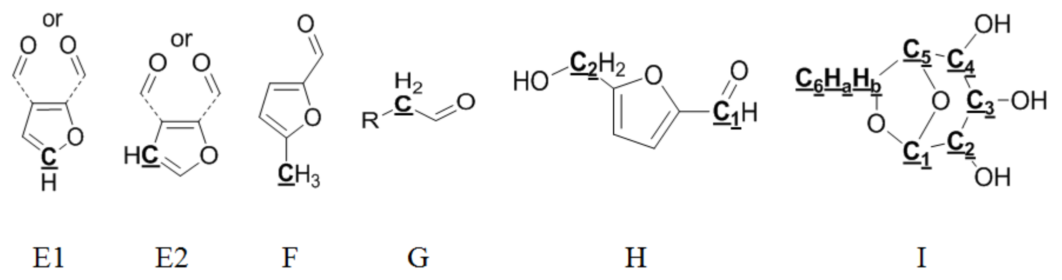


Fig.5 Detailed structures and assignments from HSQC-NMR analysis of pyrolysis oil produced from Loblolly pine residue cellulose

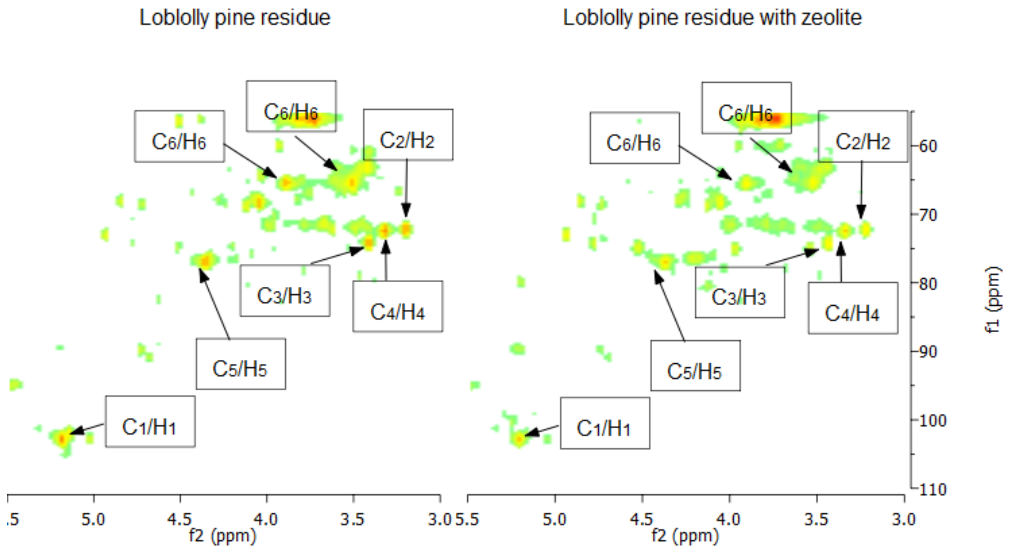


Fig.6 HSQC-NMR spectra and assignments of each carbon in levoglucosan in pyrolysis oils

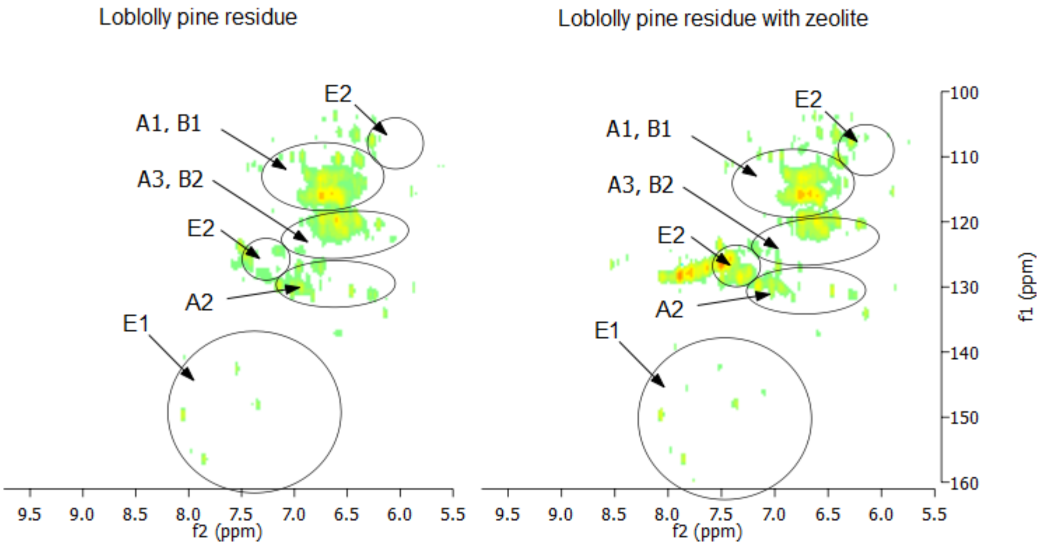


Fig.7 Aromatic C—H signals in HSQC-NMR spectra of pyrolysis oils

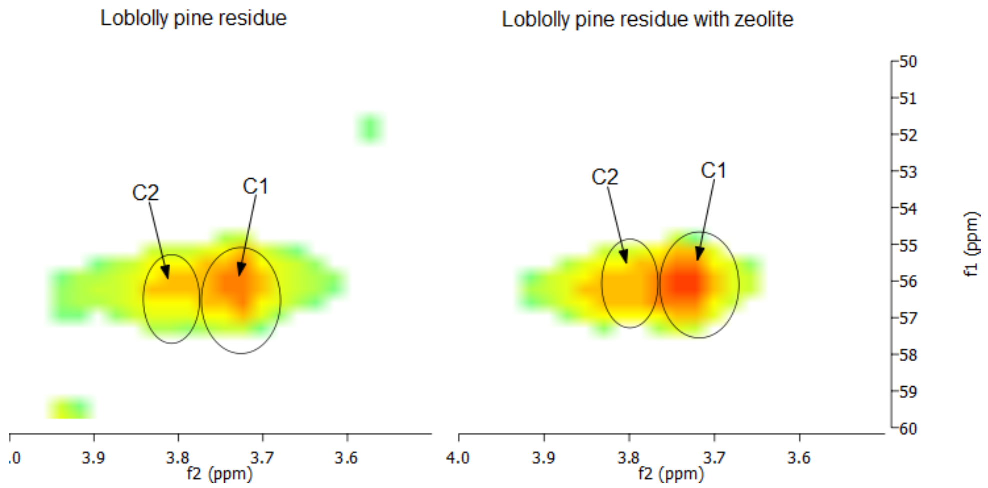


Fig.8 Methoxyl signals in HSQC-NMR spectra of pyrolysis oils

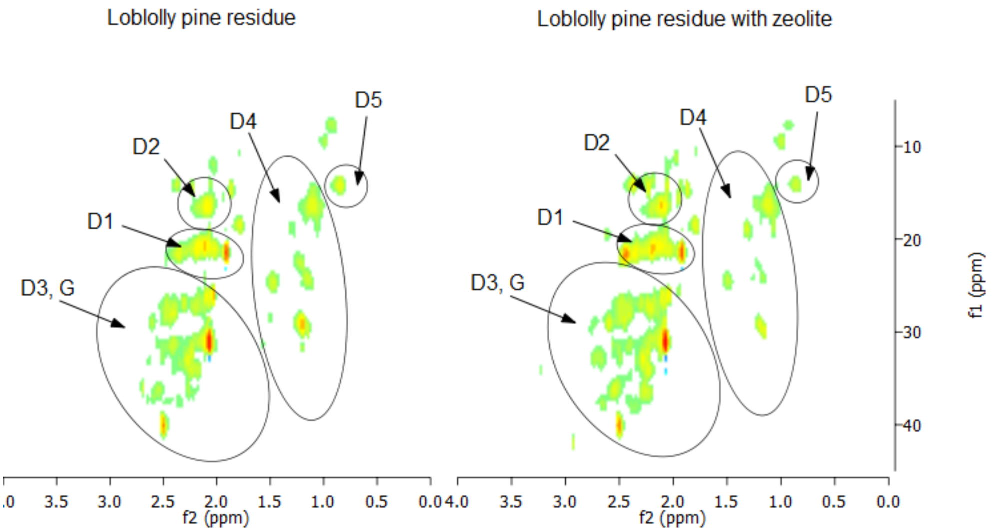


Fig.9 Aliphatic C—H signals in HSQC-NMR spectra of pyrolysis oils

3.5 Molecular weight of pyrolysis oil

The average molecular weights (M_w) of the heavy oils produced by pyrolysis of Loblolly pine residue with the zeolites at 600°C are summarized in Fig.10. Addition of the zeolite decreased the M_w of the pyrolysis oil by 19%. This indicates that the zeolite could induce catalytic degradation and produce lower molecular weight bio-oil. A similar result was reportedly achieved by using ZSM-5 zeolite for catalytic pyrolysis[34].

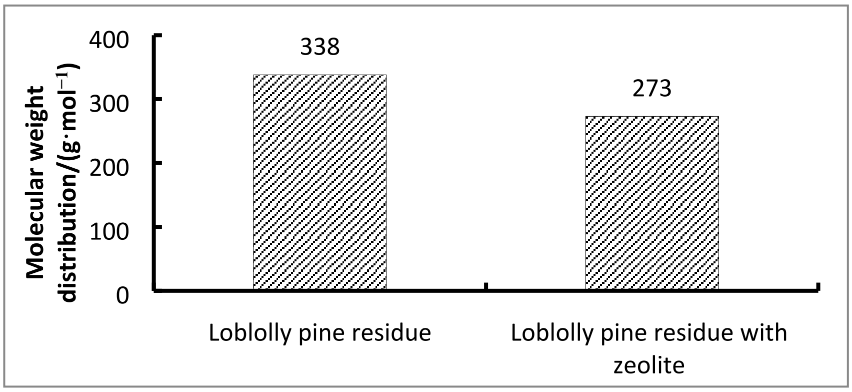


Fig. 10 Molecular weight distribution (M_w) of heavy oils produced by pyrolysis of Loblolly pine residue

3.6 ^{19}F-NMR analysis of pyrolysis oil

Table 2 shows the ^{19}F-NMR analysis of the carbonyl groups in the pyrolysis oils. Addition of the zeolite decreased the carbonyl group content by 11% and the quinone content by 25%. This tendency is in good agreement with the ^{13}C-NMR data (Fig.3).

Table 2 ^{19}F-NMR analysis of carbonyl groups in the pyrolysis oils

Samples	^{19}F-NMR analysis	
	Carbonyl (aldehyde and ketone) (mmol·g^{-1})	Quinone (mmol·g^{-1})
Loblolly pine residue pyrolysis oil	4.31	0.83
Zeolite-assisted Loblolly pine residue pyrolysis oil	3.85	0.62

3.7 Physical properties of pyrolysis oil

The physical properties of the pyrolysis oil produced from Loblolly pine residue are summarized in Table 3. The pour point of the pyrolysis oil from the zeolite-assisted process was lower than that of the pyrolysis oil from the non-zeolite-assisted process. This is because the zeolite could enhance the decomposition of carbonyl groups, as shown in Fig.3. It should be noted that the cloud points for all types of heavy oils were undetectable by this cold flow property analyzer. A possible reason is the dark color of the bio-oil, which makes the observation difficult[35]. The cetane numbers were lower than the bio-oil range due to the significant content of aromatic compounds[36] in the pyrolysis oil. This value is expected to fall in the bio-oil range after refining the pyrolysis oil. In contrast, the cetane number increased slightly after using the zeolite. The zeolite could enhance the degradation of lignin, leading to a relatively higher cetane number for the bio-oils compared with that obtained after non-zeolite-assisted pyrolysis oil. The other properties of the pyrolysis oil with ZSM-5 were similar to those achieved with non-zeolite-assisted pyrolysis oil.

Table 3 Physical properties of pyrolysis oils and bio-oil

	Bio-oil from Loblolly pine residue		
Physical properties	Pyrolysis oil without zeolite	Pyrolysis oil with zeolite	Bio-oil[35, 37-39]
Pour point/°C	−12.0	−22.5	(−36)~(−9)
Cetane number	14.3	16.9	49~62
pH value	2.5	2.4	2.0~4.0
Relative density	1.2	1.2	1.1~1.3
C/%	54.3	55.8	54~58
H/%	5.6	6.1	5.5~7.0
O/%	35.2	35.6	35.0~40.0
N/%	0.1	0.1	0.0~0.2
Flash point/℃	80	78	50~100
Viscosity (at 50℃)/(mPa•S)	105	95	40~100
HHV/(MJ·kg^{-1})	16.2	16.8	16~19

3.8 Analysis of hydrogenated pyrolysis oil

Fig.11 shows the ^{1}H-NMR spectra of the Loblolly pine residue pyrolysis oil and hydrogenated Loblolly pine residue pyrolysis oil. The integration results are shown in Table 4. The hydrogenation process eliminated 78% of the aromatic protons, and 74% of the protons was derived from the aliphatic protons with no oxygen attached to the α-carbon. This indicates that the majority of carbon in the hydrogenated pyrolysis oils was aliphatic carbons. In addition, the hydrogenated pyrolysis oils have a relatively low oxygen content, and thus represent a potential resource for bio-gasoline. Fig.12 shows the ^{1}H-NMR spectra of the pyrolysis oil from ZSM-5-assisted treatment of Loblolly pine residue and hydrogenated pyrolysis oil from ZSM-5-assisted treatment of Loblolly pine residue. The integration results are shown in Table 5. The hydrogenation process significantly increased the content of aliphatic carbons and decreased the content of aromatic carbons.

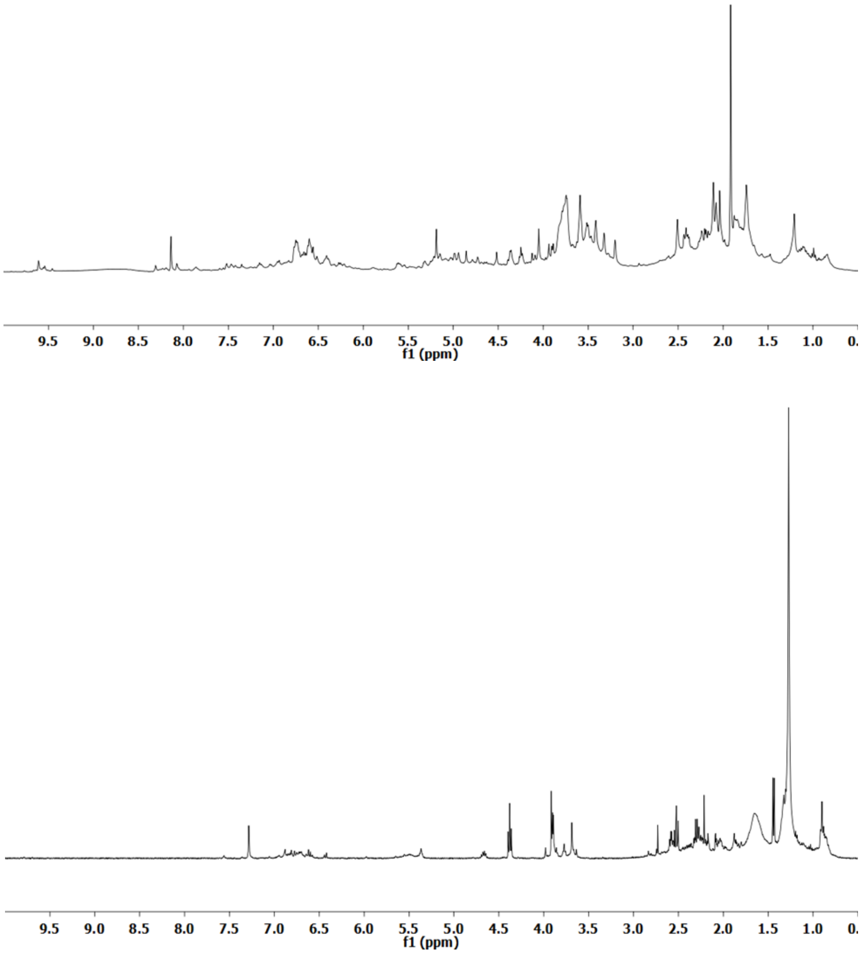


Fig.11 ^{1}H-NMR spectra of Loblolly pine residue pyrolysis oil and hydrogenated Loblolly pine residue pyrolysis oil (from top to bottom)

Table 4 ^{1}H-NMR chemical shift assignment ranges and functional group contributions for the Loblolly pine residue pyrolysis oils

Types 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

[a]Assignment ranges are on the basis of literature reports[29, 40].

[b]Results are shown as percentage hydrogen.

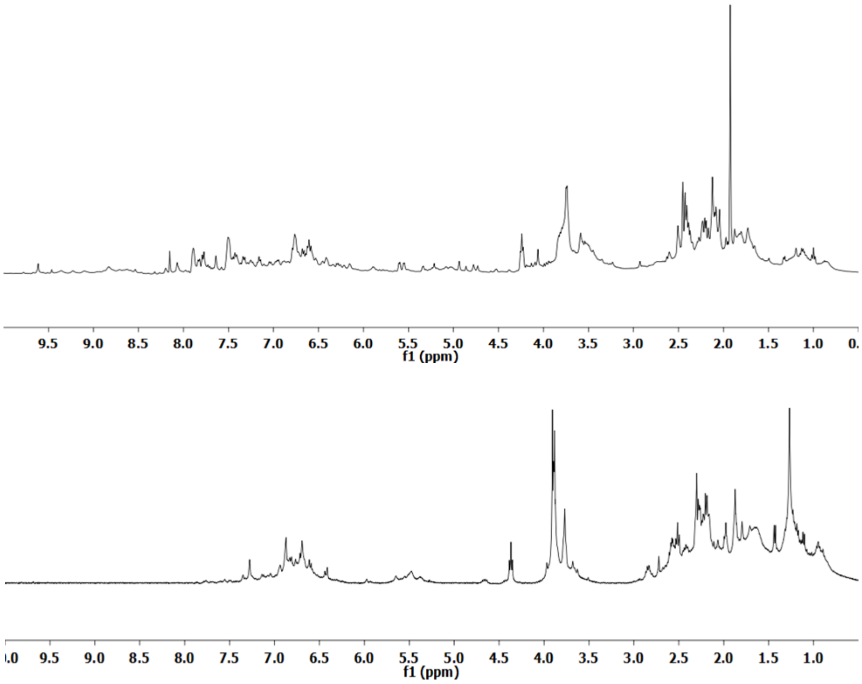


Fig.12 ^{1}H-NMR spectra of pyrolysis oil from zeolite-assisted treatment of Loblolly pine residue and hydrogenated pyrolysis oil from zeolite-assisted treatment of Loblolly pine residue (from top to bottom)

Table 5 ^{1}H-NMR chemical shift assignment ranges and functional group contributions for the zeolite-assisted pyrolysis oils

Types of protons	Range/ppm	Zeolite-assisted Loblolly pine residue pyrolysis oil	Zeolite-assisted hydrogenated Loblolly pine pyrolysis oil
—CHO, —COOH	10~9.6	0.31	0
ArH, HC=C—	8.2~6.0	24.17	13.13
—CH_n—O—, CH_n—O—	6.0~3.0	25.94	15.25
—CH_3, —CH_n—	3.0~0.5	49.58	71.62

4 Conclusions

The pyrolysis of Loblolly pine residue was carried out in the presence of ZSM-5 zeolite, and the pyrolysis oil was hydrogenated using formic acid as a source of hydrogen. NMR analysis proved that the zeolite effectively induced decarboxylation reactions and decreased the content of aliphatic hydroxyl groups in the heavy oil by 57%. The zeolite decreased the molecular weight of the pyrolysis oil by 19%. After hydrogenation, the aromatic carbon content decreased by 78%, whilst the aliphatic carbon content increased significantly.

Declaration of interests: None

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