Catalytic Hydrotreatment of Light Distillates Obtained from Bio-Oil for Use in Oxygenated Liquid Fuels

Xianwei Zheng, Jie Chang, and Yan Fu*

Bio-oil can be fractionated into three parts according to their boiling points. This research reported that light distillates could be converted into oxygenated liquid fuels through a two-stage hydrotreatment approach, using a Pd/C catalyst. The main goal of the first hydrotreatment stage was to stabilize the high active components, which contained carbon–carbon double bonds and aldehyde groups. The second hydrotreatment stage aimed to saturate the components with benzene rings and keto groups, resulting in saturated oxygenated compounds. The H/C_{eff} ratio was improved greatly after the two-stage hydrotreatment, increasing from 0.51 (in the reactant) to 1.67 (in the final products). The high heating value of the final products was 31.63 MJ/kg. After the two-stage hydrotreatment, the main products were C_5–C_9 alcohols, which were tested *via* gas chromatography–mass spectrometry. The products could be blended with gasoline directly. Based on the experiments regarding the hydrogenated model compounds, a reaction schematic for the two-stage hydrotreatment was created. Moreover, the bio-oil hydrotreatment kinetics were investigated. The order of the hydrotreatment reaction was 2.0, and the apparent activation energy (E_a) was 57.29 KJ/mol.

Keywords: Bio-oil; Hydrotreatment; Fuel; Kinetics; Pd/C

*Contact information: The Key Lab of Enhanced Heat Transfer and Energy Conservation, Ministry of Education, School of Chemistry and Chemical Engineering, South China University of Technology, Wushan Road 381, Guangzhou, 510640, China; *Corresponding author: fuyan@scut.edu.cn*

INTRODUCTION

Recent environmental concerns, coupled with growing awareness of potential future energy shortages, have boosted research on fossil fuel alternatives. Biomass is the most abundant and inexpensive sustainable feedstock used to produce renewable fuels and chemicals (Sharma and Bakhshi 1993; Bridgwater *et al.* 1999; Luo *et al.* 2004). Fast pyrolysis is the leading technology for converting biomass to liquid products (known as fast pyrolysis oil or bio-oil), which are potential fossil fuel substitutes (Chang 2003; Lu *et al.* 2007; Wang *et al.* 2010a). However, bio-oil cannot be used in conventional gasoline and diesel fuel engines because of its high oxygen and water contents, as well as its high acid content (Czernik and Bridgwater 2004; Wang *et al.* 2012a). Ideally, the bio-oil should be upgraded to obtain a mixture of organic molecules that are more compatible with current fuel infrastructures (Elliott 2007).

Raw bio-oil has been upgraded using various methods, such as esterification, hydrotreatment, and cracking (Wang *et al.* 2010b, 2012b). Hydrotreatment is considered to be an effective method for upgrading bio-oil (Huber *et al.* 2006). Ni-based catalysts have been used to hydrogenate model compounds of phenols and bio-oil (Zhao *et al.* 2010; Zhang *et al.* 2013), and the model compounds of phenols can be converted into hydrocarbons. Furthermore, noble metal catalysts have also been reported in bio-oil hydrotreatment. Wildschut *et al.* (2010) reported a bio-oil hydrotreatment study that used a Ru/C catalyst, under the conditions of 350 °C, 200 bar. According to Wildschut *et al.* (2010), an increase in the reaction time leads to a significant decrease in the oil yield, due to the formation of gas phase components. Using a one-pot hydrotreatment yields an undesirable quality of upgraded oil, and the oil yield is relatively low. Hence, a two-stage hydrotreatment approach has been proposed. First, low-temperature hydrotreatment stabilizes the bio-oil, and the subsequent high-temperature hydrotreatment is conducted to obtain the target products. Elliott *et al.* (2012) investigated two-stage catalytic hydroprocessing of pine bio-oil on a continuous-flow fixed-bed reactor system, using a Ru/C catalyst, and concluded that high yields of deoxygenated hydrocarbon products can be obtained. Vispute *et al.* (2010) have reported the results of the two-stage bio-oil hydrogenation with Ru/C and Pt/C catalysts and concluded that industrial commodity chemical feedstocks (aromatic hydrocarbons and light olefins) can be obtained. Pd/C catalyst has the potential to provide higher oil yields than Ru/C, and Pd/C also has a weaker deoxidization ability (Wildschut *et al*. 2009). Therefore, Pd/C is considered suitable for application in the preparation of oxygenated liquid fuels.

These previous studies mainly focused on upgrading all the components of bio-oil, and the high quality of liquid fuels could not be obtained because of complicated bio-oil composition. Hence, the classified separation of bio-oil prior to upgrading was proposed, which was beneficial to the enrichment of compounds with similar properties (Zheng *et al.* 2013). In addition, the number range of carbon atom in each separated bio-oil fraction is similar to gasoline, diesel, and the residual oil of petroleum. Then the upgraded bio-oil can be used either as a gasoline or diesel replacement, or as a blending material with gasoline or diesel. Guo *et al*. (2011) have reported that the upgrading process of molecular distillated fraction separated from bio-oil could greatly reduce the corrosiveness of the bio-oil and improve its storage stability.

Therefore, this study investigates a two-stage hydrotreatment approach for light distillates (C_5–C_{10}) separated from bio-oil with a Pd/C catalyst to obtain high quality of liquid fuels, which can be used as a blending material with gasoline. The reaction schematic is illustrated based on the experiments of model compounds. In addition, the kinetics of the second hydrotreatment stage is investigated to predict the product distribution and establish a reaction model.

EXPERIMENTAL

Materials

The original bio-oil provided by Xinfa Garden Engineering Co., Ltd (Shandong, China) was produced from poplar and pine sawdust. The flash pyrolysis temperature ranged from 500 °C to 700 °C. The annual bio-oil yield was 100,000 tons. The bio-oil was fractionated into three parts according to the boiling point obtained during pyrolysis. These fractions were light distillates, middle distillates, and heavy distillates. During the experiments, oil with light distillates was used. When this part of the oil was stored in a refrigerator for a certain duration, the oil separated into two phases (oil phase and aqueous phase) automatically. The extracted material used in this study was the oil phase. Table 1 presents the properties of the feedstock and upgraded products. The noble metal catalyst Pd/C, which contained 1, 3, 5, and 10 wt.% of active metal, was purchased from J&K

Scientific Co., Ltd (China). The batch set-up was obtained from Beijing Century Senlong Experimental Apparatus Co., Ltd.

Table 1. Properties of Oil Phase and Upgraded Products

	Oil phase	Upgraded products after the first hydrotreatment stage	Upgraded products after the second hydrotreatment stage
High heating value (MJ/Kg)	21.02	24.39	31.63
Elemental compositions (wt.%):			
C	55.94	62.31	60.73
H	6.35	6.91	11.82
O	31.72	30.23	27.06
N	0.44	0.55	0.39
H/C_{eff}	0.51	0.60	1.67

Hydrotreatment of the Oil Phase Obtained from Bio-oil

The oil phase was hydrotreated in a 50 mL batch autoclave setup. In the first hydrotreatment stage, bio-oil (1.0 g), H_2O (20 mL), and 5 wt.% Pd/C were added into the reactor. The reactor was purged with H_2 five times. Moreover, the reaction was produced using a stirring speed of 800 rpm. After the reaction stopped, the reactor was cooled to room temperature. The liquid phase (LP) was removed from the reactor, and the yield was calculated. This LP was the product of the first hydrotreatment stage. Liquid (2 mL) was removed, and ethyl acetate was used to extract organic compounds, which were analyzed via gas chromatography–mass spectrometry (GC–MS). In the second experimental stage, the remaining liquid and 5 wt.% Pd/C were placed in the reactor. The reactor was purged with H_2 five times. The reaction was performed with 5 MPa of H_2, both at room temperature and at 523 K, with a stirring speed of 800 rpm. After the reaction was stopped, the reactor was cooled to room temperature. The LP was removed from the reactor, and the yield was calculated. H_2O was used to wash the reactor. Filtering was conducted, and the filtrate became the product of the second hydrotreatment stage. Ethyl acetate was used to extract the organic compounds. The extracted liquid was then vacuum distilled, and the hydrogenated products were obtained. The flow scheme of experimental process is shown in Fig. 1.

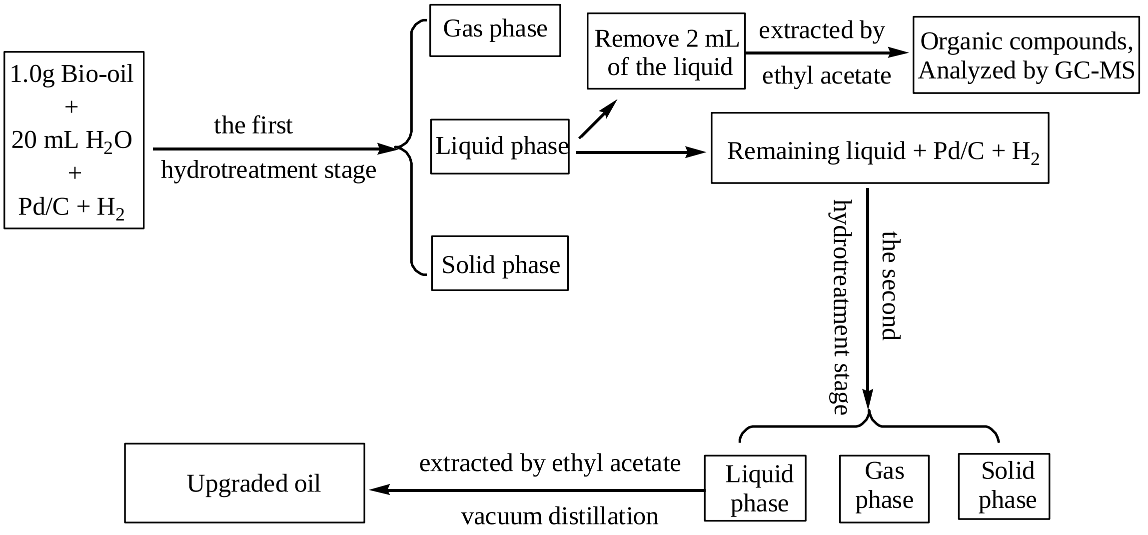


Fig. 1. The flow scheme of two-stage hydrotreatment process

External Mass Transport, Koros-Nowak (KN) Criterion Test, and Hydrotreatment Kinetics

The final product properties were mainly determined by the second hydrotreatment stage. Hence, the kinetics of the second stage was researched to predict the product distribution. To ensure favorable contact among the gas phase, the LP, and the catalyst, stirring speeds of 600, 700, 800, 900, and 1,000 rpm were used under the following conditions: 1.0 h, 523 K, and 5 wt.% Pd/C. To confirm the reaction rate independently from the internal transport phenomena, the KN criterion test was conducted using the catalyst with 1, 3, 5, and 10 wt.% active metal, under the conditions of 1.0 h, and 493 and 523 K. Moreover, the catalyst's active surface sites were measured by titration with carbon monoxide. The temperatures (493, 508, and 523 K) and a catalyst with 5 wt.% active metal were used to explore the order of the reaction, the activation energy, and the pre-exponential factor. The reaction times were 0.5, 1.0, 1.5, 2.0, 2.5, and 3.0 h.

Hydrotreatment of Model Compounds

The reaction mechanism experiments were conducted in the same reactor using pure model compounds. The hydrogenated conditions of vanillin, syringaldehyde, and 4-hydroxy-3-methoxycinnamaldehyde were 5 MPa H_2, 473 K, 2.0 h, and 800 rpm, respectively. The hydrogenated conditions of phenol, catechol, 4-methylcatechol, and 4-ethylcatechol were 5 MPa H_2, 523 K, 2.0 h, and 800 rpm, respectively. The reaction liquid was extracted with ethyl acetate and analyzed by gas chromatography-mass spectrometry (GC-MS).

Analyses Methods

The samples were diluted with ethyl acetate. The compositions of the reactants and products were analyzed using a Shimadzu QP 2010 Plus GC-MS equipped with an Rxi®-5 ms column (30 m × 0.25 × mm 0.25 μm). The injector temperature was 270 °C, and the ion source was 200 °C. The analysis conditions were as follows: the oven temperature was maintained at 40 °C for 4 min, heated at a rate of 4 °C/min to 120 °C, then increased to 280 °C at a rate of 10 °C/min, and held at 280 °C for 4 min. All the compounds were identified by means of the NIST08 and NIST08s mass spectral data library.

Elemental analyzer (Vario EL Ⅲ) determined the elemental composition (C, H, and N) of bio-oil and hydrogenated products. The oxygen content was determined by difference. The high heating value was measured with WGR-1 calorimetric bomb (ASTM D4809). UV spectrum analysis was performed with Shimadzu UV-2450, with the wavelength ranging from 190 to 500 nm.

RESULTS AND DISCUSSION

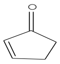
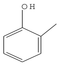
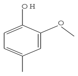
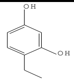
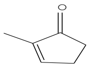
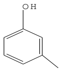
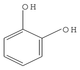
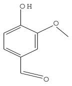
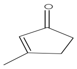
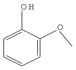
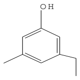
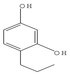
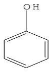
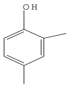
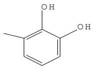
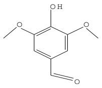
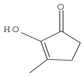
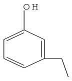
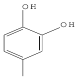
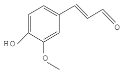
The hydrogen content of a particular feedstock could be expressed in terms of the hydrogen-to-carbon atomic effective ratio (H/C_{eff} ratio) of the feedstock, which was calculated based on the following formula (Vispute *et al.* 2010) (Eq. 1):

$$H/C_{eff} = \frac{moles\ of\ H - (2 \times moles\ of\ O)}{moles\ of\ C} \tag{1}$$

The H/C_{eff} ratio of the biomass feedstock was between 0 and 0.5, whereas that of the petroleum-based feedstock ranged from 1.0 to 2.0. Thus, the biomass-based feedstock was hydrogen deficient.

The materials used in the study had an H/C_{eff} ratio of 0.51, which was much less than the ratio of the petroleum-based feedstock. The oil phase compositions were analyzed via GC–MS. The main compounds are presented in Table 2. These compounds are divided into three categories. The first category included cyclopentene ketone and its derivatives, aromatic aldehydes, and furfural (Nos. 1, 2, 3, 5, 17, 19, and 20). The second category included phenol and its homologs, as well as catechol and its homologs (Nos. 4, 6, 7, 9, 10, 12, 13, 14, 15, 16, and 18). The third category included a small amount of guaiacol and its homologs (Nos. 8 and 11), whose properties are quite stable due to the present methoxyl groups (Zhao *et al.* 2010). These compounds were nearly unchanged during the entire hydrotreatment process. H_2O was used as solvent in this study. On the one hand, it was advantageous for the separation of products; on the other hand, water was an excellent solvent for the hydrogenation of phenols (Feng *et al.* 2014).

Table 2. Main Compounds in the Oil Phase

No.	Structure	Area%	No.	Structure	Area%	No.	Structure	Area%	No.	Structure	Area%
1		5.54	6		7.09	11		1.18	16		8.02
2		1.04	7		8.79	12		19.02	17		2.39
3		2.28	8		2.31	13		4.04	18		1.68
4		7.98	9		4.78	14		4.03	19		1.76
5		2.84	10		1.85	15		7.69	20		5.69

The First Hydrotreatment Stage of the Oil Phase

The reaction conditions and experimental results of this stage are shown in Fig. 2. Gas, liquid, and solid phases were produced after the reaction. The gas phase was analyzed *via* GC, and the main compounds were the excess of H_2. The LP, which was a yellowish-colored liquid, was the target product. The solid phase included the catalyst and the bio-oil coke (Li *et al.* 2014).

The LP was analyzed *via* GC–MS. Table 3 presents the main compounds. The compounds that contained carbon–carbon double bonds and aldehyde groups (the first category compounds in the oil phase) were converted into other substances. Cyclopentanone and methyl cyclopentanone were the hydrogenated products of cyclopentene ketone and methyl cyclopentene ketone. Furthermore, 2-Hydroxy-3-methyl-2-cyclopenteneketone, 4-hydroxy-3-methoxycinnamaldehyde, syringaldehyde, and vanillin disappeared after the reaction. The reaction path is discussed separately. The second and third categories in the oil phase remained unchanged during this stage.

As shown in Fig. 2, cyclopentene ketone was converted from 84.20% to 94.69%, and 4-hydroxy-3-methoxycinnamaldehyde was changed from 90.12% to 94.87%. Such changes were not significantly affected by the reaction conditions. By contrast, the conversions of vanillin (from 42.69% to 72.20%) and syringaldehyde (from 52.36% to 72.10%) were affected greatly by the reaction conditions. The effects of the reaction conditions were related to the activity of the functional groups. The appropriate conditions were 473 K, 5.0 MPa H_2, 2.0 h, and 0.075 g of Pd/C catalyst. At the appropriate reaction conditions for the first hydrotreatment stage, the yield of upgraded oil was 36%, and the H/C_{eff} ratio changed from 0.51 to 0.60. The high heating value was 24.39 MJ/kg. (Table 1).

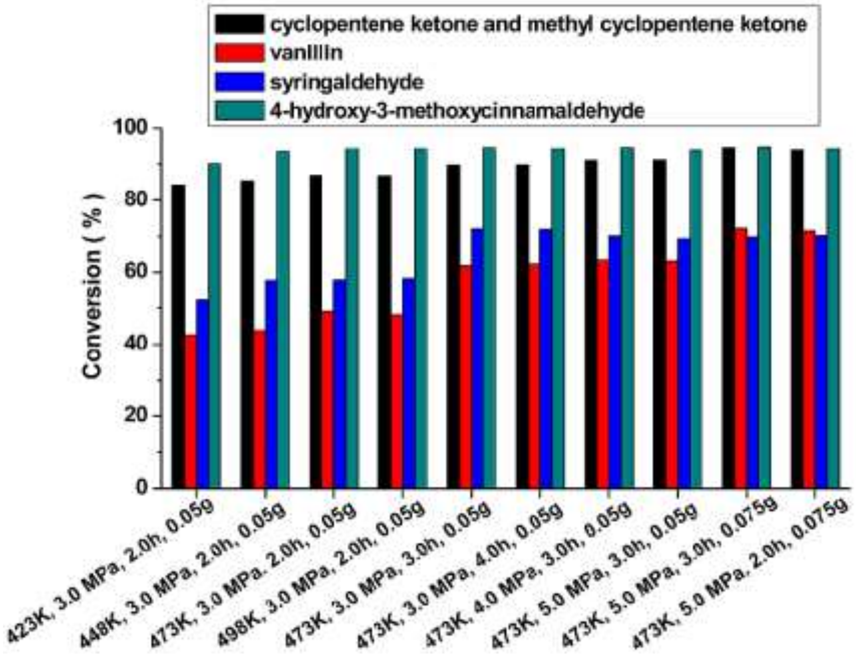


Fig. 2. Reaction conditions and experimental results of the first hydrotreatment stage

Table 3. Main Compounds after the First Hydrotreatment Stage

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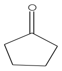
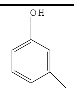
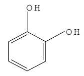
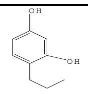
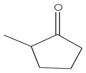
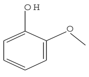
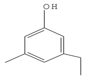
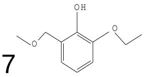
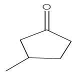
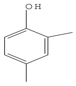
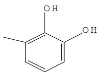
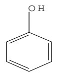
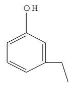
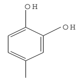
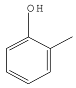
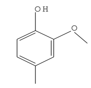
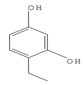
1		3.59	6		8.22	11		19.14	16		4.40
2		4.36	7		2.35	12		1.68	17		4.48
3		1.60	8		3.74	13		4.79			
4		8.08	9		4.37	14		10.14			
5		6.08	10		1.76	15		11.21			

The Second Hydrotreatment Stage of the Oil Phase

The products of the first hydrotreatment stage were used as the reactants in the second reaction stage. Figure 3 shows the experimental conditions and results. Gas, liquid, and solid phases were produced after the reaction. The gas phase was analyzed *via* GC, and the main compounds were the excess of H_2. The LP, which was a colorless liquid, was the product. The solid phase was mainly comprised of the Pd/C catalyst.

The LP was analyzed *via* GC–MS. Table 4 presents the main compounds. The compounds with benzene rings or ketone groups were converted into saturated alcohols. Cyclopentanol and its homologs were produced from cyclopentanone and its homologs. The second category compounds in the oil phase were the main materials that changed during this process. Phenol and its homologs were saturated and converted into the corresponding alcohols, whereas catechol and its homologs were transformed into other compounds (excluding saturated benzene rings) to form cyclohexanediol. The content of cyclohexanol (the hydrogenated product of phenol) was much higher than that of phenol during the first hydrotreatment stage. The cyclohexanediol content (hydrogenated product of catechol) was far less than that of catechol in the first hydrotreatment stage. The reaction mechanism was discussed separately. The third category in the oil phase still showed a few changes during this stage.

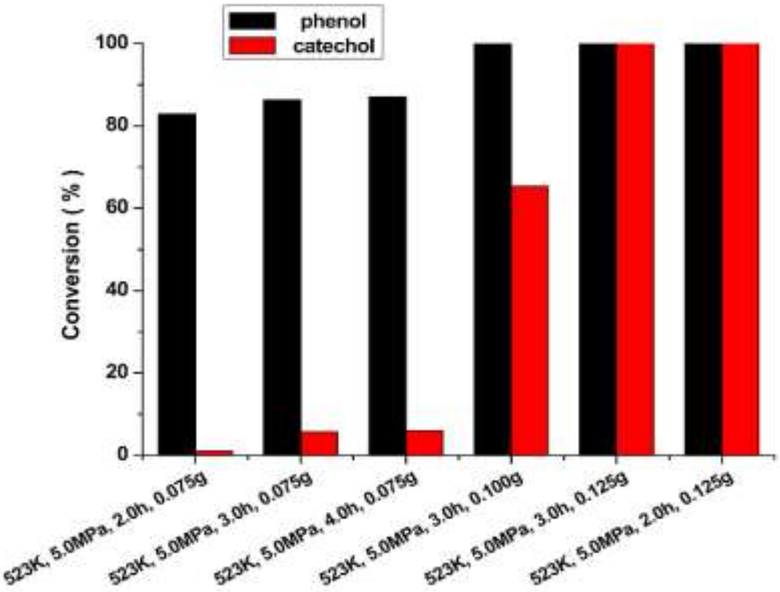
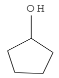
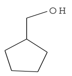
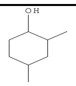
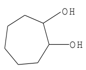
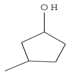
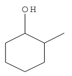
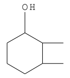
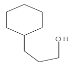
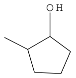
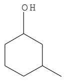
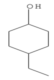
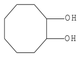
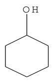
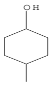
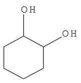
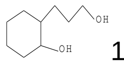


Fig. 3. Reaction conditions and experimental results of the second hydrotreatment stage

Table 4. Main Compounds of the Second Hydrotreatment Stage

No.	Structure	Area%	No.	Structure	Area%	No.	Structure	Area%	No.	Structure	Area%
1		2.63	5		3.07	9		3.15	13		6.34
2		4.06	6		9.17	10		3.36	14		2.66
3		4.83	7		5.36	11		2.45	15		17.79
4		13.72	8		4.19	12		4.29	16		12.93

As shown in Fig. 3, the conversion of phenol and catechol was observed when the reaction time and catalyst content was altered. The hydrotreatment of phenol was easier than that of catechol. The conversion of phenol and catechol could maximize at 100% under the conditions of 523 K, 5.0 MPa H_2, 2.0 h, and 0.125 g Pd/C catalyst. C_5–C_9 oxygenated liquid fuels were obtained after the second hydrotreatment stage. Under the conditions of 523 K, 5.0 MPa H_2, 2.0 h, and 0.125 g catalyst, the yield of upgraded oil was 90%, and the H/C_{eff} ratio improved greatly (ranging from 0.60 to 1.67). The high heating value was 31.63 MJ/kg (Table 1). After two-stage hydrotreatment reaction, the overall oil recovery was 30%.

UV Spectrum Analysis

The raw oil phase and the hydrogenated products were also examined using the UV spectrum, in order to trace the development of aromatic ring systems during the hydrotreatment. UV spectrum analysis has been widely used in previous studies (Wang *et al.* 2012c). Figure 4 shows the UV spectra. The oil phase and the hydrogenated products were diluted in the same concentrations. Two absorption values (257 and 275 nm) were apparent in the raw oil phase. These values implied the existence of carbon–carbon double bonds in the ketone groups and aromatic rings, respectively (Deng *et al.* 2007). After the first hydrotreatment stage, the absorption value (257 nm) decreased greatly, and the absorption value (275 nm) was nearly the same as the raw oil phase, which further explained the results of the GC–MS analysis. After the second hydrotreatment stage, the absorption peaks nearly disappeared, thereby indicating that the aromatic rings were saturated.

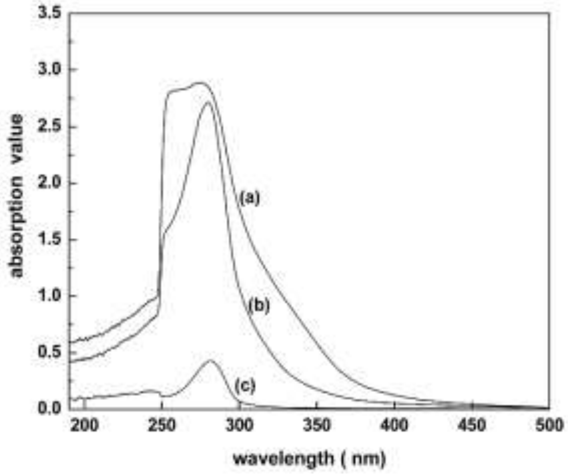


Fig. 4. UV spectrum of oil phase and hydrogenated products: (a) oil phase; (b) first stage products; (c) second stage products

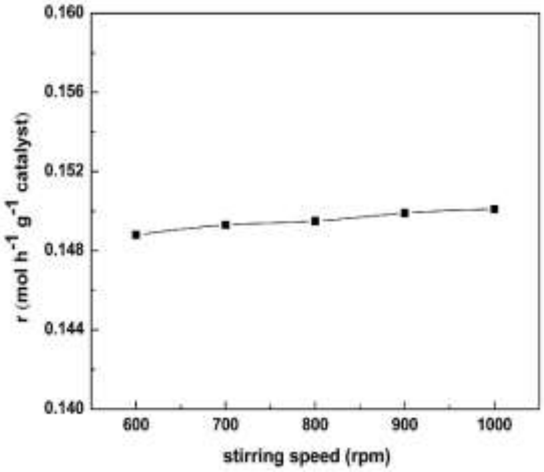


Fig. 5. The plot of reaction rate versus stirring speed

Experiment on External Mass Transport and the KN Criterion Test

To demonstrate that the kinetics were unaffected by the external mass transport, stirring speeds of 600, 700, 800, 900, and 1,000 rpm were used under the conditions of 523 K, 1.0 h, and a 5 wt.% Pd/C catalyst. The results are shown in Fig. 5. The reaction rate remained fairly constant as the stirring speed increased. Therefore, the agitation rate of 800 rpm was sufficient for external mass transport.

The KN criterion test (modified by Madon–Boudart) was performed to confirm that the reaction rate was independent of the internal transport phenomena (Madon and Boudart 1982). The criterion was based on the rate measurements for the catalyst samples, where the concentration of the catalytically active material was altered (Madon and Boudart 1982). The reaction rate for the kinetic regime should be directly proportional to the concentration of the active material. Therefore, a series of Pd/C catalysts (including 1.0, 3.0, 5.0, and

10.0 wt.%) and the respective dispersions (D) (64%, 58%, 62%, and 56%) were prepared. The hydrotreatment reactions all followed the same conditions (1.0 h, 0.125 g catalyst, and 800 rpm) at both 493 and 523 K. The KN criterion was explained by the turnover rate (s^{-1}) versus the surface moles of the active material per unit weight of catalyst, as shown in Fig. 6. The slope values were 35.15 and 24.27 at 493 and 523 K, respectively, and were obtained via linear fitting (R^2 = 0.9315, 0.9448). The values were close to constant at varying temperatures. Thus, the hydrotreatment reaction rate with the Pd/C catalyst was unaffected by the internal mass transport.

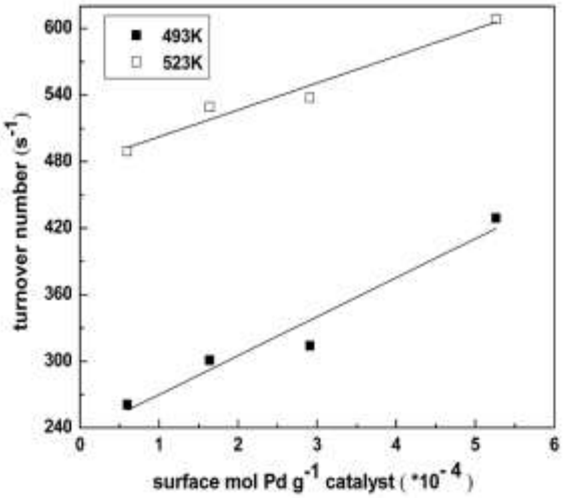


Fig. 6. The KN criterion plot of turnover rate versus surface moles Pd g^{-1} catalyst

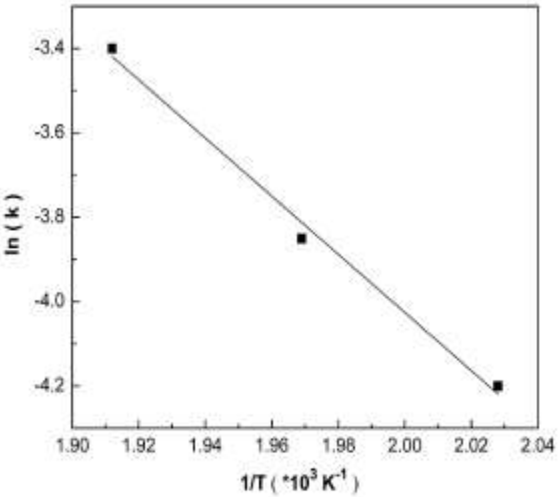


Fig. 7. Arrhenius plot of hydrotreatment with different temperatures

Kinetics Research of the Second Hydrotreatment Stage

Kinetics research was performed to predict the product distributions, as well as to set up a reaction model of the bio-oil hydrotreatment. Bio-oil contains numerous unsaturated compounds, and the hydrotreatment reaction can result at different rates and in different reaction orders because of the structural differences (Zhang *et al.* 2003). Moreover, the chemical bonds were broken and oxygen may be removed and cooked at high temperatures. Therefore, various chemical reactions occurred during the hydrotreatment, and *n*th order kinetics (with respect to the total hydrogen contents) was applied to describe the hydrogenated reaction rate. The equation for the reaction rate can be expressed as follows (Wang *et al.* 2001) (Eq. 2),

$$\frac{dC}{dt} = kC^n \tag{2}$$

where, *C* is the hydrogen content, *k* is the apparent rate constant, *t* is the reaction time, and *n* is the order of reaction. Furthermore, the equation can be integrated as follows (Eq. 3),

$$\frac{1}{n-1}\left(\frac{1}{C_0{}^{n-1}} - \frac{1}{C^{n-1}}\right) = kt \qquad (n \neq 1) \tag{3}$$

where, C_0 is the initial hydrogen contents. If the reaction order (*n*) is appropriate, then the value of *k* is constant at the corresponding reaction temperature.

Therefore, the kinetics of the second hydrotreatment stage was studied at the temperatures of 493, 508, and 523 K with a 5 wt.% active metal catalyst. The reaction times were 0.5, 1.0, 1.5, 2.0, 2.5, and 3.0 h. The elemental compositions of the product were also measured. A numerical method was used to explore the appropriate value of the reaction order (*n*). The linear plot of Eq. 3 versus the reaction time (*t*) is shown in Fig. 8. The slope represents the apparent rate constant (*k*) in Fig. 8, which is 0.016, 0.02, and 0.03 m^3/mol/h at 493, 508, and 523 K, respectively. The reaction order (*n*) was 2.0 at the corresponding temperature. The order of reaction indicated the effect of the concentration on the reaction rate. A higher reaction order indicated a more obvious reaction rate affected by the concentration (Wang *et al.* 2001).

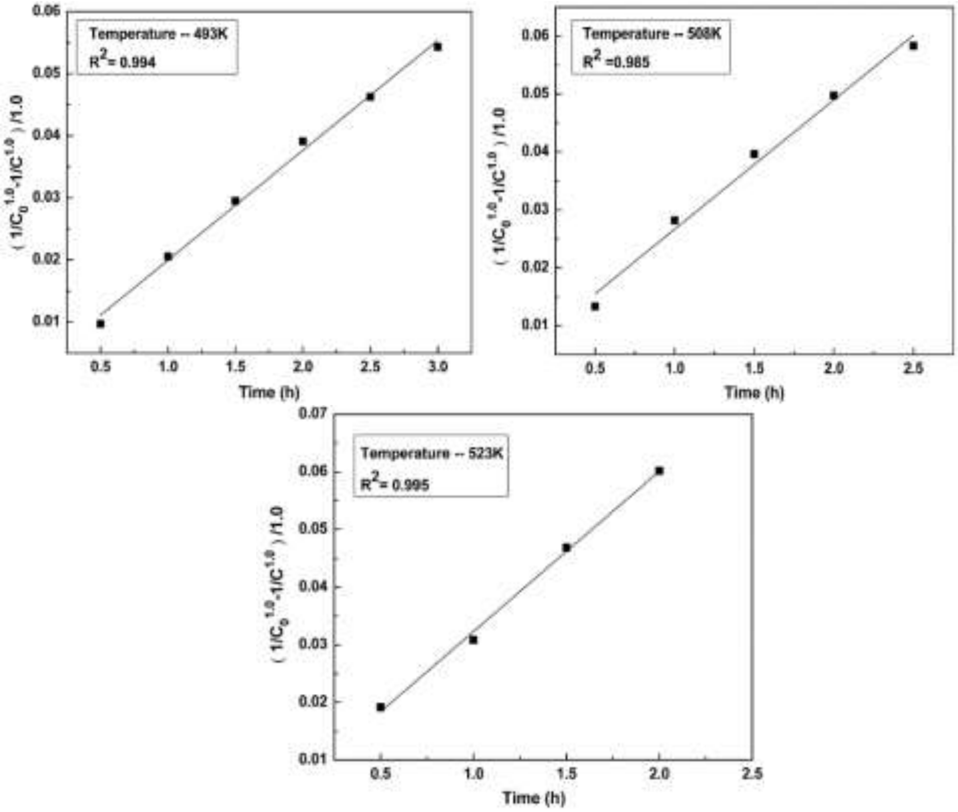


Fig. 8. The plot of kinetics experiments at different temperatures

The Arrhenius law was used to calculate the apparent activation energy (*Ea*) and the pre-exponential factor (*A*) based on the kinetics research. The equation is as follows (Eq. 4),

$$\ln k = -\frac{E_a}{RT} + \ln A \tag{4}$$

where *R* is the gas constant (8.315 J/K/mol), and *T* is the reaction temperature in Kelvin. The values were calculated via linear fitting ($R^2 = 0.986$) in Fig. 7. The activation energy (E_a) of the second hydrotreatment stage was 57.29 KJ/mol, and the pre-exponential factor (*A*) was 1.73×10^4 m^3/mol/h.

Reaction Schematic for the Two-stage Hydrotreatment

During the entire hydrotreatment process, other reaction types occurred besides the hydrogenation of unsaturated groups. As discussed above, in the first hydrotreatment stage, vanillin, syringaldehyde, and 4-hydroxy-3-methoxycinnamaldehyde disappeared. Subsequently, the model compounds were used to determine which components had been converted. The hydrogenated products of vanillin and syringaldehyde were mainly 2-norpinanol, which was not detected by GC-MS after the first hydrotreatment stage. The char could be formed because of the complicated compositions of the oil phase. Also, the hydrogenated product of 4-hydroxy-3-methoxycinnamaldehyde was a type of phenolic ether.

In the second hydrotreatment stage, catechol and its homologues were transformed into other compounds (besides saturating benzene rings) to form cyclohexanediol. Thus catechol, 4-methylcatechol, and 4-ethylresorcinol were used as model compounds. Catechol could be converted into cyclohexanol, cyclohexanediol, and cyclopentyl methanol after hydrotreatment. This could explain why the amount of cyclohexanol increased and the amount of cyclohexanediol was greatly reduced. The hydrogenated product of 4-methylcatechol was heptanediol, and 4-ethylresorcinol was converted into octanediol. The hydrotreatment reaction went through a series of complex processes, including ketone/aldehyde isomerization, dehydration, hydrogenation, and open rings reaction. The reaction schematic is shown in Fig. 9.

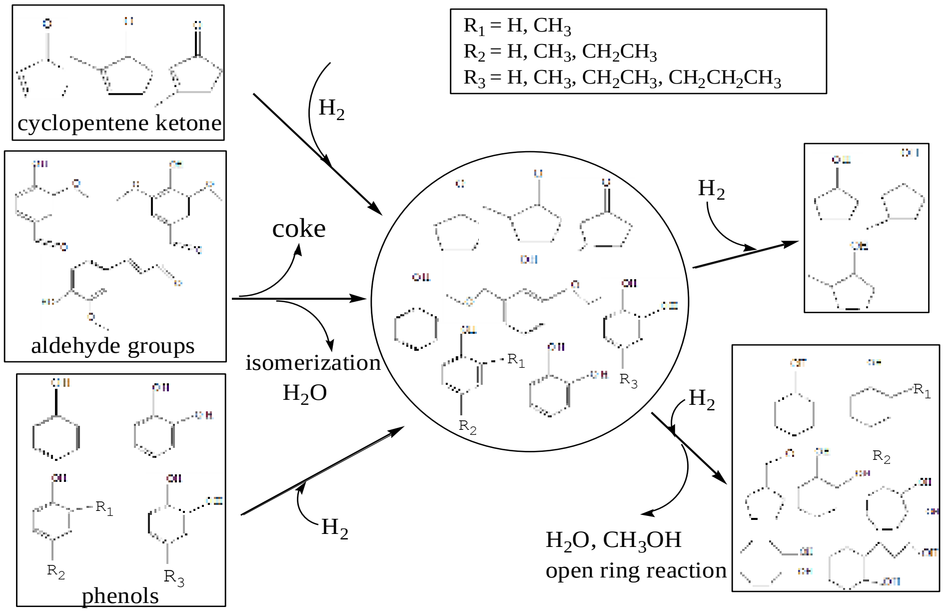


Fig. 9. Reaction schematic for two-stage hydrotreatment of light distillates obtained from bio-oil

CONCLUSIONS

This research studied the two-stage hydrotreatment of light distillates obtained from bio-oil to oxygenated liquid fuels with a Pd/C catalyst. High-quality liquid fuels were obtained. The kinetics of the hydrotreatment reaction was investigated. The results were as follows:

1. The H/C_{eff} ratio increased from 0.51 in the reactant, to 1.67 in the final products. The high heating value reached was 31.63 MJ/Kg. The main products after the two-stage hydrotreatment were C_5–C_9 alcohols, which could be directly used as blending materials with gasoline.
2. The order of the reaction was 2.0 at 493, 508, and 523 K. The apparent activation

energy (E_a) was 57.29 KJ/mol, and the pre-exponential factor (A) was 1.73×10^4 m^3/mol/h. The kinetics research could predict the product distribution.

3. The hydrotreatment reaction went through a series of complex processes, including ketone/aldehyde isomerization, dehydration, hydrogenation, and open rings reaction.

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