# UPGRADING OF BIO-OIL MOLECULAR DISTILLATION FRACTION WITH SOLID ACID CATALYST

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Molecular distillation technology has been adopted to obtain a bio-oil fraction rich in carboxylic acids and ketones. This unique bio-oil fraction was then upgraded with a La-promoted solid acid catalyst. Three washing pretreatments were used to prepare catalysts A, B, and C, with the intention of reducing the amounts of residual sulfuric acid. Model reactions were used to estimate their catalytic activities and the residual amounts of sulfuric acid. Catalyst B, with washing after calcination, displayed higher catalytic activity (80.83%) and lower residual amount of sulfuric acid (50 μmol/g). The catalysts were characterized by techniques such as BET, XRD, and SEM to explain the differences in their catalytic activities. The optimum catalyst B was used in the upgrading of the bio-oil molecular distillation fraction. After upgrading, the corrosivity of the bio-oil fraction declined and its storage stability was improved. The carboxylic acid content in the upgraded bio-oil fraction decreased from 18.39% to 2.70%, while the ester content increased from 0.72% to 31.17%. The conversion of corrosive carboxylic acids to neutral esters reduced the corrosivity of the bio-oil fraction. Moreover, the ketones with unsaturated carbon-carbon double bonds (such as 2-cyclopenten-1-one, 3-methyl-2-cyclopenten-1-one, etc.) were converted into saturated compounds, which improved the stability of the bio-oil fraction.

*Keywords: Molecular distillation; Biomass; Bio-oil; Fractions; Upgrading*

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## INTRODUCTION

The scarcity of fossil fuels and the emission of greenhouse gases have led to great interest in exploring clean, renewable energy resources. Biomass resources have great reserves and particular advantages in terms of renewability and carbon dioxide neutral characteristics (Lucia 2008; Kumarappan et al. 2009). Fast pyrolysis technology is a thermochemical process by which biomass waste can be converted into crude liquid bio-oil with high yields (Wang et al. 2010; Bridgwater and Peacocke 2000). Bio-oil has higher energy density and better transportability than solid biomass waste. However, it is still an inferior liquid fuel when compared with diesel transport fuels. It has various shortcomings, such as high water content, high oxygen content, and corrosivity (Luo et al. 2004; Barth and Kleinert 2008). Crude bio-oil has a limited ability to serve as a motor fuel, though it can be used directly as a boiler fuel (Czernik and Bridgwater 2004; Chiaramonti et al. 2007), and an upgrading process is needed if it is to be used as a transport fuel.

Bio-oil is a complex oxygenated mixture comprising hundreds of GC-detectable compounds, such as carboxylic acids and phenols (Bridgwater 2003; Ozbay et al. 2001; Oasmaa 2001). On the other hand, it also has a large content of high molecular weight lignin byproducts, which are derived from incomplete pyrolysis of lignin. Mohan carried out a quantitative analysis of bio-oil and found that crude bio-oil contained about 25% of high molecular lignin compounds (Mohan et al. 2006). Oasmaa also confirmed the existence of high molecular lignin with a content of 20% (Oasmaa and Elliott 2010).

Research related to upgrading based on crude bio-oil has hitherto been hampered by both composition analysis difficulties and catalyst coke problems. Adjaye carried out the catalytic upgrading of crude maple pyrolysis oil at temperatures between 330 and 410 $^{o}$C. Catalyst deactivation occurred, with a coke yield of 21% (Adjaye et al. 1996). Guo tried to implement a crude bio-oil upgrading process, but also encountered a coke yield of about 30% (Guo and Yan 2005; Guo et al. 2003). In order to accelerate the bio-oil upgrading process, a feasible approach would be to obtain bio-oil fractions that are rich in easily upgraded compounds and then carry out upgrading research with these bio-oil fractions.

Bio-oil is a thermally sensitive mixture that cannot be effectively separated by traditional distillation technologies. Traditional distillation technologies require high temperatures and long distillation times, which destroy the properties of bio-oil. Bio-oil turns into a solid residue when it was heated to 100 $^{o}$C during vacuum distillation (Bridgwater 2003; Murwanashyaka et al. 2001). It was converted into solid coke when it was heated to 145 $^{o}$C during vacuum rectification (Xu et al. 1999). In order to effectively separate bio-oil, a novel distillation technology that is suitable for thermally sensitive materials may be used. Molecular distillation technology is a unique liquid-liquid separation technology that relies on the various mean free paths of different substances and can be used to isolate compounds at temperatures much lower than their boiling points. Moreover, it takes only a few seconds to complete the separation process. The low distillation temperature and short heating time makes it quite suitable for the separation of thermally sensitive compounds. In fact, this distillation technology has been widely used in the fine chemical, pharmaceutical, and food-processing industries, such as in the extraction of tocotrienol from palm fatty acid distillates (Posada et al. 2007), the recovery of tocopherol from rapeseed oil (Jiang et al. 2006; Shao et al. 2007), and the purification of octacosanol (Chen et al. 2007) and monoglycerides (Fregolente et al. 2007).

Molecular distillation technology was introduced into the field of bio-oil separation by us, and gratifying results were obtained (Wang et al. 2009; Guo et al. 2009; Guo and Wang 2010). The separation characteristics of bio-oil at 70, 100, and 130 $^{o}$C were investigated in our earlier paper (Wang et al. 2009). A bio-oil distillation yield about 85% was achieved without a coking problem at 130 $^{o}$C. In another experiment a bio-oil fraction rich in carboxylic acids was produced at 50 $^{o}$C and the water in the residual bio-oil fraction was completely removed at the same time (Guo et al. 2009). Distillation evaluation models, as well as bio-oil distilled fractions, were investigated in a two-step bio-oil molecular distillation process (Guo and Wang 2010). In the work described in this paper, the distilled bio-oil fraction from a two-step bio-oil molecular distillation process was used. Also its upgrading with a La-promoted solid acid catalyst

was studied. The improvement of bio-oil properties was analyzed with reference to the variation in content of different compounds.

## EXPERIMENTAL

### Catalyst Preparation

Chemicals used in the catalyst preparation process included n-butyl titanate, anhydrous ethanol, concentrated sulfuric acid, silica, and lanthanum oxide, which were purchased from Sinopharm Chemical Reagent Co. Ltd. The titanium sol was synthesized using the referred method (Zhang 2006). Initially, 25.58 g n-butyl titanate and 20 mL anhydrous ethanol were added into a 250 mL beaker, and they were mixed together. And then 4 mL deionized water, 20 mL anhydrous ethanol, and 1.04 g concentrated sulfuric acid were mixed first and added into a separatory funnel at once. Finally, the liquid mixture in the separatory funnel was rapidly dropped into the former beaker with continuously stirring to obtain the titanium sol. After aging for 24 hours, the titanium sol was dried at 100 $^{o}$C and milled to obtain $TiO_2$ powders. $SiO_2$ and $TiO_2$ powders were mixed in a mass ratio of 4:6, and then 6wt% $La_2O_3$ was added. A sulfuric acid solution (1mol/L) was used to impregnate the porous supports by the incipient wetness impregnation method. The catalyst precursor was obtained after drying. The precursor was then subjected to three types of washing pretreatment to produce catalysts A, B, and C.

Catalyst A: No washing pretreatment was used. The catalyst precursor was directly calcined at 400 $^{o}$C for 6 h.

Catalyst B: Catalyst A was subjected to a washing pretreatment four times and then dried directly at 100 $^{o}$C overnight to produce catalyst B. For each washing, about 50 mL of deionized water was used per 10 g of catalyst A.

Catalyst C: The catalyst precursor was subjected to a washing pretreatment four times, and then dried at 100 $^{o}$C overnight before its calcinations at 400 $^{o}$C for 6 h. For each washing, about 50 mL of deionized water was used per 10 g of catalyst precursor.

### Characterization of Catalysts

Textural properties were determined by $N_2$ adsorption–desorption isotherms measured at -196 $^{o}$C on a Quantachrom-Autosorb-1-C apparatus. X-ray diffraction (XRD) patterns were recorded on a PANalytical X'Pert PRO X-ray diffractometer using Cu Kα radiation ($\lambda$ = 0.15418nm) with an angle ($2\theta$) range of 10° to 80° and a scanning speed of 5°/min. The tube voltage was 40 kV and the current was 30 mA. The morphologies of the solid products were examined by scanning electron microscopy (SEM, FEI Model SIRION-100).

### Bio-oil Production and Fractionation Method

Pine sawdust was crushed and screened to 0.45-1 mm, and then fed into a fluidized-bed reactor to produce bio-oil at 450-550 $^{o}$C. The detailed bio-oil production procedure was same with that was described in our previous paper (Wang and Luo 2010).

Pretreatment was used to remove the water and small particles in bio-oil before the molecular distillation process.

A KDL-5 molecular distillation facility was applied to separate bio-oil into fractions. Volatile compounds in bio-oil turned into vapor over the evaporator surface, and they were immediately condensed by the internal condenser to produce the bio-oil fraction. The first molecular distillation process was done under 80 $^{o}$C and 1600 Pa to produce the bio-oil fraction 1. The residual heavy fraction was subjected to the second molecular distillation process under 80 $^{o}$C and 340 Pa to produce the bio-oil fraction 2. Finally, bio-oil fractions 1 and 2 were mixed to form a new bio-oil fraction and used for the upgrading research in this paper. The total yield for bio-oil fractions was 57.02 wt%. More details about the molecular distillation process can be found in our published paper (Guo and Wang 2010).

### Experimental Procedures

All the experiments were carried out in a 300 mL stainless steel autoclave under atmospheric pressure. The reaction temperature was 90 $^{o}$C, and the amount of catalyst was 2wt%. A model reaction between acetic acid (20 mL) and propanol (52 mL) was used to investigate the catalyst activity, and a blank experiment with pure propanol (72 mL) was designed to detect the residual amounts of sulfuric acid. The catalyst activities and residual amounts of sulfuric acid were determined by NaOH titration, respectively. The optimal catalyst from the model reactions was chosen and used in the upgrading procedure of bio-oil fraction. Bio-oil fraction and propanol were added into the autoclave, and then heated to 90 $^{o}$C and held for 2 h. After the reaction, the gaseous products were released, and the liquid products were analyzed with a GC-MS system.

### Analysis of Products

The compounds in the bio-oil fraction and upgraded fraction were identified with a Trace DSQ 2 system using a 30 m x 0.25 mm x 0.25 μm Agilent DB-WAX capillary column. The oven temperature was first controlled at 40 $^{o}$C for 1 minute, and then it was heated to 240 $^{o}$C at a rate of 8 $^{o}$C /min. Finally, it was kept at 240 $^{o}$C. Samples were injected directly into the GC inlet to minimize loss of the oil components.

## RESULTS AND DISCUSSION

### Catalyst Activity and Residual Sulfuric Acid Test

The catalyst activity was estimated by model reaction between acetic acid and propanol. The conversion of acetic acid was used to indicate the catalyst activity, which is listed in Table 1. Catalysts A and B had the similar activity of about 80%, which indicated that acetic acid was effectively converted in the model reaction. The similar activity between catalysts A and B indicated that washing after calcinations did not reduce the activity of the catalysts. Catalyst C showed a much lower activity (only 57.72%) than catalyst A. The differences of their activities will be discussed further based on the catalyst characterization.

Solid acid catalyst showed excellent activity in the bio-oil upgrading process, but there was a negative residual sulfuric acid problem. The residual sulfuric acid on the catalyst made the pH value of upgraded bio-oil even lower. The washing pretreatments were applied with the intention of reducing the residual amounts of sulfuric acid. Washing both before and after calcinations reduced the amount of residual sulfuric acid from 75 μmol/g to 50 μmol/g. Catalyst B showed higher activity and a lower amount of residual sulfuric acid, and it was selected for the bio-oil fraction upgrading.

**Table 1.** Catalyst Activities and Amounts of Residual Sulfuric Acid

| Catalysts | Activity (%) | Residual $H_2SO_4$ (μmol/g) |
|---|---|---|
| A | 80.29 | 75 |
| B | 80.83 | 50 |
| C | 57.72 | 50 |

## Catalyst Characterization

The textural properties of the catalysts derived from $N_2$ adsorption–desorption isotherms are given in Table 2. The BET surface area and pore volume of catalyst A were 35.10 $m^2/g$ and 0.12 $cm^3/g$, respectively. Its pore size was 10.58 nm. Catalysts B and C had higher BET surface areas and pore volumes than catalyst A. The results indicated that washing pretreatment had a positive effect in enlarging the BET surface area and pore volume. The enlarging tendency was much more obvious in the case of washing before calcinations. $La_2O_3$ became dissolved in the sulfuric acid solution, and it existed in an ionic state ($La_2(SO_4)_3$) before the calcinations process, and so it was easily washed away by water. Hence, washing before calcinations had a much more significant influence on the catalyst structure.

**Table 2.** Textural Properties of Catalysts

| Catalysts | BET surface area ($m^2/g$) | Pore volume ($cm^3/g$) | Pore size (nm) |
|---|---|---|---|
| A | 35.10 | 0.12 | 10.58 |
| B | 76.74 | 0.42 | 17.80 |
| C | 157.41 | 0.64 | 14.43 |

The XRD patterns of the catalysts are shown in Fig. 1. The various crystalline diffractional peaks indicated the existence of amorphous $SiO_2$ and anatase $TiO_2$. No peak representing amorphous $TiO_2$ was detected in the XRD patterns because it was completely transformed into anatase at 400 $^oC$ (Xu and Zeng 2008). Catalysts A and B had good crystallization peaks intensity and their XRD patterns were quite similar. This indicated that washing after calcinations had little influence on the crystallization of the catalysts. Catalysts B and C were treated with the same amount of water, but their XRD patterns were different. Catalyst C displayed diffractional peaks of lower intensity than those of catalyst B. $La_2O_3$ had a positive effect in enhancing the crystallization of $TiO_2$ (Yang et al. 2010). The loss of $La_2O_3$ had a detrimental effect on the activity of catalyst C. The diffractional peaks of $La_2O_3$ were not detected for any of the three catalysts. This can be mainly attributed to the low content of $La_2O_3$ phase, which was highly dispersed in the silica.

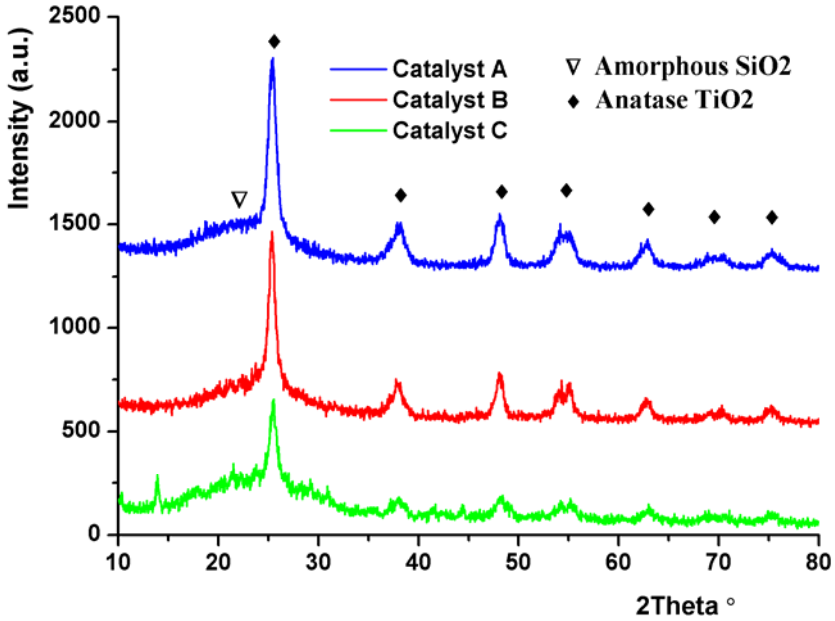
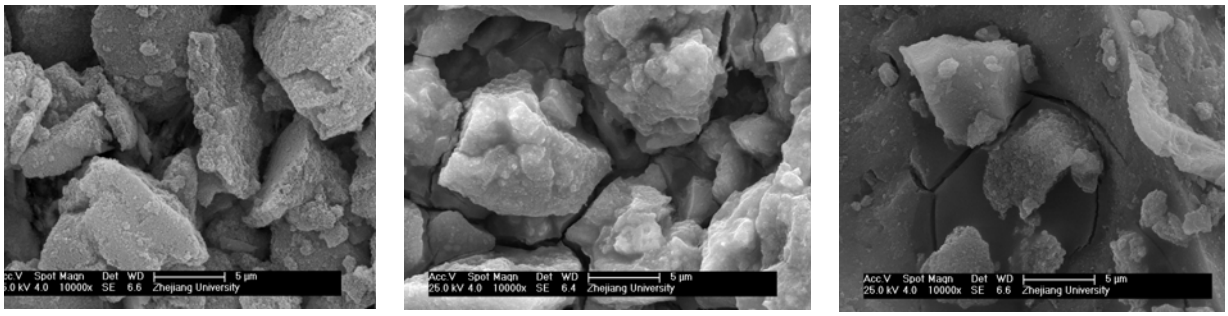



**Fig. 1.** XRD patterns of the catalysts

Figure 2 shows SEM images of the three catalysts. Their particle sizes were in the range of 5 μm to 10 μm. The surface of catalyst A was rough, and with some small particles adhering to it. Catalysts B and C showed similar surface characteristics. Their surfaces were much smoother than that of catalyst A, and meanwhile they appeared fused. The washing pretreatment removed the small particles and made the surface appear fused.



Catalyst A Catalyst B Catalyst C

**Fig. 2.** SEM images of the catalysts

## Upgrading of Bio-oil Molecular Distillation Fraction

The model reaction and residual sulfuric acid test proved that catalyst B had higher catalytic activity and a lower residual amount of acid. Catalyst B was therefore selected for the upgrading of bio-oil fractions. Gas chromatography-mass spectrometry (GC-MS) was used to detect the compositions of the bio-oil fraction and the upgraded fraction, and their respective spectra are presented in Fig. 3.

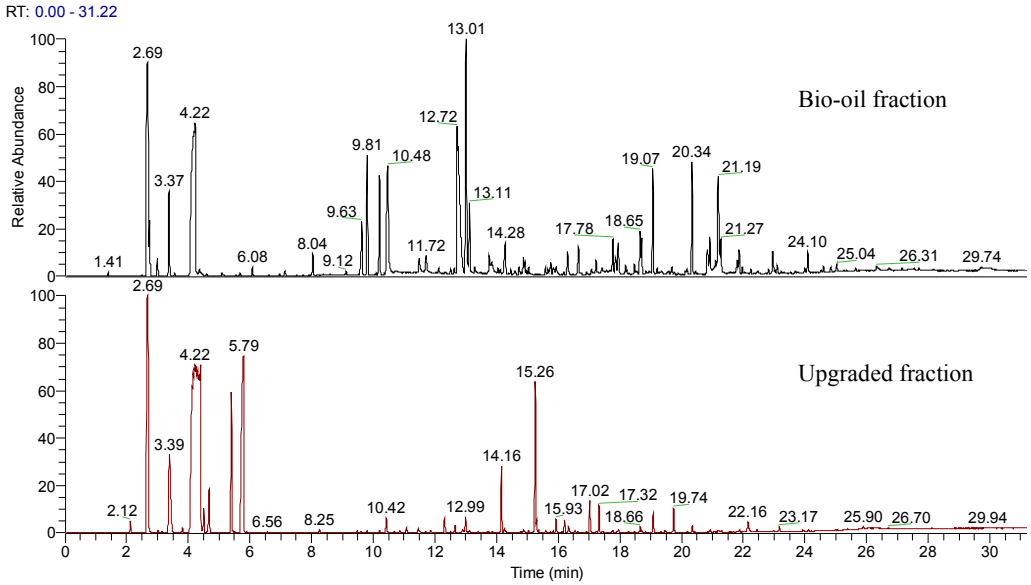



**Fig. 3.** GC-MS spectra of the bio-oil fraction and the upgraded fraction

*Overview of typical chemical groups in bio-oil fraction and upgraded fraction*

Compounds in the bio-oil fraction and the upgraded fraction could be classified into acids, esters, ethers, etc. The distribution in the amounts of the chemical groups is shown in Figure 4. Bio-oil fraction had a high content of carboxylic acids. Content of carboxylic acids decreased from 18.39% to 2.70% after the upgrading process in the autoclave. In contrast, the esters content increased sharply from 0.72% to 31.17%. The corrosive carboxylic acids were efficiently converted to neutral esters, which can be expected to have a positive effect in reducing corrosiveness of the bio-oil fraction (Czernik and Bridgwater 2004). The total amount of ethers did not show much fluctuation. The amounts of ketones, aldehydes, and especially furans were sharply reduced. Besides the esters, only the phenols showed an increasing tendency among all the bio-oil chemical groups.

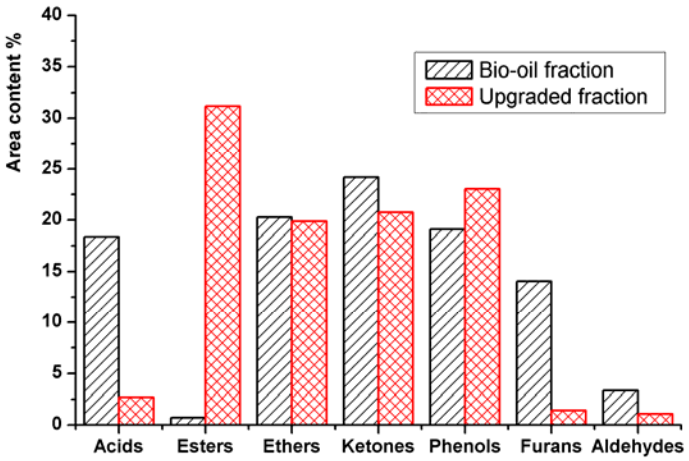



**Fig. 4.** Chemical groups in the bio-oil fraction and upgraded fraction

*Composition comparison between bio-oil fraction and upgraded fraction*

The chemical group content variation was discussed above. Here, the detailed changes of the compounds are described. The detailed compositions of the bio-oil fraction and the upgraded fraction are listed in Table 3. It is clear that the kinds of carboxylic acids were reduced. There were five carboxylic acids in the bio-oil fraction, including acetic acid, formic acid, and 2-methyl-propanoic acid. However, only acetic acid and benzenecarboxylic acid remained in the upgraded fraction. The carboxylic acids of low molecular weight were efficiently converted, while the benzenecarboxylic acid showed a lower reactivity. The esters were the corresponding derivatives of carboxylic acids and propanol, such as n-propyl formate and n-propyl acetate. The numbers of ketones also declined, and some of the ketones appearing in bio-oil fraction disappeared in the upgraded fraction. All of the ketones that disappeared shared the same characteristic. That was, they had unsaturated carbon-carbon double bonds, such as 2-cyclopenten-1-one, and 3-methyl-2-cyclopenten-1-one. The conversion of unsaturated ketones increased the stability of the bio-oil fraction. Phenols did not react during this upgrading process, and all of the phenols detected in the bio-oil fraction were still found in the upgraded fraction. Furans and aldehydes, however, were reactive, and their amounts declined.

**Table 3.** Detailed Compositions of Bio-oil Fraction and Upgraded Fraction

| Bio-oil fraction | Area % | Upgraded fraction | Area % |
|---|---|---|---|
| Acids | | | |
| Acetic acid | 15.70 | Acetic acid | 2.45 |
| Formic acid | 0.70 | Benzenecarboxylic acid | 0.25 |
| Propanoic acid, 2-methyl- | 0.52 | | |
| Butanoic acid, 2-methyl- | 1.13 | | |
| Benzenecarboxylic acid | 0.34 | | |
| Esters | | | |
| 1,2-Ethanediol, monoacetate | 0.72 | n-propyl formate | 2.79 |
| | | n-Propyl acetate | 24.54 |
| | | 2-Acetyloxy-1-ethoxyethyl acetate | 2.62 |
| | | 1,2-Ethanediol, monoacetate | 0.49 |
| | | 1,2- Terephthalic acid, diisooctyl ester | 0.72 |
| Ethers | | | |
| Ethanol, 2,2-diethoxy- | 16.43 | Propane, 2,2-diethoxy- | 8.81 |
| Pentane, 1,1-diethoxy- | 0.42 | 2-Propanone, 1,1-dipropoxy- | 1.44 |
| Heptane, 1,1-diethoxy- | 3.41 | Ethanol, 2,2-diethoxy- | 8.71 |
| | | Heptane, 1,1-diethoxy- | 0.91 |

**Table 3.** Continued

| | | | |
|---|---|---|---|
| Ketones | | | |
| 2-Butanone, 3-hydroxy- | 0.42 | 2-Propanone, 1-hydroxy- | 7.85 |
| 2-Propanone, 1-hydroxy- | 9.50 | 1-Hydroxy-2-butanone | 0.67 |
| 2-Cyclopenten-1-one | 1.01 | 2-Pentanone, 5,5-diethoxy- | 2.23 |
| 1-Hydroxy-2-butanone | 0.97 | Butyrolactone | 6.44 |
| 2-Cyclopenten-1-one, 3-methyl- | 1.52 | 2(5H)-Furanone, 5-methyl- | 0.73 |
| 2-Cyclopenten-1-one, 2,3-dimethyl- | 0.28 | 2(5H)-Furanone, 3-methyl- | 0.80 |
| 2-Pentanone, 5,5-diethoxy- | 3.02 | 2(5H)-Furanone | 1.22 |
| Butyrolactone | 0.44 | 2-Cyclopenten-1-one, 2-hydroxy-3-methyl- | 0.79 |
| 2(5H)-Furanone, 5-methyl- | 0.92 | | |
| 2(5H)-Furanone, 3-methyl- | 0.76 | | |
| 2(5H)-Furanone | 1.13 | | |
| 2-Cyclopenten-1-one, 2-hydroxy- | 1.28 | | |
| 2-Cyclopenten-1-one, 2-Hydroxy-3-methyl- | 2.56 | | |
| 4-Methyl-5H-furan-2-one | 0.36 | | |
| Phenols | | | |
| Phenol, 2-methoxy- | 5.04 | Phenol, 2-methoxy- | 9.88 |
| Phenol, 2-methoxy-4-methyl- | 4.98 | Phenol, 2-methoxy-4-methyl- | 3.55 |
| Phenol, 2-methyl- | 1.87 | Phenol, 2-methyl- | 0.53 |
| Phenol | 1.45 | Phenol | 1.20 |
| Phenol, 4-ethyl-2-methoxy- | 1.14 | Phenol, 4-ethyl-2-methoxy- | 0.98 |
| Phenol, 4-methyl- | 1.61 | Phenol, 4-methyl- | 1.54 |
| Phenol, 2-methoxy-4-propyl- | 0.22 | Phenol, 2-methoxy-4-propyl- | 1.50 |
| Eugenol | 1.24 | Eugenol | 1.28 |
| Phenol, 2-methoxy-4-(1-propenyl)- | 0.21 | phenol, 2-methoxy-4-(1-propenyl)- | 1.01 |
| Phenol, 2,6-dimethoxy- | 0.93 | Phenol, 2,6-dimethoxy- | 0.69 |
| Phenol, 4-methoxy-3-(methoxymethyl)- | 0.41 | Phenol, 4-methoxy-3-(methoxymethyl)- | 0.86 |
| Furans | | | |
| Furan, 2,5-diethoxytetrahydro- | 13.11 | Furan, 2,5-diethoxytetrahydro- | 1.05 |
| 2-Furanmethanol | 0.50 | 2-Furanmethanol | 0.37 |
| 2-Ethoxytetrahydrofuran | 0.43 | | |
| Aldehydes | | | |
| 3-Furaldehyde | 0.21 | Furfural | 1.08 |
| Furfural | 3.11 | | |

## CONCLUSIONS

Molecular distillation technology was used to produce a bio-oil fraction rich in carboxylic acids and ketones. Then its upgrading process was carried out with a La-promoted solid acid catalyst. One of the most important aims in bio-oil upgrading is to reduce its corrosiveness, which can be achieved by converting carboxylic acids into neutral esters. The commonly used solid acid catalyst showed good performance in converting carboxylic acids, but it had a negative residual sulfuric acid problem.

1. Three types of washing pretreatment were applied to produce catalysts A, B, and C in terms of reducing the residual amounts of sulfuric acid. It was found that the residual amounts of sulfuric acid can be reduced by washing both before and after the catalyst calcinations process. Residual sulfuric acid content on solid acid catalysts declined from 75 μmol/g to 50 μmol/g.
2. The catalytic activity of catalyst C (with washing before calcination) dropped obviously. Catalyst characterizations including BET, XRD, and SEM were carried out to explain the differences in their catalytic activities. The results indicated that loss of $La_2O_3$ phase led to inferior crystallization of $TiO_2$ in catalyst C. Therefore, catalyst C showed lower activity.
3. The optimal catalyst (with washing after calcination) displaying higher activity and lower amount of residual sulfuric acid was selected for bio-oil fraction upgrading. After upgrading, the carboxylic acid content of the bio-oil fraction decreased from 18.39% to 2.70% and its esters content increased from 0.72% to 31.17%. The corrosive carboxylic acids in the bio-oil fraction were successfully converted into neutral esters. The ketones in bio-oil fraction showed great reactivity. The number of kinds and amounts of ketones in the upgraded fraction were reduced. In particular, those ketones with unsaturated carbon-carbon double bonds disappeared in the upgraded fraction.
4. This upgrading process reduced corrosiveness of the bio-oil fraction and improved its storage stability according to the composition analysis of the bio-oil fraction and the upgraded fraction.

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