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ARTICLE

Development of a catalytically green route from diverse lignocellulosic biomasses to high-density cycloalkanes for jet fuels

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This study reports a novel route to manufacture high-density cycloalkanes for jet fuels from diverse lignocellulosic biomasses. The consecutive processes for manufacturing high-density cycloalkanes primarily included the catalytic microwave-induced pyrolysis of diverse lignocellulosic biomasses (hybrid poplar, loblolly pine, and Douglas fir) over a well-promoted ZSM-5 and hydrogenation process in the present of the Raney nickel catalyst. Two variables (catalytic temperature and catalyst to biomass ratio) were employed to determine the optimal condition for the production of $C_8 - C_{16}$ aromatics in the catalytic microwave pyrolysis. The maximum carbon yield of desired aromatics was 24.76%, which was achieved from catalytic microwave pyrolysis of hybrid poplar at 500 °C with the catalyst to biomass ratio of 0.25. We observed the aromatics derived from catalytic microwave pyrolysis in the *n*-heptane medium were completely hydrogenated into renewable high-density cycloalkanes for jet fuels. In the hydrogenation process, increasing catalyst loading and reaction temperature could promote the selectivity of high-density cycloalkanes. Results indicated that the hybrid poplar was the optimal feedstock to obtain the highest selectivity (95.20%) towards high-density cycloalkanes. The maximum carbon yield of cycloalkanes-enriched hyrogenated organics based on hybrid poplar was 22.11%. These high-density cycloalkanes with high selectivity can be directly used as additives in jet fuels, such as JP-5, JP-10, and RJ-5.

1. Introduction

There are immense interests in converting renewable resources and developing new generation (hydrocarbon) biofuels, with a particular focus on green aviation fuels.[1, 2] Lignocellulosic biomass is considered as a ubiquitous and sustainable source of carbon that displays promising potential in the manufacture of hydrocarbon transportation fuels and versatile chemicals.[3, 4] The agricultural and forest resources reserves in U.S. potentially satisfy one-third of the country's petroleum demand.[5] Additionally, demand for diesel and jet fuels in the United States is expected to continue increasing by 27% in the following years as opposed to gasoline [6]; thus it is essential to shift biofuel production derived from lignocellulosic biomass towards distillate-range liquid alkanes in the future.

The current jet fuels originated from fossil resources are principally comprised of linear-chain and branched-chain alkanes.[7, 8] However, lower densities (~0.76-0.78 g/mL) of linear-chain alkanes and branched-chain alkanes have to be blended with high-density hydrocarbons to meet the specifications of jet fuels.[9] Conversely, cycloalkanes (especially the polycyclic alkanes) are compact molecules within robust ring strain and contribute to a more dense jet fuel and burn cleanly with high heats of combustion and low freezing points.[10-12] To make up the shortage of chain alkanes, jet fuel range cycloalkanes or aromatic hydrocarbons should be synthesized and added into commercial jet fuels (e.g. Jet A and JP-8).[8, 13] Therefore, most efforts to substitute petroleum-based high-density tactical fuels, such as JP-5, JP-10 and RJ-5 have focused on increasing polycyclic high-density hydrocarbons.

Several technologies have been evaluated for the production of renewable drop-in fuels for aviation; Dumesic group[14, 15] and Huber *et al.*[7, 16] have pioneered a new route to synthesize the long carbon chain alkanes using the lignocellulose-derived platform chemicals. Nevertheless, these multiple steps necessitate expensive reactants and noble metal catalysts under severe reaction conditions, resulting in infeasible commercialization in biorefineries. In the current work for producing high-density biofuels, Harvey group[17] and Zou *et al.*[18] have successfully developed liquid fuels with a density of 0.94 g/mL via the dimerization of pinene followed by hydrogenation. Unfortunately the sources of some specific woods and plants used for the production of pinene are limited. Accordingly the production of high-density alkanes for jet fuels using cheap and abundant sources call for ideal

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technologies with efficient solid-phase catalysts to make the processes economically feasible.

It is widely known that oxygen content of bio-oil could be partially or even completely eliminated by zeolite cracking during fast pyrolysis of biomass.[19] Biomass-derived feedstock has been directly converted into aromatics with ZSM-5 as the catalyst in a single catalytic pyrolysis step.[20, 21] Besides, Lei group have found that microwave-induced pyrolysis could enhance the selectivity of aromatics in the upgrading bio-oil.[22-24] Yet, the evaluation of how the biomass-derived feedstock affects the chemical composition (especially for aromatic hydrocarbons) of bio-oil from catalytic pyrolysis and its impact as a precursor of cycloalkanes for jet fuels are often overlooked.[25] Wherefore understanding how biomass feedstock influences the chemical composition of the resulting bio-oil is vital to obtain specific range aromatic hydrocarbons for jet fuels.[26] For lignocellulosic biomass sources, hybrid poplar, loblolly pine, and Douglas fir have emerged as front-runners in U.S.[5] These fastest-growing and abundant biomasses in North America and are well suited for a variety of applications such as biofuels production and bio-based chemicals, providing flexibility for future biorefineries.

Furthermore, it was noticed that high density aromatics (C_8 - C_{16}) are prone to be hydrogenated into cycloalkanes.[27, 28] To this end, diverse lignocellulosic biomasses were comparably converted into aromatics by catalytic microwave pyrolysis over well-promoted ZSM-5. The organic phase of the bio-oils derived from catalytic microwave pyrolysis was thereafter extracted by the optimum solvent. In the final step, the organic mixture was hydrogenated into $C_8 - C_{16}$ high-density hydrocarbons (including cycloalkanes and minor aromatics) by using Raney nickel as the catalysts, which satisfy basic specifications of conventional jet fuels.

2. Experimental

2.1 Materials

The feedstock used was Douglas fir sawdust pellets (Bear Mountain Forest Products Inc., USA) which were approximately 7 mm in diameter and 15 mm in length. Hybrid poplar and loblolly pine samples were supplied by the Composite Materials and Engineering Center (CMEC) at Washington State University. Proximate and elemental analysis of diverse lignocellulosic biomasses was described in Table S1. Parent ZSM-5 (SiO_2/Al_2O_3 Mole Ratio: 50) was purchased from Zeolyst International, USA. Nickel-Aluminum alloy powder in a non-activated type was used as purchased from Alfa Aesar (Ward Hill, MA, USA).

2.2 Catalyst preparation

The activity of parent ZSM-5 was improved by suffering both hydrothermal and calcined treatments. Under the gentle stirring, parent ZSM-5 powder was added into deionized water (mass ratio=1) at 60 °C. After addition, the mixture was kept on stirring for 2 h under this condition. The slurry was then dried at 105 °C till constant weight. The sequential process was

the catalyst calcination: hydrothermally treated ZSM-5 was calcined at 550°C for 5 h in a muffle furnace. The catalysts were pelletized and sieved to 20 − 40 mesh. The main characteristics of the catalyst were reported in our previous study.[23, 24]

The Raney Ni catalyst was developed using a 20 wt% NaOH aqueous solution to remove Al in the following procedure. 10 g of the above Ni-Al was slowly added into 100 mL NaOH aqueous solution under gentle stirring. After addition, the slurry was kept on stirring at 80 °C for 1 h. The excess of sodium hydroxide was finally washed with distilled water until nearly neutral pH was reached. The obtained Raney Ni catalyst was stored in water. Raney Ni is notorious for its pyrophoricity, and it may ignite spontaneously when dried in air. The Raney Ni catalyst was thus dried at 60 °C till constant weight in the atmosphere of nitrogen to avoid contact with air, prior to the subsequent catalytic test.

2.3 Catalytic microwave-induced pyrolysis of diverse ligonocellulosic biomasses

Fig. S1 shows the schematic diagram of the microwave-assisted pyrolysis system integrated with the catalysis process. Detailed experimental setting was described in our previous studies.[24, 29] The feedstock was air dried at 105 °C for 24 h to remove the physically bound moisture, prior to conducting the experiments. Fixed loading (20 g) of hybrid poplar, loblolly pine, and Douglas fir for each run were placed in a 500 mL quartz flask which was placed inside a Sineo MAS-II batch microwave oven (Shanghai, China) by a constant microwave power setting (700 W). 0.05 g of activated carbon powder was used as the absorber for the microwave-assisted pyrolysis. All reactions of microwave pyrolysis were conducted at the temperature of 480 °C for 10 min. The pyrolysis volatile vapors from the flask passed through a packed bed catalysis reactor which was filled with well-promoted ZSM-5. The packed-bed reactor customized was constructed of quartz and externally heated by a heating tape. A thermocouple was introduced between the reactor and the heating tape to measure catalytic temperatures. The condensable liquid was collected as bio-oils. The non-condensable vapors escaped as gas at the end of the condensers and were collected for analysis.

2.4 Hydrotreatment of liquid organics derived from catalytic microwave pyrolysis

Based on the solvents effects in the hydrogenation of a model compound (naphthalene) in our previous study,[27] the combined bio-oils evolved from catalytic microwave pyrolysis were extracted by the optimal solvent (*n*-heptane). To produce the high-density cycloalkanes for jet fuels, a closed reaction system with a stirred stainless batch reactor of the 4592 micro stirred reactor (with a 50 mL vessel) and a 4848 reactor controller from Parr Instrument Company (Moline, IL, USA) was used (Fig. S2). The mixture of organics and the *n*-heptane medium was loaded into the reactor together with 10 wt% or 20 wt% Raney Ni catalyst (in terms of the reactants). Then the reactor was sealed and vented for five times with hydrogen to

get rid of the air present in the vessel. Hydrogen was subsequently adjusted to reach the set pressure (500 psi). The automatic controller was employed to control the temperature and the revolution of stirrer (300 rpm). The pressure inside the reactor was recorded and the reactions proceeded at a set temperature (see Table 3) for the intended time. After the experiment finished, stirring was stopped and the reactor was rapidly cooled to ambient temperature. Then, the gas was collected for analysis and the reactor was depressurized. Consequently the liquid product was filtered to remove catalyst particles.

2.5 Analytical techniques

Elemental analysis (C, H and N) of diverse biomass sources, liquid samples, char, and coke deposited on spent catalysts was conducted using a 2400 Series II CHN/O Elemental Analyzer (PerkinElmer, USA).

The textural properties of the catalyst were determined by means of N_2 adsorption–desorption (Micromeritics TriStar II 3020 Automatic Physisorption Analyzer). Fresh catalysts were degassed in vacuum at 300 °C for 1 h. The Brunauer–Emmett–Teller equation was applied to calculate the specific surface area using adsorption data at p/po= 0.05–0.25. The pore volume was evaluated by using the Barrett–Joyner–Halenda (BJH) method.

Powder X-ray diffraction (XRD) patterns were executed on a Rigaku Smartlab X-ray diffractometer equipped with a Cu Kα X-ray source operating at 40 kV and 40 mA. The scattering angle 2θ was varied from 10° to 80°.

The particle size distribution and surface morphology of the samples were measured with a scanning electron microscope (SEM, FEI Quanta 200 F).

The chemical composition of the bio-oils was characterized and qualified by Agilent 7890A GC-MS (GC–MS; GC, Agilent 7890A; MS, Agilent 5975C) with a DB-5 capillary column. The GC was first programmed to heat to 45°C for 3 min followed by heating to 300°C at a rate of 10°C/min. The injection sample size was 1 μL. The flow rate of the carrier gas (helium) was 0.6mL/min. The ion source temperature was 230°C for the mass selective detector. Compounds were identified by comparing the spectral data with that in the NIST Mass Spectral library. The area percent of changed concentrations of model compounds obtained from GC/MS results was utilized to predict product concentration in bio-oils.

The moisture content in the bio-oils was determined by a Karl Fischer (KF) compact titrator (V20 Compact Volumetric KF Titrator, Mettler-Toledo).

The gaseous product was collected in a 1L Tedlar gas bag and then offline analyzed by an INFICON 3000 Micro-GC (INFICON Inc., Santa Clara, CA, USA) system with a thermal conductivity detector (TCD). A standard gas mixture consisting of H_2, N_2, CH_4, CO, CO_2, C_2H_4, C_2H_6, and C_3H_6 was used to calibrate the yield of non-condensable gas. Alkanes and olefins (>C_4) in gas samples were either not detected or negligible in this research.

2.6 Experimental methods and data evaluation

A central composite experimental design (CCD) was employed to optimize the process conditions and liquid organics yield from hybrid poplar, loblolly pine, Douglas fir (corresponding to Table S2, S3, and S4, respectively). The catalytic temperature (X_1, °C) and catalyst to biomass ratio (X_2) were chosen as independent variables. In these experiments based on CCD, the mass of catalyst varied from 2.2 to 7.8 g, while packed bed catalytic temperature ranged from 269 to 481 °C. Two additional experiments conducted at 500 °C or with the catalyst loading of 1 g were compared as shown in Table S2, S3, and S4.

The coke mass was determined by the difference before and after catalytic pyrolysis. After the experiment of microwave-induced pyrolysis, the char was left in the quartz flask of pyrolysis reactor; while the coke was formed on the ZSM-5 catalyst in the packed-bed catalysis reactor. The weight of non-condensable gas was calculated using the following equation:

$$Gas\ mass = biomass\ mass - liquid\ mass - char\ mass - coke\ mass \quad (1)$$

Overall carbon yields of the liquid, gas, and solid products and carbon selectivity of a specific product were calculated based on the following equations.

$$Carbon\ yield = \frac{moles\ of\ carbon\ in\ a\ product}{moles\ of\ carbon\ fed\ in} \times 100\% \quad (3)$$

$$Carbon\ selectivity = \frac{moles\ of\ carbon\ in\ a\ product}{moles\ of\ carbon\ in\ identified\ products} \times 100\% \quad (4)$$

Table 1 Textural properties of Ni-Al alloy powder and home-made Raney Ni catalyst[a]

	S_{BET} (m²/g)	V_{pore} (cm³/g)	S_{pore} (m²/g)	d_{pore} nm
Ni-Al alloy powder	0.35	0	0	0
Home-made Raney Ni	52.4	0.034	35.8	3.8

[a]S_{BET}: BET surface area; V_{pore}: pore volume; S_{pore}: pore surface area; d_{pore}: average pore size

3. Results and discussion

3.1 Catalyst characterization of as-prepared Raney nickel

During alkali leaching, Al in the Ni-Al alloy powder reacted with NaOH solution. As expected, the Raney Ni catalyst is primarily composed of metallic nickel. The textural properties of as-prepared Raney Ni catalyst and the parent Ni-Al alloy powder were demonstrated in Table 1. After the alkali treatment, BET surface area, pore volume, and pore surface area were significantly improved. The BET surface area of the Raney Ni catalyst dramatically increased by dissolution of Al component from 0.35 to 52.4 m²/g. Moreover, pore volume and pore surface area progressively went up to 0.034 cm³/g and of 35.8 m²/g, respectively. The decent BET surface area of the Raney Ni catalyst assisted the adsorption of hydrogen on the surface of the catalyst for the hydrogenation reaction. The average

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pore size of the Raney Ni catalyst is 3.8 nm, which is close to the mono-cyclic aromatics diameter, thus mono-cyclic aromatics are prone to be adsorbed in the pores.[30]
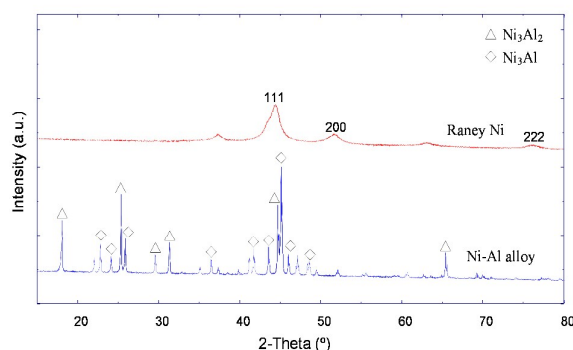

Fig. 1 The XRD patterns of the Ni-Al alloy powder and home-made Raney Ni catalyst.

Fig. 1 outlines the XRD patterns of the Ni-Al alloy powder and the as-prepared Raney Ni catalyst. The XRD patterns of Ni-Al alloy shows that it contains Ni_3Al_2 and Ni_3Al domains. After dissolving Al component by NaOH solution, the diffractions of metallic Ni were observed as amorphous nature. It mainly displayed diagnostic (111), (200), and (220) diffractions of fcc Ni at 2θ of 44.5, 51.8, and 76.3°, respectively.

The SEM images of Ni-Al alloy powder and the Raney Ni catalyst are illustrated in Fig. 2. The morphological differences between Ni-Al alloy powder and the home-made Raney Ni catalyst are readily visible from Fig. 2 (A) and (B). According to SEM images of Ni-Al alloy powder and home-made Raney Ni catalyst, the small particles of home-made Raney Ni are more dispersive, confirming a high BET surface. It was also observed that the Raney Ni catalyst was constituted by the typical fractured and angular particles, which are in line with other research;[31] while Ni-Al alloy powder shows the intact metallic structure. Therefore, the Raney Ni catalyst treated by 20 wt% NaOH solution could provide the excellent catalytic activity for the hydrogenation reaction.

3.2 Optimization of liquid organics from catalytic microwave pyrolysis

3.2.1 Product yield distributions from diverse lignocellulosic biomasses

The product yield distribution from hybrid poplar, loblolly pine, and Douglas fir are summarized as a function of catalytic temperature and catalyst to biomass ratio (for details see Table S2, S3, and S4). It was found that the yields of liquid organics and non-condensable gas were in the range from 14.44 to 22.07 wt% versus 39.20 to 50.34 wt%, 13.56 to 21.02 wt% versus 40.98 to 52.02 wt%, 13.88 to 20.88 wt% versus 38.18 to 49.66 wt%, respectively. The carbon yields of the liquid organics were compared in the following section. These results indicate that catalytic temperature had significant effects on both yields of liquids and gas. The yields of liquid organics declined with the increase of the catalytic temperature; while the yield of non-condensable gas increased with the similar increasing tendency of catalytic temperatures. These outcomes indicate that the elevated catalytic temperature could facilitate catalytic cracking rate of large molecule compounds into small molecules, thereby reducing the liquid organics yields. Due to the scissions of the C-O and C-C bonds at high catalytic temperature, the yields of gases fractions (CO, CO_2, and small hydrocarbons) were enhanced. The yields of liquid organics were also visualized in accordance to the response surface and contour line in Fig. 3 (A) for hybrid poplar, (B) loblolly pine, and (C) for Douglas fir. For ANOVA analysis, the P-value of the three models are all less than 0.05, suggesting the models are significant to present the relationships between product yields and reaction conditions. The coefficient of determination (R^2) for the three models are all larger than 0.95, evidencing that these models fairly represent the relationships with regard to the independent variables. Accordingly, these models can be used to predict the maximum mass yields of liquid organics according to the two variables. It is worth noting that the product yields were also affected by the catalyst to biomass ratio. Increasing the ratio contributed to improving the yield of gas, whereas the yield of liquid organics gradually decreased. It was found that when
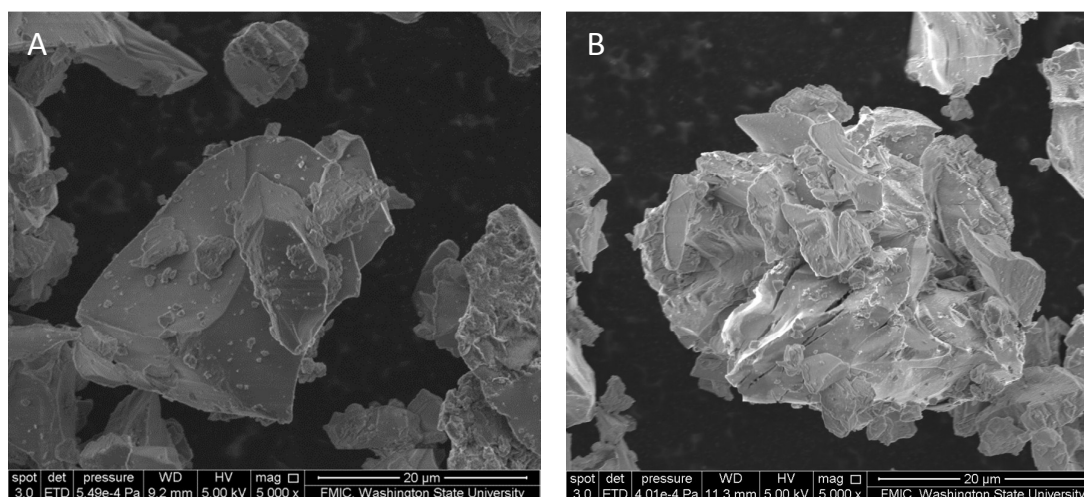
Fig. 2 SEM images of the Ni-Al alloy powder (A) and the as-prepared Raney Ni catalyst (B).

more catalysts were loaded; more spare active sites would be provided for catalytic cracking reactions in the fixed time, resulting in the varied yields of the products. Of the three biomasses, the optimal biomass species for maximizing the organic yields was hybrid poplar. When pyrolysis without catalyst; the liquid organic yield of hybrid poplar went up to 22.07 wt%, exceeding those from loblolly pine and Douglas fir. Similar phenomenon was observed by other studies as a result of catalytic temperature and catalyst to biomass ratio affecting product yields.[23, 29]

Solid carbonaceous residue (char and coke) from pyrolytic and catalytic processes can be distinguished due to the *ex-situ* catalysis. The char yield evolved from diverse biomass species (hybrid poplar, loblolly pine, Douglas fir) remained virtually constant at 22.50 wt%, 20.20 wt%, and 21.50 wt%, respectively. It was claimed that high ash and lignin contents could incur the high formation of solid residues including char and coke in the pyrolytic process.[26, 32] The proportion of cellulose, hemicellulose and linin in various biomass sources was shown in Table S5. Hence high ash content in hybrid poplar[33] and high lignin content in Douglas fir[22] caused the higher formation of char. Given the coke deposited on the catalyst leading to deactivation of the active sites and micropores blockage, the carbonaceous compounds were a crucial element to be taken into consideration in the study of formation mechanism when zeolites are employed as catalysts. The coke deposition yields of hybrid poplar, loblolly pine, and Douglas fir as a function of catalytic temperature and catalyst to biomass ratio were also depicted in Table S2, S3, and S4, varying from 1.27 to 3.57 wt.%, 1.18 to 3.99 wt%, 1.95 to 4.02 wt%, respectively. The less formation of coke from hybrid poplar was mainly attributed to less lignin content,[33] comparing to higher contents in loblolly pine and Douglas fir.
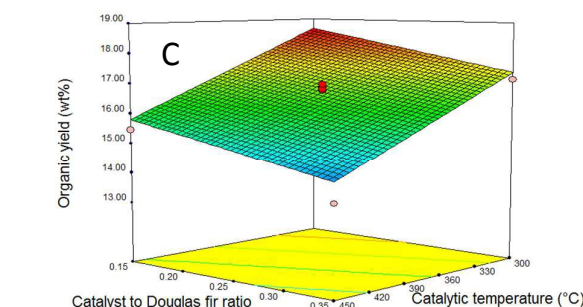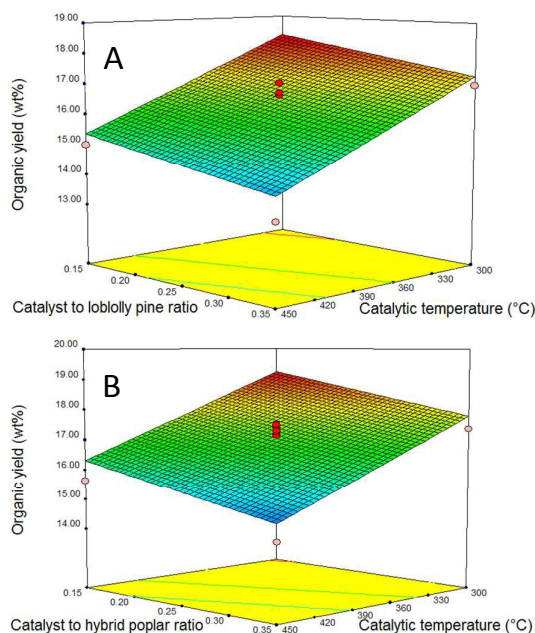

Fig. 3 Effect of the interaction of the independent variables on organic yield from hybrid poplar (A), loblolly pine (B) and Douglas fir (C) yields (red pots represent actual experimental values).

3.2.2 Chemical composition of liquid organics from catalytic microwave pyrolysis of diverse biomass sources

As previous work reported, catalyst temperature had a significant effect on the chemical composition of bio-oils by using ZSM-5 as the catalyst.[23, 29] In this sense, catalytic temperature was chosen as the variable to investigate and even optimize the quality of liquid organics. Representative results of liquid organics regarding the chemical compounds from diverse biomass species in light of catalytic temperature at the same catalyst to biomass ratio (0.25) are shown in Fig. S3, S4, and S5. In comparison with the liquid organics obtained by non-catalytic pyrolysis of hybrid poplar, loblolly pine, and Douglas fir, the selectivity towards aromatic hydrocarbons significantly increased, which was attributed to microporous structure of ZSM-5 catalyst and active sites generated in the micropores. It was found that the selectivity of aromatic hydrocarbons ranged from 17.95 to 94.33%, 23.75 to 93.16%, 2.72 to 92.62% as catalytic temperature increased to 500 °C, implying that the elevated catalytic temperature accelerated reaction rates of cracking, dehydration, decarbonylation, decarboxylation, and aromatization in the short time, giving rise to high selectivity towards aromatic hydrocarbons. It was reported that cellulose as the feedstock for catalytic pyrolysis produced higher amount of aromatic hydrocarbons than hemicellulose and lignin.[34] It could also be inferred from these results that higher amount of aromatic hydrocarbons from catalytic pyrolysis of hybrid poplar was due to higher cellulose content (see Table S5).

Phenols and guaiacols were the most abundant compounds in raw organics without using the catalyst, which was mainly derived from the direct decomposition of lignin; whereas these compounds dramatically declined at 500 °C, and guaiacols were even not detected from all biomass sources. These results indicate that high catalytic temperature favored the scission of methoxy and hydroxyl groups from phenyl to form aromatic hydrocarbons. Other minor oxygenated aromatics could be ignored when catalytic temperature from the three biomass sources were set at 500 °C.
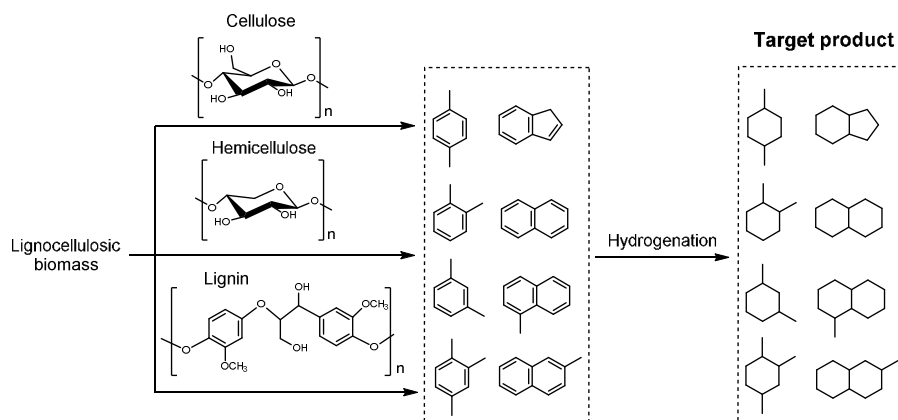
Scheme 1 Proposed reaction pathways for the conversion of lignocellulosic biomass into high-density cycloalkanes for jet fuels

Table 2 Products distribution and main aromatics carbon selectivity from diverse lignocellulosic biomasses at 500 °C[a]

	Biomass sources		
	Hybrid poplar	Loblolly pine	Douglas fir
Overall carbon selectivity (C mol%)			
Gas	42.34	43.08	40.53
Char	30.63	31.73	34.29
Coke	2.27	2.28	3.66
Aromatics	24.76	22.91	21.52
Aromatics carbon selectivity (C mol%)			
Toluene	4.77	5.18	4.32
Ethylbenzene	2.60	2.39	1.79
p-xylene/*m*-xylene	13.34	12.03	12.54
Trimethylbenzene	5.22	4.05	4.37
Indane	2.49	2.08	2.99
Indane	5.86	4.05	5.06
Phenol	1.34	1.86	1.52
p-cresol/*m*-cresol	1.59	1.55	2.03
Naphthalene	17.83	13.59	10.77
1-methylnaphthalene	2.87	3.72	1.68
2-methylnaphthalene	14.20	16.70	12.30
Anthracene	0.78	1.59	1.25
Pyrene	1.20	0.26	2.40

[a]Reaction condition: Catalyst, 25 wt% with respect to biomass; Reaction temperature, 480 °C; Reaction time, 10 min.

3.2.3 Catalytic transformation of diverse lignocellulosic biomass into C_8- C_{16} aromatics

It was assured that the optimal condition to maximize the amount of aromatics was set at 500 °C. To produce jet fuel range cycloalkanes, the novel synthetic route was proposed in Scheme 1. Therefore, the transformation of lignocellulosic biomass into $C_8 - C_{16}$ aromatics is primarily required. In this regard, the catalytic temperature was held at 500 °C and catalyst to biomass ratio was kept constant at 0.25. The catalytic microwave pyrolysis was duplicated for three times for all biomass species in order to gain abundant liquid organics which were stepwise mixed together for the hydrogenation process. The overall carbon yield distribution and partial aromatics carbon selectivity from catalytic microwave pyrolysis of diverse biomass species are shown in Table 2. It was noteworthy that the non-condensable gas and char were found to be the dominant compositions from all biomasses. The non-condensable gas was mainly comprised of hydrogen, carbon dioxide, carbon monoxide, methane.

In addition, It was also noted that 24.76% carbon yield of aromatics was obtained from catalytic microwave pyrolysis of hybrid poplar, which was higher than those of loblolly pine (22.91%) and Douglas fir (21.92%). In contrast, the carbon yields of catalyst coke were all much lower than other studies reported elsewhere.[20, 21, 35, 36] Since the ex-situ catalysis could make the indirect contact between biomass and catalyst, the catalyst could not be poisoned by the inorganic elements in the biomass and solid carbonaceous char could not deposit on the catalyst, contributing to the low carbonaceous residue formed on the catalyst. In general, hybrid poplar could be considered as the better resource for the production of aromatics.

The main aromatics carbon selectivity from catalytic microwave pyrolysis of diverse biomass sources is also depicted in Table 2. Generally the typical compositions belong to the lumps of $C_8 - C_{16}$ aromatics, including mono-cyclic and poly-cyclic aromatic hydrocarbons. Carbon selectivity towards xylenes from all biomass sources was comparable between 12 and 14%. Other mono-cyclic aromatic hydrocarbons among the three biomasses, e.g. toluene, phenol, indane, and indene, were also comparable. Two-ring aromatic hydrocarbons were the dominant compositions including naphthalene and its derivatives, originating from oligomerization reactions of mono-cyclic aromatic hydrocarbons. As the pore diameter of the well-promoted ZSM-5 catalyst is similar to the diameters of two-ring aromatic hydrocarbons, two-ring aromatic hydrocarbons formed could be prone to diffusing out. Carbon selectivity of naphthalene and 2-methylnaphthalene from hybrid poplar were 17.83% and 14.20 %, respectively. The carbon selectivity was comparable with those of loblolly pine, yet a little higher than that of Doulas fir (10.77% and 12.30%, respectively). Other poly-cyclic aromatic hydrocarbons with

three rings all had low carbon selectivity, most of which corresponding to carbon number did not exceed C_{16}.

3.3 *Hydrotreatment of extracted organics*

3.3.1 The effect of catalytic temperature on the chemical composition of hydrogenated organics

Given the water influence in the hydrogenation process, the bio-oils from the catalytic pyrolysis step were extracted by the optimum solvent (*n*-heptane). The liquid organics together with *n*-heptane from each biomass were separated and weighed to measure the loss of organics in the extracting step. The loss of organics in water phase can be neglected if considering that all recoveries of organics exacted by *n*-heptane could reach ~94 wt%, most of which were aromatic hydrocarbons. Since the liquid organics produced by catalytic microwave pyrolysis of intact biomasses principally consisted of C_8 - C_{16} aromatics, the controllable adjustment of aromatics with 8 - 16 carbon numbers are considered as precursors of jet fuels. According to hydrogenation of the model compound in the medium of *n*-heptane, naphthalene with 99% carbon selectivity was transformed into saturated decalin.[27] Thus the mass ratio of reactant to solvent was set at 1:7 in light of hydrogenation reaction of the model compound. The extracted organics within C_8 - C_{16} aromatics were stepwise hydrogenated in terms of several variables.

Table 3 Products distribution and partial cycloalkanes carbon selectivity from Douglas fir as a function of reaction temperature[a]

	Temperature (°C)		
	150	200	250
Overall selectivity (% in area)			
Cycloalkanes	54.82	70.83	83.34
Cycloolefins	8.32	7.32	3.20
Hydro-aromatic hydrocarbons	20.07	10.22	6.32
Hydro-cyclic alcohols	5.34	5.19	3.78
Aromatic hydrocarbons	8.19	3.20	1.88
Other oxygenated aromatics	3.26	3.24	1.48
Cycloalkanes selectivity (C mol%)			
1,4-dimethylcyclohexane	1.32	1.18	2.68
1,3-dimethylcyclohexane	2.27	4.54	5.04
1,2-dimethylcyclohexane	1.45	2.57	2.23
Ethylcyclohexane	2.34	3.07	4.67
1,2,4-trimethylcyclohexane	0.78	0.69	1.36
Propylcyclohexane	1.06	1.49	1.90
Hexahydroindan	9.86	10.40	11.64
Decalin	14.78	16.03	16.28
Bicyclohexyl	1.01	1.74	1.56
Perhydrofluorene	1.45	1.54	1.34
Tetradecahydroanthracene	2.67	2.89	3.02

[a]Reaction condition: Initial pressure, 500 psi; Raney Ni catalyst, 10 wt% with respect to reactant mass; Reaction time, 2 h.

In order to further understand the effect of the Raney Ni catalyst on the chemical reactions and obtain more insight into hydrogenated organics, the chemical compounds of hydrogenated organics from Douglas fir are elucidated as a function of reaction temperature in Table 3. The selection of Douglas fir is because Douglas fir was the typical feedstock, obtaining appropriate ratio mono-ring and poly-ring aromatic hydrocarbons from catalytic microwave pyrolysis, which can be more readily investigated into the conversions of the aromatic hydrocarbons. It is noticeable that the reaction temperature significantly influenced the hydrogenation reactions. Cycloalkanes was formed through hydrocycloaddition of corresponding aromatic hydrocarbons or other ring-unsaturated hydrocarbons. The gross amount of cycloalkanes progressively increased with the increment of reaction temperatures. It can be seen that cycloalkanes were in the range from 54.82% at 150 °C to 83.34% as reaction temperatures went up to 250 °C, suggesting that increasing the reaction temperature could facilitate the reaction rate of hydrogenation, resulting in enhancement of cycloalkanes during the fixed reaction time. In this regard, more than half of the aromatic intermediates were converted into jet fuel range cycloalkanes, whose amount in hydrogenated bio-oils was equal to that in JP-5 [37]. Moreover, there is a minor selectivity for cycloolefins, generally declining from 8.32 to 3.20% along with the increasing of reaction temperatures. Therefore, elevated temperature could facilitate the hydrogenation of cyclic olefins into cycloalkanes. Hydro-aromatic hydrocarbons and aromatic hydrocarbons show decreased trend (20.07 to 6.32% and 8.19 to 1.88%, respectively). It was found that the amount of hydro-cyclic alcohols was much lower at 250 °C than that at 200 °C, and other oxygenated aromatics was also declined at 250 °C. These outcomes imply that the higher reaction temperature possibly favored the scission of hydroxyl group from phenyl to form aromatic hydrocarbons through hydrogenolysis reactions.[38] These aromatic hydrocarbons could be further transformed into ring-saturated hydrocarbons. In addition, less than 1 vol% small hydrocarbons (such as methane, ethane, and propane) were produced at 250 °C, which were possibly from hydrocracking of larger hydrocarbons. Hence, hydrogenolysis and hydrocracking reactions could simultaneously occur at high reaction temperatures in the hydrogenation system.

Reaction temperatures also had a significant effect on the carbon selectivity of specific cycloalkanes. It was noteworthy that the carbon selectivity of mono-cyclic alkanes significantly increased as the reaction temperature increased, especially from 150 to 200 °C. Meanwhile, 1, 3-dimethylcyclohexane (C_8H_{16}) and ethylcyclohexane (C_8H_{16}) gradually increased from 2.27 to 5.04% and 2.34 to 4.67%, which indicates that high reaction temperatures presumably accelerated hydrocracking reactions of poly-cyclic aromatic hydrocarbons after being partially hydrogenated. Because aromatic and alkane ring in hydro-aromatic hydrocarbons are not coplanar, the hydrogenated alkane ring could be continuously hydrocracked on the Raney Ni catalyst and finally opened to form branched chains attached on the aromatic ring. The carbon selectivity of

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hexahydroindan (C_9H_{16}) was slightly impacted by alterations of reaction temperature. Likewise, there were small upward tendency of decalin ($C_{10}H_{18}$) carbon selectivity, which gradually increased from 16.03 to 16.28% when it was set in the range of 200-250 °C. It showed that all naphthalene was completely hydrogenated into decalin under these conditions. Carbon selectivity of other poly-cyclic alkanes showed a steady increment, implying that the hydrogenation rate of polycyclic aromatic intermediates could also be facilitated by increasing reaction temperatures.

3.3.2 The effect of catalyst loading on the chemical composition of hydrogenated organics

Yet the C_8-C_{16} aromatics were not thoroughly converted into jet fuel range cycloalkanes, even when the reaction temperature was carried out at 250 °C. Other effects such as catalyst loading were further investigated into the chemical compositions of hydrogenated organics from Douglas fir. The products distribution is summarized as a function of catalyst loading (10 wt% and 20 wt% with respect to reactant mass) in Fig 4 (A). It was observed that the selectivity towards cycloalkanes were 70.83% and 84.59% depending on alterations of catalyst loadings. The more catalysts loaded into the reactor could provide more reactive sites for the hydrocycloaddition of unsaturated hydrocarbons, thus improving the hydrogenated efficiency. Unsaturated hydrocarbons (hydro-aromatic hydrocarbons and cycloolefins) partially hydrogenated in the process accounted for 10.22 – 4.60% and 7.32 – 2.83%, respectively. The variation of hydro-aromatic hydrocarbons (e.g. tetralin) was significantly impacted by the catalyst loading. Adequate catalyst loading could impel the hydro-aromatic hydrocarbons to be hydrogenated into cycloalkanes. The decreases of the unsaturated hydrocarbons, as more catalysts were employed, were mainly due to the transformations into corresponding cycloalkanes. Catalyst loading also had an influence in the selectivity of hydro-cyclic alcohols, occupying from 5.19 to 3.84%. The amount of aromatic hydrocarbons decreased with the increasing of catalyst loading, implying that more active sites were provided for converting the aromatic intermediates into hydro-aromatic hydrocarbons or cycloalkanes. Other oxygenated aromatics showed slight variations, varying from 3.24 to 2.15%. These results indicate that the chemical compositions of hydrogenated organics were essentially influenced by the catalyst loading.

The effect of catalyst loadings on partial cycloalkanes carbon selectivity is explained in Fig. 4 (B). Catalyst loading had a slight influence on the carbon selectivity of mono-cyclic cycloalkanes, including dimethylcyclohexanes and ethylcyclohexane. These results indicate that mono-cyclic aromatic hydrocarbons were prone to being hydrogenated into mono-cyclic alkanes even in the presence of low catalyst loading. Two aromatic rings of naphthalenes were coplanar and one aromatic ring was readily converted into a saturated ring, however the aromatic ring and cyclic alkane ring of tetralin was no longer coplanar after hydrogenation.[39] Thus the opposite aromatic ring was directed away from the

catalyst surface. Once more adequate catalysts were applied; the other aromatic ring was still hydrogenated at the spare active sites. It is obvious that the carbon selectivity of both hexahydroindan and decalin increased since more Raney Ni catalyst were introduced. In addition, the carbon selectivity of bicyclohexyl ($C_{12}H_{22}$), perhydrofluorene ($C_{13}H_{22}$), and tetradecahydroanthracene ($C_{14}H_{24}$) gradually increased as more catalysts were employed. Consequently, more catalyst loading offered more active sites on the Raney Ni catalyst surface and inside the structure, giving rise to more hydrocycloaddition reactions.
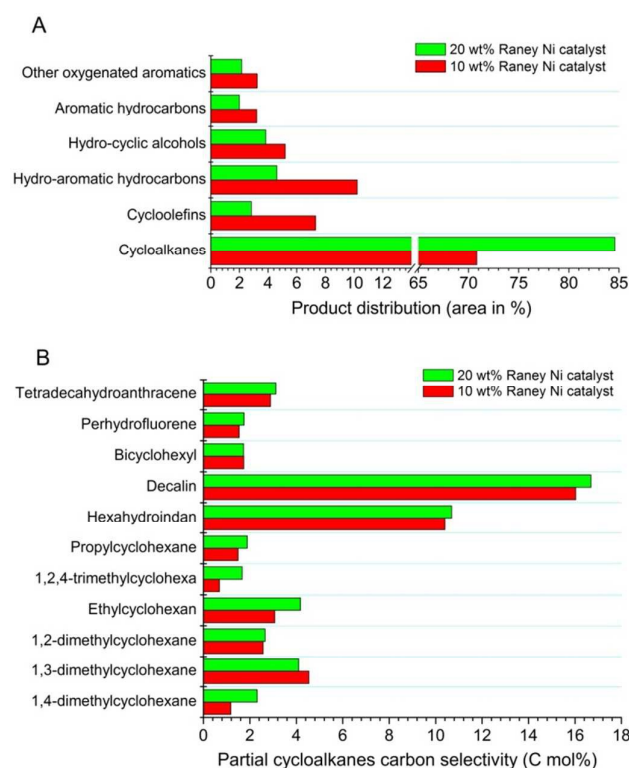

Fig. 4 Overall products distribution (A) and partial cycloalkanes carbon selectivity (B) with respect with catalyst loading. Reaction condition: Reaction temperature, 200 °C; Initial pressure, 500 psi; Reaction time, 2h.

3.3.3 The effect of diverse biomass sources on the chemical composition of hydrogenated organics

Apart from reaction temperature and catalyst loading, biomass source was another crucial factor that influenced product distribution and carbon selectivity of the cycloalkanes. The chemical composition of hydrogenated organics from diverse biomass sources (hybrid poplar, loblolly pine, Douglas fir) is depicted in Table 4. After the hydrogenation process, the recovery of the hydrogenated organics from the diverse biomass sources were all over 95 wt%. Compared with the overall product distribution from loblolly pine and Douglas fir,

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Table 4 Products distribution and partial cycloalkanes carbon selectivity as a function of diverse biomass sources[a]

	Biomass sources		
	Hybrid poplar	Loblolly pine	Douglas fir
Overall selectivity (% in area)			
Cycloalkanes	95.20	94.06	92.70
Cycloolefins	1.01	0.89	1.20
Hydro-aromatic hydrocarbons	0.23	0.22	0.34
Hydro-cyclic alcohols	2.67	3.12	3.56
Aromatic hydrocarbons	0.67	1.20	1.05
Other oxygenated aromatics	0.22	0.51	1.15
Cycloalkanes selectivity (C mol%)			
1,4-dimethylcyclohexane	4.23	5.48	1.52
1,3-dimethylcyclohexane	5.20	3.27	5.23
1,2-dimethylcyclohexane	2.34	1.53	2.11
Ethylcyclohexane	5.87	4.59	5.03
1,2,4-trimethylcyclohexane	3.06	2.29	1.36
Propylcyclohexane	1.32	0.88	1.79
Hexahydroindan	10.34	11.23	10.84
Decalin	16.76	16.34	17.05
Bicyclohexyl	1.23	1.65	1.32
Perhydrofluorene	1.89	2.05	1.34
Tetradecahydroanthracene	3.02	3.76	3.49

[a]Reaction condition: Initial pressure, 500 psi; Raney Ni catalyst, 20 wt% with respect to reactant mass; Reaction temperature, 250 °C; Reaction time, 2 h.

the result for the production of jet fuel range cycloalkanes from hybrid poplar was more superior to the others under the same condition. As mentioned above, the higher compositions of cellulose in hybrid poplar contributed to the shares of aromatics derive from catalytic microwave pyrolysis, therefore giving rise to higher content of cycloalkanes via hydrocycloadditions of aromatics. It was observed that 95.20% selectivity towards cycloalkanes was achieved from hybrid poplar. From the optimal result of hybrid poplar, approximately 0.028 mole of hydrogen were consumed by the parent aromatics (1 g) by the hydrogenation reactions. The minor amount of hydrogen consumed in the process was affirmed that hydrogen preferentially acted as the H-donor to undergo the hydrocycloaddition of ring-unsaturated hydrocarbons to generate cycloalkanes, rather than the hydrodeoxygenation of oxygenates to form water. Because of the high content of the cycloalkanes in the hydrogenated organics, the hydrogenated organics can be directly regarded as the high density jet fuels. As a result, the carbon yields of the high density jet fuel based on the three lignocellulosic biomasses (hybrid poplar, loblolly pine, and Douglas fir) were 22.11%, 20.46%, and 19.22% respectively.

The gross amount (~1%) of cycloolefins was comparable, which amount meets the specifications (less than 5%) of commercial jet fuels. Small amounts of hydro-aromatic hydrocarbons and aromatic hydrocarbons were detected in

the hydrogenated organics from all biomass sources, suggesting that aromatic intermediates were thoroughly hydrogenated into cycloalkanes. As such, the content of hydro-cyclic alcohols derived from phenols were much lower under this condition , which indicates that partial hydro-cyclic alcohols could be converted into cycloalkanes via the scission of hydroxyl group substituted on the phenyl and subsequent hydrocycloaddition of the received aromatic hydrocarbons. There was trace amount of other oxygenated aromatics in the hydrogenated organics from all biomasses sources, implying that hydrogenolysis reactions also took place in the process. Small hydrocarbons detected in the gas revealed that these hydrocarbons with small volume were from the hydrocracking and hydrogenolysis of larger hydrocarbons.

It was found that the carbon selectivity of both dimethylcyclohexanes and ethylcyclohexane were maximum from hybrid poplar. Other mono-cyclic alkanes such as trimethylcyclohexane were also shown the largest carbon selectivity. Therefore hybrid poplar was the optimal biomass source for the production of mono-cyclic alkanes. Of the biomass sources, hybrid poplar displayed the lowest carbon selectivity of hexahydroindan. Unlike the hexahydroindan, the carbon selectivity towards decalin, bicyclohexyl, perhydrofluorene, and tetradecahydroanthracene was all comparable from three biomasses. Accordingly, these outcomes imply that employing hybrid poplar as the feedstock in the integral steps could finally improve the overall yield of cycloalkanes, and obtain the highest carbon selectivity of mono-cyclic alkanes.

Conclusions

In summary, the microwave-induced pyrolysis followed by hydrogenation is a profound approach for the production of renewable high-density cycloalkanes from lignocellulosic biomass. Diverse lignocellulosic biomasses (hybrid poplar, loblolly pine, and Douglas fir) were taken consideration to manufacture liquid organics in the catalytic microwave pyrolysis. The optimal condition to maximize the C_8 - C_{16} aromatics in the step of catalytic microwave pyrolysis was at 500 °C with the catalyst to biomass ratio of 0.25. It was observed that the maximum carbon yield (24.76%) of aromatics and highest selectivity (94.33%) towards aromatic hydrocarbons in liquid organics were both from catalytic microwave pyrolysis of hybrid poplar.

These aromatics in *n*-heptane medium were thoroughly hydrogenated into jet fuel range cycloalkanes at 250 °C in the presence of 20 wt% (based on the mass of liquid aromatics) the Raney Ni catalyst. The hybrid poplar derived products obtained the highest selectivity (95.20%) towards high-density cycloalkanes for jet fuels under very mild conditions. From lignocellulosic biomass to cycloalkanes-enriched hydrogenated organics through the integral processes, the maximized carbon yield of the hydrogenated organics from hybrid poplar was 22.11%. Increasing the reaction temperature and catalyst loading could facilitate the hydrogenation reaction to improve the production of cycloalkanes. It is more likely that in the

future these cycloalkanes can be directly used as additives in jet fuels or hydrocracked into linear and branched alkanes in the jet fuel range through hydrocracking and isomerization reactions.

Acknowledgements

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A novel pathway for producing high-density cycloalkanes for jet fuels from diverse lignocellulosic biomasses and determining the optimal biomass source *via* catalytic microwave-induced pyrolysis and hydrogenation process