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From lignocelluloic biomass to renewable cycloalkanes for jet fuels

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A novel pathway was investigated to produce jet fuel range cycloalkanes from intact biomass. The consecutive processes for converting lignocellulosic biomass into jet fuel range cycloalkanes principally involved the use of the well-promoted ZSM-5 in the process of catalytic microwave-induced pyrolysis and Raney nickel catalysts in the hydrogen saving process. Up to 24.68% carbon yield of desired C_8 – C_{16} aromatics was achieved from catalytic microwave pyrolysis at 500 °C. We observed that solvents could assist in the hydrogenation reaction of naphthalene; and the optimum result for maximizing the carbon selectivity (99.9%) of decalin was from the reaction conducted in the *n*-heptane medium. The recovery of organics could reach ~94 wt. % after the extracting process. These aromatics in the *n*-heptane medium were eventually hydrogenated into jet fuel range cycloalkanes. Various factors were employed to determine the optimal result under mild conditions. Increasing catalyst loading, reaction temperature, and prolonged time could enhance the hydrogenation reactions to improve the selectivity of jet fuel range cycloalkanes. Three types of hydrogenation catalysts (NP Ni, Raney-Ni 4200, home-made Raney Ni) were chosen to evaluate the catalytic performance. Results indicated that the home-made Raney nickel was the optimal catalyst to obtain the highest selectivity (84.59%) towards jet fuel range cycloalkanes. These cycloalkanes obtained can be directly used as additives to make the desired jet fuels by blending with other hydrocarbons. Hence integrating catalytic processes and conversion of lignocellulosic biomass pave a new avenue for the development of green bio-jet fuels over inexpensive catalysts under mild conditions.

1. Introduction

Growing concerns about global climate change and rapid diminishing fossil-based petroleum reserves have spurred immense interest in the utilization of renewable resources for developing new generation (hydrocarbon) biofuels, with a particular focus on green aviation fuels.[1, 2] The development of alternative aviation fuels received more attention in order to reduce dependence on fossil sources. Lignocellulosic biomass is a ubiquitous and sustainable source of carbon that displays promising potential in the manufacture of hydrocarbon transportation fuels and versatile chemicals.[3, 4]

The commercial aviation fuels designed for use in aircrafts are jet fuels, which are exclusively derived from petroleum refining.[5] The current jet fuels originated from fossil resources are rich in straight-chain alkanes.[6, 7] It was found that both straight-chain alkanes and branched-chain alkanes are highly susceptible to pyrolytic cracking, resulting in coking in a jet engine, increasing deposition and fouling of fuel control units and injectors, and increasing operating costs due to the increased maintenance.[8, 9] On the other hand, the thermal stability of a jet fuel can be greatly enhanced by utilizing liquids rich in cycloalkanes; because cycloalkanes 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, comparing with straight-chain alkanes and branched-chain alkanes with lower densities (~ 0.76-0.78 g/mL).[8, 10] However, commercial petroleum fuels normally do not have very high cycloalkane contents and it is difficult to concentrate the cycloalkanes on a commercial scale.[11] To fulfill the demand of increasing the density and volumetric heating, it is imperative for cycloalkanes to be synthesized and added into jet fuels (e.g. Jet A and JP-8).[7] Therefore, most efforts to produce jet fuels have focused on increasing the cycloalkanes content, for example JP-5 navy fuel contains 52.8% cycloalkanes.[12]

To produce renewable drop-in fuels for aviation, Dumesic group[13, 14] and Huber et al.[6, 15] have discovered a new route by aldol condensation of furfural and acetone to synthesize the long carbon chain intermediates of C_8 - C_{15}. The hydrodeoxygenation process was stepwise introduced to obtain the branched alkanes with high thermal stability and energy density, which could be used as drop-in fuels for

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aviation. In general, most studies emphasized on manufacturing jet fuel range (C_8 - C_{16}) straight-chain alkanes and/or branched-chain alkanes from the lignocellulose-derived platform compounds, which cannot meet the specification of cycloalkanes in jet fuels.[16-18] In addition, these multiple processes necessitate expensive reactants and noble metal catalysts, resulting in infeasible commercialization in biorefineries comparing with commercial formulations based on petroleum derived jet fuels.

In addition, fast pyrolysis has also received special recognition and it is one of the viable process options to convert lignocellulosic biomass to pyrolysis oil.[19, 20] The pyrolysis oil is unable for use as a transportation fuel because of detrimental properties, including a much lower energy density than petroleum fuels, poor thermal and chemical stabilities, and high viscosity.[21, 22] To circumvent these problems, raw pyrolysis oil has to be upgraded to eliminate total or partial oxygenates and unsaturated degree prior to its practical application as transportation fuel.[23] Among the upgrading approaches for jet fuels, hydrodeoxygenation (HDO) is deemed to be a promising and effective process.[7] The HDO process conditions are rather severe (300 – 400 °C, 80 - 300 bar H_2 pressure).[21, 22] It is widely known that the oxygen content in the fast pyrolysis oils was removed through HDO process in the form of H_2O. In this regard, large amount of costly hydrogen was consumed by the dehydration reaction, which significantly reduces the hydrogenating efficiency. Since advanced jet fuels from HDO process are expected to be enlarged in a biorefinery scale, high capital costs caused by tolerance of severe condition and low selectivity of liquid products render these processes uneconomical.[24, 25] Accordingly, the production of jet fuels from renewable biomass resources calls for ideal technologies with efficient solid-phase catalysts to make the processes economically feasible under a mild, environmentally friendly reaction condition.

In contrast, oxygen content of bio-oil can be partially or even completely eliminated by zeolite cracking during fast pyrolysis of biomass.[26] Carlson et al. have reported that biomass-derived feedstock can be directly converted into aromatics with ZSM-5 as catalyst in a single catalytic pyrolysis step.[27, 28] Lei and his colleagues have focused on the production of aromatics through catalytic microwave-induced pyrolysis of biomass-derived feedstock.[29, 30] Up to 92.60% selectivity towards aromatic hydrocarbons was obtained, belonging to jet fuel range (C_8 – C_{16}) aromatics. In this sense, the certain range aromatics with low oxygen content are prone to be hydrogenated into cycloalkanes together with minor aromatics under low-severity conditions. The hydrogenated process is regarded as a hydrogen saving process, in which hydrogen is converted in the form of cycloalkanes rather than water.

It is more reasonable to use Ni-based catalysts for hydrotreating bio-oil because of their high activity of hydrogenation and low cost. Raney-type nickel is widely used as a versatile catalyst in such a hydrotreating process for reductive transformations of organic compounds.[31] Moreover, Raney-type nickel is utilized in other widespread fields for fine chemical manufacturing owing to its good catalytic performance.[22] In addition to catalyzing liquid products, costly hydrogen derived from aqueous-phase reforming could also be obtained over a tin-promoted Raney-nickel catalyst by Huber and his colleagues.[32] It was found that water molecule was easily fixed to the Raney nickel surface by oxygen bonding, thereby inhibiting the adsorption of organic substrates to the metallic surface.[33] Hence the removal of water in bio-oils is an essential step to enhance the catalytic performance in the hydrogen saving process. Some solvents (e.g. ethyl acetate) can be used to extract the organic mixture from pyrolysis oils. However, far too little attention has been paid to evaluate the impact of the solvents as part of the catalytic system.[34] Unlike the organic synthesis literature, in which the influence of solvents has been well-demonstrated and understood; while the effect of solvents for hydrogenation and hydrogenolysis reactions are commonly neglected and/or rarely comprehended.[35] Thus advance towards understanding the effect of solvents on the hydrogenation of bio-oils can lay the foundations for valorization of bio-oils.

According to aforementioned consideration, the direct conversion of lignocellulosic biomass into jet fuels by integrated processes was conducted. Lignocellulosic biomass was firstly converted into jet fuel range (C_8 – C_{16}) 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 after evaluating the solvent influence on the hydrogenation reaction of model compounds. In the final step, the organic mixture was hydrogenated into desired C_8 – C_{16} hydrocarbons (including cycloalkanes and minor aromatics) which satisfy basic requirements of conventional jet fuels by using Raney nickel as the catalysts. Since the coupling of three main steps (catalytic microwave pyrolysis, liquid-liquid extraction, and downstream hydrogen saving process) over regular catalysts has not been previously reported on the direct use of lignocellulosic biomass, this study demonstrates proof-of-principle of a novel consecutive three-step process to produce cycloalkanes for 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. Proximate and elemental analysis of raw Doulgas fir sawdust pellets were described in Table S1. It was evidenced that pelleted biomass could be maximally decomposed into pyrolytic volatile vapors by microwave heating, which could be thereafter catalyzed into targeted products.[29, 30] Parent ZSM-5 (SiO_2/Al_2O_3 Mole Ratio: 50) was purchased from Zeolyst International, USA. Methanol (99.8%), 2-propanol (99.7%), ethyl acetate (99.5%), benzene (99.5%), *n*-hexane (99%), cyclohexane (99%), toluene (99.7%), n-heptane (99%), methylcyclohexane (99%), p-xylene (99%), ethylbenzene (99%), 1H-indene (97%), indane (95%), naphthalene (99.6%), 1,2,3,4-tetrahydronaphthalene (97%), decahydronaphthalene (98%), 1-methylnaphthalene (96%), 2-methylnaphthalene (97%), *n*-dodecane (99%), anthracene (99%), pyrene (98%), Nickel-Aluminum alloy powder in an non-activated type were used as purchased from Alfa Aesar (Ward Hill, MA, USA). 1,2-dimethylcyclohexane (99%), 1,3-dimethylcyclohexane (99%), 1,4-dimethylcyclohexane (99%), ethylcyclohexane (99%), 1,2,4-trimethylbenzene (98%), 1,2,4-trimethylcyclohexane (97%), propylcyclohexane (99%), hexahydroindan (99%), bicyclohexyl (99%), perhydrofluorene (97%), tetradecahydroanthracene (99%), Raney Ni 4200 (slurry in water) in an activated form were supplied by Sigma-Aldrich Corporation (St. Louis, MO, 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.[36]

Non-pyrophoric Raney nickel (referred as NP Ni) was prepared from metallic alloy powders. Under gentle stirring, Ni-Al alloy powders (2 g) were slowly impregnated with 1.2 wt. % NaOH aqueous solution (20 mL) at room temperature. After addition, the temperature was elevated from room temperature to 80 °C and hold at the temperature for 30 min. Additional 2 mL of 12 wt. % NaOH aqueous solution was added to the slurry and stirred gently at 80 °C for 30 min for further alkali leaching. Subsequently the sample was washed to neutrality using distilled water and reserved in water for future catalytic use.

The home-made Raney nickel catalyst was developed using 20 wt. % NaOH aqueous solution to remove Al in the following procedure. 2 g of the above Ni-Al was slowly added into 20 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 nickel catalyst was stored in water. In order to test the catalytic performance of Raney nickel manufactured from the process, Raney nickel 4200 (referred as Raney-Ni 4200) purchased in the activated form was used as criterion for catalyzing the hydrogenation reaction of bio-oils. Raney nickel is notorious for its pyrophoricity, and it may ignite spontaneously when dried in air. The Raney-Ni 4200 slurry and home-made Raney nickel catalyst were 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 ligonocellulosic biomass

A Sineo MAS-II batch microwave oven (Shanghai, China) with a rated microwave power of 1000 W was employed for microwave pyrolysis. Detailed experimental setting was described in our previous studies.[29, 37] Fig. S1 shows the schematic diagram of the microwave-assisted pyrolysis system integrated with the catalysis process. Fixed loading of Douglas fir sawdust pellets (25 g) for each run were placed in a 500 mL quartz flask inside the microwave oven. 0.05g of activated carbon powder was used as the absorber for the microwave-assisted pyrolysis. The system was purged with nitrogen on a flow rate of 1000 mL/min for 15 min prior to pyrolysis reaction to maintain an oxygen-free environment. The microwave pyrolysis was conducted at the temperature of 480 °C for 10 min, which could maximize the pyrolytic volatiles yield as reported in our previous studies.[29, 38, 39] The pyrolysis volatile vapors from the flask passed through a packed bed catalysis reactor which was filled with catalyst. The packed-bed reactor customized is 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. As previous work reported, the optimal condition to maximize the composition of jet fuel range aromatics was set at 500 °C.[29] In this regard, the catalytic temperature was hold at 500 °C and catalyst (7.5 g) to biomass ratio was kept consistently at 0.3. The condensable liquid was collected as bio-oil. The non-condensable vapors escaped as gas at the end of the condensers and were collected for analysis. The catalytic microwave pyrolysis was duplicated for two times in order to gain abundant bio-oils which were stepwise mixed together for the hydrogenated process.

2.4 Hydrogenation of model compounds in diverse solvents

To evaluate the effect of diverse solvents on the hydrogenation of model compounds, a closed reaction system with a stirred stainless batch reactor of the 4592 micro stirred reactor (with a 50mL vessel) and a 4848 reactor controller from Parr Instrument Company (Moline, IL, USA) was used (see Fig. S2). In our previous study, naphthalene and its derivatives were the most abundant compositions in the bio-oils from catalytic microwave pyrolysis of Doulgas fir sawdust pellets;[29] thus it is more appropriate to use naphthalene as the model compound for the hydrogenation reaction. Naphthalene (1 g), Raney-Ni 4200 (0.1 g), solvent (7 g) were placed in the reactor. Solvents used were methanol, 2-propanol, ethyl acetate, benzene, *n*-hexane, cyclohexane, toluene, *n*-heptane, methylcyclohexane, decalin, and *n*-dodecane. 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 (200 °C) for 2 h. 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 Hydrotreatment of bio-oil derived from catalytic microwave pyrolysis

The combined bio-oils evolved from catalytic microwave pyrolysis were extracted by the optimal solvent after determining the effects of all solvents in the hydrogenated system. To produce the jet fuel range cycloalkanes, the mixture of organics and the optimum solvent was loaded into the reactor together with 10 wt. % or 20 wt. % catalysts (in terms of the reactants). The reactor was flushed with hydrogen and then tightly closed. The experiments for each run were performed at 150, 200, or 250 °C under stirring (300 rpm) for the intended time. The final step conducted was the same as aforementioned hydrogenation of model compounds.

2.6 Analytical techniques

Elemental analysis (C, H, N, and O) of Douglas fir sawdust pellets, 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 smaples 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.

2.7 Data evaluation

The coke mass was determined by the difference before and after catalytic pyrolysis. The weight of non-condensable gas was calculated using the following equation:

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

Conversion of naphthalene, overall carbon yields of the liquid, gas, and solid products, carbon yield of a specific product were calculated based on the following equations.

$$Conversion\ of\ naphthalene = \frac{moles\ of\ naphthalene\ reacted}{moles\ of\ naphthalene\ fed\ in} \times 100\% \quad (2)$$

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

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

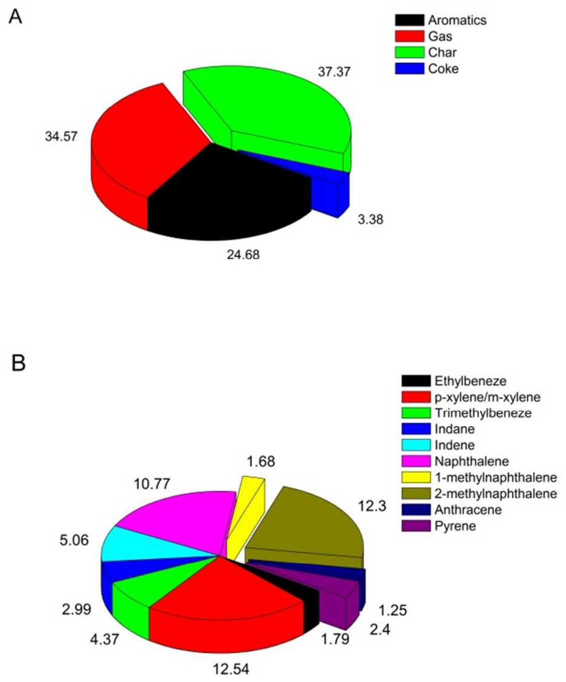


Fig. 1 Overall carbon yield distribution (A) and main aromatics carbon selectivity (B) for extracted bio-oils from catalytic microwave pyrolysis of Douglas fir sawdust pellets

3. Results and discussion

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

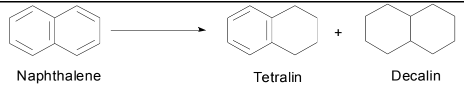
To produce jet fuel range cycloalkanes, the transformation of lignocellulosic biomass into jet fuel range (C_8 – C_{16}) aromatics is primarily required. The water content of bio-oils obtained was close to 20 wt% (based on biomass loading), which was derived from both the moisture of raw biomass and the subsequent dehydration reaction during biomass pyrolysis. The yield of organics (7.52 g) in the bio-oils accounted for 15.04 wt. %, prior to extracting process. The overall carbon yield distribution from catalytic microwave pyrolysis of biomass is shown in Fig. 1(A). It is noteworthy that the char were found to be the dominant composition, occupying 37.37% (Table S2). It was also noted that the carbon yield (34.57%) of non-condensable gas was calculated by difference. The gas was mainly comprised of hydrogen, carbon dioxide, carbon monoxide, methane, originating from decarboxylation, decarbonylation, cracking, and oligomerization reactions. In addition, 24.68% carbon yield of aromatics was obtained after mixing all bio-oils from catalytic microwave pyrolysis of Doulas fir sawdust pellets (for details see Table S3). In contrast, the carbon yield (3.38%) of catalyst coke was much lower than other studies reported elsewhere.[27, 28, 40, 41]

The carbon selectivity of main aromatics from catalytic microwave pyrolysis of Douglas fir sawdust pellets is depicted in Fig 1(B). Generally the typical compositions belong to the lumps of jet fuel range aromatic hydrocarbons, including mono-cyclic and poly-cyclic aromatic hydrocarbons. Carbon selectivity towards xylenes was 12.54%, which was the dominant share in the liquid organics. Other mono-cyclic aromatic hydrocarbons, e.g. indene (5.06% carbon selectivity) and indane (2.99% carbon selectivity), were also obtained. The large amount of poly-cyclic aromatic hydrocarbons including naphthalene and its derivatives was evolved from oligomerization reactions of mono-cyclic aromatic hydrocarbons.[42, 43] Carbon selectivity of naphthalene and 2-methylnaphthalene were 10.77% and 12.30%, respectively. The results imply that total amounts of poly-cyclic aromatic hydrocarbons were the most abundant compounds. Other poly-cyclic aromatic hydrocarbons with three rings had low carbon selectivity, most of which corresponding to carbon number did not exceed C_{16}.

3.2 Solvents effect on the hydrogenation of naphthalene

Aiming to ultimately determine the solvents effect on the hydrogenation of aromatics-enriched bio-oils evolved from catalytic microwave pyrolysis, we first explored the influence of various solvents in the hydrogenation reaction of a model compound (naphthalene). Table 1 summarize the results from hydrogenation of naphthalene with Raney-Ni 4200 performed in several solvents under 500 psi H_2 (initial pressure) at 200 °C for 2 h. As for all experiments, only unreacted hydrogen was detected at the end of reactions, implying that the reactions were not carried out under hydrogen starved conditions. The solvents effect on the hydrogenation of naphthalene demonstrates that the reaction medium could promote the catalytic transformation. The experiment conducted in methanol achieved only 22.6% conversion of naphthalene (entry 1). Trace amount of decalin (7.5% toward carbon selectivity) was detected in this solvent. The results imply that Raney-Ni 4200 could be poisoned when hydrogenation was conducted in neat methanol, which is identical to the study reported elsewhere.[35] Unlike the inhibited effect of methanol, both 2-propanol and ethyl acetate led to almost full conversion of the substrate. 47.0% carbon selectivity of decalin in 2-propanol medium was obtained from the hydrogenation reaction of naphthalene, which is remarkably superior to 22.90% carbon selectivity conducted in the medium of ethyl acetate. It is well developed that 2-propanol could serve as H-donor in the hydrogen transfer during hydrogenation.[44] Hence, 2-propanol as the reaction medium could facilitate the hydrogenation reaction of tetralin to decalin.

Table 1 Effect of various solvents on the hydrogenation reaction of naphthalene[a]



Entry	Solvent	Conv. (%)	Carbon selectivity (C mol%)	
			Tetralin	Decalin
1	Methanol	22.6	15.1	7.5
2	2-propanol	99.9	52.9	47.0
3	Ethyl acetate	100	77.1	22.9
4	Benzene	95.2	86.1	9.1
5	*n*-hexane	99.9	7.1	92.8
6	Cyclohexane	99.9	13.4	86.5
7	Toluene	98.9	86.8	12.1
8	*n*-heptane	100	0.1	99.9
9	Methylcyclohexane	99.9	30.4	69.5
10	Decalin	100	0.5	99.5
11	*n*-dodecane	100	32.6	67.4

Reaction condition: naphthalene (0.0078 mol), solvent (7 g), Raney-Ni 4200 (0.1 g, 10 wt. % with respect to reactant mass), 500 psi H_2 (initial pressure), 200 ^{o} C for 2 h.

Among the solvents of aromatic hydrocarbon (benzene and toluene), over 95% naphthalene was converted; however poor conversions were gained in decalin (9.1% and 12.1%, respectively). It was probably attributed to the unsaturated solvents which could first attach to the surface of Raney-Ni 4200 and then reacted with hydrogen absorbed at the surface. The competitive reaction resulted in insufficient hydrogen and active sites of catalyst for the hydrogenation reaction of tetralin to decalin. Conducting the reaction in alkanes (entry 5-6, 8-11), however, contributed to very high to full conversion: *n*-hexane (99.9%), cyclohexane (99.9%), *n*-heptane (100%), methylcyclohexane (99.9%), decalin (100%), *n*-dodecane (100%). For maximizing the hydrogenation of naphthalene to decalin, *n*-heptane showed the best conversion (99.9% carbon selectivity), comparing with n-hexane (92.8%), cyclohexane (86.5%), methylcyclohexane (69.5%), decalin (99.5%), *n*-dodecane (67.4%). As *n*-heptane does not dissolve with water but display good extracting performance,[35] therefore, *n*-heptane is the desired solvent that should be used for extracting the aromatics-enriched bio-oils. Moreover *n*-heptane is an essential compound in JP-4 and Jet A,[2] the hydrogenated mixture including cycloalkanes and *n*-heptane can be directly utilized as jet fuels or drop-in fuels. Meanwhile, pure cycloalkanes can be separated with *n*-heptane through vaporization. Accordingly, results revealed that the hydrogenation reaction heavily depended on the solvents employed; *n*-heptane was the optimal solvent, which was then used for extracting aromatics-enriched bio-oils and hydrogenation reactions.

3.3 *In suit* hydrogenation of extracted bio-oils

3.3.1 The effect of catalyst loading on the chemical composition of hydrogenated bio-oils

Given the water influence in the hydrogenation process, the mixed bio-oils from catalytic microwave pyrolysis were extracted by the optimum solvent. 7.02 g of liquid organics (~14 wt. %, based on biomass mass) were extracted using *n*-heptane (40 g). The loss of organics (0.5 g) in water phase can be neglected if considering that the recovery of organics could reach ~94 wt. %. Since the bio-oils produced by catalytic microwave pyrolysis of intact biomass principally consisted of C_8 - C_{16} range aromatics, the controllable adjustment of aromatics with 8 - 16 carbon numbers are considered as precursors of jet fuels. According to the hydrogenation reaction of model compound in the medium of *n*-heptane, naphthalene of 99.9% carbon selectivity was converted into saturated decalin. It is well known that decalin is the most abundant cycloalkane in jet fuels.[45] These conditions set a standard for designing the following hydrogenation reaction of extracted bio-oils, thus the ratio of reactant to solvent was set at 1:7. In this respect, additional solvent (9.14 g) was added into the extracted bio-oils, maintaining the ratio at 1:7. Subsequently, the extracted bio-oils (C_8 - C_{16} aromatics) were hydrogenated by several variables under low-severity conditions.

The products distribution is summarized as a function of catalyst loading (10 wt. % and 20 wt. % with respect to reactant mass) in Fig 2 (A). It was observed that cycloalkanes as significant composition of jet fuels were in the range from 32.22 to 58.90% based on the GC/MS peak area, depending on alterations of catalyst loadings. More than half of the aromatic intermediates were converted into jet fuel range cycloalkanes using 20 wt. % Raney-Ni 4200, whose amount in hydrogenated bio-oils was equal to that in JP-5. Unsaturated hydrocarbons (hydro-aromatic hydrocarbons and cycloolefins) partially hydrogenated in the process accounted for 36.81 – 11.01% and 9.04 – 10.31%, 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. Catalyst loading also had a crucial influence on the selectivity of hydro-cyclic alcohols, occupying from 4.74 to 11.74%, which suggests that phenols were completely hydrogenated into hydro-cyclic alcohols under the condition of sufficient catalyst loading. The amount of aromatic hydrocarbons decreased as the catalyst loading was increased, implying that more active sites were offered for catalyzing the aromatic intermediates to hydro-aromatic hydrocarbons or cycloalkanes. Other oxygenated aromatics showed slight variations influenced by catalyst loading, varying from 7.50 to 5.77%. These results indicate that hydrogenated reactions were remarkably impacted by the catalyst loading.

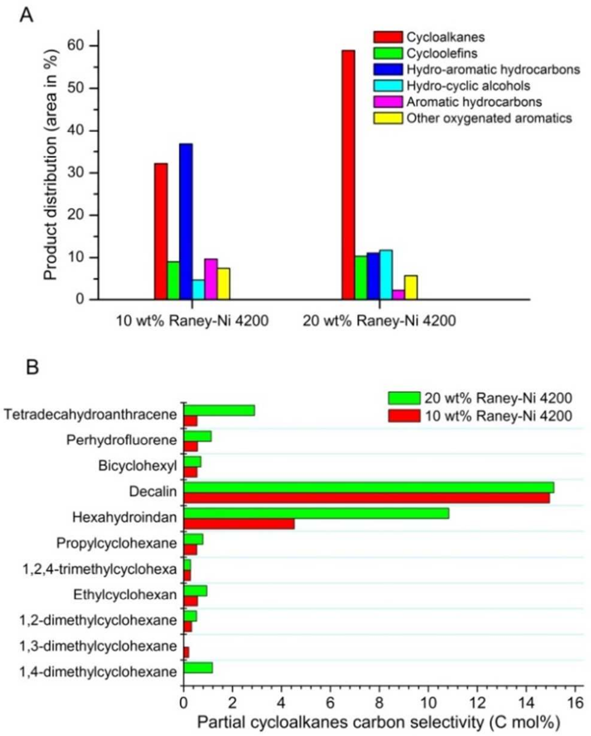


Fig. 2 Overall products distribution (A) and patial aromatics carbon selectivity (B) with resptect with catalyst loading. Reaction condition: Reaction temperature, 200 °C; Initial pressure, 500 psi; Reaction time, 2h.

The effect of catalyst loadings on partial cycloalkanes carbon selectivity is explained in Fig. 2 (B). Catalyst loading did not have a vital influence on the carbon selectivity of mono-cyclic cycloalkanes. These results indicate that mono-cyclic aromatic hydrocarbons were prone to be 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 hydrogenated into a saturated ring; however the aromatic ring and cyclic alkane ring of tetralin was no longer coplanar after hydrogenation.[31] The other aromatic ring was thus directed away from the catalyst surface, resulting in lack of reduction. If more adequate catalysts were provided, the other aromatic ring could also be hydrogenated at the spare active sites. It is obvious that the carbon selectivity of both hexahydroindan (C_9H_{16}) and decalin ($C_{10}H_{18}$) increased when more Raney-Ni 4200 catalyst were added in the reactor. 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. These results reveal that more catalyst loading, which means that more active sites were offered on the Raney-Ni 4200 surface, gave rise to more hydrogenated reactions.

Table 2 Products distribution and partial cycloalkanes carbon selectivity as a function of reaction temperature[a]

	Temperature (°C)		
	150	200	250
Overall selectivity (% in area)			
Cycloalkanes	47.43	58.90	63.34
Cycloolefins	9.48	10.31	5.20
Hydro-aromatic hydrocarbons	20.76	11.07	16.09
Hydro-cyclic alcohols	8.34	11.74	3.78
Aromatic hydrocarbons	8.32	2.20	6.88
Other oxygenated aromatics	5.67	5.77	4.71
Cycloalkanes selectivity (C mol%)			
1,4-dimethylcyclohexane	1.06	1.18	1.35
1,3-dimethylcyclohexane	1.23	-	1.80
1,2-dimethylcyclohexane	-	0.53	0.40
Ethylcyclohexane	0.87	0.95	3.90
1,2,4-trimethylcyclohexane	0.23	0.29	0.35
Propylcyclohexane	0.68	0.79	1.71
Hexahydroindan	9.43	10.84	10.66
Decalin	12.67	15.13	15.63
Bicyclohexyl	0.67	0.71	1.14
Perhydrofluorene	1.04	1.13	-
Tetradecahydroanthracene	2.01	2.90	2.49

[a]Reaction condition: Initial pressure, 500 psi; Raney-Ni 4200, 20 wt. % with respect to reactant mass; Reaction time, 2 h.

3.3.2 The effect of reaction temperature on the chemical composition of hydrogenated bio-oils

Based on the previous result, catalyst loading of 20 wt. % was feasible for the following experiments. In order to further understand chemical reactions in the process and obtain more insight into hydrogenated bio-oils, the chemical compounds of hydrogenated bio-oils are elucidated as a function of reaction temperature in Table 2. It can be seen that the reaction temperature had a significant effect on the *in situ* hydrogenation reactions. The amount of total cycloalkanes progressively increased with the increasing of reaction temperatures. It was noticed that cycloalkanes were in the range from 47.43% at 150 °C to 63.34% as reaction temperature increased to 250 °C, implying that a high reaction temperature favored the hydrogenation reactions. Furthermore, there is a minor selectivity for cycloolefins, generally decreased from 9.48 to 5.20% alongside the increment of reaction temperatures. Therefore, elevated temperature could enhance the hydrogenation reaction of olefins into cycloalkanes. Hydro-aromatic hydrocarbons and aromatic hydrocarbons experienced declined tendencies (20.76 – 11.07% and 8.32 to 2.20%, respectively) as the reaction temperature went up to 200 °C; whereas the two compositions displayed an increased trend as reaction temperatures increased from 200 °C to 250 °C. That is because the elevated reaction temperature possibly favored the scission of hydroxyl group from phenyl to form aromatic hydrocarbons through hydrogenolysis reactions.[46] It was found that the amount of hydro-cyclic alcohols was much lower at 250 °C than that at 200 °C. It can also be seen that other oxygenated aromatics was also declined to 4.71% at 250 °C. In the gas fraction, total amount (less than 1 vol. %) of small hydrocarbons (such as methane, ethane, propane) were also detected at 250 °C, which could be produced from hydrocracking of lager hydrocarbons. These results suggest that hydrogenolysis and hydrocracking except hydrogenation reactions could take place at high reaction temperatures.

Reaction temperatures also had a significant influence on the carbon selectivity of specific cycloalkanes. It was noteworthy that mono-cyclic alkanes significantly increased as the reaction temperature increased, especially from 200 to 250 °C. Meanwhile, ethylcyclohexane (C_8H_{16}) dramatically increased from 0.95 to 3.90%, which suggests that high reaction temperatures improved hydrocracking reactions of poly-cyclic alkanes after being hydrogenated. The carbon selectivity of hexahydroindan was slightly influenced by the changed reaction temperature when it was set in the range of 200 - 250 °C. It showed that all indane and indene in the extracted bio-oils were completely hydrogenated into hexahydroindan under these conditions. Likewise, there were small upward tendency of decalin carbon selectivity, which gradually increased from 12.67 to 15.63%. Carbon selectivity of other poly-cyclic alkanes showed a steady increment, which implies that the hydrogenated reactions of polycyclic aromatic intermediates could also be facilitated by increasing reaction temperatures.

Table 3 Products distribution and partial cycloalkanes carbon selectivity on the basis of reaction time[a]

	Reaction time (h)		
	1	2	3
Overall selectivity (% in area)			
Cycloalkanes	39.62	58.90	71.92
Cycloolefins	9.27	10.31	11.15
Hydro-aromatic hydrocarbons	29.24	11.07	0.51
Hydro-cyclic alcohols	5.22	11.74	10.06
Aromatic hydrocarbons	9.67	2.20	1.82
Other oxygenated aromatics	6.98	5.77	4.55
Cycloalkanes selectivity (C mol%)			
1,4-dimethylcyclohexane	1.02	1.18	-
1,3-dimethylcyclohexane	1.11	-	1.47
1,2-dimethylcyclohexane	0.23	0.53	-
Ethylcyclohexane	0.87	0.95	3.04
1,2,4-trimethylcyclohexane	0.34	0.29	1.00
Propylcyclohexane	0.76	0.79	0.94
Hexahydroindan	5.02	10.84	10.26
Decalin	14.15	15.13	14.51
Bicyclohexyl	0.64	0.71	0.77
Perhydrofluorene	0.67	1.13	0.77
Tetradecahydroanthracene	2.22	2.90	3.23

[a]Reaction condition: Initial pressure, 500 psi; Raney-Ni 4200, 20 wt. % with respect to reactant mass; Reaction temperature, 200 °C.

3.3.3 The effect of reaction time on the chemical composition of hydrogenated bio-oils

Apart from catalyst loading and reaction temperature, reaction time was another crucial factor that influenced product distribution and cycloalkanes carbon selectivity as shown in Table 3. Especially, the product distribution in the resulting product prominently shifted towards the cycloalkane (39.62 – 71.92%) with increasing reaction time, suggesting that hydrogenation reactions were enhanced because of longer reaction duration. The amount of cycloolefins appeared to increase slightly to 11.15% at prolonged reaction time (3 h). The total amount of hydro-aromatic hydrocarbons distantly declined, ranging from 29.24 to 0.51%. Likewise, the selectivity of aromatic hydrocarbons experienced a downward trend from 9.67 to 1.82%. Prolonged reaction time could give rise to ring reduction of aromatic hydrocarbons, which resulted in the decrease of aromatic hydrocarbons to form hydro-aromatic hydrocarbons. Owing to more time provided for the reaction, the production of cycloalkanes was likely facilitated by means of hydrogenating related hydro-cyclic aromatic hydrocarbons. It was noted that the total amount of hydro-cyclic alcohols was significantly impacted by prolonged reaction time especially going from 1 to 2 h.

The carbon selectivity for mono-cyclic alkanes increased, especially for ethylcyclohexane (0.87-3.04%), as the reaction time was elevated; whilst the carbon selectivity of hexahydroindan and decalin were decreased from the period of 2 - 3 h. Aromatic intermediates have already been converted into corresponding cycloalkanes under the condition of 2 h. Prolonged time (3 h) could render the cycloalkanes to be hydrocracked and oligomerized, forming mono-cyclic alkanes or derivatives. For the gas result from the reaction of 3 h, trace volume of hydrocarbons was found, suggesting that the hydrocracking and oligomerization reactions have taken place in the process. In contrast, polycyclic aromatic hydrocarbons with three rings are very difficult to be hydrogenated due to their structures. Prolonging reaction time to until 3 h could make these polycyclic aromatic intermediates be totally hydrogenated, thereby improving the carbon selectivity of poly-cyclic alkanes. Wherefore these result indicate that prolonging reaction can principally enhance the hydrogenation reactions; hydrocracking and oligomerization reactions may also occur jointly in the process after 2 h reaction time.

Table 4 Products distribution and partial cycloalkanes carbon selectivity in the presence of various catalysts[a]

	Catalyst categories		
	NP Ni	Raney-Ni 4200	Home-made Raney Ni
Overall selectivity (% in area)			
Cycloalkanes	59.51	58.90	84.59
Cycloolefins	8.94	10.31	2.83
Hydro-aromatic hydrocarbons	12.33	11.07	0.60
Hydro-cyclic alcohols	9.93	11.74	6.84
Aromatic hydrocarbons	3.09	2.20	0.99
Other oxygenated aromatics	6.20	5.77	4.15
Cycloalkanes selectivity (C mol%)			
1,4-dimethylcyclohexane	-	1.18	-
1,3-dimethylcyclohexane	3.80	-	4.10
1,2-dimethylcyclohexane	0.36	0.53	0.66
Ethylcyclohexane	0.99	0.95	4.18
1,2,4-trimethylcyclohexane	0.39	0.29	1.37
Propylcyclohexane	1.09	0.79	1.65
Hexahydroindan	11.05	10.84	8.09
Decalin	14.29	15.13	16.69
Bicyclohexyl	0.69	0.71	1.13
Perhydrofluorene	0.64	1.13	1.04
Tetradecahydroanthracene	2.47	2.90	3.12

[a] Reaction condition: Initial pressure, 500 psi; Catalyst, 20 wt.% with respect to reactant mass; Reaction temperature, 200 °C ; Reaction time, 2 h.

3.3.4 The effect of catalysts selection on the chemical composition of hydrogenated bio-oils

The chemical composition of hydrogenated bio-oils in the presence of various catalysts (NP Ni, Raney-Ni 4200, and home-made Raney Ni) is depicted in Table 4. Compared with the overall product distribution over Raney-Ni 4200 in the purchased form, the result over NP Ni was similar under the same condition; while the result for producing cycloalkanes in the presence of home-made Raney nickel was more superior to the others. It was observed that 84.59% selectivity towards cycloalkanes was achieved, which was even better than the result using Raney-Ni 4200 when the reaction time was 3 h. The total amount (less than 5%) of cycloolefins was acquired in the presence of home-made Raney Ni, which amount meets the specifications of commercial jet fuels. Small amounts of hydro-aromatic hydrocarbons and aromatic hydrocarbons were detected when using home-made Raney Ni, suggesting that aromatic intermediates were thoroughly hydrogenated into cycloalkanes. As such, the content of hydro-cyclic alcohols had the same tendency as hydro-aromatic hydrocarbons and aromatic hydrocarbons, which indicates that partial hydro-cyclic alcohols could be converted into cycloalkanes via the scission of hydroxyl group. There was the lowest amount of other oxygenated aromatics in the hydrogenated bio-oils using home-made Raney Ni as the catalyst, 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 dimethylcyclohexane and ethylcyclohexane were maximum in the presence of home-made Raney Ni. Other mono-cyclic alkanes such as propylcyclohexane and trimethylcyclohexane were also shown the largest carbon selectivity. Therefore home-made Raney Ni was the optimal catalyst for the production of mono-cyclic alkanes. Of the catalysts, home-made Raney Ni displayed the lowest carbon selectivity of hexahydroindan. These results indicate that hexahydroindan formed was possibly hydrocracked over the catalyst, thereby forming more mono-cyclic alkanes. Unlike the hexahydroindan, the carbon selectivity for decalin, bicyclohexyl, tetradecahydroanthracene was all the highest when using the home-made Raney Ni as the catalyst. These outcomes imply that employing home-made Raney Ni as the catalyst could improve the overall selectivity of cycloalkanes, and obtain the highest carbon selectivity of mono-cyclic alkanes.

Table 5 Textural properties of Ni-Al alloy, NP Ni, Raney-Ni 4200 and home-made Raney Ni catalysts[a]

	S_{BET}	V_{pore}	S_{pore}	d_{pore}
	(m^2/g)	(cm^3/g)	(m^2/g)	nm
Ni-Al alloy	0.35	0	0	0
NP Ni	157.7	0.048	38.2	5.0
Raney-Ni 4200	38.1	0.112	43.0	10.4
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.

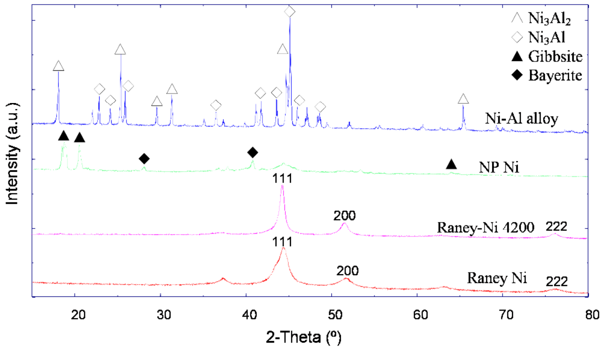


Fig. 3 The XRD patterns of the Ni-Al alloy powder, NP-Ni, Raney-Ni 4200, and home-made Raney Ni.

3.4 Catalyst characterization

During alkali leaching, Al in the Ni-Al alloy powder reacted with NaOH solution. In this respect, it is expected that Raney Ni is primarily comprised of metallic nickel. When the Al/NaOH stoichiometry is more than 1, insoluble $Al(OH)_3$ was also formed by the reaction between Al and the water.[47] Therefore NP-Ni produced with insufficient amount of NaOH is regarded as a Ni-$Al(OH)_3$ catalyst. However, there is also small amount of residual hydrated alumina absorbed in the spongy structure of Ranye Ni, as illuminated by Zhu *et al.*[47] The textural properties of NP-Ni, Raney-Ni 4200 and home-made Raney Ni, compared with the parent Ni-Al alloy powder, are illustrated in Table 5. BET surface area, pore volume, and pore surface area of all catalysts were significantly improved by the alkali treatments. After dissolution of Al component, the BET surface area of home-made Raney Ni dramatically increased from 0.35 to 52.4 m^2/g, which is higher than that of purchased Raney-Ni 4200 (38.1 m^2/g) and other Raney Ni catalyst.[48] The decent

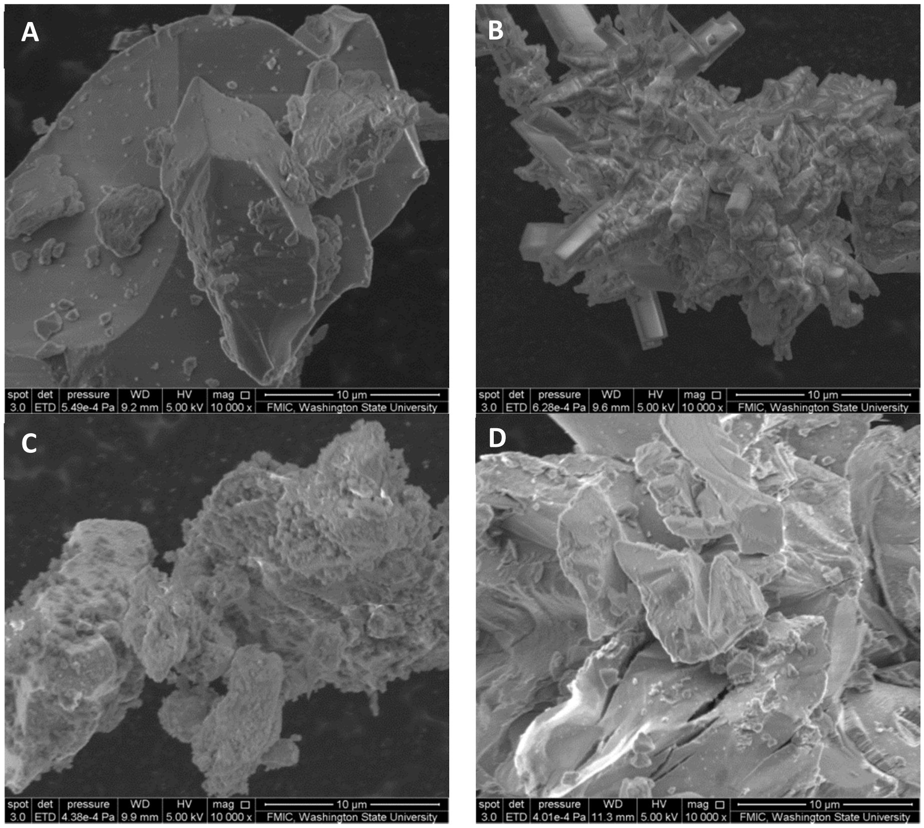


Fig. 4 SEM images of the Ni-Al alloy powder (A), NP-Ni (B), Raney-Ni 4200 (C), and home-made Raney Ni (D).

BET surface area of home-made Raney Ni assisted the adsorption of hydrogen on the surface of the catalyst for the hydrogenation reaction. The catalytic activity of NP-Ni was probably inhibited by the large amount of hydrated alumina adsorbed in the structure, although the NP-Ni has the highest BET surface area. Besides 0.034 cm^3/g of pore volume and 35.8 m^2/g of pore surface area for home-made Raney Ni were also generated. The average pore size of home-made Raney Ni is 3.8 nm. The suitable average size is close to the mono-cyclic aromatics diameter, thus mono-cyclic aromatics are prone to be adsorbed in the pores.[49]

Fig. 3 outlines the XRD patterns of the Ni-Al alloy, NP Ni, Raney-Ni 4200 and home-made Raney Ni. The XRD patterns of Ni-Al alloy indicates that it consists of the two kinds of Ni_3Al_2 and Ni_3Al domains. After dissolving Al component by 20 wt. % NaOH solution, the diffractions with respect to metallic Ni were observed as amorphous nature for both Raney-Ni 4200 and home-made Raney Ni. They mainly displayed diagnostic (111), (200), and (220) diffractions of fcc Ni at 2θ of 44.5, 51.8, and 76.3°, respectively.[50] With regarding to NP Ni, the large content of $Al(OH)_3$ was formed and identified according to the peaks assignable to gibbsite and bayerite.

The SEM images of Ni-Al alloy powder, NP-Ni, Raney-Ni 4200 and the home-made Raney Ni are shown in Fig. 4. The morphological differences between Ni-Al alloy powder and the other three catalysts are readily visible from Fig. 4 (A), (B), (C), and (D). It was observed that both Raney-Ni 4200 and home-made Raney Ni are constituted by the typical fractured and angular particles, which are in line with other research;[51] while Ni-Al alloy powder shows the intact metallic structure. The small particles of home-made Raney Ni are more dispersive in comparison with Raney-Ni 4200, confirming a higher BET surface. For NP Ni, it is composed of nickel angular particles and irregularly oriented aluminum crystal-like particles.[47]

3.5 Reaction pathway for the conversion of lignocellulosic biomass into jet fuel range cycloalkanes

These observations are the key point to propose the reaction pathway for the conversion of lignocellulosic biomass into jet fuel range cycloalkanes. Based on the quantified products distribution in this study, and related results from direct microwave pyrolysis of woody biomass and catalytic microwave pyrolysis of cellulose,[36, 38] the overall reactions network (including catalytic microwave pyrolysis and hydrogen saving process) is summarized and shown in Fig. 5. In the primary route from lignocellulosic biomass to jet fuel range cycloalkanes, cellulose underwent a series of dehydration, decarboxylation, and decarbonylation to form furan compounds during catalytic pyrolysis.[36, 52] These furans then went through decarbonylation, aromatization, and oligomerization reactions inside the pores of well-promoted ZSM-5 to form aromatic hydrocarbons. Likewise, we observed that hemicellulose was decomposed into furan compounds,[38] which was identical to the result using cellulose as feedstock.[36] These furan compounds also diffused into the well-promoted ZSM-5 pores, which underwent dehydration, decarboxylation, decarbonylation, and oligomerization reactions to generate aromatic hydrocarbons. Monomeric phenolic compounds were primarily generated from decomposition of lignin in lignocellulosic biomass, which were thereafter catalyzed into aromatic hydrocarbons through a series of dehydration, cracking, and oligomerization reactions.[28, 52]

Single or multiple aromatic rings were transformed into single or multiple alkane rings by hydrogenation reactions in the presence of Raney nickel catalysts. As a result, the achieved aromatic hydrocarbons in the jet fuel range could be converted into jet fuel range cycloalkanes from the hydrogen saving process under very mild conditions. Trace volume of small hydrocarbons was also produced by hydrocracking reactions. The cycloalkanes (together with minor aromatics and cycloolefins) can be used as additives to make the desired jet fuels by blending with other hydrocarbons. The cycloalkanes produced in the hydrogen saving process can be further upgraded through the hydrocracking and hydroisomerization process to from both straight and branched alkanes.[53, 54] The straight and branched alkanes blend with cycloalkanes according to the proportions, which can produce different commercial and military jet fuels.

Conclusions

This study demonstrated that the integrated processes were potentially profound approaches when targeting production of jet fuel range cycloalkanes from lignocellulosic biomass. The integral processes detailed here were illustrated to deliver up to 84.59% selectivity of jet fuel range cycloalkanes from intact biomass under very mild conditions. In the first step, the overall carbon yield of jet fuel range aromatics from catalytic microwave pyrolysis was 24.68%. The bio-oils were extracted by n-heptane and the recovery of organics could reach ~ 94 wt. %. These aromatics in *n*-heptane medium were hydrogenated into jet fuel range cycloalkanes. Compared with the conventional HDO process in the presence of noble catalyst, the process is a hydrogen saving process, resulting in the costly hydrogen being transformed in the form of cycloalkanes, rather than water. The home-made Raney nickel was the optimum catalyst to obtain the highest selectivity of jet fuel range cycloalkanes. It is more likely that these high-yield cycloalkanes mixing with minor aromatics and cycloolefins can be potentially used as additives in jet fuels. From this perspective, these integrated processes by using inexpensive catalysts and intact biomass under the mild conditions deliver a novel and feasible route, specifically targeting jet fuel range cycloalkanes. Future efforts direct towards improving the carbon yield of aromatics from catalytic microwave pyrolysis and implement an economic analysis in a biorefinery based on the integral process.

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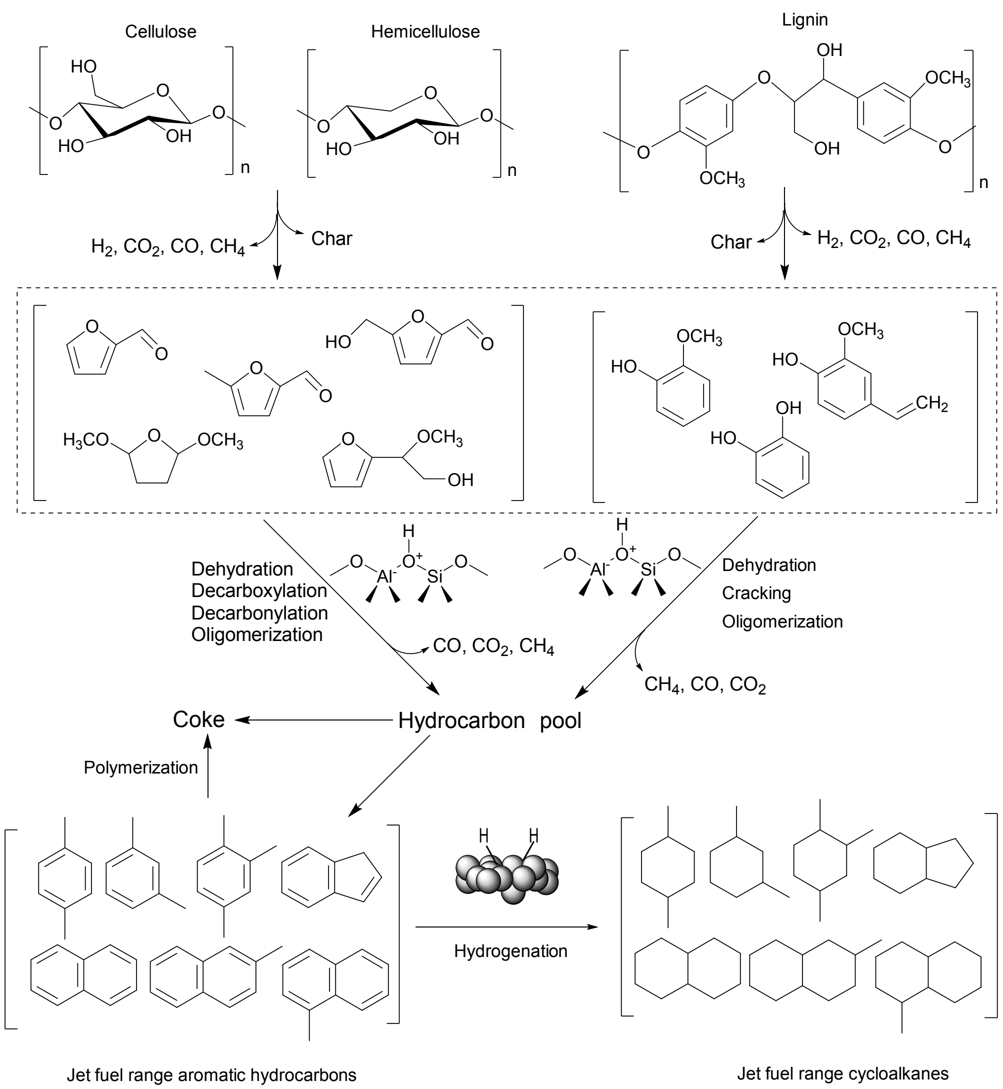

Fig. 5 Proposed reaction pathways for the conversion of lignocellulosic biomass into jet fuel range cycloalkanes.

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