Enhancement of jet fuel range alkanes from co-feeding of lignocellulosic biomass with plastics *via* tandem catalytic conversions

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ABSTRACT: Enhanced carbon yields of jet fuel range alkanes were manufactured from co-feeding of lignocellulosic biomass with plastics. The consecutive processes proceeded *via* the co-feed catalytic microwave-induced pyrolysis and hydrogenation process. In the co-feed catalytic microwave pyrolysis by using ZSM-5 as the catalyst, parent ZSM-5 fabricated by hydrothermal and calcined treatments contributed to the increase of surface area as well as the formation of more mesopores. Liquid organics with enhanced carbon yield (40.54%) were more principally lumped in the jet fuel range from the co-feed catalytic microwave pyrolysis performed at the catalytic temperature of 375 °C with the plastics to biomass ratio of 0.75. To manufacture home-made Raney Ni catalyst, the BET surface area, pore surface area, and pore volume of the home-made Raney Ni catalyst were considerably improved when the Ni-Al alloy was dissolved by the NaOH solution. In the hydrogenation process, we observed the three species of raw organic derived from the co-feed catalytic microwave pyrolysis were almost completely converted into saturated hydrocarbons under a low-severity condition. The improved carbon yield (38.51%) of hydrogenated organics regarding co-reactants of biomass and plastics predominantly match jet fuels. In the hydrogenated organics, over 90% selectivity toward alkanes with the carbon number in the jet fuel range was attained. In this respect, these hydrogenated organics with high amounts of renewable cycloalkanes can be potentially served as high-density jet fuels or additives for

blending with civilian jet fuels.

KEYWORDS: Bio-jet fuels; well-promoted ZSM-5; home-made Raney Ni; co-feed catalytic microwave pyrolysis; hydrogenation; cycloalkanes

1 Introduction

The limitation of fossil resources accompanied with huge environmental issues accelerate the exploitation of renewable resources to substitute petroleum hydrocarbon fuels, with a particular concentration on the development of new generation biofuels [1-3]. Lignocellulosic biomass has attracted essential attention as a carbon-neutral resource for promising potentials to produce transportation biofuels and versatile chemicals [4, 5]. Catalytic fast pyrolysis (CFP) of lignocellulose to valuable biofuels and chemicals is recognized as the most prevailing and promising route in a single process [6-11]. Dozens of lignocellulose and biomass-derived feedstock have been subjected to catalytic pyrolysis for the production of advanced biofuels with more favorable properties [6-8, 12, 13]. Zeolite-based catalysts (e.g., ZSM-5) have been recognized as the highest-efficiency catalysts to produce considerable petrochemicals (aromatics and olefins) [9, 14, 15].

However, even in the presence of highly efficient catalyst, catalytic pyrolysis of lignocellulose can solely manufacture low carbon yield (10 – 30%) of aromatic hydrocarbons; large amounts of solid residues, including both biochar and coke (carbon yields usually above 30%), are achieved in the process [10, 16-19]. As aromatics are considered as the high energy-density hydrocarbons

1 production [11], such low carbon yield of aromatic hydrocarbons from catalytic pyrolysis is not
2 cost-effective to scale up the process in a biorefinery. Further, the process is commonly plagued
3 by the high production of coke deposited on the catalyst because the coke could rapidly
4 deactivate the catalyst and reduce its lifetime, resulting in the catalytic process to be
5 impractical[20]. Therefore, these are the huge challenges in the face of commercializing the
6 catalytic pyrolysis for the production of renewable petrochemicals.

7
8 It is discerned that the petrochemicals with the low carbon yield of aromatics and high coke
9 formation are mainly associated with the oxygen-enriched intrinsic nature and hydrogen
10 deficiency of lignocellulose [16, 18, 21]. In addition, the hydrogen to carbon effective (H/C_{eff})
11 ratio plays a significant role in coke formation and converting efficiency of biomass into
12 advanced biofuels [8, 22, 23]. Thus the hydrogen-deficient (H/C_{eff} usually less than 0.3) biomass
13 produces low carbon yields of petrochemicals and large formation of coke when the
14 lignocellulose were transformed over zeolite catalysts [9, 15]. In order to improve the carbon
15 efficiency of aromatics and minimize the coke formation, it is reasonable that the incorporation
16 of high H/C_{eff} ratio co-reactants with biomass in the catalytic pyrolysis could help mitigate these
17 issues. It is observed that co-feeding of lignocellulose with hydrogen-rich feedstock in the
18 catalytic pyrolysis can modify the reaction mechanism of oxygen removal by substituting
19 decarbonylation and decarboxylation with dehydration [10, 22, 24, 25]. Waste plastics represent
20 a cheaper and abundant hydrogen sources, which can be used to improve carbon efficiency of
21 aromatics and lower the coke formation in the catalytic co-pyrolysis [9, 15, 18, 21, 26].
22 Tremendous quantities of waste plastics are generated each year worldwide. Among the waste
23 plastics, polyethylene formed by the polymerization of olefins with a H/C_{eff} ratio of 2 accounts

for up to 40% of gross waste plastics [27]. Hence co-feeding of lignocellulose with waste plastics in catalytic pyrolysis is remarkably beneficial for the environment and energy recapture.

Although the co-feeding of biomass with plastics in catalytic pyrolysis has a significant synergy for aromatic production and coke reduction, these aromatics are commonly mono-ring aromatic hydrocarbons with low carbon numbers ($C_6 - C_8$) [21, 23, 25, 26]. Yet, these aromatics with low carbon numbers cannot satisfy the requirement of jet fuels [19]; that is due to the fact that the current jet fuels are principally comprised of linear-chain and branched-chain alkanes in the range of $C_8 - C_{16}$ [28, 29]. It is well known that cycloalkanes in jet fuels can be burned cleanly with high heats of combustion; that is because cycloalkanes are compact molecules within robust ring strain [30, 31]. To promote the qualities of current jet fuels, cycloalkanes with the carbon numbers in the jet fuel range can be synthesized and added into civilian jet fuels [29, 32]. The representative techniques on bio-jet fuel production include catalytic hydrodeoxygenation of vegetable oils [33, 34] and Fischer-Tropsch synthesis of biomass-derived syngas [5, 11]. Nonetheless, aromatics and cycloalkanes cannot be generated by the two technologies. On the other hand, the promising pathway for the production of cycloalkanes are the hydro-cycloaddition of aromatic hydrocarbons [35-38]. To pursue the precursors of renewable cycloalkanes for jet fuels, highly desirable aromatic hydrocarbon in the jet fuel range ($C_8 - C_{16}$) should be generated.

Due to conventional ZSM-5 zeolite with microporous structure, it contributes to mono-ring aromatics with low carbon numbers. In our previous study, moderate treatments were used to

fabricate ZSM-5 properties including its porosity and acidity, which is vital for improving product selectivity toward aromatic hydrocarbons [39, 40]. It was shown that the mild hydrothermal and calcined modifications favored the generation of mesopores and more catalytic sites. Accordingly our well-modified catalyst is suitable for the production of aromatic hydrocarbons in the $C_8 - C_{16}$ range. Besides we have developed a combined process to manufacture renewable cycloalkane from lignocellulosic biomass, albeit obtaining a low carbon yield [35]. In addition, it is manifested that microwave-assisted pyrolysis technology is one of the most promising techniques to enhance the degradation reactions because of rapid heat rate by microwave irradiation [41]. In comparison with conventional pyrolysis, microwave-assisted pyrolysis encloses the advantages of rapid heating, easy control, and low energy input [42, 43]. In the hydro-cycloaddition process, the catalytic performance of home-made Raney Ni catalyst was superior to purchased Raney Ni catalysts, producing higher yields of cycloalkanes under the same system [35]. During the process, the aromatics in the *n*-heptane medium were almost completely converted into saturated hydrocarbons under a low-severity condition.

Initially, the production of $C_8 - C_{16}$ aromatics was the target compounds from the co-feeding of lignocellulosic biomass and plastics in the catalytic pyrolysis. To best of our knowledge, the co-feed catalytic microwave-induced pyrolysis has not yet been explored. The main objective of this research presented in this paper was the production of jet fuel range alkanes with enhanced carbon yield. In this respect, there is no literature reported on the production of jet fuel range alkanes from the co-feeding of lignocellulosic biomass with plastics. Furthermore, the reaction mechanisms regarding the co-feeding of lignocellulosic biomass with plastics through catalytic combined conversions have never been established. Therefore, this study can fill this research

gap in the production of jet fuels from co-feeding of lignocellulosic biomass and plastics via tandem catalytic processes.

The innovations aspects of this study were the novel pathways from co-feeding of lignocellulosic biomass with plastics by using modified catalysts, namely well-promoted ZSM-5 catalyst and home-made Raney Ni catalyst with the purpose of enhancing the carbon yield of aromatics and lowering the coke formation and improving the carbon selectivity of jet fuel range alkanes. Herein, biomass and plastics were co-pyrolyzed using a tandem microwave-induced pyrolysis system and a catalytic system, aiming to determine whether there is an apparent synergy between co-feeding of biomass and plastics in the catalytic microwave-induced pyrolysis. For maximizing the carbon efficiency of jet fuel range alkanes, the various species of bio-oils derived from co-feed catalytic microwave-assisted pyrolysis was first extracted by the optimum solvent (*n*-heptane). The organic mixture was subsequently hydrogenated into saturated hydrocarbons by using home-made Raney Ni catalyst. The influence of organic species on the carbon yield and product distribution of saturated hydrocarbon in the jet fuel range was also evaluated.

2 Experimental sections

2.1 Materials

Douglas fir sawdust pellets (7 mm in diameter and 15 mm in length) were leveraged as lignocellulosic biomass, which were supplied by Bear Mountain Forest Products Inc., USA. Low-density polyethylene pellets (LDPE) was purchased from Sigma-Aldrich Corporation (St. Louis, MO, USA). Its density and melting point are 0.925g/cm³ and 116 °C, respectively. The

1 elemental compositions of Douglas fir sawdust pellets and LDPE are listed in Table 1. Parent
2 ZSM-5 ($\text{SiO}_2/\text{Al}_2\text{O}_3$ Mole Ratio: 50) was supplied by Zeolyst International, USA. Nickel-
3 Aluminum alloy powder in a non-activated form was purchased from Alfa Aesar (Ward Hill,
4 MA, USA).

6 *2.2 Catalyst preparation*

7 The parent ZSM-5 was fabricated by hydrothermal and calcined treatments. Parent ZSM-5
8 powder was added into deionized water (mass ratio=1) at 60 °C under the gentle stirring. The
9 slurry was kept at this condition for 2 h. The slurry was subsequently dried at 105 °C until the
10 weight was constant. The sequential process was calcination: parent ZSM-5 tailored by
11 hydrothermal treatment was calcined at 550°C for 5 h in a muffle furnace. The obtained solid
12 was pelletized and sieved to 20 – 40 mesh. For the regeneration of promoted ZSM-5, the spent
13 catalysts were burned at 550°C for 2 h in a muffle as well.

15 Home-made Raney Ni catalyst was fabricated by using a 20 wt% NaOH aqueous solution to
16 dissolve Al composition in the Ni-Al alloy powder. In this case, 10 g of Ni-Al alloy powder was
17 slowly added into 20 wt% NaOH aqueous solution (100 mL) under gentle stirring. After addition,
18 the slurry was held on stirring at 80 °C for 1 h. The excess of NaOH solution was consequently
19 washed by distilled water until neutral pH was reached. Since Raney Ni is notorious for its
20 pyrophoricity, it can ignite spontaneously when it is exposed in air. The obtained home-made
21 Raney Ni catalyst was therefore stored in water. Prior to the subsequent catalytic test, the Raney
22 Ni catalyst was dried at 60 °C in the atmosphere of nitrogen to avoid contact with air.

2.3 Co-feed catalytic microwave-induced pyrolysis of lignocellulosic biomass and plastics

The schematic diagram of the microwave-assisted pyrolysis system integrated with the catalysis system was presented in Fig. S1. Detailed experimental description was shown in our previous research [44, 45]. Prior to the experiments, Douglas fir sawdust pellets were air dried at 105 °C for 24 h to remove the physically bound moisture. The co-feeding of Douglas fir sawdust pellets with LDPE pellets were placed in a 500 mL quartz flask, which was put 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 leveraged as microwave absorbers for the microwave-assisted pyrolysis. All runs for microwave-assisted pyrolysis in the microwave oven chamber were implemented at 480 °C for 10 min.

2.4 Hydrogenation of liquid organics derived from co-feed catalytic microwave pyrolysis

Due to the solvents influence in the hydro-cycloaddition of a model compound (naphthalene) in our previous study [35], the mixed bio-oils from co-feed catalytic microwave pyrolysis were extracted by the optimal solvent (*n*-heptane). For the hydrogenation process of extracted organics, 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 employed (Fig. S2). Herein, the mixture of organics and the *n*-heptane medium was placed into the vessel with 20 wt% home-made Raney Ni catalyst (with respect to the reactants). Then the reactor was sealed and vented for three times by hydrogen to expel the air in the vessel. Hydrogen was subsequently adjusted to the set pressure (500 psi). The automatic controller was

used to control the temperature and the revolution of stirrer (350 rpm). The pressure inside the reactor was recorded and the reactions were conducted at 200 °C for 2 h. After the experiment was quenched, stirring was stopped and the vessel was rapidly cooled to ambient temperature. Then, the gas was collected by a 1L Tedlar gas bag and the reactor was depressurized. Consequently the liquid products were filtered to remove catalyst particles.

2.5 Analytical techniques

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

The textural properties of the catalysts were evaluated in light of N₂ adsorption–desorption (Micromeritics TriStar II 3020 Automatic Physisorption Analyzer). Fresh catalysts (well-promoted ZSM-5 catalyst and home-made Raney Ni catalyst) were degassed in vacuum at 300 °C for 1 h. The Brunauer–Emmett–Teller equation was utilized to figure out the surface area by using adsorption data at $p/p_0 = 0.05 - 0.25$. The pore volume was measured through the Barrett–Joyner–Halenda (BJH) method.

The acidity was determined by temperature-programmed desorption (TPD) of ammonia with a Micromeritics AutoChem II 2920 Chemisorption Analyzer equipped with a PFEIFFER mass spectrometer. The samples were initially saturated with NH₃ at the room temperature in a flow of 10% NH₃ in nitrogen. After NH₃ saturation, the weakly bound NH₃ was desorbed prior to the

1 measurement at 120 °C for 1 h at a He flow rate of 25 mL/min. The desorption curve was finally
2 calculated at a heating ramp of 10 °C/min from 120 °C to 550 °C with a He flow rate of 25
3 mL/min.

4
5 Powder X-ray diffraction (XRD) patterns were applied on a Rigaku Smartlab X-ray
6 diffractometer equipped with a Cu K α X-ray source, which was operated at 40 kV and 40 mA.
7 The scattering angle 2θ was changed from 10° to 80°.

8
9 The particle size and surface morphology of the samples were evaluated with a scanning electron
10 microscope (SEM, FEI Quanta 200 F).

11
12 The chemical composition of all liquid samples was characterized and qualified by Agilent
13 7890A GC-MS (GC-MS; GC, Agilent 7890A; MS, Agilent 5975C) with a DB-5 capillary
14 column. The GC was first heated to 45°C for 3 min, followed by heating to 300°C at a rate of
15 10°C/min. The injection of the sample volume was 1 μ L. The flow rate of the carrier gas (helium)
16 was 0.6mL/min. The ion source temperature was 230 °C for the mass selective detector.
17 Compounds were identified by comparing the spectral data with that in the NIST Mass Spectral
18 library. All the measurements were triplicated to ensure reproducibility.

19
20 The moisture content in the bio-oils was measured by a Karl Fischer (KF) compact titrator (V20
21 Compact Volumetric KF Titrator, Mettler-Toledo).

The gas 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 including H₂, N₂, CH₄, CO, CO₂, C₂H₄, C₂H₆, and C₃H₆ was quantify to calibrate the yield of non-condensable gas. The gas composition (>C₄) were either not detected or negligible in this research. All the measurements were triplicated to assure reproducibility.

2.6 Experimental methods and data evaluation

A central composite experimental design (CCD) was employed to optimize the process conditions and product yields from co-feeding of biomass with plastics in catalytic microwave pyrolysis (Table 2). The catalytic temperature (X₁, °C) and plastics to biomass ratio (X₂) were used as independent variables. The loading of Douglas fir sawdust pellets was 20 g for each run, while the catalyst to reactants ratio was constantly held at 0.2 in co-feed catalytic microwave pyrolysis. In these experiments based on CCD, the mass of LDPE pellets varied from 8 to 22 g, while the catalytic temperature ranged from 269 to 481 °C. Four additional experiments were conducted as the controls (Entry 14 – 17, Table 2).

The coke mass was calculated by the difference before and after catalytic process. Because of *ex-situ* catalysis, char was left in the quartz flask inside microwave over chamber; while the coke was formed on the ZSM-5 catalyst in the packed-bed catalysis reactor. The weight of gas product was determined using the following equation.

$$\text{Weight of gas} = \text{initial reactants mass} - \text{liquid mass} - \text{char mass} - \text{coke mass} \quad (1)$$

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

$$\text{Carbon yield} = \frac{\text{moles of carbon in a product}}{\text{moles of carbon fed in}} \times 100\% \quad (2)$$

$$\text{Carbon selectivity} = \frac{\text{moles of carbon in a product}}{\text{moles of carbon in identified products}} \times 100\% \quad (3)$$

3 Results and discussion

3.1 Catalyst characterization

After the integral treatments, the BET surface area, pore surface area, and pore volume were considerably improved. Besides, it was found that parent ZSM-5 fabricated by means of the integrated treatments led to the generation of mesopores in the ZSM-5 zeolite matrix as listed in Table 3. The average pore size of the promoted ZSM-5 is 5.2 nm, which is identical to naphthalene diameter (5.5 nm), therefore double-ring aromatics are readily adsorbed in the mesopores.[46] The overall acid amounts can be determined by the relative peak areas of the NH₃ desorption curves; it can be seen that the acidity are comparable (Fig. 1). For the promoted ZSM-5 catalyst, the maximum peak shifted to low temperatures, accompanying with a decrease of strong acid sites. The decrease of strong acid sites could reduce the extent of catalytic cracking of large molecules into gaseous molecules, thereby increasing the carbon yield of liquid organics. However, the minimum peak was not impacted by the integrated treatments. The total

1 acidity (0.18 mmol NH₃/g) of the well-promoted ZSM-5 catalyst is a bit less than that of parent
2 ZSM-5 due to the decrease of strong acid sites.

3
4 For the manufacture of home-made Raney Ni catalyst, Al in the Ni-Al alloy powder reacted with
5 NaOH solution during alkali leaching. The textural properties of Ni-Al alloy and home-made
6 Raney Ni catalyst were also demonstrated in Table 3. According to the alkali treatment, BET
7 surface area, pore surface area, and pore volume were substantially enhanced. The BET surface
8 area of home-made Raney Ni catalyst dramatically increased from 0.35 to 52.4 m²/g. Moreover,
9 pore surface area and pore volume progressively went up to 35.8 m²/g and 0.034 cm³/g,
10 respectively. Accordingly, the decent BET surface area of the Raney Ni catalyst contributed to
11 the adsorption of hydrogen for the hydrogenation reaction. The average pore size of the Raney
12 Ni catalyst is 3.8 nm, which is suitable for the diffusion of mono-cyclic aromatics in the pores.
13 [46]

14
15 Fig. 2 shows the XRD patterns of the Ni-Al alloy powder and home-made Raney Ni catalyst. It
16 can be seen that the XRD patterns of Ni-Al alloy is comprised of the two categories of Ni₃Al₂
17 and Ni₃Al domains. As the Al component dissolved by 20 wt. % NaOH solution, the diffractions
18 regarding metallic Ni were shown as amorphous nature. It was also found that the home-made
19 Raney Ni catalyst mainly presented diagnostic (111), (200), and (220) diffractions of fcc Ni at 2θ
20 of 44.5, 51.8, and 76.3°, respectively.[47]

21
22 The SEM images of Ni-Al alloy powder and home-made Raney Ni catalyst are displayed in Fig.

3. The morphological difference between Ni-Al alloy powder and home-made Raney Ni catalyst are readily visible from Fig. 3 (A) and (B). The home-made Raney Ni catalyst is constituted by the typical fractured and angular particles, which is identical to other research;[48] whereas Ni-Al alloy powder only had the intact metallic structure. In addition, it is observed that the small particles of home-made Raney Ni catalyst are dispersive, reaffirming the high BET surface.

3.2 Product yield distributions from co-feed catalytic microwave pyrolysis

The product yield distribution from co-feeding of lignocellulosic biomass with plastics in the catalytic microwave pyrolysis are summarized on the basis of catalytic temperature and plastics to biomass mass ratio in Table 2. It was found that the mass yields of bio-oil and gas were considerably impacted by the two variables in the range from 30.57 to 47.00 wt% versus 36.18 to 49.56 wt%, respectively. Without the addition of plastics, the yield of bio-oil derived from catalytic microwave pyrolysis of lignocellulosic biomass alone was much less than that of bio-oils from the co-feed catalytic microwave pyrolysis of biomass with plastics. The water content in the bio-oil varied from approximately 10 to 30 wt% depending upon the reaction conditions. Without the introduction of plastics in the catalytic microwave pyrolysis, the water content could reach 30 wt%, while the water content from the co-feed catalytic microwave pyrolysis was ~ 10 – 20 wt%. When the optimal condition of plastics to biomass ratio for minimizing the water content was executed at 1.45, the water content was declined to 9.54 wt%. It is evidenced that plastics-derived olefins could react with furan compounds from the decomposition of cellulose and hemicellulose to generate aromatics through Diels-Alder reactions followed by dehydration [24, 49]. As a result, if the extent of dehydration reaction was enhanced in the co-feed catalytic

microwave pyrolysis; the increasing trend of water content in the bio-oil was observed. In addition, the yield of olefins produced via catalytic cracking and subsequent cyclization for the production of aromatics could also be influenced by the two independent variables.[45] Accordingly, the catalytic temperature and plastics to biomass ratio play an essential role bio-oil and gas yields. The maximum bio-oil yield was observed at the catalytic temperature of 200 °C with the plastics to biomass ratio of 0.75; while the maximum gas yield was found at 500 °C with the ratio of 0.75.

Owing to the *ex-situ* catalysis, char derived from microwave-assist co-pyrolysis and coke from catalytic step can be distinctly separated. It was also found that catalytic temperature and plastics to biomass ratio affected both mass yields of char and coke as well. The char yield was in the range from 9.09 wt% at the highest plastics to biomass ratio of 1.45 to 21.69 wt% without the introduction of plastics. Thus the char residue from the catalytic microwave co-pyrolysis of lignocellulosic biomass with plastics was lower than that from biomass alone. These results indicate that co-feeding of biomass with plastics in the catalytic microwave pyrolysis was discerned to have a pronounced impact at the char formation. It is mainly attributed to the fact that with in the surrounding of hydrogen from the direct decomposition of plastics, the polymerization reactions of oxygenates were partially inhibited for the char formation [26, 50]. In addition, lignin as the main component of lignocellulosic biomass (Table S1) generated reactive free radicals upon pyrolysis [51]. These free radicals were relatively unstable and could readily polymerize during pyrolysis; therefore, the free radicals became strong hydrogen acceptors [52]. Hydrogen evolved from plastics could be likely absorbed by free radicals, and the polymerization and cross-linking reactions to form char were thus suppressed [21]. As a result,

1 the formation of char was strongly reduced when biomass was co-pyrolyzed with plastics. From
2 other studies reported elsewhere, the HHV of the resulting char could be obviously improved in
3 the co-pyrolysis of biomass and plastics as well. [50, 53]

4
5 Since the coke deposited on the catalyst could cause the deactivation of zeolite-based
6 catalysts,[40] the co-feed catalytic microwave pyrolysis should aid in reducing coke formation
7 and extending catalyst lifetime. The coke yield with regard to catalytic temperature and plastics
8 to biomass ratio is also outlined in Table 2, ranging from 1.02 to 3.85 wt%. As expected, the
9 coke formation was notably affected by the co-feeding of plastics. It can be seen that the highest
10 coke yield was obtained without the addition of plastics. The catalyst coke was attenuated as the
11 plastics was co-fed, declining to ~ 1 wt%. It has been reaffirmed that in the presence of the well-
12 promoted ZSM-5 catalyst, the resultant furan compounds could react with plastics-derived
13 olefins via Diels-Alder reactions rather than polymerization reactions, thereby reducing the coke
14 formation [8, 9]. Furthermore, the hydrogen-deficient oxygenates from the thermal
15 decomposition of cellulose and hemicellulose could accept the hydrogen from plastics
16 degradation or olefins oligomerization, resulting in the decrease of coke formation [26]. For
17 most phenolic compounds from the thermal degradation of lignin were too large to enter zeolite
18 pores [54]; these phenolic compounds could easily deposit on the catalyst surface and further
19 polymerize to form coke [21]. Conversely, these phenolic compounds could abstract hydrogen
20 atoms from evolutions of plastics during the co-feed catalytic microwave pyrolysis. Hence these
21 phenolic compounds were stabilized and the polymerization reaction for the generation of coke
22 could be inhibited. In the ANOVA analysis based on CCD, the *P*-value from the four models
23 (bio-oil, gas, char, and coke yield) are all smaller than 0.05, implying that these models are

appropriate to present the relationships between all product yields and the two independent variables as sketched in Fig. S3 - S6. The coefficient of determination (R^2) of these models are all more than 0.95, which evidences that these models are favorable to mimic the relationships. Accordingly, these models can be employed to predict the maximum product yields regarding the two independent variables.

3.3 The effect of catalytic temperature on the co-feed catalytic microwave pyrolysis

As reported in our previous work, catalyst temperature played a vital in the product distribution [40, 44]. In this case, catalytic temperature was also used to investigate the product distribution and evaluate the qualities of liquid organics. Representative results of product distribution during co-feed catalytic microwave pyrolysis in light of catalytic temperature are shown in Fig. 4. As expected, the carbon yield of char did not significantly vary alongside the changes of catalytic temperature because of the *ex-situ* catalysis. Increasing the catalyst temperature during co-feed catalytic microwave pyrolysis lowered the carbon yield of catalyst coke. It was noted that direct degradation of plastics could produce a large amount of long-chained waxes.[21] However, these waxes with long carbon chains could be readily adsorbed on the catalytic surface at the low catalytic temperatures, forming the waxy coke that finally enclosed the whole catalyst. Meanwhile, phenolic compounds could also be abstracted on the catalyst and stepwise polymerize to yield coke at the low catalytic temperatures [23]. When the elevated catalytic temperatures implemented, catalytic cracking of waxes and phenolic compounds was favored, generating lighter compounds which were more easily accessible to enter the mesopores. Consequently, the carbon yield of coke was reduced at the expense of large molecules as the

1 catalytic temperature was enhanced.

2
3 Since the degradation of plastics to generate olefins is an endothermic reaction, the yield of
4 olefins should go up as the catalytic temperature increased at the tested region [15]. The
5 increased yield of olefins could strengthen the Diels-Alder reaction, contributing to the increase
6 of aromatics [23]. Nonetheless, an excessively high catalytic temperature can favor reverse
7 Diels-Alder reactions to form light olefins instead of aromatics [8, 26]. It was also manifested
8 that increasing catalytic temperature improved the decomposition of biomass-derived oxygenates
9 into small molecular, preventing the formation of liquid aromatics [6, 8]. As a result, the carbon
10 yield of liquid organics gradually decreased due to the enhanced catalytic cracking reactions in
11 the catalytic temperature region. On the contrary, the carbon yield of gas monotonically
12 promoted at the expense of liquid organics degradation as the catalytic temperature went up,
13 reaching 46.22% at 500 °C.

14
15 Table 4 gives a detailed carbon yield and selectivity on the basis of catalytic temperature. In
16 comparison with the liquid organics obtained by co-feed catalytic microwave pyrolysis at 200 °C,
17 the aliphatic olefins and oxygenates were the primary species in the liquid organics. This result
18 indicates that such low catalytic temperature could not favor the zeolite-catalyzed reactions to
19 form aromatics. As the catalytic temperature was elevated to 375 °C, the carbon selectivity
20 toward aromatic hydrocarbons remarkably increased. There was still a low amount of aliphatic
21 hydrocarbons in the liquid organics (at 375 °C). Besides, there was a trace amount of aromatic
22 oxygenates (such as phenol) existing in the liquid organics, whose content was much lower than

1 those from catalytic microwave pyrolysis of biomass alone under the same conditions [44]. It is
2 likely that plastics-derived olefins participated in the Diels-Alder reaction with furan compounds
3 followed by dehydration reaction to expel these oxygenates. Aromatic hydrocarbons obtained
4 were predominantly made up of toluene, xylenes, trimethylbenzenes, naphthalene, and their
5 derivatives. It was obtained that the carbon selectivity toward toluene and xylenes ranged from
6 10.72 to 18.42% and 18.78 to 27.41%, respectively; whilst the carbon selectivity toward
7 trimethylbenzene decreased from 17.13 to 9.01% as catalytic temperature went up from 375 to
8 500 °C. These outcomes evidence that the dealkylation reaction of aromatics was also promoted
9 at the elevated catalytic temperature, leading to increased amounts of simple aromatics.[15, 21] It
10 is noted that a trace amount of oxygenates was obtained at the catalytic temperature of 500 °C. It
11 could be inferred from these results that under such condition, hydrogen transfer reactions could
12 enhance the cracking of the side chains substituted on phenyl to yield aromatic hydrocarbons.[54]
13 It is also possible that the stabilized phenolic compounds could be directly deoxygenated via
14 demethoxylation followed by dehydroxylation to obtain simple aromatic hydrocarbons.[21] To
15 make the precursors match the jet fuels, these results suggest that the aromatic hydrocarbons
16 obtained at catalytic temperature of 375 °C are more desirable.

17
18 Non-condensable gas was another major co-product from co-feeding of biomass with plastics in
19 the catalytic microwave pyrolysis. The composition of gaseous fraction regarding catalytic
20 temperature is also listed in Table 4. Because of the co-feeding of biomass with plastics in the
21 catalytic microwave pyrolysis, oxygen content was expelled from furan compounds by reacting
22 with olefins through Diels-Alder reaction followed by dehydration reaction with the water as
23 product, instead of decarbonylation and decarboxylation reactions [7, 8, 49]. Thus the carbon

yields of CO and CO₂ are very low. However, it was observed that the carbon yields of CO increased as the catalytic temperature went up from 375 to 500 °C. It is discerned that higher catalytic temperature had a negative impact at the Diels-Alder reaction [21], resulting in rejecting oxygen content from furans by decarbonylation reaction. It is noteworthy that the carbon yield of ethylene dramatically increased as the catalytic temperature went up to 500 °C. These results indicate that increasing catalytic temperature favored the catalytic cracking of long-chain waxes into light olefins. In addition, elevated catalytic temperature also prevented the aromatization reaction of light olefins to form aromatic hydrocarbons. [10, 15]

3.4 The effect of plastics to biomass ratio on the co-feed catalytic microwave pyrolysis

It was manifested that the optimal condition to obtain aromatic hydrocarbons lumped in the jet fuels range was set at 375 °C. Since lignocellulosic biomass is more abundant and cheaper than waste plastics, it is desired to enhance the mass ratio of cellulosic biomass in the co-reactants if this cannot decrease the carbon yield of liquid organics substantially. In order to investigate the effect of plastics proportion in the co-feed catalytic microwave pyrolysis, the overall carbon yield of product distribution at 375 °C with respect to plastics to biomass ratio is depicted in Fig. 5. It can be seen that the carbon yield of liquid organics increased nonlinearly with the augment of plastics to biomass ratio. Comparing with liquid organics without using plastics as the co-reactant, the liquid carbon yield rapidly increased as the ratio went up to 0.75. This increasing tendency indicates that there was a positive synergy between the two reactants. Furthermore, the substantial trend was attributed to the fact that large amounts of olefins with high H/C_{eff} ratio reacted with furan compounds by the Diels-Alder reaction to enhance liquid organics yield [55,

56]. According to our previous study [45], the highest yield (above 30%) of liquid organics from catalytic microwave pyrolysis of LDPE alone was much less than the yield of liquid organics from co-feed catalytic microwave pyrolysis. Yet as the plastics to biomass ratio went up from 0.75 to 1.45, the carbon yield of liquid organics slightly augmented. Thus, this slight tendency suggests that the co-feeding of biomass and plastics in catalytic microwave pyrolysis through the Diels-Alder reaction for the enhancement of liquid organics yield could not take place to a larger extent or could even reach the ceiling.

Both the carbon yields of char and coke gradually declined with an increasing plastics to biomass ratio as shown in Fig. 5. The carbon yields dramatically first decreased as the plastics to biomass ratio went up to 0.75; whereas they represent slight augmented trends as the ratio started 0.75 to 1.45. These could be explained by the fact that there was a significantly synergistic effect between the two feedstock in the ratio range from 0 to 0.75; whereas the synergy could not be further appreciably enhanced as more plastics were employed. Hence, there exists an optimal plastics to biomass ratio (0.75) for the Diels-Alder reaction in co-feed catalytic microwave pyrolysis if considering high value of waste plastics. As stated above, the Diels-Alder reaction could not be further enhanced at the high ratios (0.75 – 1.45), thus the light olefins derived from the catalytic cracking improved the carbon yield of non-condensable gas.

Table 5 lists how the carbon selectivity toward aromatics changes with the addition of plastics. In general, the carbon selectivity toward monocyclic aromatics went up as the plastics to biomass ratio increased; whilst the carbon selectivity toward polycyclic aromatics gradually declined. For

instance, the maximum carbon selectivity of aromatic hydrocarbons was xylenes, which increased appreciably from 4.28 to 21.33%. As such, the second highest carbon selectivity of aromatics was trimethylbenzene, displaying the same tendency as xylenes from 8.32 to 16.25%. By contrast, the carbon selectivity toward polycyclic aromatics experienced a remarkable drop with the increasing plastics to biomass ratio. It is due to the reason that Diels-Alder reaction between aromatics and light olefins, or hydrogen could suppress the polymerization reaction of monocyclic aromatics to generate polycyclic aromatics [21, 22, 26]. Meanwhile, light olefins alone were prone to the formation of monocyclic aromatic hydrocarbons by using ZSM-5 catalyst in the catalytic microwave pyrolysis. [45] In this regard, the aromatics with the carbon number in the jet fuel range were preferred from the experiment conducted at the low plastics to biomass ratio.

The gaseous composition with regard to plastics to biomass ratio is also illustrated in Table 5. The carbon yield of methane retains at around 12% with the maximum yield at the ratio of 0.75, whereas, the carbon yield of both CO and CO₂ decreased with the increase of plastics to biomass ratio. It is mainly attributed to the Diels-Alder reaction that was accelerated between biomass and plastics, instead of the decarbonylation and decarboxylation reaction. Unlike the CO and CO₂, the carbon yield of ethylene was found to augment in the most pronounced way from 5.32 to 56.34%. These outcomes verifies that the introduction of plastics in the catalytic microwave pyrolysis enhanced the H/C_{eff} ratio; and biomass-derived oxygenates was further transformed into more aromatics and olefins. Besides, biomass-derived oxygenates could promote the degradation of large molecules to light olefins in the co-feed catalytic pyrolysis.[15]

3.5 Process robustness: the recyclability of the well-promoted ZSM-5 catalyst

Irrespective of conversion extent of co-feed catalytic microwave pyrolysis, an appreciable reaction condition was employed to determine the process robustness and reuse of the well-promoted ZSM-5 catalyst. That is because the catalyst recyclability is of essential importance for a heterogeneous process [57]. Thus, the spent catalyst was regenerated to evaluate the recyclability in the co-feed catalytic microwave pyrolysis. The conversions were all conducted at the catalytic temperature of 375 °C with the plastics to biomass ratio of 0.75 as presented in Fig. 6. Since the co-feeding of biomass and plastics in the microwave reactor was pyrolyzed under the same condition, the carbon yield of char did not significantly change along with the recycle times of the catalyst. However, the carbon yield of liquid organics was dramatically affected by the catalyst recycle times, showing a slight decrease with the increase of recycle times. This result verifies that although coke deposited on the catalyst surface could be removed, the mesopores were permanently blocked by the coke, triggering the loss of active sites. Thus the Diels-Alder reaction between the biomass and plastics for the improvement of liquid organics yield was inhibited as well. Interestingly, the carbon yield of coke first decreased then increased. The decreased carbon yield of coke was possibly due to the fact that the Diels-Alder cycloaddition was inhibited in the pores; yet the catalytic cracking still took place on the surface of the catalyst active sites, which could mitigate the polymerization to form coke. For the increased carbon yields, the active sites on the catalyst surface were also be deactivated, leading to the waxes absorbed on the catalyst that could not be cracked. According to the trend of gas yield, it is reaffirmed that the active sites inside the catalyst pores was first deactivated by the pore blockage, the active sites on the catalyst surface were subsequently inhibited with the

1 increasing recycle times of the catalyst.

2
3 Table 6 describes the detailed carbon yields and product carbon selectivity with respect to
4 catalyst reused times. It was found that carbon selectivity toward all aromatics species decreased
5 with the increasing reused times. Nonetheless, a large amount of aliphatic hydrocarbons were
6 detected in the liquid organics. The results indicate that the aromatization and oligomerization of
7 olefins to form aromatics were suppressed due to catalyst pores blockages; the Diels-Alder
8 cycloaddition between the co-reactants for improving aromatics carbon selectivity was thus
9 inhibited. It is noticed that both the carbon selectivity of CO and CO₂ first decreased and then
10 went up; whilst the carbon selectivity of C₂H₄ showed an inverse tendency, first increasing and
11 then decreasing from the fresh to the fifth usage. It is manifested that the catalytic cracking of
12 both waxes and oxygenates occurred individually on the catalyst surface, forming these relevant
13 gas in the first phase (from the fresh use to the third use). However, as the active sites was
14 deactivated on the surface from the third use to the fifth use, the catalytic cracking of waxes and
15 oxygenates was suppressed as well.

16 17 *3.6 Hydrogenation of liquid organics derived from co-feed catalytic microwave pyrolysis for jet* 18 *fuels*

19 Given the Raney Ni catalyst could be poisoned by water in the hydrogenation process [36], the
20 water in the raw bio-oil samples should be removed. Since *n*-heptane served as the vital
21 medium in the hydrogenation process [35], two phase of mixed bio-oil samples was separated by
22 the optimum solvent (*n*-heptane). The liquid organics mixed with *n*-heptane from every samples

1 were separated and weighed to measure the loss of organics. ~94 wt% of liquid organics were
2 existing in the organic phase by extracting all samples. Since liquid organics produced from
3 catalytic microwave co-pyrolysis (at 375 °C with the plastics to biomass ratio of 0.75) were
4 principally comprised of aromatics from C₈ – C₁₆, these aromatics are viewed as precursors for
5 civilian jet fuels. In addition, the run that obtained the maximum liquid carbon yield (at 375 °C
6 with the ratio of 1.45) and the run that gained the liquid organics within lowest oxygenated
7 content (at 500 °C with the ratio of 0.75) were also hydrogenated for the optimization of jet
8 fuels. As reported, naphthalene in *n*-heptane was completely transformed into saturated decalin
9 [35], thus the mass ratio of reactant to *n*-heptane was set at 1:7 in terms of adding certain mass of
10 *n*-heptane.

11
12 The product distribution and carbon selectivity toward main alkanes from the hydrogenation of
13 diverse raw organics are elucidated in Table 7. After all the reactions, more than 99 vol% of
14 unreacted hydrogen was detected, indicating that the hydrogenation reactions were not
15 implemented under hydrogen-starved conditions. The overall carbon yields of these
16 hydrogenated organics (R-1, R-2, and R-3) with respect to the co-reactants of biomass and
17 plastics were 38.51, 32.92, and 40.53%, respectively. These carbon yields of hydrogenated
18 organics were much higher than that in our previous research [35]. Compared with the overall
19 product distribution of hydrogenated R-1 and R-3, the result regarding the production of
20 cycloalkanes from hydrogenated R-2 was more superior to the others under the same condition.
21 It was observed that ~ 90% selectivity toward cycloalkanes was achieved from hydrogenated R-2.
22 The high amounts of high-density cycloalkanes can be potentially used as the replacement of
23 high-density jet fuels (e.g., JP-10 and RJ-5). For the production of aliphatic alkanes,

hydrogenated R-3 obtained the maximum amount, which is close to 30%. In this sense, the contents of hydrogenated R-3 were identical to that in JP-5 navy fuel (31.23% of aliphatic alkanes, 53.06% of cycloalkanes, and 15% of aromatic hydrocarbons) [58]. The total amounts of hydro-aromatic hydrocarbons and aromatic hydrocarbons were comparable in all hydrogenated organics, whose amounts satisfy the regulations (less than 15%) of current jet fuels. A trace amount of other compounds were detected in all hydrogenated organics. Likewise, lower than 1 vol% of small hydrocarbons (e.g., methane, ethane, and propane) were achieved under the low-severity condition, reaffirming that there was almost no carbon loss in the hydrogenation system.

It was discerned that hydrogenated R-3 attained the maximum carbon selectivity toward monocyclic alkanes, except dimethylcyclohexane. Dimethylcyclohexane derived from the hydrocycloaddition of xylenes presented the highest carbon selectivity in hydrogenated R-2. That is because the dealkylation reaction was facilitated at the high catalytic temperature (500 °C), giving rise to high yield of xylenes. It is also noticeable that the maximum carbon selectivity toward aliphatic alkanes was attained in hydrogenated R-3 and none of unsaturated aliphatic hydrocarbons was found, suggesting that these high amounts of unsaturated aliphatic hydrocarbons were completely transformed into saturated aliphatic hydrocarbons under the mild reaction condition. Of the three raw organics for hydrogenation, the hydrogenated organics derived from R-1 obtained the highest amounts of saturated alkanes lumped in the jet fuel range. With the consideration of both reaction condition and product distribution, the raw organics (R-1) is the optimal source to manufacture renewable jet fuels with high carbon yield.

3.7 Reaction pathway for the conversion regarding co-feeding of biomass with plastics into jet fuels

These observations are the key support to show the reaction route for the conversion regarding co-feeding of lignocellulosic biomass with plastics into jet fuels. The resultant observation of the hydrogenated organics is manifested that the reaction pathway was much more complicated than those proposed previously [9, 14, 26]. Based on the quantified products in this research, related results from catalytic microwave-induce degradation of LDPE alone [45], and lignocellulosic biomass to jet fuel through combined catalytic conversions [40, 59]; the overall reactions network (co-feed catalytic pyrolysis and hydrogenation process) is outlined in Fig. 7. For the dominant route in lignocellulosic biomass, cellulose went through a sequence of dehydration, decarbonylation, and decarboxylation to generate furan compounds in the thermal degradation [17, 40]. As such, it was evidenced that hemicellulose was likely to depolymerized into furan compounds [59], which was comparable with the result of cellulose degradation [40]. Unlike cellulose and hemicellulose, lignin in lignocellulosic biomass was primarily decomposed into phenolic compounds. As for the degradation of plastics in another route, thermal degradation of plastics usually occurred through two mechanisms (random scission and chain-end scission) [60, 61]. The two abovementioned mechanisms took place simultaneously, generating free radicals together with the long carbon chains [62]. At the same time, the radical fragments could be transformed into straight chain hydrocarbons via hydrogen transfer reactions [62]. The hydrogen from the thermal degradation of plastics was provided for biomass-derived oxygenates that acted as the strong acceptor, suppressing the char formation.

1 The waxes with large molecule weigh from the thermal degradation of plastics subsequently
2 underwent catalytic cracking over ZSM-5 through two carbocationic mechanisms, giving rise to
3 light olefins [60, 63]. These olefins thereafter reacted with furan compounds by the Diels–Alder
4 reaction followed by the dehydration reaction to form aromatic hydrocarbons. Meanwhile, these
5 plastics-derived olefins could individually subject to cyclization, aromatization, and
6 oligomerization reactions to obtain aromatic hydrocarbons [21]. Likewise, these furan
7 compounds could individually go through decarbonylation, aromatization, and oligomerization
8 reactions inside the mesopores of well-promoted ZSM-5 to form aromatic hydrocarbons as well.
9 As previously reported, it is confirmed that the interaction via the hydrocarbon pool mechanism
10 could be found in addition to Diels–Alder reaction [9]. Since the carbon yield of liquid organics
11 significantly increased and the coke yield dramatically decreased, the Diels–Alder reaction was
12 the dominant reaction pathway during the co-feed catalytic pyrolysis in comparison with the
13 hydrocarbon pool mechanism. In addition, phenolic compounds were individually converted into
14 aromatic hydrocarbons over ZSM-5 catalyst by the dehydration, cracking, and oligomerization
15 reactions [17, 64].

16
17 The liquid organics resulting from the co-feed catalytic microwave pyrolysis mostly gave rise to
18 a mixture of aromatic and aliphatic hydrocarbons. As hydrogenation of unsaturated hydrocarbons
19 primarily occurs in bio-oil hydrotreatment by using metal catalysts under mild reaction
20 conditions [65], and Raney-Ni catalysts in the hydrotreating process are in favor of catalyzing
21 the hydrogenation reactions due to the porous structure of active nickel [66]; hence, it was shown
22 that the hydrogenation of aliphatic olefins was the first step to take place in the hydrogenation
23 system [67]. The aromatic hydrocarbons were stepwise hydrogenated into cyclic alkanes or

hydro-aromatic hydrocarbons through hydro-cycloaddition reactions in the presence of home-made Raney Ni catalyst. Furthermore, the hydroisomerization reaction could take place among the dimethylcyclohexanes; and a trace volume of small hydrocarbons was also generated by hydrocracking reactions. As a result, these hydrogenated organics can be potentially used as alternatives of civilian jet fuels or additives to manufacture desired jet fuels by mixing with other hydrocarbons.

4 Conclusions

In summary, the microwave-induced co-pyrolysis followed by hydrogenation process is a profound route for the improved carbon yield of jet fuel range alkanes from co-feeding of lignocellulosic biomass with plastics. Two variables (catalytic temperature and plastics to biomass ratio) were evaluated in the co-feed catalytic microwave pyrolysis to improve the carbon yield of aromatics with the carbon number in the jet fuel range. The results showed that there was a positive synergy between lignocellulosic biomass and plastics in the co-feed catalytic microwave pyrolysis, which could significantly improve the carbon yield of liquid organics and suppress the formations of char and coke. Although the optimal condition to maximize the carbon yield (42.66%) of liquid organics in the step of co-feed catalytic microwave pyrolysis was at 375 °C with the plastics to biomass ratio of 1.45, the compounds with low carbon numbers (e.g. toluene) was also obtained, which cannot meet the specifications of jet fuels. Yet the chemical compounds of liquid organics with high carbon yield (40.54%), which was derived from the reaction conducted at 375 °C with the ratio of 0.75 primarily satisfy the specifications in the jet fuel range.

After the hydrogenation process by using home-made Raney Ni as the catalyst under a low-severity condition, the overall carbon yield of three hydrogenated organics (R-1, R-2, and R-3) regarding raw lignocellulosic biomass and plastics were 38.51, 32.92, and 40.53%, respectively. Given the overall carbon yield and product distribution, the raw organics conducted at the catalytic temperature of 375 °C with the biomass to plastics ratio of 0.75 in the co-feed catalytic microwave pyrolysis is more suitable for the production of renewable alkanes for advanced jet fuels (especially for high-density jet fuels). Herein, ~ 90% selectivity toward jet fuel range alkanes was obtained from such raw organics, and up to 75% selectivity belongs to high-density cycloalkanes. It is more likely that in the future these alkanes can be potentially used as additives or replacements for jet fuels.

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Table 1 Elemental analyses of Douglas fir sawdust pellets and low-density polyethylene

<i>Elemental analysis (wt%)</i>	Douglas fir sawdust pellets	Low-density polyethylene
Carbon	47.90	85.71
Hydrogen	6.55	14.29
Nitrogen	0.08	0
Oxygen ^a	45.57	0
^a Determined by difference		

Table 2 Experimental design and product yield distribution^a

Entry ^b	Catalytic Temperature (°C)	Plastics to biomass ratio	Yield (wt%)			
			Bio-oil	Gas	Char	Coke
1	300	0.5	39.97	39.27	17.21	3.55
2	300	1	45.32	39.93	11.86	2.89
3	450	0.5	34.55	45.73	16.74	2.98
4	450	1	40.24	46.07	12.02	1.67
5	375	0.75	42.54	41.33	13.11	3.02
6	375	0.75	41.38	42.44	13.20	2.98
7	375	0.75	42.09	41.93	12.87	3.11
8	375	0.75	41.68	42.00	13.44	2.88
9	375	0.75	41.77	42.24	13.02	2.97
10	375	0.4	35.22	43.61	17.57	3.60
11	375	1.1	43.85	41.72	11.56	2.87
12	269	0.75	42.85	40.57	13.24	3.34
13	481	0.75	38.23	47.56	12.78	1.43
14	375	1.45	45.57	42.76	9.09	2.58
15	200	0.75	47.00	36.18	13.28	3.54
16	500	0.75	36.47	49.56	12.95	1.02
17	375	0	30.57	43.89	21.69	3.85

^a reaction condition: reaction temperature 480 °C; reaction time, 10 mins.

^b Entry-1 to Entry-13 were conducted based on central composite design; Entry-14 and Entry-16 were added as the controls; Entry-17 is the control in the absence of plastics.

Table 3 Textural properties of well-promoted ZSM-5 and home-made Raney Ni catalysts^a

	S_{BET}	V_{pore}	S_{pore}	d_{pore}	T_{acidity}
	(m ² /g)	(cm ³ /g)	(m ² /g)	nm	mmol NH ₃ /g
Parent ZSM-5	386.9	0.078	55.3	5.7	0.20
Well-promoted ZSM-5	396.2	0.097	74.1	5.2	0.18
Ni-Al alloy	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; T_{acidity} : total acidity.

Table 4 Detailed carbon yield distribution and product carbon selectivity as a function of catalytic temperature ^a

	Catalytic temperature (°C)				
	200	269	375	481	500
<i>Overall carbon yield (C mol%)</i>					
Liquid organics	42.23	40.84	40.54	36.22	34.65
Char	18.02	17.56	17.87	18.34	17.67
Coke	5.98	5.42	4.23	2.78	1.46
Gas ^b	33.77	36.18	37.36	42.66	46.22
<i>Liquid carbon selectivity (C mol%)</i>					
Toluene	4.97	6.48	10.72	14.62	18.42
Ethylbenzene	1.18	1.63	2.29	2.66	1.99
<i>p</i> -xylene/ <i>m</i> -xylene	2.50	7.67	18.78	25.27	27.41
Trimethylbenzene	4.35	16.74	17.13	10.41	9.01
Indane	0.39	0.72	-	2.24	2.00
Indene	1.60	1.30	0.79	1.91	1.59
Phenol	1.92	1.78	1.51	1.46	1.19
<i>p</i> -cresol/ <i>m</i> -cresol	2.96	2.19	1.74	1.52	1.09
Naphthalene	5.51	3.90	5.33	6.96	6.43
1-methylnaphthalene	-	1.12	5.29	7.08	7.50
2-methylnaphthalene	-	0.97	2.13	0.90	0.95
Anthracene	-	-	0.85	1.29	1.28
Pyrene	-	0.12	-	0.09	0.24
<i>Gaseous carbon selectivity (C mol%)</i>					
Methane	12.45	13.11	13.65	14.02	14.25
Carbon monoxide	30.32	26.54	16.43	18.61	20.11
Carbon dioxide	22.45	20.45	18.98	20.10	20.32
Ethylene	18.45	24.20	31.45	36.54	40.22
Ethane	7.18	8.43	11.23	5.09	2.91
Propane	9.15	7.27	8.26	5.64	2.19

^a Reaction condition: Catalyst, 20 wt% with respect to feed; Plastics, 75 wt% with respect to biomass; Reaction temperature, 480 °C; Reaction time, 10 min.

^b Determined by difference

Table 5 Detailed carbon yield distribution and product carbon selectivity on the basis of plastics to biomass ratio^a

	Plastics to biomass ratio				
	0	0.4	0.75	1.1	1.45
<i>Overall carbon yield (C mol%)</i>					
Liquid organics	25.64	34.18	40.54	41.34	42.66
Char	40.55	27.27	17.87	14.88	11.25
Coke	7.53	5.65	4.23	3.87	3.34
Gas ^b	26.28	32.90	37.36	39.91	42.75
<i>Liquid carbon selectivity (C mol%)</i>					
Toluene	2.85	4.04	10.72	8.09	10.82
Ethylbenzene	1.43	1.54	2.29	2.86	3.20
<i>p</i> -xylene/ <i>m</i> -xylene	4.28	7.53	18.78	18.24	21.33
Trimethylbenzene	8.32	13.23	17.13	17.73	16.25
Indane	-	1.31	-	1.58	1.31
Indene	2.65	2.11	0.79	0.96	0.60
Phenol	4.53	1.92	1.51	1.11	0.80
<i>p</i> -cresol/ <i>m</i> -cresol	6.31	3.51	1.74	0.83	0.58
Naphthalene	8.02	7.78	5.33	4.16	3.23
1-methylnaphthalene	6.07	5.64	5.29	4.60	3.13
2-methylnaphthalene	3.13	2.63	2.13	1.86	1.54
Anthracene	1.82	0.45	0.85	0.91	0.24
Pyrene	0.35	0.34	-	0.21	0.12
<i>Gaseous carbon selectivity (C mol%)</i>					
Methane	12.94	13.22	13.65	12.44	11.68
Carbon monoxide	40.40	25.67	16.43	13.12	10.75
Carbon dioxide	28.12	22.36	18.98	14.39	11.25
Ethylene	5.32	23.19	31.45	46.84	56.34
Ethane	6.54	8.74	11.23	7.32	5.75
Propane	6.68	6.82	8.26	5.89	4.23

^a Reaction condition: Catalyst, 20 wt% with respect to feed; Reaction temperature, 480 °C; Catalytic temperature, 375 °C; Reaction time, 10 min.

^b Determined by difference

Table 6 Detailed carbon yield distribution and product carbon selectivity with respect to catalyst reused times ^a

	Recycle times				
	Fresh	2nd	3rd	4th	5th
<i>Overall carbon yield (C mol%)</i>					
Liquid organics	40.54	39.23	38.01	37.98	36.77
Char	17.87	18.02	17.75	18.22	17.68
Coke	4.23	3.88	3.35	4.34	4.89
Gas ^b	37.36	38.87	40.89	39.46	40.66
<i>Liquid carbon selectivity (C mol%)</i>					
Toluene	10.72	8.18	7.84	6.23	5.96
Ethylbenzene	2.29	3.02	3.39	2.55	3.96
<i>p</i> -xylene/ <i>m</i> -xylene	18.78	18.05	18.61	15.20	14.25
Trimethylbenzene	17.13	17.03	16.68	17.20	16.60
Indane	-	-	1.78	-	1.37
Indene	0.79	1.46	1.41	1.19	0.95
Phenol	1.51	1.58	1.60	1.69	1.96
<i>p</i> -cresol/ <i>m</i> -cresol	1.74	2.07	1.98	1.99	2.27
Naphthalene	5.33	5.57	5.86	4.72	3.87
1-methylnaphthalene	5.29	5.38	4.66	3.23	3.15
2-methylnaphthalene	2.13	1.01	0.96	1.02	0.72
Anthracene	0.85	0.32	1.27	0.34	0.21
Pyrene	-	0.53	0.34	0.27	0.22
<i>Gaseous carbon selectivity (C mol%)</i>					
Methane	13.65	14.54	13.22	12.55	13.76
Carbon monoxide	16.43	16.33	15.65	20.11	22.44
Carbon dioxide	18.98	18.78	17.44	23.44	24.59
Ethylene	31.45	36.76	40.15	33.01	27.44
Ethane	11.23	7.45	6.24	4.56	6.35
Propane	8.26	6.14	7.30	6.33	5.42
^a Reaction condition: Catalyst, 20 wt% with respect to feed; Plastics, 75 wt% with respect to biomass; Reaction temperature, 480 °C; Catalytic temperature, 375 °C; Reaction time, 10 min.					
^b Determined by difference					

Table 7 Products distribution and partial alkanes' carbon selectivity for hydrogenation of diverse liquid organics^a

	Organics species ^b		
	R-1	R-2	R-3
<i>Overall selectivity (% in area)</i>			
Aliphatic alkanes	14.04	2.15	29.24
Cycloalkanes	74.28	89.27	59.21
Hydro-aromatic hydrocarbons	3.03	3.24	1.12
Aromatic hydrocarbons	6.13	4.17	8.56
Others	2.52	1.17	1.87
<i>Alkanes selectivity (C mol%)</i>			
1,4-dimethylcyclohexane	3.64	5.27	3.43
1,3-dimethylcyclohexane	12.38	17.26	12.67
1,2-dimethylcyclohexane	5.23	7.98	7.23
Ethylcyclohexane	3.02	3.87	4.05
Octane	0.75	0.17	0.98
1,2,4-trimethylcyclohexane	16.67	10.76	15.89
Propylcyclohexane	2.29	3.54	1.27
Nonane	0.88	0.14	1.72
Hexahydroindan	2.89	4.56	2.02
Decalin	5.76	7.87	3.71
Decane	0.58	-	1.02
Undecane	2.12	0.77	3.15
Dodecane	0.85	-	1.14
Tridecane	0.34	0.21	1.21
Tetradecane	0.63	0.15	1.32
Pentadecane	0.45	-	1.23
Hexadecane	0.49	0.14	0.98

^a Reaction condition: Initial pressure, 500 psi; Raney Ni catalyst, 20 wt% with respect to reactant mass; Reaction temperature, 200 °C; Reaction time, 2 h.

^b R-1: reactant from the experiment conducted at catalytic temperature of 375 °C with plastics to biomass ratio of 0.75; R-2: reactant from the experiment conducted at catalytic temperature of 500 °C with plastics to biomass ratio of 0.75; R-3: reactant from the experiment conducted at catalytic temperature of 375 with plastics to biomass ratio of 1.45.

Fig. 1 NH₃-TPD profiles of parent ZSM-5 and well-promoted ZSM-5 catalyst.

Fig. 2 The XRD patterns of the Ni-Al alloy powder and home-made Raney Ni catalyst.

Fig. 3 SEM images of Ni-Al alloy powder (A) and home-made Raney Ni catalyst (B).

Fig. 4 The overall carbon yields regarding product distribution from co-feed catalytic microwave pyrolysis in light of catalytic temperature at the same plastics to biomass ratio (0.75).

Fig. 5 The overall carbon yields regarding product distribution from co-feed catalytic microwave pyrolysis as a function of plastics to biomass ratio at the same catalytic temperature (375 °C).

Fig. 6 The overall carbon yields regarding product distribution from co-feed catalytic microwave pyrolysis on the basis of catalyst recycle times at the catalytic temperature of 375 °C with the plastics to biomass ratio of 0.75.

Fig. 7 Proposed reaction pathways for the conversion of lignocellulosic biomass and plastics into jet fuel range alkanes.

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Improvement of renewable alkanes for jet fuels from co-feed catalytic microwave-assisted pyrolysis and hydrogenation process