



# Optimizing carbon efficiency of jet fuel range alkanes from cellulose co-fed with polyethylene via catalytically combined processes



Xuesong Zhang, Hanwu Lei\*, Lei Zhu, Xiaolu Zhu, Moriko Qian, Gayatri Yadavalli, Di Yan, Joan Wu, Shulin Chen

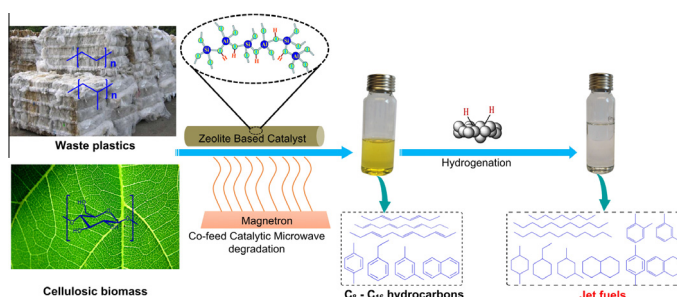
Department of Biological Systems Engineering, Washington State University, Richland, WA 99354-1671, USA

## HIGHLIGHTS

- It is the first time to convert co-reactants of biomass and plastics into jet fuels.
- There was a positive synergy for aromatics in catalytic microwave co-pyrolysis.
- Modified catalysts were employed in respective processes.
- Over 39% overall carbon yield of hydrogenated organics were gained.
- ~90% selectivity toward jet fuel range alkanes was attained.

## GRAPHICAL ABSTRACT

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



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## ABSTRACT

Enhanced carbon yields of renewable alkanes for jet fuels were obtained through the catalytic microwave-induced co-pyrolysis and hydrogenation process. The well-promoted ZSM-5 catalyst had high selectivity toward C<sub>8</sub>–C<sub>16</sub> aromatic hydrocarbons. The raw organics with improved carbon yield (~44%) were more principally lumped in the jet fuel range at the catalytic temperature of 375 °C with the LDPE to cellulose (representing waste plastics to lignocellulose) mass ratio of 0.75. It was also observed that the four species of raw organics from the catalytic microwave co-pyrolysis were almost completely converted into saturated hydrocarbons; the hydrogenation process was conducted in the *n*-heptane medium by using home-made Raney Ni catalyst under a low-severity condition. The overall carbon yield (with regards to co-reactants of cellulose and LDPE) of hydrogenated organics that mostly match jet fuels was sustainably enhanced to above 39%. Meanwhile, ~90% selectivity toward jet fuel range alkanes was attained.

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## 1. Introduction

Municipal solid waste (MSW) has been found as one of the major challenges in the face of the modern world (Fang et al.,

2016); in particular, the sustainable disposal management of MSW was intensively appealed in the industrialized and developing countries (Lemoine et al., 2013). MSW is comprised of various categories of materials. Among it, biomass co-existing with plastics make up a majority of the composition (Cheng and Hu, 2010). Yet, the conventional methods for the disposal of MSW takes away valuable land and causes numerous environmental issues (Cheng and Hu, 2010). More attentions are paid to energy-efficient, eco-

\* Corresponding author.

E-mail address: [hlei@wsu.edu](mailto:hlei@wsu.edu) (H. Lei).

friendly and economically sound technologies for the disposal of MSW. Because discarded MSW represents a tremendous energy source; MSW-to-energy technologies not only mitigates negative impacts on the environment, but also provides sustainable energy. Catalytic fast pyrolysis (CFP) is recognized as the most prevailing and promising pathway in a single process (Cheng and Huber, 2012; Li et al., 2013, 2015). Zeolite-based catalysts (e.g. ZSM-5) have been proved as the most efficient catalysts to produce important petrochemicals (Dorado et al., 2014; Li et al., 2013; Zhang et al., 2014).

However, even in the presence of ZSM-5 catalyst, catalytic pyrolysis of lignocellulose alone only generated low carbon yields (10–30%) of aromatic hydrocarbons; large amounts of solid residues (carbon yields usually above 30%) were also achieved in the process (Li et al., 2015; Liu et al., 2014; Yao et al., 2015). It is plagued by the high yield of coke deposited on the catalyst. That is because the coke could rapidly deactivate the catalyst and further reduce the lifetime, triggering the catalytic process to be impractical. These aforementioned phenomenon is principally due to the intrinsically oxygen rich nature and hydrogen deficiency of biomass (Liu et al., 2014; Xue et al., 2016; Yao et al., 2015). It was found that the hydrogen to carbon effective ( $H/C_{\text{eff}}$ ) ratio plays a vital role in the efficiency for converting biomass to biofuel and coke formation (Cheng and Huber, 2012; Dorado et al., 2015; Zhang et al., 2015a). Thus the hydrogen-deficient ( $H/C_{\text{eff}}$  usually less than 0.3) biomass produce low yields of petrochemicals, but large amounts of coke when they were converted over zeolite-based catalysts (Li et al., 2013; Zhang et al., 2014).

To improve the carbon efficiency of aromatic production and reduce the formation of coke, the incorporation of hydrogen-enriched co-reactant in the catalytic pyrolysis of biomass could mitigate these problems. It is mostly likely that co-fed hydrogen-rich feedstock in the catalytic pyrolysis of biomass could change reaction mechanism of oxygen removal from biomass by substituting decarbonylation and decarboxylation with deoxygenation (Dorado et al., 2015; Green et al., 2016; Li et al., 2015). It is widely known that waste plastics represent a cheaper and abundant hydrogen source (Li et al., 2014b; Li et al., 2013; Xue et al., 2016; Yao et al., 2015; Zhang et al., 2014), which were utilized to improve carbon yield of aromatic production and lower the coke formation in the co-feed catalytic pyrolysis. For example, polyethylene accounts for up to 40% of gross waste plastics in MSW (Miskolczi et al., 2004). Accordingly, the co-feeding of biomass with waste plastics from MSW in catalytic pyrolysis is beneficial for the environment and energy recapture.

On the other hand, the co-feeding of biomass with plastics in catalytic pyrolysis commonly gave rise to mono-ring aromatic hydrocarbons with low carbon number ( $C_6$ – $C_8$ ) (Green et al., 2016; Li et al., 2014b; Xue et al., 2016; Zhang et al., 2015a). These hydrocarbons with low carbon numbers cannot suit current jet fuels within  $C_8$ – $C_{16}$  hydrocarbons. Linear-chain and branched-chain alkanes predominantly make up  $C_8$ – $C_{16}$  hydrocarbons in the current jet fuels (Bi et al., 2015; Huber et al., 2006). By contrast, cycloalkanes are compact molecules within robust ring strain and can be burned cleanly with high heats of combustion (Li et al., 2014a; Zhang et al., 2015f). As expected, jet fuel range cycloalkanes should be synthesized and added into commercial jet fuels (e.g. Jet A and JP-8). It was noteworthy that aromatic hydrocarbons are prone to be transformed into cycloalkanes by hydro-cycloaddition reactions under a mild reaction condition (Zhang et al., 2015d,e). To pursue renewable cycloalkanes, highly desirable aromatic hydrocarbon ( $C_8$ – $C_{16}$ ) as the precursors should be synthesized in co-feed catalytic pyrolysis, rather than mono-ring aromatic hydrocarbons with low carbon numbers.

Parent ZSM-5 zeolite used for aromatic production with low carbon number are not suitable for the production of jet fuel range

aromatics in the catalytic pyrolysis. Nonetheless, moderate treatments were employed to tailor zeolite properties for modifications of porosity and acidity, which is essential for improving product selectivity of  $C_8$ – $C_{16}$  aromatic hydrocarbons in our previous study (Zhang et al., 2015b). The mild hydrothermal and calcined conditions favored the generation of mesopores for the diffusion of double-ring aromatics, and catalytic sites for specific efficiency. In this regard, we have developed a tandem process to produce renewable cycloalkane for jet fuels derived from lignocellulosic biomass individually, albeit achieving a low carbon yield (24.68%) (Zhang et al., 2015e). It is manifested that microwave-assisted pyrolysis technology is one of the most promising methods for enhancing and accelerating chemical reactions due to effective heat transfer through microwave irradiation (Luque et al., 2012). In comparison with conventional pyrolysis, microwave-assisted pyrolysis encloses the potentials of fast and selective heating, easy control of reaction conditions, low reaction temperatures and energy requirements (Lidstrom et al., 2001). In the hydrotreating process, Raney-type Ni is widely employed as a versatile catalyst for reductive conversions of organic compounds (Gross et al., 2001). It was discerned that the catalytic activities of home-made Raney Ni catalyst used was superior to as-purchased Raney Ni catalysts (Zhang et al., 2015e). We observed that aromatics from catalytic microwave pyrolysis were almost completely converted into high-density cycloalkanes in the *n*-heptane medium under a low-severity condition.

This present work aims to unravel the key interactions between cellulose and low-density polyethylene (LDPE), which act as the model compounds of lignocellulosic biomass and waste plastics in MSW. To this end, cellulose and LDPE were first co-pyrolyzed using a tandem microwave-induced system coupled with a downstream catalysis system. For converting aromatics into renewable cycloalkanes for jet fuels, several species of liquid organics extracted by the optimum solvent (*n*-heptane) was transformed into saturated hydrocarbons by using home-made Raney Ni catalyst in the hydrogenation process. The influence of organic species in the overall carbon yield and product distribution of saturated hydrocarbon in the jet fuel range was also evaluated.

## 2. Materials and methods

### 2.1. Materials

Cellulose (CAS number 9004-34-6), in the form of microcrystalline powders and particle sizes is averaged at 50  $\mu\text{m}$ , was purchased from Sigma–Aldrich Corporation (St. Louis, MO, USA). Low-density polyethylene (LDPE) (CAS number 9002-88-4) in the form of pellets was purchased from Sigma–Aldrich Corporation (St. Louis, MO, USA). The density and melting point of LDPE are 0.925  $\text{g}/\text{cm}^3$  at ambient temperature and 116  $^\circ\text{C}$ , respectively. The elemental composition of cellulose and LDPE is described in Table 1. Parent ZSM-5 ( $\text{SiO}_2/\text{Al}_2\text{O}_3$  Mole Ratio: 50) was purchased from Zeolyst International, USA. Nickel–Aluminum alloy powder in a non-activated type was used as purchased from Alfa Aesar (Ward Hill, MA, USA).

### 2.2. Catalyst preparation

The activity of parent ZSM-5 was improved by both hydrothermal and calcined treatments. Under the gentle stirring, parent ZSM-5 powder was added into deionized water (mass ratio = 1) at 60  $^\circ\text{C}$ . After addition, the mixture was kept on stirring for 2 h under this condition. The slurry was then dried at 105  $^\circ\text{C}$  till constant weight. The sequential process was the catalyst calcination: hydrothermally treated ZSM-5 was calcined at 550  $^\circ\text{C}$  for 5 h in a

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