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Co-upgrading of raw bio-oil with kitchen waste oil through fluid catalytic cracking (FCC)

Wenchao Ma[a], Bin Liu[b], Ruixue Zhang[a], Tianbao Gu[a], Xiang Ji[a,c], Lei Zhong[a], Guanyi Chen[d,a,b,*], Longlong Ma[e,*], Zhanjun Cheng[a], Xiangping Li[a]

[a] Tianjin Engineering Research Center of Bio Gas/Oil Technology, School of Environmental Science and Engineering, Key Laboratory of Efficient Utilization of Low and Medium Grade Energy (Tianjin University), Ministry of Education, Tianjin University, Tianjin 300072, China
[b] Qingdao Institute for Ocean Engineering of Tianjin University, Qingdao 266235, China
[c] School of Life Science and Technology, Inner Mongolia University of Science and Technology, Baotou 014010, China
[d] School of Science, Tibet University, Lhasa 850012, China
[e] Key Laboratory of Renewable Energy and Gas Hydrate, Guangzhou Institute of Energy Conversion, Chinese Academy of Sciences, Guangzhou 510640, China

HIGHLIGHTS

- Bio-oil upgrading through fluid catalytic cracking were performed.
- Synergetic effect occurs during co-catalytic cracking of bio-oil and kitchen waste oil.
- Bio-oil upgrading mixed with kitchen waste oil produce more olefins and aromatics.
- Kitchen waste oil provide hydrogen for oxygenated compounds convert into hydrocarbons.
- Kitchen waste oil mixed into bio-oil can inhibit the formation of coke precursor.

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ABSTRACT

Raw bio-oil was produced from fast pyrolysis of pine sawdust in a fluidized-bed boiler at 550 °C. Then the raw bio-oil is partially mixed with kitchen waste oil (100:0, 50:50, 0:100 by weight) and subsequently subjected to off line co-catalytic cracking process for upgrading over HZSM-5. The raw bio-oil mixed with kitchen waste oil test shows that the co-catalytic cracking improves the organic bio-oil yield and inhibits the coke formation. The oxygen content of organic bio-oil decreased significantly after upgrading. The reaction pathway of co-upgrading is proposed, which shows that kitchen waste oil, as a hydrogen supplier, transform hydrogen from high saturation degree to the unsaturation oxygenated compounds to form hydrocarbons. Co-catalytic cracking process of raw bio-oil and kitchen waste oil not only can be used in raw bio-oil upgrading but also can recycle kitchen waste oil with relatively low cost. Moreover, the deactivation catalysts are analyzed by TG-FTIR (Thermogravimetric-Fourier Transform Infrared spectroscopy) and SEM (Scanning Electron Microscope).

1. Introduction

Biomass, as one of the new energy source, is the only renewable source of organic carbon. Bio-oil, from pyrolysis of biomass, can be used as fuel mixed with diesel, or as feedstocks for the manufacture of value-added products (such as hydrocarbons and hydrogen production) [1], which also receives wide attention due to its lower net CO_2 emissions. Pine sawdust, a common waste material from many forestry factories, which considered as a potential bio-oil feedstock [2].

Light olefins and light aromatics are the basic materials in the petroleum and chemical industry. Traditionally, they are produced from naphtha, light diesel, or heavier hydrocarbons. However, supply of naphtha is scarce in China [3]. Fortunately, bio-oil contains some olefins and aromatics, and their contents can be significantly increased via bio-oil catalytic upgrading. The fast pyrolysis for bio-oil production in fluidized bed is the most common technology for biomass conversion, which can produce 45–58 wt.% raw bio-oil (the total of organic phase and water phase) (e.g. from pine sawdust) [2,4,5]. However, bio-oil from direct pyrolysis exhibits some undesirable properties: high acidity, high water content, high oxygen content, etc [6,7]. These

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[*] Corresponding authors at: Tianjin Engineering Research Center of Bio Gas/Oil Technology, School of Environmental Science and Engineering, Key Laboratory of Efficient Utilization of Low and Medium Grade Energy (Tianjin University), Ministry of Education, Tianjin University, Tianjin 300072, China (G. Chen).

E-mail addresses: chen@tju.edu.cn (G. Chen), mall@ms.giec.ac.cn (L. Ma).

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properties limit its direct use as a source of chemical feedstock and require upgrading technology to improve its quality.

Traditionally, there are two routes for bio-oil upgrading to improve the contents of olefins and light aromatics: hydrodeoxygenation (HDO) and catalytic cracking. HDO is performed at moderate temperature (300–600 °C), high hydrogen pressure (10–20 MPa), over a variety of catalysts with the removal of oxygen as H_2O, CO_2 or CO. The catalysts used for HDO upgrading of pine sawdust bio-oil are usually zero valent metals (such as zinc metal) [8] or metal modified catalysts (such as Ru/WZr, Pd/C, Ni/C, Co/C, Ru/TiO_2, Ru/Al_2O_3, $MoNi/\gamma\text{-}Al_2O_3$) [9–11]. The main disadvantage of HDO is the excess cost, due to the use of high pressure and hydrogen. In catalytic cracking process, oxygen containing bio-oils are catalytically decomposed to hydrocarbons, while the oxygen gets removed as CO_2 and H_2O, thereby elevating the energy density. There are two kinds of catalytic cracking processes, i.e. offline and online catalytic cracking, which use bio-oil and pyrolysis vapours as raw feedstock, respectively [7,12]. Additionally, a good option can be to co-feed the bio-oil with conventional fluid (co–)catalytic cracking (FCC) feedstocks to upgrade raw bio-oil.

FCC, the most important technology in petrochemical industry, can transform high molecular weight hydrocarbons to more gasoline products [13,14]. Its units are usually designed for treating complex and heavy feeds [15]. According to the characteristics of FCC, it is great possible to be used for bio-oil upgrading. It is interesting to upgrade bio-oil in the modern refineries using FCC, on one hand to produce a material with high hydrocarbons contents, and on the other hand with a minimum investment in existing refineries [14,16–18]. However, development of the FCC process for bio-oil upgrading faces an important obstacle, which is the deposition on the catalyst of carbonaceous material formed by the polymerization of lignin-derived molecules of the biomass [19].

Zeolite is a universal choice for bio-oil catalytic upgrading due to their ability to deoxygenate pyrolysis vapors [20]. HZSM-5 zeolite with 3-dimensional sinusoidal and straight channels of molecular dimension has been used to enhance the light olefins and aromatics production via dehydration, decarboxylation, decarbonylation, aromatization and isomerization reactions occurred inside their internal structure [21]. But the zeolite suffers from heavy deactivation by coke, some researchers attributed to the low H/C_{eff} ratio (the effective ratio of hydrogen to carbon, $H/C_{eff} = (H\text{-}2 * O)/C$ [22]) in the feedstock. Thus, co-pyrolysis or co-catalytic cracking process with high H/C_{eff} ratio of materials, such as deoiled asphalt ($H/C_{eff} = 1.16$) [23], plastic polymers (e.g. polyethylene ($H/C_{eff} = 2.67$)) [21], ethanol ($H/C_{eff} = 2$) [12] have been promoted. Comparatively, co-pyrolysis or co-catalytic cracking with higher H/C_{eff} compounds are supposed to have positive effects on the quality and quantity of the bio-oil product. The synergetic effect between raw materials and the hydrogen transfer from hydrogen-rich material to unsaturation oxygenated compounds under co-pyrolysis or co-catalytic cracking have been reported. Krerkkaiwan et al. [24] evidenced a synergetic effect has been occurred in the co-pyrolysis of biomass and coal, which can be explained by the transferring of active OH and H radicals from the biomass to the coal. Cai et al. [25] investigated the hydrogen supply and transfer behaviors in hydrogenation-cracking, the results shows that methanol ($H/C_{eff} = 2$) could supply hydrogen to promote the conversion of components in a distilled fraction of bio-oil to aromatic hydrocarbon.

The kitchen waste oil with an annual generation of over 5 million tons in China is facing the disposal problem [26]. The co-catalytic cracking process of raw bio-oil mixed with kitchen waste oil can be also a good solution for treating and recycling kitchen waste oil with relatively low cost. Moreover, kitchen waste oil, as a hydrogen supplier for raw bio-oil upgrading, with higher H/C_{eff} ratio and low price seems to be more promising than the high value of alcohols. In our previous study, it was found that co-pyrolysis of corn cob and kitchen waste oil was effectively improving the bio-oil production as well as the bio-oil quality [27]. To the best of our knowledge, no more information has been given on the co-catalytic cracking of bio-oil and kitchen waste oil.

Few studies have been conducted to explore the conversion rate of bio-oil derived from pine sawdust and kitchen waste oil to olefins and aromatics by FCC over HZSM-5. In this paper, raw bio-oil from the fast pyrolysis of pine sawdust is partially mixed with kitchen waste oil, and then subsequently offline catalytic cracking process as an approach for upgrading is carried out. The objective is to co-upgrade bio-oil with kitchen waste oil by FCC over HZSM-5. This paper aim to provide a technology that easy to scale-up and can be further apply to industrial production of high olefins and aromatics contents and kitchen waste utilization.

2. Material and methods

2.1. Feedstocks

Pine sawdust, collected from Jing Hai country, Tianjin, China, sieved to 20–60 mesh particle size, and then dried in an oven at 80 °C for 24 h. The raw bio-oil was produced from fast pyrolysis of pine sawdust in a fluidized bed boiler with a feed rate of 2.5 kg/h by screw feeder with a temperature of 550 °C. The yield of organic bio-oil phase and water phase were 18.7 wt.% and 15.9 wt.%, respectively. Char production is approximately 46.2 wt.%, while gas represents 19.2 wt.% by difference.

Kitchen waste oil was obtained after using edible vegetable oils several times for frying, provided from student restaurant of Nankai University in Binhai, Tianjin, China. The proximate and elemental analysis of the feedstock is shown in Table 1. The kitchen waste oil contains higher carbon and hydrogen content and lower oxygen content compare with pine sawdust, which lead to the H/C_{eff} of kitchen waste oil much higher than pine sawdust. The compositions of kitchen waste oil analyzed by GC–MS show that they are all aliphatic acids, in which the oleic acid and linoleic acid are the main components.

2.2. FCC upgrading

The bio-oil upgrading process was performed in a quartz fluidized bed, its schematic diagram shown in Fig. 1. The unit mainly consisted of a gas-supplying unit, a preheating unit, a fluidized bed boiler with an inner diameter of 4 cm and a height of 50 cm, a condensation unit, an accumulative flowmeter and gas-collecting unit. After the catalytic cracking, the product vapors were passed through condensation unit to

Table 1
Elemental, proximate analysis and GC–MS composition of feedstocks.

Feedstock	Pine sawdust	Raw bio-oil	Kitchen waste oil
Elemental analysis (wt.%)			
C	48.28	31.76	75.18
H	7.31	8.54	12.17
O[*]	43.41	59.61	12.56
N	0.25	0.09	0.01
S	0.23	–	–
H/C_{eff}	0.47	0.41	1.69
Proximate analysis (wt.%, dry basis)			
Volatile	84.10		
Fixed carbon	15.20		
Ash	0.70		
Water content (wt.%, wet basis)	9.10	46.0	
GC–MS composition			
Palmitic acid (C16:0)			8.5
Stearic acid (C18:0)			3.1
Oleic acid (C18:1)			21.2
Linoleic acid (C18:2)			55.2
Linolenic acid			5.9
Other acids			6.1

[*] Calculated by difference.