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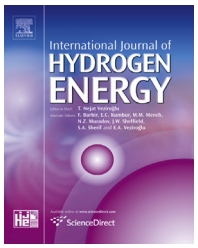

Production of hydrogen rich bio-oil derived syngas from co-gasification of bio-oil and waste engine oil as feedstock for lower alcohols synthesis in two-stage bed reactor

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ABSTRACT

High efficient production of lower alcohols (C_1–C_5 mixed alcohols) from hydrogen rich bio-oil derived syngas was achieved in this work. A non-catalytic partial oxidation (NPOX) gasification technology was successfully applied in the production and conditioning of bio-oil derived syngas using bio-oil (BO) and emulsifying waste engine oil (EWEO) as feedstock. The effects of water addition and feedstock composition on the gasification performances were investigated. When the BO_{20} and $EWEO_{30}$ was mixed with mass ratio of 1: 0.33, the maximum hydrogen yield of 93.7% with carbon conversion of 96.7% was obtained, and the hydrogen rich bio-oil derived syngas was effectively produced. Furthermore, a two-stage bed reactor was applied in the downstream process of lower alcohols synthesis from hydrogen rich bio-oil derived syngas ($H_2/CO/CO_2/CH_4/N_2$ = 52.2/19.5/3.0/9.4/15.9, v/v). The highest carbon conversion of 42.5% and the maximum alcohol yield of 0.18 kg/kg_{cat} h with selectivity of 53.8 wt% were obtained over the $Cu/ZnO/Al_2O_3(2.5)//Cu_{25}Fe_{22}Co_3K_3/SiO_2(2.5)$ catalyst combination system. The mechanism and evaluation for lower alcohols synthesis from model bio-oil derived syngas and model mixture gas were also discussed. The integrative process of hydrogen rich bio-oil derived syngas production and downstream lower alcohols synthesis, potentially providing a promising route for the conversion of organic wastes into high performance fuels and high value-added chemicals.

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Introduction

Lower alcohols (C_1–C_5 mixed alcohols) synthesis has been developed for decades. They are extensively produced using syngas (a fuel gas mixture consisting primarily of hydrogen, carbon monoxide, and very often some carbon dioxide, which can be generated from coal, natural gas, biomass, etc. [1]) as feedstock. As a potential alternative fuel/additive or chemical raw materials, the lower alcohols have many advantages including complete combustion, higher octane numbers, lower toxic exhaust gas (CO, NO_x) emission, excellent substitute for methyl *tert*-butyl ether (MTBE) and higher added value [2,3]. So the catalytic conversion of syngas to lower alcohols is now attracting renewed attention for both industrial application and fundamental research. At present, many researches and reviews about lower alcohols synthesis have been reported with regard to catalyst exploration, reaction mechanism, kinetics study, etc. [3–7]. However, there are limited studies investigating the synthesis of lower alcohols using biomass as feedstock [8].

Biomass is the sole carbonaceous renewable energy which can be directly converted into fuels and chemicals by thermal-chemical technologies [9–11], such as pyrolysis to bio-oil (BO) [12–14] and gasification to bio-syngas [15–17]. The bio-syngas derived from biomass gasification generally contains gas components (H_2, CO and CO_2 with similar fraction), tar and undesirable contaminants like alkali compounds [17]. Furthermore, because of the disadvantages of biomass, such as variable composition, wide geographical dispersion and low energy density, the direct gasification of biomass would not be suitable for a large-scale bio-fuels production. In contrast, the bio-syngas derived from BO gasification by steam reforming or partial oxidation has a better application prospect [18]. The liquid bio-oil can be continuously supplied under pressure through oil pump, and the problem of slag draining resulted from ash melting doesn't exist. Therefore, it is essential to precondition biomass into BO before gasification to bio-syngas in the future energy system [19].

On the other hand, a great deal of waste engine oil (WEO) is generated from machinery, chemical and transportation industry in China every year. The WEO with high carbon content, well thermal conductivity and fine hydrogen production ability, also is a potential source of high-value fuel and chemical feedstock [20]. At present, most of WEOs are refined into new lubricating oil or burned in special furnaces to heat buildings after processing. However, these methods are leading to a major environmental concern due to produced SO_2 and NO_x during combustion and residual heavy metal compounds after combustion. Pyrolysis technologies, such as electric resistance and electric arc heated pyrolysis [21], microwave-heated pyrolysis [20,22,23], have recently shown promise as an economic and environmentally friendly method to disposal of WEO, which can produce pyrolysis oils, incondensable gases and char. Lam et al. [23] studied the microwave-heated pyrolysis of WEO. It was found that the reclaimed gas (41 wt% yield) contained significant amount of light aliphatic hydrocarbons (65–86 vol.%) which was mainly composed of C_1–C_6 alkenes and valuable gases (13–35 vol.% of syngas) that could be reformed to produce hydrogen.

Recent years, the non-catalytic partial oxidation (NPOX) technology has been applied in the conversion of methane, natural gas, coke oven gas, coal, heavy oil, etc. However, only a few of works about the conversion of whole bio-oil to syngas by NPOX are reported [24,25]. Marda et al. [24] developed a system for the volatilization and conversion of bio-oil mixed with methanol to syngas through NPOX using an ultrasonic nozzle to feed the mixture. For lower alcohols synthesis and Fischer–Tropsch (F–T) synthesis processes, the syngas is preferable when the H_2/CO ratio is above than 2.0 and $H_2/(2CO + 3CO_2)$ ratio is slightly greater than 1.0 [26]. Generally, crude bio-oil derived syngas includes a mount of CO_2, thus resulting in higher CO_2/CO ratio and lower $H_2/(CO + CO_2)$ ratio [27]. In order to effectively adjust the composition of crude bio-oil derived syngas, different technologies have been adopted in the downstream process, such as methane reforming, Water–gas shift (WGS) reaction and CO_2 removal by chemical or physical absorption. Xu et al. [28] developed a novel approach for high efficient conversion of the CO_2-rich bio-syngas into the CO-rich bio-syngas by reaction of CO_2 with biomass char over Ni/Al_2O_3 catalyst. In the present work, BO mixing with WEO was used as feedstock during the NOPX gasification process so as to obtain hydrogen rich bio-oil derived syngas with high yield and desirable composition ($H_2/CO > 2.0$ and $H_2/(2CO + 3CO_2) > 1.0$) for lower alcohols synthesis.

According to the catalytic reaction mechanism and product distribution, catalyst for lower alcohols synthesis from syngas ($H_2/CO/CO_2$) can be classified as (1) modified methanol synthesis catalysts applied to produce methanol and branch alcohols and (2) modified F–T synthesis catalysts used to produce linear alcohols with small amounts of branched alcohols [3]. Our previous study indicated that the catalyst $Cu_{25}Fe_{22}Co_3K_3/SiO_2$ (simplified as $Cu_{25}Fe_{22}Co_3K_3$) showed the highest activity and space-time yield (STY) of C_{2+} alcohols [29]. As we all known, the $Cu/ZnO/Al_2O_3$ catalyst is a typical methanol synthesis catalyst, which has been widely applied in industrial processes at elevated pressures (5–10 MPa) and temperatures (200–300 °C) [30]. In order to increase the conversion of CO, the yield and selectivity of lower alcohols, a two-stage bed catalyst combination system of $Cu_{25}Fe_{22}Co_3K_3$ and $Cu_{4.5}Zn_{4.5}Al_1$ (screened $Cu/ZnO/Al_2O_3$ catalyst with Cu/Zn/Al mole ratio of 4.5/4.5/1, and simplified as $Cu_{4.5}Zn_{4.5}Al_1$) was explored by our group [31]. The demonstrated thermal coupling reaction condition by lumped kinetics study over the catalyst combination system with the optimal loading volume ratio of 2.5/2.5 was $T = 280$ °C, $P = 5.5$ MPa and gas hourly space velocity (GHSV) = 2800 h^{-1}. In this work, lower alcohols was produced from hydrogen rich bio-oil derived syngas over the two-stage bed catalyst combination system of $Cu_{25}Fe_{22}Co_3K_3$ and $Cu_{4.5}Zn_{4.5}Al_1$ under their thermal coupling reaction conditions. The mechanism and evaluation for lower alcohols synthesis from model bio-oil derived syngas and model mixture gas were also studied.

Experimental method

Feedstock and catalyst

The BO (obtained from Renewable Clean Energy Laboratory, University of Science and Technology of China) was