Energy Conversion and Management 171 (2018) 211–221

Contents lists available at ScienceDirect

Energy Conversion and Management

journal homepage: www.elsevier.com/locate/enconman

Direct conversion of simulated propene-rich bio-syngas to liquid iso-hydrocarbons via FT-oligomerization integrated catalytic process

Qian Zhang[a,b,c,d], Tiejun Wang[a,b,c], Yujing Weng[a,b,c,d], Huiyan Zhang[e], Tharapong Vitidsant[f], Yuping Li[a,b,c], Qi Zhang[a,b,c], Rui Xiao[e], Chenguang Wang[a,b,c,*], Longlong Ma[a,b,c,*]

[a] *Guangzhou Institute of Energy Conversion, Chinese Academy of Sciences, Nengyuan Road No. 2, Guangzhou, PR China*
[b] *CAS Key Laboratory of Renewable Energy, Nengyuan Road No. 2, Guangzhou, PR China*
[c] *Guangdong Provincial Key Laboratory of New and Renewable Energy Research and Development, Nengyuan Road No. 2, Guangzhou, PR China;*
[d] *University of Chinese Academy of Sciences, Beijing 100049, PR China*
[e] *Ministry of Education of Key Laboratory of Energy Thermal Conversion and Control, School of Energy and Environment, Southeast University, Nanjing 210096, PR China*
[f] *Department of Chemical Technology, Faculty of Science, Chulalongkorn University, Bangkok 10330, Thailand*

ARTICLE INFO

Keywords:
FT-Oli
Biomass
Bio-syngas
Fischer-Tropsch synthesis (FTS)
Oligomerization
Isomerized hydrocarbon

ABSTRACT

The bio-syngas formed from the catalytic cracking of bio-oil include two types of useful components which are light olefin and H_2, CO. The integration of FTS and olefinic polymerization seems potential way for the production of hydrocarbon bio-fuels while fully utilizing the olefin-rich bio-syngas. This work aimed to develop an integrated process for the production of liquid hydrocarbons directly from the olefin-rich bio-syngas through a one-stage process, which included the synthesis of liquid hydrocarbons via the oligomerization of light olefin over HZSM-5 along with the FT (Fischer-Tropsch) synthesis of H_2, CO over FeMn catalyst. A series of integration configuration composed of Fe-based catalyst (FeMn) and acidic zeolite (HZSM-5) were investigated, it was found that the undesired hydrogenation of lower olefin on the nearby metal active site seems greatly affected the yield of C5+ . More significantly, the proximity of the two active components plays a crucial role in suppressing the undesired hydrogenation reaction and contributing to the high selectivity of liquid hydrocarbons. The optimal catalytic performance yields a high selectivity to gasoline-range hydrocarbons (87.3%) with excellent low olefin hydrogenation selectivity (7.4%). Meanwhile, the obtained gasoline-range hydrocarbon showed high degree of isomerization. The integrated transformation process potentially provides an alternative way for the production of gasoline range isomerized hydrocarbon fuels using olefin-rich bio-syngas.

1. Introduction

Recent years, there is a world-wide attention on the gradual depletion of fossil fuel resources and the deteriorating environmental problems [1,2]. To alleviate these problems, the production of liquid fuels from renewable resources has received widespread attention [3]. Biomass, as an extensive carbon-containing renewable resource, has attracted great attention [4,5]. Besides, utilization of biomass resource also provides an alternative route to valuable bio-fuels and chemicals [6,7].

The route of biomass conversion is promising and is receiving more and more attention as it is a renewable, environmentally benign, and low-cost strategy compared with the conventional energy production. Among the pathways of biomass conversion, the biomass-to-liquid (BTL) process is a key technology from biomass to hydrocarbon liquid fuels. In general, the core of the BTL process is syngas (CO and H_2) production and transformation which comprise a series of steps, such as gasification of biomass, gas cleaning and compression, Fischer-Tropsch synthesis (FTS), hydrocracking [8], etc. Traditionally, the FTS is a promising way to convert syngas into hydrocarbons with wide range and high value-added chemicals that can be utilized as alternatives to petroleum products [9–11]. However, the FT process has two unfavorable dis-advantages, namely nonselective product distribution controlled by Anderson-Schulz-Flory (ASF) polymerization kinetics and its product are mainly linear hydrocarbons with low octane value [12]. In recent years, the production of isoparaffin-rich hydrocarbons has drawn a lot of attention for its advantages in high-octane value fuel. Lots of investigations have been made to obtain iso-paraffin by adopting catalyst with FT active metal dispersed on acidic supports such as acidic zeolite or other [13,12]. Unfortunately, low catalytic activity and severe methanation acquired, which ascribed to the extremely low reduction degree of active metal due to the strong

---

* Corresponding authors at: Guangzhou Institute of Energy Conversion, Chinese Academy of Sciences, Nengyuan Road No. 2, Guangzhou, PR China.
E-mail addresses: wangcg@ms.giec.ac.cn (C. Wang), mall@ms.giec.ac.cn (L. Ma).

https://doi.org/10.1016/j.enconman.2018.05.057
Received 6 February 2018; Received in revised form 27 April 2018; Accepted 16 May 2018

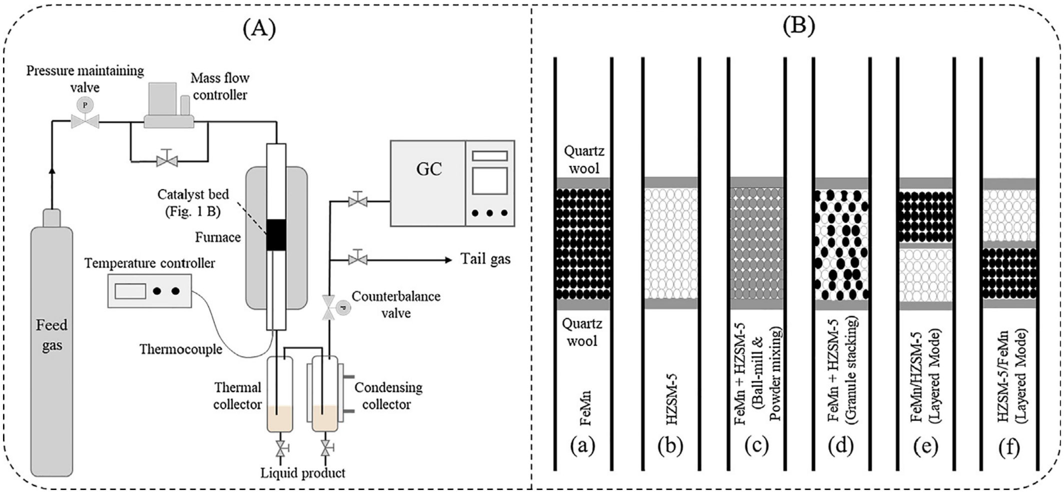

Fig. 1. Schematic experimental setup of the fixed-bed flowing reactor system for FT & Oli catalytic process (A) and different manners of the active components (B): (a) FT process on FeMn catalyst, (b) Oli process on HZSM-5 catalyst, (c) FT-Oli process on FeMn/HZSM-5-B or FeMn/HZSM-5-M (Ball-milling or Power-mixing configuration), (d) FT-Oli process on FeMn/HZSM-5-GS (Granule stacking configuration) and (e,f) FT-Oli process on FeMn/HZSM-5 or HZSM-5/FeMn (Dual-bed configuration).

interaction between the metal and support [14].

Nowadays, the olefin-rich bio-syngas was widely investigated as it can be obtained from biomass-derived bio-oil. Bio-oil is convenient for transportation and storage, its refining equipment also could share by using already existent petroleum refining infrastructures [15]. Recent researches indicated that the catalytic cracking of bio-oil could conveniently produce bio-syngas, which mainly contain C2-C4$^{=}$ light olefins, H_2, CO, CO_2, CH_4, and other gas alkanes [16–19,27]. In general, this kind of bio-syngas is able to prepare the liquid hydrocarbon through olefinic polymerization process according to our previous work [20,26]. Moreover, bio-syngas obtained from the catalytic cracking of bio-oil provides another useful carbon component which is CO.

Here, the oligomerization of light olefin in bio-syngas is considered a significant route to produce synthetic liquid fuels [21]. Meanwhile, the synthesis fuel produced from olefins oligomerization usually showed high degree of isomerization which contribute to the high-octane rating. It also can be potential used as engine fuels as its advantage in free of sulfur and other harmful impurities [22,23]. Therefore, considering the useful carbon resource of both light olefin and H_2, CO in bio-syngas, the combination of FTS and olefinic polymerization seems to provide a potential way to effectively transfer the available carbon resource in bio-syngas. Besides, the light olefin produced from FTS process can be reutilized thought the olefinic polymerization process during the coupling process. Therefore, the integration of FTS and olefinic polymerization for the conversion of bio-syngas seems to be a potential way for high yield of liquid fuels, and realize the anti-ASF product distribution as well as fully utilizing the useful carbon resource. So far, there are many reports about the production of the liquid fuels by FTS or olefin polymerization respectively [17,24–27], and the tandem process of oligomerization and FTS was also studied [46]. Nevertheless, the systematic study of FT-Oligomerization integrated catalytic process were rarely investigated so far.

With the excellent activity of water gas shift (WGS) reaction in FTS processes, Fe-based catalyst has drawn great attention in the hydrogen-poor environment. That makes Fe-based catalyst a desirable catalyst for the direct integrated process. Moreover, Mn-promoter is usually adopted as an efficient promoter for Fe-based catalyst due to its ability of improving the dispersion of Fe particles [28,29]. And it's also believed play an important role as the electron transfer or electronic interaction promoter to modify the electronic character of Fe active phases [30], which contribute to the high FTS activity associate with the enhanced absorption of CO. As for the oligomerization, HZSM-5 is considered a preferred choice of acidic catalyst for the integrated process due to its following advantages: its shape-selective property that limits the formation of heavy hydrocarbons, and its high acidity property that favorable for the acid catalyzed oligomerization process. Therefore, the combination of Mn-promoted Fe catalyst and acidic HZSM-5 catalyst was adopted for the direct integrated process in this work.

In this work, the FT-Oli integrated catalytic process for producing branched liquid hydrocarbons from olefin-rich bio-syngas was investigated, which contain the synthesis of liquid hydrocarbons via Fischer-Tropsch process over FeMn catalyst and the oligomerization of light olefin over HZSM-5. Here, several integration manners of the FT and oligomerization catalysts were adopted to further investigate the integration process. The present integrated catalytic process provides a potential approach for the production of branched-rich hydrocarbon fuels from bio-syngas.

2. Experimental

2.1. Feed gas

On the basis of the previous researches, the bio-oil can be catalytically converted to olefins-rich bio-syngas with typical composition of C2-4$^{=}$/CO/H_2/other gas = 30/30/10/30 (in volume ratio). Meanwhile, nearly complete conversion of bio-oil and olefins yield about 43.8 C-mol% were achieved. In this work, in order to further investigate the FT and oligomerization integrated process, the syngas is supposed to be more simplified and representative. Therefore, the simulate olefin-rich syngas (model gas) with the composition of C_3H_6/CO/H_2/N_2 = 20/30/10/40 was employed for the experiment, which contains two useful components: light olefin and H_2, CO.

2.2. Catalyst preparation

Here, the HZSM-5 with a Si:Al molar ratio of 20 was purchased from Nankai catalyst Co. Ltd. The FeMn catalyst with Fe/Mn molar ratio of 2:1 was prepared by a co-precipitation method. See the Supporting Information for preparation details.

For the preparation of composite catalysts shown in Fig. 1c, FeMn and HZSM-5 powder with same mass were evenly mixed together by stirring, followed by pressurizing to a self-supported block by the hydraulic tablet machine, then crushing and finally sieving to the range of 40–60 mesh. The obtained catalyst was denoted as FeMn/HZSM-5-M. Another composite catalyst was prepared by a ball-milling technique.