Chemical Engineering Science 105 (2014) 1–11

Contents lists available at ScienceDirect

Chemical Engineering Science

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

Fischer–Tropsch synthesis in a bench-scale two-stage multitubular fixed-bed reactor: Simulation and enhancement in conversion and diesel selectivity

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HIGHLIGHTS

- A process based on a two-stage multitubular fixed-bed reactor is presented for Fischer–Tropsch synthesis (FTS).
- A two-dimensional pseudohomogeneous reactor model is proposed for bench-scale FTS.
- The two-stage multitubular fixed-bed process increases CO conversion, diesel range selectivity and stability.
- The simulations demonstrate the understandable enhanced CO conversion and products distribution shift toward diesel-range hydrocarbon.
- We suggest a novel method of improving products distribution and increasing carbon efficiency by multi-stage short reactor rather than one long reactor for FTS.

ARTICLE INFO

Article history:
Received 11 July 2013
Accepted 23 September 2013
Available online 14 October 2013

Keywords:
Fischer–Tropsch synthesis
Two-stage fixed-bed reactor
Bench-scale
Pseudohomogeneous reactor model
Simulation
Conversion and selectivity control

ABSTRACT

A process based on a two-stage multitubular fixed-bed reactor is presented to enhance in conversion and diesel selectivity for the Fischer–Tropsch synthesis (FTS) process, which is characterized by the condensation and separation of liquid products and water from the outlet of the first-stage reactor. A two-dimensional pseudohomogeneous reactor model is proposed to simulate the temperature profile and CO conversion of the two-stage fixed-bed process. Model calculations indicate that the condensation and separation of liquid products and water between the two stages of the multitubular fixed-bed reactor plays an important role by changing temperature profile and synthesis gas partial pressure of the second-stage reactor. The model validation has been verified on the basis of the bench-scale test data in a single-stage and two-stage fixed-bed reactor, respectively, which demonstrates the understandable products distribution shift toward diesel-range hydrocarbon. The combined action of higher temperature, syngas/H_2 partial pressure and readsorption of olefins at the two-stage fixed-bed reactor make CO conversion and C_{5+} selectivity increase, while CH_4 and CO_2 selectivity keep decreasing trends. Compared with the single-stage fixed-bed reactor process, the total CO conversion increases from 79% to 89% in the two-stage fixed-bed reactor process. The high valuable diesel range (C_{12}–C_{22}) increases significantly from 67% to 78%, while the gasoline range (C_5–C_{11}) decreases from 27% to 18%. The catalysts exhibit more stability and less deactivation rate over the two-stage fixed-bed process. The results are helpful to obtain more valuable diesel products and effective utilization of the syngas by the multi-stage fixed-bed process without tail gas recycling, which provides a practical case for multi-stage short reactor rather than one long reactor for FTS to improve products distribution.

1. Introduction

The low temperature Fischer–Tropsch synthesis (FTS) is considered nowadays the most promising route for environmentally sound production of transportation fuels and chemical feedstocks from natural gas, coal and biomasses (Bae et al., 2011; dela Osa et al., 2012; Zhang et al., 2010). In recent years, the availability of cheap natural gas and raw materials like coal and biomass has given momentum to FTS. The capacities will increase in the near future with natural gas favoured as feedstock, and around 2015 the global annual production rate of fuels via FTS will be about 30 million tons, mostly produced in countries like South Africa, Malaysia, and Qatar (Jess and Kern, 2012).

It is believed that the major impediment of the GTL popularization via FTS is the economical feasibility, which is related to the productivity, lifespan and CH_4 selectivity of catalysts besides the

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0009-2509/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.ces.2013.09.057

price of natural gas. In this respect, the manufacture of syngas is by far the most capital-intensive part of a gas conversion plant. Therefore, the FTS unit should focus on utilizing syngas as efficiently as possible, and selectivity considerations are then extremely important in the design of the FTS section, which is of industrial interest (Geerlings et al., 1999; Lira, et al., 2008; dela Osa et al., 2012; Teiseh et al., 2012). The present emphasis has shifted towards maximizing the yield of high-cetane diesel products from the FTS process, which is virtually free of sulfur and aromatic compounds, low particulate and NOx emissions (Bermúdez et al., 2011; Szeto et al., 2012). Due to its high activity, high C_{5+} hydrocarbons selectivity, lower activity for the water-gas shift (WGS) reaction and long life, cobalt-based catalyst is currently the catalyst of choice for the conversion of syngas to liquid fuels (Sadeqzadeh et al., 2012; Wang et al., 2013; Zhang et al., 2005). The highly exothermic nature of the FT reaction combined with the high activity of the Co catalyst makes the removal of heat from the reactor of critical importance, because the local reaction temperature is critical in controlling the process selectivity as the unwanted methanation reaction becomes dominant at high temperatures, while moderate temperatures are crucial to extend the catalyst life time and prevent thermal runaways. Therefore, the effectiveness of heat transfer determines the temperature profile of the reactor and catalyst particle. Various types of reactors, including fixed bed, fluidized bed and slurry phase, are used to efficiently remove the reaction heat by FT reaction, but fixed-bed reactor process remains an attractive approach because it has the highest volumetric catalyst loading volume (catalyst loading/reactor volume), the highest potential of productivity (Davis, 2005; Mazidi et al., 2013). Moreover, it doesnot require separating the catalyst from the products and is easy to scale up from a single tube test (Yang et al., 2010), which has been persuasively exemplified by the large-scale commercial operations of Sasol and Shell (Dry, 1996; Sie, 1998). In multitubular fixed-bed reactor, a large amount of reaction heat is generated at the entrance of the catalyst bed, where the reactant partial pressures and temperature rapidly declined due to increased water partial pressure (Raq et al., 2011; Sharma et al., 2011; Kölbel, 1959; Wang et al., 2003). To remove the reaction heat and increase the syngas conversion, the multitubular fixed-bed reactor contains many tubes filled with catalyst immersed in boiling water for heat removal, or a considerable fraction of the liquid reaction products has to be recycled to the fixed reactor, which increases pressure drops and makes the reactor more tricky to be operated and less flexible to be scaled up (Jess and Kern, 2009; Sie and Krishna, 1999). Another disadvantage in fixed-bed multitubular reactors is low catalyst utilization (Wu et al., 2010). It is vitally necessary to maximize the products value for diesel distillate and carbon utilization efficiency with rising energy and raw material prices. In FTS, water is the major byproduct. Many researchers have investigated its effects on the catalyst performances in various reaction systems. The water may affect the syngas conversion, hydrocarbon selectivity, product distribution and catalyst longevity by changing syngas adsorption, chain initiation, chain growth, methanation, hydrogenation to paraffins and dehydrogenation to olefins (Dalai and Davis, 2008). The effect of water on the activity of cobalt catalysts depends on catalyst composition, nature of the support, catalyst preparation method and pretreatment. The water effects are reported to be either negligible (Huber et al., 2001), negative (Rahimpour et al., 2011a, 2011b; Bezemer et al., 2010), or positive (Lualdi et al., 2011; Bertole et al., 2002). The negative is linked to the formation of inactive oxides of cobalt or the formation of irreducible cobalt support compounds. Furthermore, water and heavy hydrocarbons are main sources of catalyst deactivation (Bezemer et al., 2010; Zhang et al., 2006; Van Berge et al., 2000). It is well known that the catalyst deactivation is not significant at low partial pressures of water, but a much more rapid decrease in conversion can be observed in the presence of more significant amounts of water, because it increases the CoO surface coverage and leads to a more severe sintering. Sadeqzadeh et al. (2012) confirmed the absolute water pressure increase in the reactor and the high P_{H_2O}/P_{H_2} ratio will enhance cobalt sintering. Therefore, keeping the P_{H_2O}/p_{H_2} below its critical value by removing the water may enhance the catalyst lifetime significantly.

Herein, to maximize reactor volume productivity, a process based on a two-stage multitubular fixed-bed reactor is presented to enhance CO conversion and diesel production from FTS, which is characterized by the condensation and separation of liquid products and water from the outlet of the first-stage reactor. A two-dimensional pseudohomogeneous reactor model is proposed to simulate the temperature profiles and CO conversion profiles of the two-stage multitubular fixed-bed reactor process, which demonstrates the understandable products distribution shift toward diesel-range hydrocarbon. The process is investigated in a bench-scale single-stage and two-stage multitubular fixed-bed reactor using cobalt-based catalyst. The results are helpful to obtain more valuable diesel products and effective utilization of syngas by simple multi-stage multitubular fixed-bed process, which provide a practical case for multi-stage short reactor rather than one long reactor for FTS to improve products distribution, as well as increase the carbon efficiency.

2. Experimental section

2.1. Material preparation

2.1.1. Preparation of Al_2O_3-modified SiO_2 support

The SiO_2 support (Qingdao Haiyang Chemical Co., average particle size Ø 3.2 mm) was soaked with 0.05 mol/L HNO_3 for 3 h by slowly stirring, and washed three times with distilled water. Then the resulting SiO_2 support was dried at 373 K for 10 h, followed by calcining at 873 K for 5 h. The pretreated SiO_2 support was modified with calculated amounts of $Al(NO_3)_3$ $9H_2O$ by incipient wetness impregnation, and dried at 323 K for 24 h and at 373 K for 12 h, then calcined at 873 K for 8 h.

2.1.2. Preparation of ZrO_2 promoted Co_3O_4/Al_2O_3–SiO_2 catalyst

The resulting Al_2O_3-modified SiO_2 was used as support, and prepared by the incipient wetness co-impregnation method with an aqueous solution of $Co(NO_3)_2$ $6H_2O$ and $ZrO(NO_3)_2$ $6H_2O$ (Industrial products, Shandong Zibo Zhaoyi Chemical Co.) for 24 h, followed by drying at 313 K for 10 h, and at 383 K for 2 h, then calcined at 723 K for 10 h.

2.2. Material characterization

2.2.1. X-ray diffraction characterization

The crystal structures were determined by a powder X-ray diffractometer (Shimadzu XRD 6000), using Cu Kα radiation ($\lambda = 1.54184$ Å) combined with a nickel filter operating at 40 kV and 10 mA. The diffractometer data were recorded for 2θ values between 10° and 90° with a scanning rate of 4deg/min.

2.2.2. Surface area and pore volume

Nitrogen adsorption/desorption was measured by using a Micromeritics, ASAP 2405N analyzer at −196 °C in liquid nitrogen. Prior to N_2 sorption measurements, the samples were degassed at 250 °C, under vacuum, for at least 16 h. The Brunauer–Emmett–Teller (BET) surface area was calculated using experimental points at a relative pressure of $P/P_0 = 0.05$–0.30. The pore size distribution