Fuel Processing Technology 91 (2010) 1839–1844

Contents lists available at ScienceDirect

Fuel Processing Technology

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

Investigation of Fischer–Tropsch synthesis performance and its intrinsic reaction behavior in a bench scale slurry bubble column reactor

Heon Jung, Jung-Il Yang *, Jung Hoon Yang, Ho-Tae Lee, Dong Hyun Chun, Hak-Joo Kim

Clean Fossil Energy Research Center, Korea Institute of Energy Research, Daejeon 305-343, Korea

ARTICLE INFO

Article history:
Received 9 March 2010
Received in revised form 23 July 2010
Accepted 6 August 2010

Keywords:
Fischer–Tropsch synthesis
Bench scale
Slurry bubble column reactor
Space velocity
Superficial velocity
Reaction temperature

ABSTRACT

A bench scale slurry bubble column reactor (SBCR) with active-Fe based catalyst was developed for the Fischer–Tropsch synthesis (FTS) reaction. Considering the highly exothermic reaction heat generated in the bench scale SBCR, an effective cooling system was devised consisting of a U-type dip tube submerged in the reactor. Also, the physical and chemical properties of the catalyst were controlled so as to achieve high activity for the CO conversion and liquid oil (C_{5+}) production. Firstly, the FTS performance of the $FeCuK/SiO_2$ catalyst in the SBCR under reaction conditions of 265 °C, 2.5 MPa, and $H_2/CO = 1$ was investigated. The CO conversion and liquid oil (C_{5+}) productivity in the reaction were 88.6% and 0.226 g/g_{cat}-h, respectively, corresponding to a liquid oil (C_{5+}) production rate of 0.03 bbl/day. To investigate the FTS reaction behavior in the bench scale SBCR, the effects of the space velocity and superficial velocity of the synthesis gas and reaction temperature were also studied. The liquid oil production rate increased up to 0.057 bbl/day with increasing space velocity from 2.61 to 3.92 SL/h-g_{Fe} and it was confirmed that the SBCR bench system developed in this research precisely simulated the FTS reaction behavior reported in the small scale slurry reactor.

1. Introduction

Synthetic fuels produced by the Fischer–Tropsch synthesis (FTS) process are a realistic alternative to replace conventional oils. Thus, the need for the FTS technology is globally on the rise. However, only a limited number of companies are available to supply the commercial FTS technology. This technology barrier has spurred many institutions on to development efforts of FTS technology. Among them, Chinese company has been very active in proving their FTS technology to a demonstration scale of 3500 bbl/day [1].

In the FTS reaction, the slurry bubble column reactor (SBCR) and multi tubular fixed-bed reactor (FBR) are currently used in industry. The advantages and disadvantages of SBCR and FBR technologies in the FTS reaction are summarized in Table 1 [2]. Sasol began the development of an iron (Fe)-based SBCR and, after a 10-year research program, a semi-commercial scale SBCR with a capacity of 2500 bbl/day was put into operation at Sasol in 1993 [3]. Especially, in the FTS reaction, the commercialization of slurry phase reactor technology was made possible by the development of Sasol's intrinsic solution for catalyst/wax separation. Shell started to develop the Shell Middle Distillate Synthesis (SMDS) process in 1973 using an FBR with cobalt (Co) catalysts and began building a plant with a capacity of 12,500 bbl/day in Bintulu, Malaysia, which was finally commissioned in 1993 [4].

The metals, Fe, Ni, Co, and Ru, have Fischer–Tropsch synthesis activity [5], but only Fe and Co catalysts are in industrial use, as described above. Fe and Co catalysts share similarities in the FTS reaction, being very active and producing a broad range of straight chain hydrocarbons [6]. Furthermore, the product distribution afforded by these catalysts follows the ASF distribution. However, Fe and Co catalysts are also quite different in many respects. Fe catalysts are active in the form of Fe carbides, whereas the active form of Co catalysts is Co metal. Also, from the point of view of the technological preferences, a precipitated Fe catalyst is preferable to a slurry bed reactor with a synthesis gas (H_2/CO) ratio of 2/3, mainly due to its low cost, high tolerance to contaminants, and water-gas shift reaction activity, but a supported Co catalyst is more suitable for a fixed-bed reactor with a synthesis gas ratio of 2/1, mostly because of its high cost, high activity, and long catalyst life (i.e., the lifetime of Co is 10 times that of Fe) [7]. Furthermore, the amount of S compounds in the synthesis gas feed for both Fe and Co catalysts has to be very low, but Co catalysts require an additional step for the purpose of lowering the S contaminant level from the low 100's ppb (e.g., ~200 ppb) for Fe catalysts to the low 10's ppb (e.g., ~20 ppb) [7].

CTL/GTL processes utilize 3 distinct steps to convert coal or natural gas into synthetic transport fuels, viz. synthesis gas generation, the Fischer–Tropsch synthesis reaction, and product upgrading [8]. As a key step in the CTL process, the Fischer–Tropsch synthesis reaction that converts the synthesis gas generated by coal gasification into

---

* Corresponding author. Tel.: +82 42 860 3795; fax: +82 42 860 3134.
E-mail address: yangji@kier.re.kr (J.-I. Yang).

0378-3820/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.fuproc.2010.08.008

Table 1
Advantages (+) and disadvantages (−) of SBCR and FBR technologies in FTS reaction (partly from [2]).

	SBCR	FBR
Catalyst effective factor	+ (close to unity)	− (below unity)
Catalyst pore diffusion	+	−
Catalyst content in reactor	−	+
Catalyst concentration gradient	−	+
Gas-liquid mass transfer	−	+
Isothermal behavior	+	−
Catalyst exchange	+	−
Catalyst attrition	−	+
Mixing behavior	+	−
Distribution of reactants	+	−
Liquid-solid separation	−	+
Gas-liquid separation	−[a]	+
Scale-up	−	+
Reactor costs	+	−

[a] Foam formation in a slurry bubble column reactor.

liquid oil continues to be an important research field. Therefore, in this study, a highly effective FTS reaction system was developed, consisting of an SBCR with Fe catalyst, for CTL applications. Especially, a bench scale SBCR with active Fe-based catalyst was invented and the liquid oil (C_{5+}) productivity in the FTS reaction was evaluated. Furthermore, the FTS reaction behavior in the bench scale SBCR was investigated as a function of the space velocity and superficial velocity of the synthesis gas and reaction temperature.

2. Experimental

2.1. Catalysts

A catalyst with a nominal composition of 100Fe/5Cu/5 K/18SiO_2 (in parts per weight) was prepared by the conventional co-precipitation technique (FeCuK/SiO_2). In brief, the requisite amount of a SiO_2 suspension was added to a solution containing both $Fe(NO_3)_3$ and $Cu(NO_3)_2$ at the desired ratio. Then, the solution was precipitated at 80 ± 1 °C using a sodium carbonate solution until the pH reached 8.0 ± 0.1. The precipitate slurry was filtrated, washed with distilled water, and subsequently re-slurried in distilled water. After repeating the washing process several times, the filtrated cake was withdrawn and then dried at 95 °C for at least 8 h to completely remove the residual moisture. The dried precipitate was crushed and sieved to less than 75 μm (200 mesh), and the requisite amount of K_2CO_3 solution was added via the incipient wetness pore-filling technique. The final precipitate powder was calcined in air at 400 °C for 8 h. A commercial catalyst was also provided for the sake of comparing the FTS performance of the two catalysts.

Prior to the FTS reaction, 720 g of fresh catalyst was loaded in the reactor and suspended in 2880 g of liquid paraffin (Mineral oil, Aldrich Co.). Thus, the concentration of the catalyst in the slurry was fixed at 20 wt.% and the catalyst was activated *in-situ* in the slurry phase. The catalysts were activated using an *in-situ* reduction procedure with a flow rate of synthesis gas ($H_2/CO = 1$) of 3.0 l/min at 0.1 MPa and 265 °C for 25 h.

The surface area, pore size, and pore volume of the FeCuK/SiO_2 and commercial catalysts were measured by BET using a Micromeritics 2010 system. The results are summarized at Table 2. The surface basicities of the catalysts were analyzed by means of temperature-programmed desorption using CO_2 as an adsorbent (CO_2-TPD). The catalysts were heated up to 400 °C for several tens of minutes until the TCD baseline leveled off. After cooling the catalysts to 50 °C, CO_2 was introduced into the sample cell for 30 min, followed by purging with He for 1 h to remove the weakly adsorbed species. The CO_2-TPD was carried out at temperature of up to 400 °C in flowing He at a heating rate of 2 °C/min.

Table 2
The physical properties of the FeCuK/SiO_2 and commercial catalysts.

Catalyst	BET surface area/$m^2 \cdot g^{-1}$	*Ave.* Pore diameter / Å	*Ave.* Pore volume / $cm^3 \cdot g^{-1}$
FeCuK/SiO_2	181	82	0.369
Commercial	195	55	0.268

2.2. Reaction system

The FTS reaction was carried out in a stainless steel bubble column reactor (0.05 m in diameter and 2.5 m in height with an effective volume of 3.6 *l*) equipped with a sintered metal filter to allow the removal of waxy products from the reactor. The filtered wax was collected in a wax reservoir. A schematic diagram of the experimental apparatus is shown in Fig. 1. The level of the slurry in the reactor was continuously monitored by measuring the temperature across the height of the reactor. As the level of slurry within the reactor went up due to the formation of waxy products in the slurry during the FTS, these waxy products were regularly sampled from the filter depending on the level of slurry and the maximum level in the reactor remained near the top of the reactor, as shown in Fig. 1.

The reactor temperature was controlled using 11 external jacket furnaces whose temperatures were automatically controlled by a PID controller (Hanyoung Science, Korea). To prevent the sudden increase of the reaction temperature during the FTS reaction, a cooler system consisting of a U-type dip tube submerged in the slurry was designed. Furthermore, considering the severe axial temperature gradient in the reactor, two U-type dip tubes were installed across the height of the reactor. Therefore, the reaction temperature was automatically controlled to the initial set point by allowing the coolant (cold water at 25 °C) to flow through the dip tube whenever there was a sudden increase of the reaction temperature caused by the severe exothermic reaction heat generated in the FTS. Prior to the FTS reaction, the bubble column reactor was charged with a slurry consisting of the catalyst and liquid paraffin using a slurry pump (BRAN + LUEBBE, Germany). The feed gas was preheated and then introduced into the reactor from the sparger placed at the bottom with a corresponding free plate area of 0.14%. The flow rate of the inlet gas was controlled and monitored using a pre-calibrated mass flow controller (MKP, Seoul, Korea). The vent gas was passed through a hot trap (150 °C) to separate the high-boiling products, and then a cold trap to collect the liquid products via a condenser maintained at 0 °C to condense the remaining liquid products. Finally, the flow rate of the tail gas was measured using a dry gas flow meter (Shinogawa, Tokyo, Japan). All instruments were connected to a PC via LabVIEW program (LabVIEW 7.1, NI Co.) to record the experimental data automatically and to precisely measure the FTS reaction behavior at each part.

2.3. Reactant and product analysis

The reactant and product gases in the FTS reaction were analyzed online by a gas chromatograph (DS6200; DONAM INSTRUMENTS, INC., Korea) equipped with a thermal conductivity detector (TCD) and a downstream flame ionization detector (FID). H_2, CO, CH_4, and CO_2 were analyzed with a stainless steel packed column (Carboxen-1000, 2 m × 0.3 mm) and a TCD. Also, hydrocarbons (C_2-C_4) were analyzed with a capillary column (GS-GasPro, 30 m × 0.32 mm) and an FID. The liquid product distribution was analyzed by the simulated distillation (SIMDIS) technique using the ASTM D2887 method and HPLC grade carbon disulfide (CS_2, 99.9 + %, Aldrich Co.) as the solvent. A calibration mix (C_5–C_{44}, Analytical Controls) and reference mix (140–400 °C, Analytical Controls) were used as calibration standards for the SIMDIS.