Hydrogenation of CO on supported cobalt γ-Al₂O₃ catalyst in fixed bed and slurry bubble column reactors

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Abstract−Fischer-Tropsch synthesis for the production of C_5+ hydrocarbons from syngas was carried out in a tubular fixed bed reactor (TFBR) and in a slurry bubble column reactor (SBCR). The Co-based catalysts for FTS were prepared by the conventional wet-impregnation of γ-Al₂O₃. Effects of operating conditions such as GHSV (1,000-4,000 ml/g·hr), reaction temperature (220-250 ºC) and pressure (0.5-3.0 MPa) on the CO conversion and product selectivity of Co/γ-Al₂O₃ catalyst were examined in the TFBR and SBCR. The C_5+ selectivity and olefin selectivity in an SBCR were found to be higher than that in a TFBR, whereas C_2-C_4 selectivity showed a reverse trend. The CO conversion and product distribution in an SBCR were less sensitive than that in a TFBR with variations of reaction conditions.

Key words: Fischer-Tropsch Synthesis, Tubular Fixed Bed Reactor, Slurry Bubble Column Reactor, Co Catalyst

INTRODUCTION

Increasing international oil prices and rapid development of the world economy have made the global energy and environmental problems increasingly serious. Thus, the development of technologies for producing clean fuel adopting gas-to-liquid (GTL) processes including Fischer-Tropsch synthesis (FTS), methanol synthesis and dimethyl ether (DME) synthesis is very important for the sustainable development of the economy and of the energy supply [1]. FTS has been recognized as an important alternate technology to petroleum refining in the production of liquid fuels and chemicals using syngas derived from gasification of coal (CTL), reforming of natural gas (GTL) and other carbon-containing materials (BTL, etc.) [2].

Reactors for FTS, including the multi-tubular fixed bed reactors (MTFBR) [3], fluidized bed reactors (FBR) [4,5], and slurry bubble column reactors (SBCR) [6,7], are different approaches selected to achieve temperature control, and to arrive at a better choice of the catalyst and reaction products. MTFBR is simple to operate and is able to operate under plug flow of gas phase. It can be used over wide temperature ranges irrespective of whether the FT products are gaseous or liquids, or both [8]. There is also no problem in separating liquid products from the catalyst and the scale-up is easy. Therefore, it is well suited for wax production. On the other hand, MTFBR is expensive to construct, but it has a high differential pressure over the reactor in the high gas flow rate and imparts temperature gradients in the axial directions. Also, since all FT catalysts loose activity with time on stream (TOS), they have to be replaced periodically.

Circulating fluidized bed reactors (CFBR, Synthol reactor) designed by Sasol for FT synthesis have performed very successfully. These reactors use iron-based catalysts of high densities to achieve the desired turbulent fluidization, but a high drag force is required, i.e., a high gas velocity has to be used. Although these reactors are complex to operate, due to high gas velocity, film diffusion limitations at both the particle surfaces and the heat exchanger walls are minimized. In addition, frequent direct physical contact between hot catalyst particles and the heat exchanger tube walls also significantly contributes to enhanced heat exchange. The combination of all these factors results in a much higher efficiency in heat exchange in fluidized beds as compared to fixed beds. This in turn means that less heat exchange area is required for fluidized bed reactors, which lowers the relative cost of the reactor. It is in any event cheaper to construct a large empty reactor vessel and then install cooling coils into it than to construct an equivalent capacity MTFBR [3].

Recently, SBCR has been considered for the advanced gas-to-liquid (GTL) process technology including FT synthesis. It has the advantage of simple construction and lower capital requirement for a large-scale slurry reactor, good performance in temperature control, feasibility for large capacity, lower pressure drop that considerably saves the compression cost, online removal and addition of catalyst and lower catalyst amount than the MTFBR due to high catalyst efficiency in a slurry reactor. As a result, there is a trend to shift from the fixed bed reactor to the slurry reactor in gas-to-liquid processes [9,10]. Although the SBCR for FT synthesis has a number of advantages over the MTFBR, several investigators have studied to improve the attrition of the catalysts, to separate fine catalyst particles efficiently from liquid products using the separators such as hydrocyclone or modified geometric devices, to estimate closely the bubble phenomena and to elevate the heat and mass transfer coefficient in slurry bubble column.

However, Co-based or Fe-based catalysts are selected according to products required in FTS. Fe-based catalyst is often selected because of its WGS activity to work in a wide range of H₂/CO feed ratio. Further, iron is much less expensive than Co catalyst, and it

has lower methane and higher olefin selectivity. On the other hand, Co against Fe-based catalyst is often selected in the process for having the lower CO_2 and the higher paraffin wax selectivity. Fe and Co catalysts also contain some additives to stabilize the active components and to improve the productivity as reduction, structural and chemical promoters [2,11,12].

In the present study, we compare the performance of an impregnated Co/Al_2O_3 catalyst in a tubular fixed bed reactor (TFBR) and in an SBCR for the production of C_5+ hydrocarbons with change in operation variables such as temperature, pressure and space velocity. The aim of the present investigation is to generate useful data for optimum operating conditions and design (and scale-up) of practical TFBR and SBCR.

EXPERIMENTS

1. Catalyst Preparation

The γ-Al_2O_3 support was obtained by calcination in air of the aluminum boehmite phase (Catapal-B Condea high purity) at 600 °C.

The Co-based catalyst was prepared by the conventional wet-impregnation of the γ-Al_2O_3. The impregnation of the γ-Al_2O_3 with an aqueous cobalt nitrate in required composition was carried out with continuous stirring for 12 h at room temperature. The sample was then dried in a rotary evaporator before being subjected to calcination at 450 °C in air for 5 h. The ratio of cobalt metal component to γ-Al_2O_3 in the finished catalyst was fixed at 20/100 by weight.

2. Activity Test in TFBR

A catalytic activity test in a TFBR (I.D.=10.0 mm) was carried out with a catalyst of 1.0 g. Prior to the reaction, the catalyst was reduced at 400 °C for 12 h in a flow of 5% H_2 balanced with helium. After reduction, the synthesis gas (H_2/CO=2) was fed into the reactor. FTS was carried out subsequently under the following reaction conditions: T=220-250 °C, P=1.0-2.5 MPa and SV=1,000-4,000 ml/g_{cat}·h. Effluent gas from the reactor was analyzed by an online gas chromatograph (YoungLin Acme 6000 GC) employing GS-GASPRO capillary column connected with FID for the analysis of hydrocarbons and Porapak Q/molecular sieve (5A) packed column connected with TCD for the analysis of carbon oxides, hydrogen,
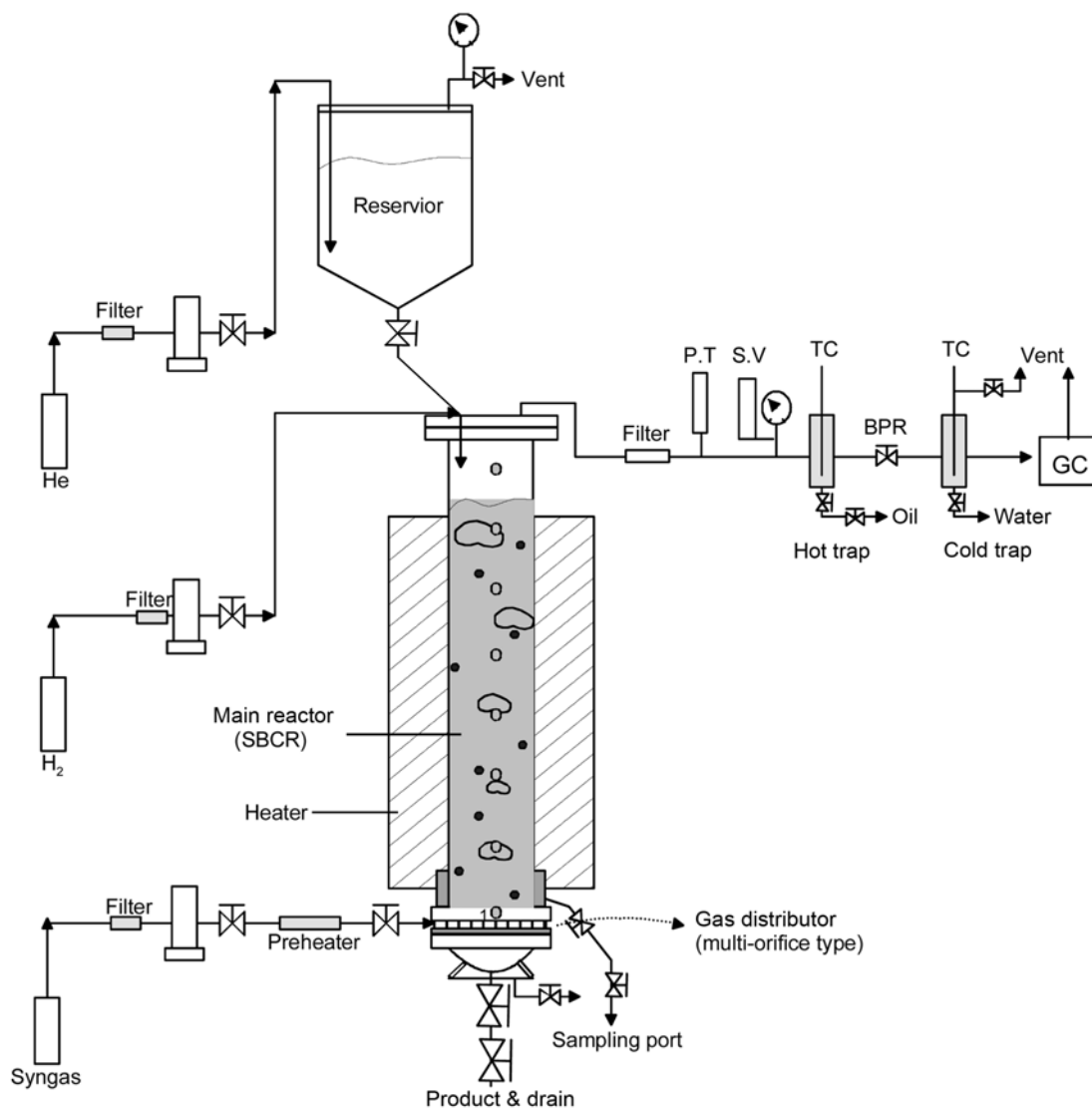

Fig. 1. Scheme of slurry bubble column reactors for Fischer-Tropsch synthesis.

methane and internal standard gas (Ar).

3. Activity Test in SBCR

A schematic of the SBCR apparatus is shown in Fig. 1. An activity test was also performed in an SBCR of 22.1 mm in I.D. and 1.0 m in height with an effective reactor volume of 0.38 L. Squalane ($C_{30}H_{62}$) of 130 g was used as liquid medium and the concentration of solid catalyst applied was 20 wt%. The synthesis gas supplied by the gas distributor of orifice type near the bottom of the reactor vessel was passed continuously through the reactor. The gas distributor was designed by a triangle pitch method and had three orifices of 0.3 mm, which orifice number and size were determined by a Weber dimensionless number as well as overall cross sectional area of orifices. The ratio of slurry-phase height and column diameter (H/D) was selected at nearly 30 at the steady state, in order to exhibit a similar performance of a slurry phase CSTR. The liquid products accumulated in the SBCR were separated by the porous sintered metal filter (5 μm grade) located underneath the distributor. The product gas and unreacted syngas (tailing gas) exit the overhead vessel, and then middle hydrocarbons and H_2O collect in a warm trap (50 °C, 2.0 MPa). In the SBCR, the catalyst was reduced under the same conditions as that of TFBR. After reduction, squalane was injected as liquid medium into the SBCR and then slurry phase was formed by using bubbles of syngas. FTS was carried out subsequently under the following reaction conditions: T=220-250 °C, P= 0.5-3.0 MPa and SV=1,000-4,000 ml/g_{cat}·h. The effluent gas was analyzed by the same methods of TFBR.

RESULTS AND DISCUSSION

For producing transportation fuels such as gasoline and diesel or chemicals such as light olefins and waxy hydrocarbons from syngas, TFBR (gas-phase reaction) and SBCR (slurry-phase reaction) are most widely used for FTS real plants. SBCR shows a different performance with variations of bubble properties and hydrodynamics in the reactor. For that reason, we designed the SBCR, especially the gas distributor and height/diameter aspect ratio, in order to exhibit a similar performance of a slurry-phase CSTR. And then we compared those two F-T reaction systems with variations of operating conditions so as to determine the optimum operating condition and to examine the activity of catalysts in those two systems. Especially, we examined the effects of the operating conditions such as reaction temperature, pressure, and space velocity on the CO conversion and selectivity of products in a TFBR and SBCR for FTS.

1. Effects of GHSV

Figs. 2 and 3 show the effects of GHSV on the CO conversion and selectivity to products in a TFBR and SBCR. In the case of TFBR, the space velocity has a linear influence upon the residence time in the reactor, and has an effect on the intra- and extra-diffusion in the catalyst. However, in the case of fluidization systems such as SBCR, CFBR and FBR, the gas velocity (superficial gas velocity) is affected by the hydrodynamic characteristics (size, rising velocity and frequency of bubble, the mixing of each phases, etc.). In particular, they can be controlled by the design of gas or liquid distributor and the reactor geometry deriving information from the flow of phases in the reactors. In TFBR of Figs. 2 and 3, the CO conversion and selectivity to C_5+ hydrocarbons decrease with the increase of space velocity, but C_2-C_4 selectivity and olefin selectivity in C_2-C_4 is larger

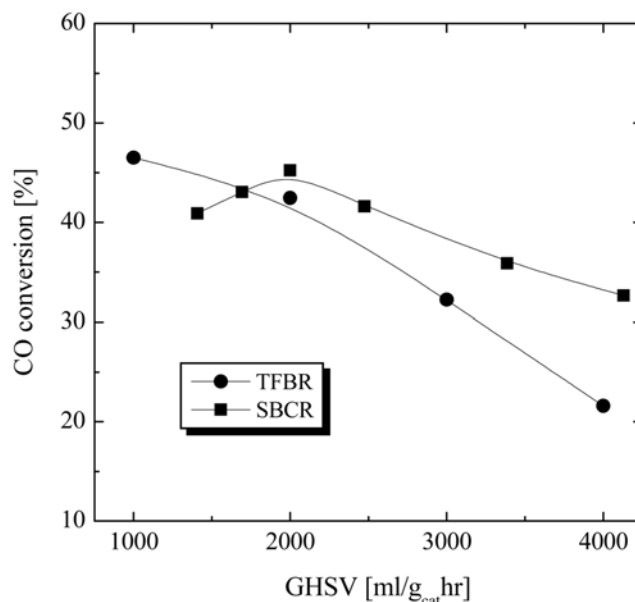

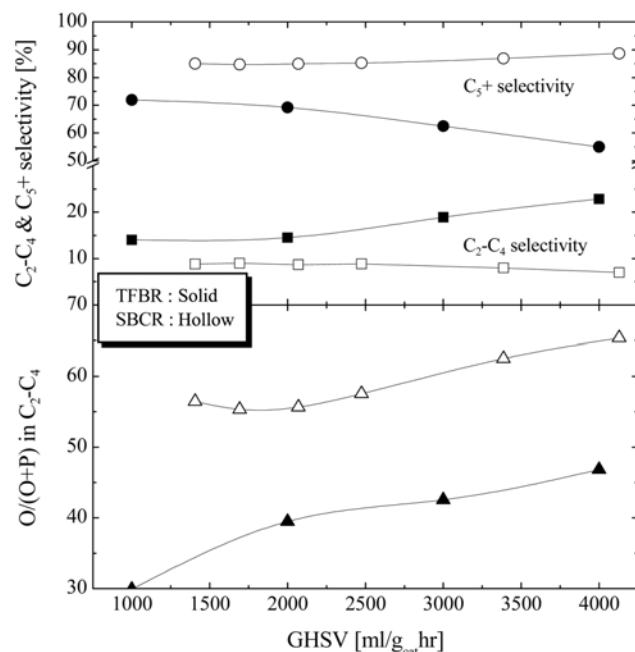Fig. 2. Effect of gas hourly space velocity (GHSV) on the CO conversion in a TFBR (T=230 °C, P=2.0 MPa) and in a SBCR (T=240 °C, P=2.0 MPa).

Fig. 3. Effect of gas hourly space velocity (GHSV) on the selectivity of products in a TFBR and in a SBCR (T=240 °C, P=2.0 MPa).
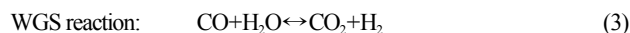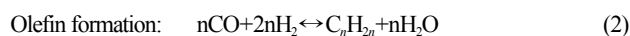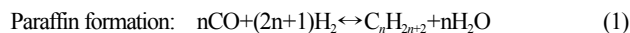
when CO conversions are lower at higher space velocities. These observations indicate that the secondary hydrogenation of olefin cannot occur on the catalyst under the present reaction conditions [13]. Also, with the higher space velocity, the chain growth occurring on the catalyst surface is deficient because of the short residence time.

The CO conversion in an SBCR, as shown in Fig. 2, exhibits a local maximum value at a space velocity of 2,000 ml/g_{cat}·h or superficial gas velocity of 12-16 cm/s. It may be due to the minimum

fluidization gas velocity for syngas-catalyst well mixing in an SBCR. In the case of the SBCR, the gas velocity among various variables has a large effect on the flow regimes: homogeneous, heterogeneous (churn-turbulent) and slug flow and transition regime for gas-liquid bubble column system [14]. Transition regime as a boundary layer of each flow can shift depending on the experimental setup and system used. Therefore, some investigators proposed that the operation of a pilot-scale SBCR should be carried out in the churn-turbulent flow regime of around 12-23 cm/s. With the further increase of gas velocity, since gas holdup in the reactor increases according to power-law equation as $\varepsilon_G = U_G^n$, a transition occurs from the homogeneous to heterogeneous flow regime. Moreover, as shown in Fig. 3, a high increase of gas velocity can cause an increase of undesired olefin ratio because of the short residence time of the gas phase and large bubbles. Therefore, the determination of optimum conditions in an SBCR in contrast to the TFBR must take into consideration both CO conversion and selectivity to desired products. Deckwer [15] reported on the available approaches for improving product selectivity, based on the operating conditions, reactor design and development for highly selective catalysts from the experimental results of previous studies. It is possible to optimize the optimum process parameters for the selective synthesis toward light olefins or heavy paraffins according to the type of F-T reactor.

2. Effects of Temperature

As reported, the FTS over iron- or cobalt-based catalysts proceeds via sequential steps:

Paraffin formation: $nCO+(2n+1)H_2 \leftrightarrow C_nH_{2n+2}+nH_2O$ (1)

Olefin formation: $nCO+2nH_2 \leftrightarrow C_nH_{2n}+nH_2O$ (2)

WGS reaction: $CO+H_2O \leftrightarrow CO_2+H_2$ (3)

The main FTS reactions (Eqs. (1) and (2)) have the optimum composition of hydrogen and carbon monoxide with a ratio 2.0 or so. A water gas shift (WGS) reaction (Eq. (3)) takes place in combina-
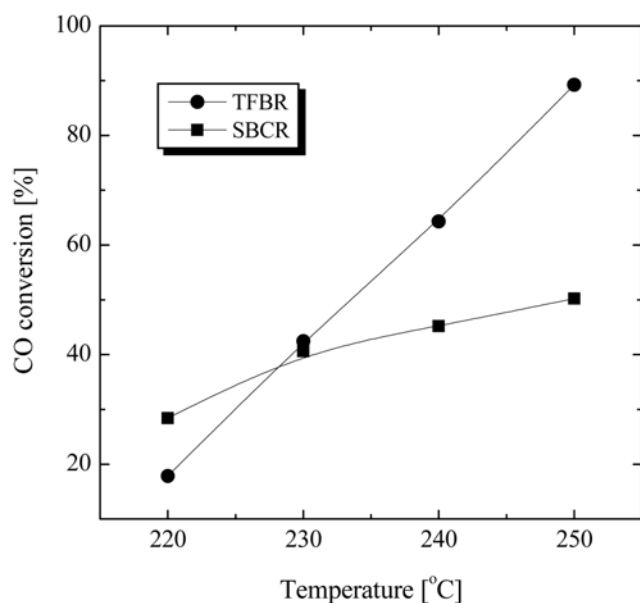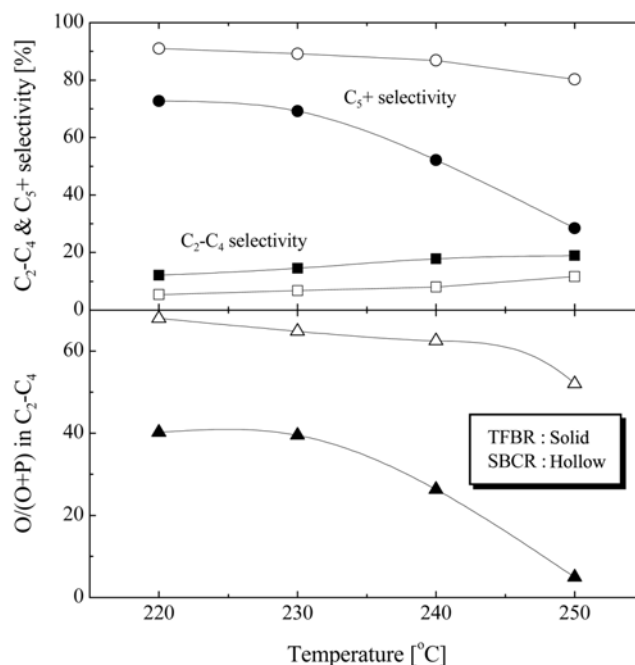

Fig. 5. Effect of reaction temperature on the selectivity of products in a TFBR and in a SBCR (P=2.0 MPa, SV=2,000 ml/ g_{cat}·h).

tion with the FTS on iron-based catalysts in the condition of low H_2/CO ratio [16]. In particular, WGS proceeds at high temperature in the range of 370-500 °C with iron-based catalysts.

Increase of CO conversion with reaction temperature can be found in FTS two reactors kinetically as well as thermodynamically as observed in Fig. 4. Fig. 5 shows C_2-C_4 and C_5+ selectivities of products in a TFBR and SBCR. It is obvious that C_1 and C_2-C_4 selectivities increased with an increase in the reaction temperature, but C_5+ selectivity and olefin selectivity in C_2-C_4 showed a reverse trend. The olefin selectivity in C_2-C_4 hydrocarbons in a TFBR is consistently lower than that in an SBCR under similar reaction conditions. Satterfield et al. [13] reported that paraffin- and methane-rich products are favored in a TFBR, whereas olefin-rich and methane-lean products are favored in a stirred slurry reactor. The variation of C_2-C_4 and C_5+ selectivities in the two reactors can be easily understood as the selectivity toward C_2-C_4 fraction increases, while the selectivity to C_5+ decreases with temperature. Because the Fischer-Tropsch polymerization reaction is exothermic, an increase of reaction temperature always shifts the product towards lower carbon number hydrocarbons [17]. However, the olefin selectivity in C_2-C_4 products is well established that olefin selectivity depends not only on the primary olefin selectivity in F-T synthesis but also on the activity of secondary hydrogenation of the primary product. With the increase of temperature, because the secondary reaction of olefin hydrogenation was inhibited, decreased olefin selectivity in C_2-C_4 hydrocarbons and increased CH_4 selectivity were observed.

3. Effects of Pressure

Figs. 6 and 7 show the effect of reaction pressure on the CO conversion and the product selectivity, in which it is seen that the CO conversion as well as the C_5+ selectivity increased with the increase in reaction pressure, while C_2-C_4 selectivity and olefin selectivity in
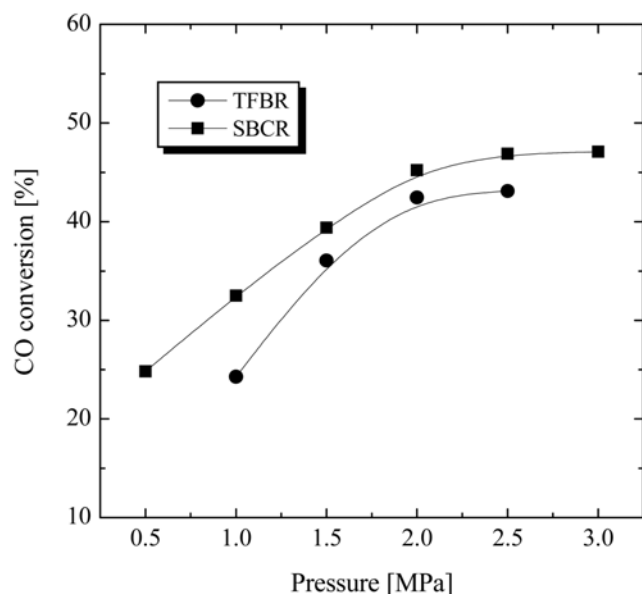

Fig. 4. Effect of reaction temperature on the CO conversion in a TFBR and in a SBCR (P=2.0 MPa, SV=2,000 ml/g_{cat}·h).

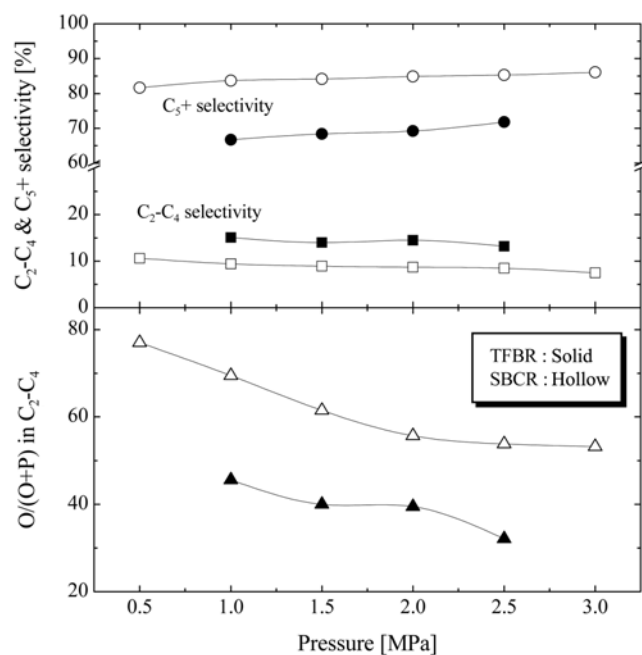Fig. 6. Effect of reaction pressure on the CO conversion in a TFBR (T=230 °C, SV=2,000 ml/g$_{cat}$·h) and in a SBCR (T=240 °C, SV=2,000 ml/g$_{cat}$·h).

Fig. 7. Effect of reaction pressure on the selectivity of products in a TFBR and in a SBCR (T=240 °C, SV=2,000 ml/g$_{cat}$·h).

Fig. 8. Relationship between CO conversion and C$_5$+ selectivity of products in F-T reactors.

elevated pressure is influenced by the hydrodynamics (such as phase holdup and bubble properties) or diffusion between syngas and catalysts. Gas holdup increases with increasing pressure and is associated with rising velocity and number density of bubbles in the reactor. Also, the pressure affects the hydrodynamics in the reactor through the variations of bubble size and its distribution. The increase of gas holdup with pressure is mainly due to the increase of small gas bubbles [18]. In addition, the distribution of bubble size is narrow, and the size and intensity of wakes decrease with decreasing bubble size, trapping fewer trailing bubbles. The difference in bubble velocities decreases by increasing size uniformity, and non-uniformity of the local flow field decreases since the bubble size and wake intensity decrease [19]. In an SBCR, although the reaction pressure increases highly, the decrease of bubble size has a limitation. Therefore, as seen in Figs. 6 and 7, the increase in the rate of CO conversion and C$_5$+ selectivity decreases gradually with pressure.

Fig. 8 shows the relationship between CO conversion and C$_5$+ selectivity. In Fig. 8, the C$_5$+ selectivity of both reactors has a decreasing trend with increasing CO conversion. In this work, a high CO conversion can be obtained at the operation condition of low space velocity or high temperature and pressure. In general, C$_5$+ selectivity and olefin selectivity in C$_2$-C$_4$ in an SBCR is higher than that in a TFBR. Also, at mostly similar operating conditions, CO conversion and product distributions in a TFBR are more sensitive than that in an SBCR with a change in the reaction conditions, due to the lubricant action of liquid medium in an SBCR. The stable trend of CO conversion and product distributions in an SBCR is also because the catalysts are diluted by the liquid phase, which diminishes their concentration and thus reduces the secondary hydrogenation [13].

CONCLUSION

FTS for the production of C$_5$+ hydrocarbons from syngas was performed in a TFBR and in an SBCR with cobalt catalyst. Under

C$_2$-C$_4$ hydrocarbons decreased. In a TFBR under elevated pressure, the residence time of gas phase is proportional linearly to the reaction pressure. As seen in Fig. 7, C$_5$+ selectivity increases with the increase of CO conversion and by the formation of heavy hydrocarbons chain growths because of the long residence with the time increased of pressure. The SBCR results are similar to the results of TFBR. Although C$_5$+ selectivity in an SBCR increases with the increase of pressure, the residence time of syngas in the reactor is not proportional to the reaction pressure. Especially, SBCR under
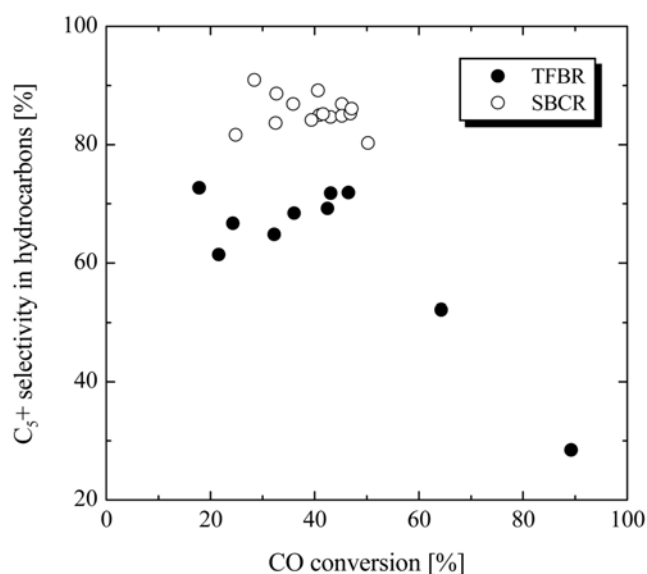
similar operating conditions, the C_5+ selectivity and olefin selectivity in an SBCR are higher than that in a TFBR. In particular, CO conversion and C_5+ selectivity in an SBCR is insensitive to changing operating conditions such as gas hourly space velocity, temperature and pressure. These results indicate that SBCR for the hydrogenation processes of CO to hydrocarbons over Co/Al_2O_3 catalysts shows better stable FTS performance than that of TFBR.

ACKNOWLEDGMENT

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