Raising Distillate Selectivity and Catalyst Life Time in Fischer-Tropsch Synthesis by Using a Novel Dual-Bed Reactor

Tavasoli, Ahmad*+; Sadaghiani, Kambiz
Research Institute of Petroleum Industry (RIPI), P.O. Box 18745-4163 Tehran, I. R. IRAN

Khodadadi, Abbas Ali; Mortazavi, Yadollah
Department of Chemical Engineering, University of Tehran, P.O. Box 11365-4563 Tehran, I. R. IRAN

ABSTRACT: *In a novel dual bed reactor Fischer-Tropsch synthesis was studied by using two diffrent cobalt catalysts. An alkali-promoted cobalt catalyst was used in the first bed of a fixed-bed reactor followed by a Rutenuim promoted cobalt catalyst in the second bed. The activity, product selectivity and accelerated deactivation of the system were assessed and compared with a conventional single bed reactor system. The methane selectivity in the dual-bed reactor was about 18.9 % less compared to that of the single-bed reactor. The C_{5+} selectivity for the dual-bed reactor was 10.9 % higher than that of the single-bed reactor. Accelerated deactivation of the catalysts in the dual-bed reactor was 42 % lower than that of the single-bed reactor. It was revealed that the amount of catalysts activity recovery after regeneration at 400 ^oC in the dual-bed system is higher than that of the single-bed system.*

KEY WORDS: *Fischer-Tropsch, Cobalt catalyst, Dual-bed, Selectivity, Life time.*

INTRODUCTION

Incorporation of olefins has been used as a means of raising the yield of liquid hydrocarbons in Fischer-Tropsch Synthesis (FTS). Linear α-olefins are known to be the main primary products of FTS. Once formed they can readsorb on the catalyst surface and undergo secondary reactions: hydrogenation, isomerization, re-insertion and hydrogenolysis. The final product can thus have been affected by these secondary reactions [1-6]. These secondary reactions have been studied by olefin co-feeding.

Increased formation rates of compounds with higher carbon numbers than the respective added olefin during FT synthesis with different kinds of catalysts and reaction conditions have also been reported. *Jordan* and *Bell* [1] studied co-feeding of ethene over a SiO_2-supported Ru catalyst. They showed that the hydrogenation of CO to hydrocarbons is strongly influenced by the presence of ethene. High selectivity to C_{3+} products and low selectivity to CH_4 were observed for C_2H_4 high partial pressures.

Table 1: Catalysts compositions.

Catalyst	Cobalt wt %	Ru/Co Wt. Ratio	K /Co Wt. Ratio	Void Fractions	Size (microns)
C_1	15	0.01	-	0.63	350-600
C_2	15	-	0.046	0.63	350-600

Iglesia and *Madon* [2] showed that by introducing ethylene to the reactor bed at a point below 10 % of the distance from the top to the bottom of the reactor bed and above a point 10 % above the bottom of the reactor bed to the top of the reactor, the CH_4 selectivity decreased from 8.3 % to 7.2 % and the C_{5+} selectivity increased from 92.9 % to 93.9 %. *Schulz* and *Claeys* [3] by co-feeding of C_2-C_{11} α-olefins during Fischer-Tropsch synthesis with a cobalt catalyst in a slurry reactor showed that the addition of an α-olefin led to a shift in the curves of formation rates of compounds with carbon numbers higher than the olefin which had been added. *Kibby* [4] claimed, without presenting experimental data, that by using a combination of iron and cobalt catalysts it would be possible to reduce methane selectivity and enhance C_{5+} selectivity.

Another important parametr in FTS is catalyst lifetime. Cobalt FTS catalysts are too expensive therefore, lowering their deactivation rates is one of the main challenges facing the commercial development of GTL technology. Several research groups recently have investigated the deactivation rates of these catalysts [7-9]. *Kiss et al.,* [7] studied hydrothermal deactivation of silica supported cobalt catalysts. They demonstrated that high partial pressure of water resulted in the formation of a phase containing mixed oxides of support and cobalt which is inactive for the synthesis. *Li et al.,* [8], by cofeeding of water, observed a decrease in CO conversion. They found that at low P_{H2O}/P_{CO} ratios, the extent of deactivation was low and reversible. However, at higher ratios deactivation was high and permanent. *Tavasoli et al.,* [9] have shown that Al_2O_3-supported cobalt catalysts, and especially those with promoters Re and Ru, which are suitable for improving the reducibility of the catalysts, deactivate faster. They attributed this effect to higher reaction rates which in turn increases the partial pressure of water which is known to be one of the major sources for deactivation. They recognized that water-induced oxidation of cobalt, cobalt-alumina interactions, irreducible cobalt aluminates formation, sintering or cluster growth and finally refractory coke formation are the main sources of activity loss.

It was shown previously that methane is produced mainly at the very beginning of the catalytic bed and it was also demonstrated that the addition of potassium oxide to the Co/Al_2O_3 increases α-olefins of the type $R-CH=CH_2$ significantly [10].

In present work, in order to affect final product distribution and catalysts lifetime, we used a dual-bed reactor. A catalyst with very low methane selectivity and high α-olefins selectivity was charged to the first bed of the dual-bed reactor. In the second bed of the reactor, a catalyst with a high activity was charged. This way it might be possible to suppress methane selectivity and enhance the selectivity of higher molecular weight hydrocarbons via olefins readsorption (formed in the first bed) in the second catalytic bed of the daul-bed reactor. Also in order to decrease the unfavorable effects of water and heavy hydrocarbons, the effluent of the first bed was cooled in order to condense water and C_{10+} hydrocarbons. Unconverted syngas and C_1-C_{10} hydrocarbons which mostly are α-olefins of the type $R-CH=CH_2$ in the effluent of the first bed were fed into the second catalytic bed.

EXPERIMENTAL
Catalyst preparation

One Ruithenum promoted (Ru/Co=0.010 by weight) and an alkali-promoted cobalt catalyst (K/Co=0.046 by weight) were prepared. The two catalysts were prepared with 15 wt % of cobalt. γ-alumina was used as the support. The support was calcined at 500 °C for 10 h prior to the impregnation. The compositions of the catalysts prepared are listed in table 1. The catalysts were prepared by aqueous impregnation of the support with the appropriate solutions of the cobalt nitrate $(Co(NO_3)_2.6H_2O)$, Ruthenium(III) nitrosylnitrate $(Ru(NO)(NO_3)_3)$ and potassium oxide. The catalyst samples were dried at 120 °C and calcined at 450 °C for 3.5 h afterwards.

Activity and Selectivity Tests

The dual-bed reactor was adapted by combination of C_1 and C_2 catalysts. 1.0 g of C_1 and 2.0 g of C_2 catalysts were charged into the first and the second beds of 1/4" tubular

micro-reactor respectively. The two beds were set in series in such a way that the effluent from the first bed went into a first separator and the gaseous effluent of the first separator directly went into the second bed. The effluent of the second bed went into the second separator.The total length of the beds was 90 cm. The reactor was placed in a molten salt bath with a stirrer to ensure a uniform temperature along the catalyst beds. The temperature of the bath was controlled via a PID temperature controller. The pressure of the reactor and separators were controlled via a Brooks pressure controler. Separate Brooks 5850 mass flow controllers were used to add H_2 and CO at the desired rate to a mixing vessel that was preceded by a lead oxide-alumina containing vessel to remove metal carbonyls before entering to the reactor. Prior to the activity tests, the temperature was raised to 400 $^{\circ}$C with a heating rate of 1 K/min and the catalysts were reduced in a flow of H_2 at 400 $^{\circ}$C for 12 h. The experiments were performed at a temperature of 210 °C, a total pressure of 20 bar, total feed flow rate of 90 ml/min, and H_2/CO ratios of 2 for a peroid of 24 hr. The temperature of the separators were set at 100 $^{\circ}$C in order to condence water and heavy hydrocarbons. Analyses of CO, CO_2, and C_1-C_{30} hydrocarbons in the second separator gaseous effluent and the liquid samples collected in the two separators were performed in a modified refinery gas analyzer (Varian 3800). Anderson-Schultz-Floury (ASF) distributions were plotted and the chain growth probability α, was calculated. The experimental setup is shown in Fig. 1.

In the second set of these experiments, 1.0 g of C_1 and 2.0 g of C_2 catalysts were mixed and charged into the reactor. In these series of experiments the second bed of the reactor and the second separator were bypassed. The reduction procedure, the reaction conditions, and the calculation methods were the same as the first set of experiments. The results of this set were used for the evaluation of performance of the dual-bed reactor.

Accelerated tests

A series of experiments were designed to study the accelerated deactivation of the cobalt catalysts in the dual-bed and single bed reactors. 0.75 g of C_1 and 0.75 g of C_2 catalysts were charged into the first and the second beds of the micro-reactor respectively. Prior to the activity tests, the temperature was raised to 400 $^{\circ}$C with a
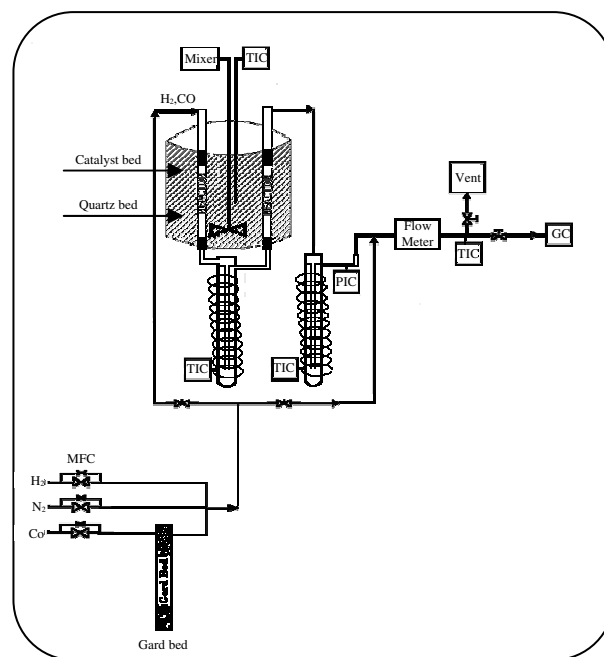

Fig. 1: Experimental setup.

heating rate of 1 K/min and the catalysts were reduced in a flow of H_2 at 400 $^{\circ}$C for 12 h (first treatment step). The FT synthesis (first synthesis step) was carried out at 260 °C, a total pressure of 1 bar, and a H_2/CO ratio of 2. Also a low feed flow rate of 30 mL/min was used to achieve high conversions and high water partial pressures that futher accelerate the deactivation of the catalyst. The temperature of the separators were set at 80 $^{\circ}$C. Analyses of CO and products, were performed every one-hour and CO conversion and selectivity (the percentage of the converted CO that appears as a given product) of the products were calculated based on the chromatograms of the products obtained from the GC. After 48 h of the first FT synthesis step, the flow of CO was switched off and catalysts were treated (second treatment step) in a flow rate of 120 mL/min H_2 at 260 $^{\circ}$C for 4 h. Then the second FT synthesis step was carried out under the same conditions of the first synthesis step and the activity (g HC produced/ g cat/ min) and selectivity of the system were measured. The third treatment step of the catalysts were performed at 400 °C for 6 h. Subsequently the reactor was cooled to 260 °C and the third FT synthesis step was carried out undert the same conditions of the previous synthesis steps.

In the second set of these experiments, 0.75 g of C_1 and 0.75 g of C_2 catalysts were mixed and charged into the
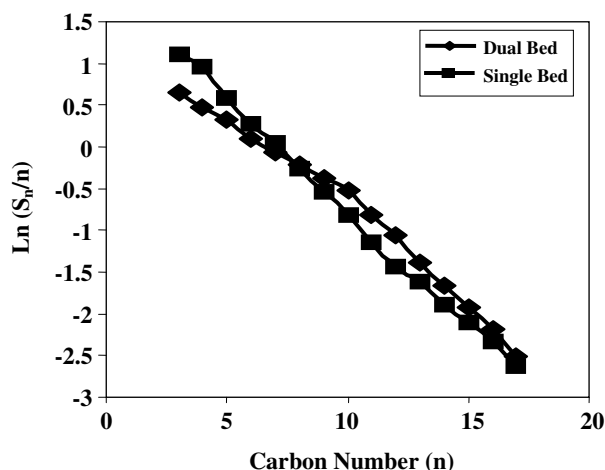
Fig. 2: ASF plots for dual bed and single bed systems (T=210 ^{o}C, P=20 bar, H$_2$/CO=2).

Fig. 3: Prod. Sele. and CO conversion of the dual and single-bed reactors (T=210 ^{o}C, P=20 bar, H$_2$/CO =2).

first bed of the reactor. In these series of experiments the second bed of the reactor and the second separator were bypassed.

The reduction procedure, the reaction conditions, and the calculation methods were the same as the first set of experiments. The results of this set were used for the evaluation of performance of the dual-bed reactor.

RESULTS AND DISCUSSION

Fig. 2 compares the ASF plots of the dual-bed and single reactors. Operating conditions of the reactor were as follows, T= 210 °C, P= 20 bar, and H$_2$/CO =2. The temperature of the first separator was set at 100 ^{o}C. In the dual bed reactor, water and C$_{10+}$ hydrocarbons produced at the first bed of the reactor condensed at this separator. unconverted syngas and C$_1$-C$_{10}$ hydrocarbons which mostly are α-olefins of the type R-CH=CH$_2$ went to the second bed. The amount of liquid products in the separators were weighted and analysed. The analysis of liquid products in the two separators are shown in table 2. In the dual bed reactor, the ratio of the amount of collected liquid hydrocarbons in the second separator to the liquid hydrocarbons of the first separator was about 5. As shown in Fig. 2 the dual-bed reactor serves to increase the average carbon number of the products produced during the FT synthesis. The high chain growth may be attributed to the effective participation of α-olefins produced at the first bed of the reactor, and to the carbon-carbon chain propagation at the second bed of the dual-bed reactor [1-3].
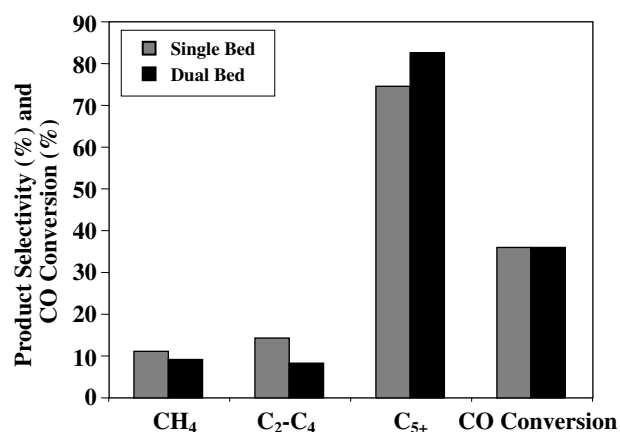
Fig. 3 compares the product selectivity and CO conversion for the dual-bed and the single-bed reactors. As shown in Fig. 3, methane selectivity in the dual-bed reactor is 9.09 % and that of the single bed reactor is 11.21 %. This shows that the methane selectivity in the dual-bed reactor is about 18.9 % less compared to that of single-bed reactor. The liquid C$_{5+}$ selectivity for the dual-bed reactor is 82.63 % and that of single bed reactor is 74.53 %. This proves that the liquid C$_{5+}$ selectivity increases about 10.9 % in the dual-bed reactor. Also C$_2$-C$_4$ selectivity for the dual-bed reactor is 8.28 % and that of the single bed reactor is 14.26 %. This demonstrates that C$_2$-C$_4$ selectivity in the dual-bed reactor is about 41.9 % less compared to that of single-bed reactor. These results show that, in the dual-bed system C$_{2+}$ olefins produced in the first bed of the reactor can readsorb and act as chain starters in the second bed of the reactor, and by this way modify the chain growth probabilities and product distributions (i.e. C$_{5+}$ selectivity).

The decrease in methane selectivity in the dual-bed system is mainly attributed to the suppression of methane formation rate by using C$_1$ catalyst at the first catalytic bed. Also it is important to note that increasing the formation rates of compounds with high carbon numbers due to olefin readsoption and as a result increasing the C$_{5+}$ selectivity causes a decrease in the selectivity of methane and light gaseous C$_2$-C$_4$ hydrocarbons selectivity. Interestingly CO conversion is about the same for both single bed and dual-bed reactors.

Table 2: Analysis of liquid products in the separators of the two reactors (T=210 ^{o}C, P=20 bar, H$_2$/CO =2).

Component	Single Bed Reactor Separator (wt. fraction)	Dual Bed Reactor: First Separator (wt. fraction)	Dual Bed Reactor: Second Separator (wt. fraction)
C6	0.00829793	0.00421287	0.00467308
C7	0.025819331	0.012776986	0.014172733
C8	0.040158693	0.020148872	0.022349917
C9	0.058508343	0.054790948	0.060776264
C10	0.057669097	0.054799171	0.05961009
C11	0.054468469	0.054792367	0.055915611
C12	0.052016569	0.054981231	0.053950333
C13	0.049589209	0.052042558	0.05106676
C14	0.044488707	0.04816817	0.047265017
C15	0.042704338	0.045438685	0.04458671
C16	0.041954592	0.044710152	0.043871837
C17	0.040842237	0.042846675	0.0420433
C18	0.038520954	0.041230905	0.040457826
C19	0.036370387	0.037938944	0.037227588
C20	0.034660899	0.036901181	0.036209284
C21	0.032625793	0.034285786	0.033642928
C22	0.031073928	0.033647036	0.033016155
C23	0.03083384	0.032658182	0.032045841
C24	0.030558784	0.032050312	0.031449368
C25	0.030921945	0.032570475	0.031959779
C26	0.029658683	0.031733851	0.031138841
C27	0.02909684	0.03109729	0.030514216
C28	0.028109565	0.029830292	0.029270974
C29	0.026472032	0.027131743	0.026623023
C30	0.02448407	0.025371469	0.024895754
C31$^+$	0.080552898	0.08391562	0.082342202
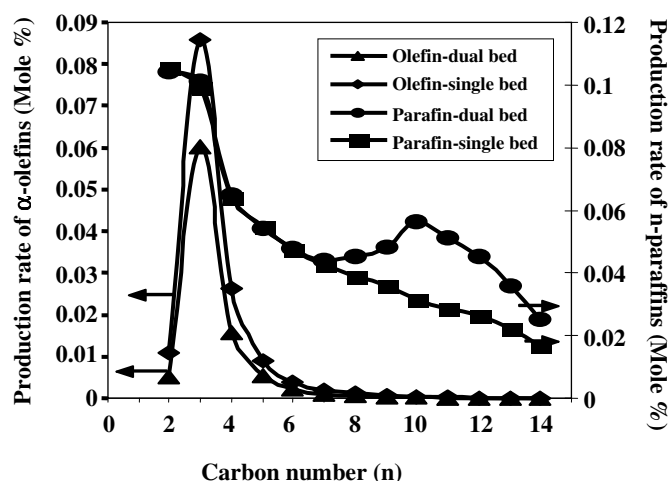
Fig. 4: The production rates of n-paraffins and α–olefins (T=210 °C, P=20 bar, H$_2$/CO=2).

Fig. 5: Relative activity of catalysts with time on stream in the dual bed single bed reacrtors (T=260 °C, P= 20 bar, H$_2$/CO=2).

Fig. 4 presents the formation rates of C_2-C_{14} n-paraffins and α-olefins for both single bed and dual bed systems at a pressure of 20 bars and 210 °C and H$_2$/CO ratio of 2. As may be seen the paraffin content in the products of single bed reactor decreases as the carbon number increases. The same trend can be seen for α-olefins except C_3. Comparing the production rates of α-olefins in the two systems, the mole % of α-olefins in the products of the dual bed reactor is about 50-75 % less than that of single bed reactor in the range of C_2-C_{15}. The mole % of paraffins in the products of the dual bed reactor is the same for both systems in the range of C_2-C_7, but the production rate of the paraffins with carbon numbers larger than 8, increases significantly in the dual bed system.

The results clearly show that the increasing paraffin content arises predominantly from the net disappearance of C_2-C_7 α-olefins and not from their direct hydrogenation to the corresponding n-paraffin. C_2-C_7 α-olefins production rate decreases in the dual bed system without a corresponding increase in C_2-C_7 n-paraffins, leading to a net increase in the fraction of the converted CO that appears as C_{8+} paraffins. The observed increase in the C_{8+} n-paraffins actually results from the effects of enhanced readsorption of C_2-C_7 α-olefins in the dual bed system.

Fig. 5 presents the relative activity changes with the duration of FT synthesis before and after different hydrogen treatment steps. Relative activity is defined as the CO conversion at a specified time to the initial CO
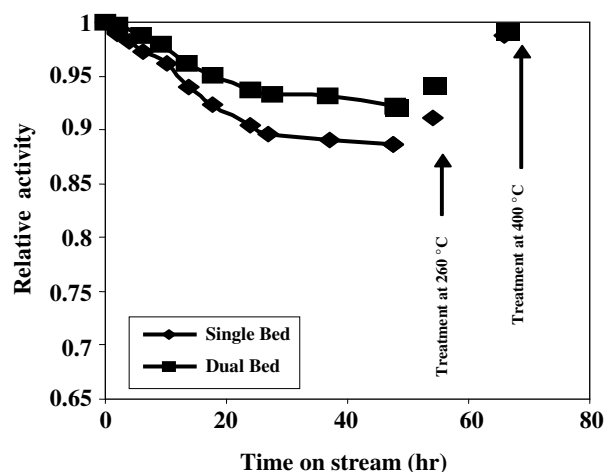
conversion of the FT synthesis. As is observed during the 48 h FT synthesis the relative activity of the single-bed and dual bed systems reduce upto about 24 h time on stream, then levels off. The relative activity changes is higher in single-bed reactor.

For single-bed reactor, the relative activity declines by 9.9 % in the 24 h while the activity fall for dual bed reactor is 6.2 %. After second hydrogen treatment step at 260 °C the relative activities increases by 2.4 % and 2 % for the single-bed and dual bed systems, respectively. It has been suggested that in FT synthesis on alumina-supported cobalt catalysts at high conversion, the loss in active sites is caused by water-induced oxidation of cobalt [11,12]. The larger deactivation observed for a single-bed reactor is due to higher patrtial pressure of water and as well as a higher amount of long chain hydrocarbons present in the catalytic bed of the single bed reactore. This water-induced back-oxidation of cobalt can be largly reversed and catalytic activity can be recovered by hydrogen treatment at or close to FT synthesis conditions. This deactivation process does not involve metal-support interactions but rather entails cobalt redox transformation with no support participation [11,12].

Finally, after the third reduction step at 400 °C, the relative activities increase by 7.8 % and 5 % for the single-bed and dual bed systems respectively. After this hydrogen treatment step, the relative activities of the the single-bed and dual bed reactors are recovered by 98.8 and 99.3 %, respectively. This recovery of the
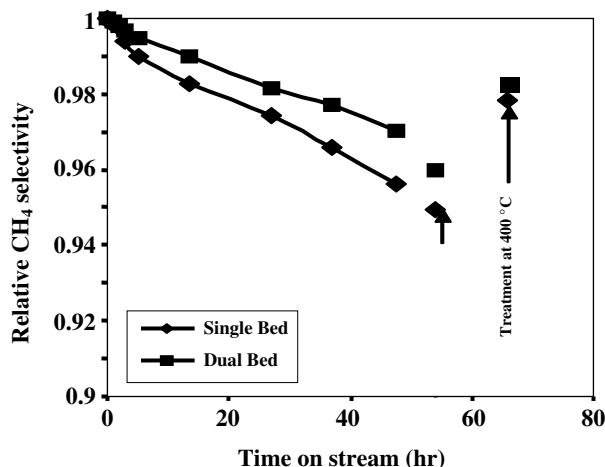
114

Fig. 6: Relative CH$_4$ selectivity of catalysts with time on stream in the dual bed and single bed reactors (T=260 ^{o}C, P= 20 bar, H$_2$/CO=2).

Fig. 7: Relative C$_{5+}$ selectivity of catalysts with time on stream in the dual bed and single bed reacrtors (T=260 ^{o}C, P= 20 bar, H$_2$/CO=2).

activities for dual bed reactor is higher than that for the single-bed reactor. This is due to higher rate of deactivation observed during the 48 h FT synthesis on the single-bed reactor, which is not recovered during the second mild hydrogen treatment step. The larger recovery of deactivation observed for the single-bed reactor seems to be caused by regeneration of more refractory forms of oxidized cobalt generated by cobalt-alumina interactions [13]. The extent of this type of deactivation depends on the partial pressure of water produced during Fischer-Tropsch synthesis. It was suggested that water promotes interaction between cobalt oxide species and γ-Al$_2$O$_3$ support [13].

The results suggest that catalysts charged in the single-bed reactor are more susceptible to reoxidation and cobalt-alumina interactions than the catalysts charged in the daul-bed reactor. Lower deactivation rates observed for the daul-bed reactor can likely be attributed to lower water partial pressure in the reactor. Condensation of water produced in the first bed of the daul-bed reactor in the first separator between the two beds, decreases the total partial pressure of water inside the reactor.

The percentages of relative activity that could not be recovered by hydrogen treatment at 400 ^{o}C (Fig. 5) are 1.2 % and 0.7 % for the single-bed and dual bed systems, respectively. Formation of some types of irreducible cobalt aluminates, sintering or cluster growth and finally refractory coke formation may be the sources of this irrevesible activity loss[13].
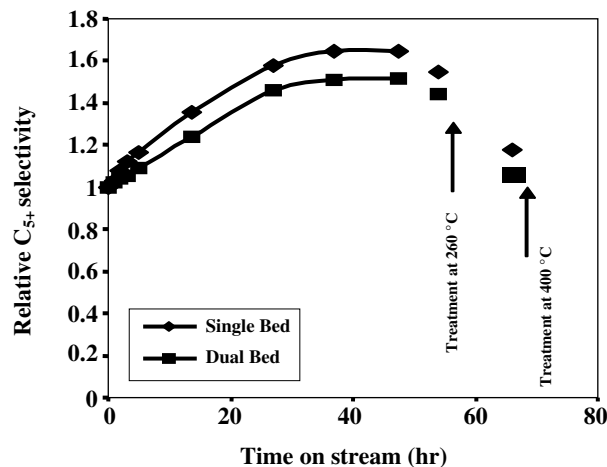
Figs. 6 and 7 show the methane and C$_{5+}$ selectivity variations with reaction time for both single bed and dual bed systems. Fig. 6 displays that, for both systems, CH$_4$ selectivity decreases with time on stream in the 48 h FT synthesis at 260 ^{o}C, while the C$_{5+}$ selectivity increases at the same time (Fig. 7). There are a monotonous decrease in CH$_4$ selectivity of the two systems, but the decrease in the CH$_4$ selectivity of the daul-bed system is lower than that of the single bed system.

Fig. 7 shows that the C$_{5+}$ selectivity, for the two systems, increase until about 24 h, then level off. Enhancement of C$_{5+}$ selectivity with time on stream in the single bed reactor is higher than that of the dual bed reactor. Smaller cobalt particles deactivate faster than the larger clusters [12]. The larger cobalt particles are more selective to higher molecular weight hydrocarbons [12,14,15]. It is speculated that the smaller particles, selective for methane, are deactivated first, leading to enhancement of C$_{5+}$ selectivity with time on stream. The higher CH$_4$ and C$_{5+}$ selectivity changes with time on stream in the single bed reactor is due to a higher rate of deactivation of smaller cobalt particles in this system. Also the removal of heavy, probably unsaturated, hydrocarbons between the two catalytic beds in the dual bed reactor enhances the hydrogenolysis of the heavy hydrocarbons, resulting in lower methane selectivities. After the second hydrogen treatment at 260 ^{o}C, the methane selectivity decreases for the two systems. The slight decrease in methane selectivity, after treatment at 260 ^{o}C, suggest that the smaller cobalt particles are not

115

regenerated in this treatment step. As was mentioned, the small catalyst particles interact more strongly with alumina as the support. The third hydrogen treatment at 400 ^{o}C causes the methane selectivity to slightly increase. Both treatment steps result in an increase in C_{2-4} hydrocarbons. At the same time after the second hydrogen treatment at 260 ^{o}C, C_{5+} selectivity decrease and the third hydrogen treatment at 400 ^{o}C causes the C_{5+} selectivity to further decrease.

CONCLUSIONS

Using a dual bed Fischer-Tropsch synthesis reactor in which the first bed has a catalyst with low methane and high α-olefins selectivities, and the second bed has a catalyst with relatively high chain growth probability, it is possible to produce an integrated process which has a very good distillate yield and low CH_4 selectivity. Increasing readsorbtion and chain initiation of alpha olefins against their hydrogenation causes the dual bed system to give a better selectivity toward distillates. Also separation of water and heavy hydrocarbons between the two catalytic beds of the dual bed reactor decreased the deactivation rate of the catalysts. The amount of catalysts activity recovery after regeneration at 400 ^{o}C in the dual-bed system is higher than that of the single-bed system.

Nomenclatures

P	Pressure (bar)
T	Temperature (^{o}C)

Greek symbols

α	Chain growth probabili

Abbreviations

GTL	Gas-to-liquid
FTS	Fischer-Tropsch Syn.
ASF	Anderson-Schultz-Floury
GC	Gas chromatograph
R	Hydrogen or an alkyl group
S	Selectivity

Subscripts

n	Carbon number

REFERENCE

[1] Jordan, D. S. and Bell, A. T., Influence of Ethylene on the Hydrogenation of CO Over Ruthenium", *J. Phys. Chem.*, **90**, 4797 (1986).

[2] Iglesia, E. and Madon, R., Reducing Methane Production and Increasing Liquid Yileds in Fischer-Tropsch Reactions, U. S. Patent 4754092, Jun. 28, (1998).

[3] Suhulz, H. and Claeys, M., Reaction of α-olefin of Different Chain Length Added During Fischer-Tropsch Synthesis on a Cobalt in a Slurry Reactor, *App. Catal.*, **186**, 71 (1999).

[4] Kibby, C.L., Increased Liquid Sensitivity During Fischer-Tropsch Synthesis by Olefin Incorporation, U.S. Patent 6331573, Dec. 18 (2001).

[5] Iglesia, E., Reyes, S. C. and Madon, R. J., Transport-Enhanced α-olefin Readsorption Pathways in Ru-Catalyzed Hydrogen Synthesis, *J. Catal.,* **129**, 238 (1991).

[6] Kuipers, E. W., Vinkenburg, I. H., Osterbeek, H., Chain Length Dependence of α-olefin Readsorption in Fischer-Tropsch Synthesis, *J. Catal.*, **152**, 137 (1995).

[7] Kiss, G., Kliewer, C.E., DeMartin, G.J., Culross, C.C., Baumgartner, J.E., Hydrothermal Deactivation of Silica-Supported Cobalt Catalysts in Fischer-Tropsch Synthesis, *J. Cat.*, **217**, 127 (2003).

[8] Li, J., Zhang, Y., Jacobs, G., Das T., Davis, B.H., Fischer- Tropsch Synthesis: Effects of Water on the Deactivation of Pt Promoted Co/Al2O3 Catalysts, *App. Cat.*, **228**, 203 (2002).

[9] Tavasoli, A., Mortazavi, Y., Khodadadi, A., Karimi, A., Effects of Different Loadings of Ru and Re on Physico-Chemical Properties and Performance of 15 % Co/Al$_2$O$_3$ FTS Catalysts, *Iran. J. Chem. and Chem. Eng.*, **24** (2), p. 9 (2005).

[10] Tavasoli, A., Mortazavi, Y., Khodadadi, A., Sadagiani, K., Lowering Methane and Raising Distillates Yields in Fischer-Tropsch Synthesis by Using Promoted and Unpromoted Cobalt Catalysts in a Dual-Bed Reactor, *Fuel Proc. Tech.*, **87** (7), 641 (2006).

[11] Krishnamoorthy, S., Tu, M., Ojeda, M.P., Pinna, D., Iglesia, E., An Investigatin of the Effects of Water on Rate and Selecvtivity for the Fischer- Tropsch Synthesis on Cobalt-Based Catalysts, *J. Cat.*, **211**, 422 (2002).

[12] Tavasoli, A., Khodadadi, A., Mortazavi Y., karimi A., Accelerated Deactivation and Activity Recovery Studies of Ruthenium and Rhenium Promoted Cobalt Catalysts in Fischer- Tropsch Synthesis, *Iran. J. Chem. and Chem. Eng.*, **24** (2), p. 25 (2005).

[13] Jacobs, G., Patterson, P.M., Zhang, Y., Das, T., Li, J., Davis B.H., Fischer-Tropsch Synthesis: Deactivation of Noble Metal-Promoted Co/Al$_2$O$_3$ Catalysts, *App. Cat.*, **233**, 215 (2002).

[14] Bechara, R., Balloy, D., Vanhove, D., Catalytic Properties of Co/Al2O3 System for Hydrocarbon Synthesis, *App. Cat.*, **207**, 343 (2001).

[15] Fan, L., Sun S., Fujimoto, K., Symposium on Advances in FT Chemistry, 219th National Meeting, American Chemical Society, San Francisco, CA (2000).