

Effect of Recycle Gas on Activity and Selectivity of Co-Ru/Al₂O₃ Catalyst in Fischer-Tropsch Synthesis

A.A.Rohani, B.Hatami, L.Jokar, F.khorasheh, A.A.Safekordi

Abstract—In industrial scale of Gas to Liquid (GTL) process in Fischer-Tropsch (FT) synthesis, a part of reactor outlet gases such as CO₂ and CH₄ as side reaction products, is usually recycled. In this study, the influence of CO₂ and CH₄ on the performance and selectivity of Co-Ru/Al₂O₃ catalyst is investigated by injection of these gases (0-20 vol. % of feed) to the feed stream. The effect of temperature and feed flow rate, are also inspected. The results show that low amounts of CO₂ in the feed stream, doesn't change the catalyst activity significantly but increasing the amount of CO₂ (more than 10 vol. %) cause the CO conversion to decrease and the selectivity of heavy components to increase. Methane acts as an inert gas and doesn't affect the catalyst performance. Increasing feed flow rate has negative effect on both CO conversion and heavy component selectivity. By raising the temperature, CO conversion will increase but there are more volatile components in the product. The effect of CO₂ on the catalyst deactivation is also investigated carefully and a mechanism is suggested to explain the negative influence of CO₂ on catalyst deactivation.

Keyword—Alumina, Carbon dioxide, Cobalt catalyst, Conversion, Fischer Tropsch, Selectivity

I. INTRODUCTION

IN the twenty-first century, natural gas is expected to become an increasingly important raw material for manufacturing clean fuels and chemicals [1]–[3]. Fischer-Tropsch (FT) synthesis is a major part of gas-to-liquids (GTL) technology, which converts Syngas gas (H₂ and CO) into liquid fuels with very low sulfur and aromatic content [1]–[4]. Production of Syngas from methane, coal, and biomass followed by subsequent conversion of Syngas to a wide range of fuels and chemicals, is of particular interest as the worldwide reserves of crude oil are being depleted.

Supported cobalt catalysts have been particularly attractive for the conversion of synthesis gas to valuable long-chained hydrocarbons, because of their high activity, high stability, relatively low cost, high selectivity for long chain paraffins and low water–gas shift (WGS) reaction [5]–[7].

A.A.Rohani, Research institute of petroleum, Industry National Iranian Oil Company P.O.Box:14665-1998, Tehran, Iran. Phone: +98 (21) 44739540-60 (Ext.2357); fax: +98 (21) 44739779; e-mail: rohaniaa@ripi.ir,

B.Hatami, Research institute of petroleum Industry, National Iranian Oil Company, Tehran, Iran (e-mail: hatami_1344@yahoo.com)

L.Jokar, F.khorasheh, A.A.Safekordi, Department of Chemical engineering and petroleum, Sharif University of technology, Tehran, Iran. (e-mail: lila_jd64@yahoo.com, khorasheh@sharif.edu, safekordi@sharif.edu).

The economical value of the process is related to the value of the products. Thus the product selectivity and the overall efficiency of the process are the main parameters of any gas converting design. In industrial scale, the gas products are separated from the desired products and after the condensation of water vapor, a part of this gas is recycled to the reactor in order to increase the efficiency of the process. This recycle gas includes: H₂ and CO (as unconverted feed), CO₂ and CH₄ (as side products) and other volatile hydrocarbons. Each of these gases has a different effect on the catalyst activity, product selectivity and deactivation of the catalyst. Many experiments have been performed to investigate the effect of olefins on the activity and selectivity of several catalysts by adding the olefin to the feed stream directly [8]–[11]; but there is little research about the influence of CO₂ and CH₄, which contribute to a significant part of the recycle gas, in the literature [12].

In this study, the effect of CO₂ and CH₄ on the product selectivity and the performance of the Co-Ru /Al₂O₃ catalyst were investigated by adding these gases to the feed stream (0-20 vol. % of the feed). On the other hand, Cobalt catalyst is more expensive than Iron based catalysts, so the deactivation rate of this catalyst is an important parameter [13]–[17]. In the other part of this study, the effect of CO₂ on the deactivation rate of Co-Ru /Al₂O₃ catalyst was inspected. The reaction was carried out in a fixed bed synthesis reactor operating at atmospheric pressure. The effects of feed flow rate and temperature were also investigated.

II. EXPERIMENTAL

A. Catalyst preparation

The catalyst used in this study, was made by the wet impregnation method. At first, Lanthanum was impregnated on Al₂O₃ using the Lanthanum Nitrate solution. After filtration, the sample was heated for 1 hour to reach 120°C in an oven and was kept at this temperature for 2.5 hours. Calcination was done at 450°C in a furnace. After the sample cooled down, Cobalt and Ruthenium were impregnated using the aqueous solution of Cobalt Nitrate and Ruthenium Nitrosyl Nitrate at the same time in one stage. The Cobalt weight loading was fixed at 15 wt. % and Lanthanum and Ruthenium were both fixed at 1 wt. % of the total weight of the catalyst.

B. Catalyst characterization

The catalyst elements were determined by XRF method and the quantity of each element was obtained by Atomic Absorption method. UOP303 standard was used to measure the amount of Cobalt and UOP873 for the promoters. In all cases 95-100% of the predicted amount of the elements was impregnated on the Alumina. The powder X-ray diffraction (XRD) patterns were obtained with a Philips diffractometer using Cu-K α radiation.

C. The fixed bed reactor system

The micro reactor used in this study, is a fixed bed column with 6 mm internal diameter and 50 cm length. Reactants are fed to the reactor with the ratio of H₂/CO = 2 using two mass controllers. Feed gases are mixed by a mixer and enter to the top of the reactor. Some crushed Quartz with the particle sizes greater than the catalyst particles, is located at the top and the bottom of the reactor to avoid the flow of catalyst in the reactor. An agitated bath of melted salt is used to release the heat of the reaction and the temperature is controlled by a PID controller.

The gas product is sent to a GC (Varian-3800) equipped with a Flame Ionization Detector (FID) and a Thermal Conductivity Detector (TCD). The volumetric flow rate of these gases is determined before the GC system. In order to prevent the condensation of the gas products, the temperature of the exit line is kept at 20°C more than the previous parts. The outlet line and the gas sampling loop of the GC are also washed by Nitrogen before each injection to avoid the condensation of gases and the agglomerate of heavy hydrocarbons. The inlet line is connected to the GC by a bypass stream in order to analyze the feed.

The mass controllers are calibrated by the Brooks Vol-U-Meter Calibrator (220 VAC) and the thermometers and temperature controllers are calibrated by the Hermetzet B 4001 Simens by the comparison method.

D. Activity and selectivity tests

For all experiments, 1 gram of catalyst with 30 to 100 μ m particle sizes was loaded into the micro reactor. The reduction of catalyst was done by Hydrogen with 30 ml/min volumetric flow rate. The reactor temperature was increased to 400°C and was kept at this temperature for 12 hours. After the reduction process, the temperature was reduced from 400°C to the desired reaction temperature in 2 hours.

To determine the effect of temperature on the catalyst activity and selectivity, the reaction was performed at 200, 210 and 220°C at atmospheric pressure. The feed flow rate was 45 ml/min. The influence of the feed rate was investigated at 220°C and atmospheric pressure at 30, 45 and 90 ml/min flow rates. To investigate the effect of CO₂ on the catalyst activity and selectivity, the reaction was carried out at atmospheric pressure and at 220 and 240°C. To investigate the effect of CO₂ on the deactivation of catalyst, the reaction was carried out at 260°C. The volumetric flow rate was 60 ml/min and CO₂ was injected to the feed stream from a storage tank (0-20 vol. % of feed). For all runs, the total pressure of the tank was 12 bars. In order to have a constant feed flow rate,

nitrogen was used in all runs. The influence of CH₄ was examined in the same situation, as CO₂, but only at 220°C.

For all experiments, the mole fraction of each component in the outlet of the reactor was determined and the feed conversion and rate of hydrocarbon production per unit mass of the catalyst was subsequently calculated. Product selectivity was estimated from the rate of production of each component and the total amount of the consumed CO.

III. RESULTS AND DISCUSSION

A. Physicochemical properties of Co-Ru/Al₂O₃

The catalyst elements were determined by XRF method and the XRF patterns are shown in Fig.1 in which, the Aluminum, Cobalt and Ruthenium peaks can be seen clearly.

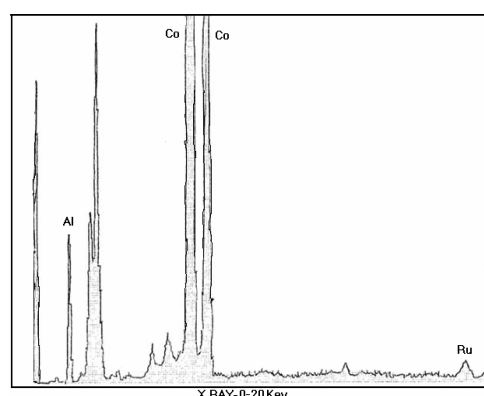


Fig.1 the XRF pattern of Co-Ru/Al₂O₃

Quantitative analysis of the catalyst elements was done by Atomic Absorption method and the result is shown in Table I. In all cases, 95-100% of the predicted amount of the element was impregnated on the Alumina.

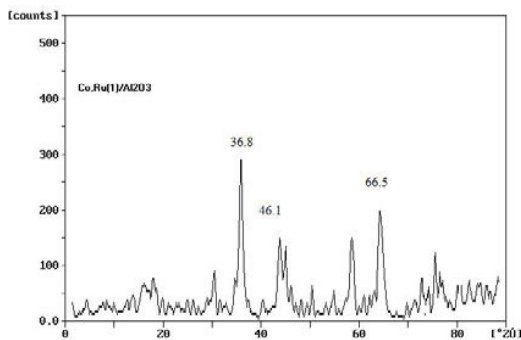
TABLE I
RESULT OF ATOMINC ABSORPTION TEST

Component	Co	Ru	La
Approximated fraction	15	1	1
Ultimate fraction	14.7	1	1

Fig. 2 shows the XRD pattern of the Co-Ru/ γ -Al₂O₃ catalyst. The Al₂O₃ exhibits reflection peaks at $2\theta = 46.1^\circ$ and 66.5° . The other peaks show the different crystalline types of CO₃O₄. The sharpest peak is observed at $2\theta = 36.8^\circ$.

B. Temperature effects

The temperature effect was inspected at atmospheric pressure with 45 ml/min feed flow rate at 200, 210 and 220°C and H₂/CO=2. Fig.3 shows that both the CO conversion and the reaction rate increase with increasing reaction temperature.

Fig.2 XRD pattern of Co-Ru/Al₂O₃

As shown in Fig.4, increasing the temperature causes a decrease in C₅+ selectivity and an increase in CH₄ and C₂-C₄ selectivity. This means that by increasing temperature, there are more volatile hydrocarbons in the products.

C. Effects of feed flow rate

Fig.5 shows the effect of feed flow rate on CO conversion at 220°C, atmospheric pressure and H₂/CO=2. Increasing the feed flow rate resulted in a decrease in the conversion of CO due to lower residence times.

As shown in Fig.6, selectivity of volatile hydrocarbons increased with increasing feed flow rate as. By raising the flow rate, the residence time of olefins on the catalyst surface

would decrease reducing the probability of olefin adsorption and regrowth thus increasing the selectivity for more volatile hydrocarbons in the products.

D. CO₂ effect

To investigate the effect of CO₂ on the catalyst activity and selectivity, the reaction was carried out at atmospheric pressure and at 220 and 240°C with 60 ml/min feed flow rate and H₂/CO=2. Fig.7 shows the effect of CO₂ on CO conversion at 220°C. Adding small amounts of CO₂ to the feed stream did not change the CO conversion significantly. By injection of about 10 vol. % and more, however, the CO conversion would decrease. The Lanthanum promoter which is a basic metal adsorbs CO₂ on the catalyst surface. By increasing the amount of CO₂ in the feed, the adsorption of this gas on the catalyst surface would increase the surface concentration of CO₂ and consequently decrease the surface concentration of H₂. Since the reaction rate is directly related to the surface H₂ concentration, the reaction rate would also decrease. As shown in the Fig.7, by adding 20 vol. % CO₂ to the feed stream, there will be 36.7% reduction in the CO conversion.

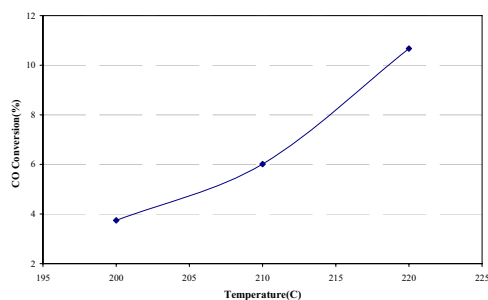


Fig. 3 temperature effect on CO conversion

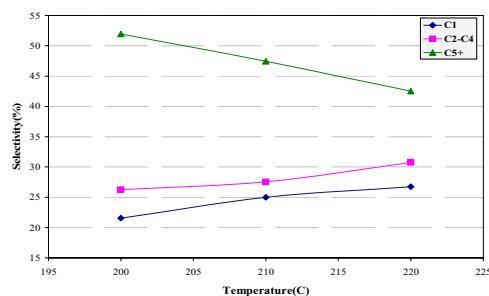


Fig. 4 temperature effect on product selectivity

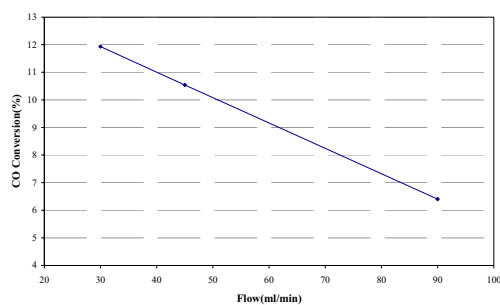


Fig. 5 effect of feed flow rate on CO conversion

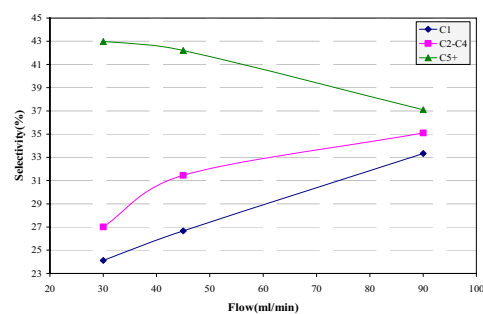
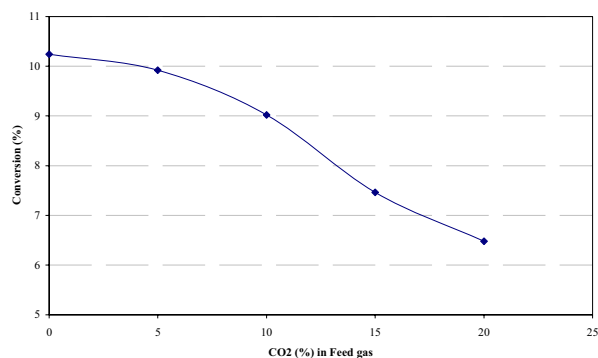
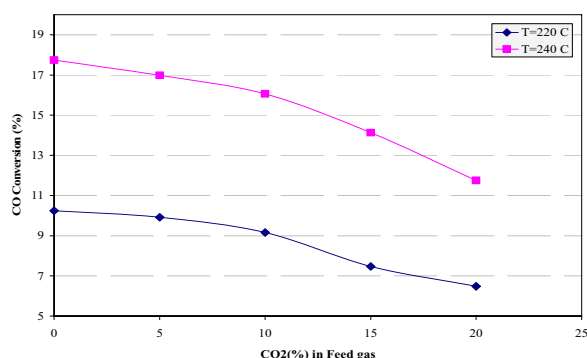


Fig. 6 effect of feed flow rate on product selectivity

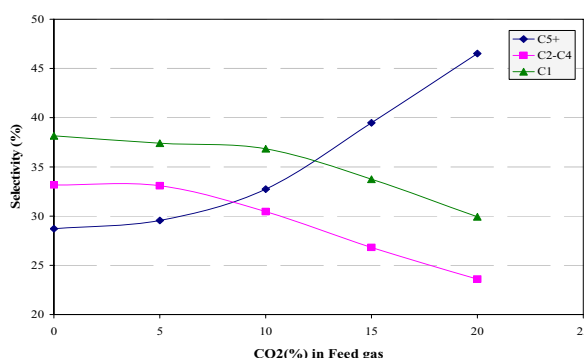
Fig. 7 effect of CO₂ on CO conversion at 220°CFig. 9 the effect of CO₂ on CO conversion at 220°C and 240°C

The effect of CO₂ on the product selectivity is shown in Fig.8. It can be seen that adding small amounts of CO₂ (less than 10 vol. %) would not significantly affect the product selectivity. Further increases in the amount of CO₂ in the feed, however, would decrease the selectivity for CH₄ and other volatile hydrocarbons and increase those for the heavy components (C₅+). Increasing the amount of CO₂ in the feed and the consequent reduction of surface H₂ concentration, would suppress hydrogenation reactions and therefore the chain growth and the product selectivity for heavy components would increase. The production of saturated paraffin hydrocarbons would decrease due to lower rate of hydrogenation reactions leading to the presence of more olefins in the products [18], [19].

Increasing the amount of CO₂ in the feed would increase the product selectivity for heavy components and liquid hydrocarbons and decrease the overall reaction rate. Similar trends were observed at the higher temperature of 240°C. The reduction in CO conversion, however, is more significant at the lower temperature. As shown in Fig.9 at 240°C, addition of 20 vol. % of CO₂ to the feed stream would result in 33.8% reduction in the CO conversion. The effect of CO₂ on the product selectivity at 240°C is shown in Fig.10. The C₅+

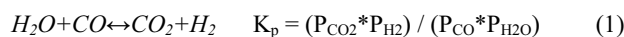
selectivity at this temperature are lower than those at 220°C over the entire range of the amounts of CO₂ added to the feed.

To investigate the effect of CO₂ on catalyst deactivation, the reaction was carried out under conditions that both the reaction rate and the CO conversion were high; namely at 260°C, atmospheric pressure, 60 ml/min feed flow rate and H₂/CO=2 for 30 hours. The results are shown in Fig.11 for different amounts of CO₂ added to the feed stream. The relative activity is defined as the ratio of CO conversion at a given time to the CO conversion at the start of the reaction. As illustrated in Fig.6, if there is no CO₂ in the feed, the relative activity of catalyst would decrease by 21.8% in the first 15 hours. With 20% CO₂ in the feed, however, the relative activity would decrease by 39.8% over the same time period. For all experiments, the reduction in activity was only significant over the first 15 hours after which the relative

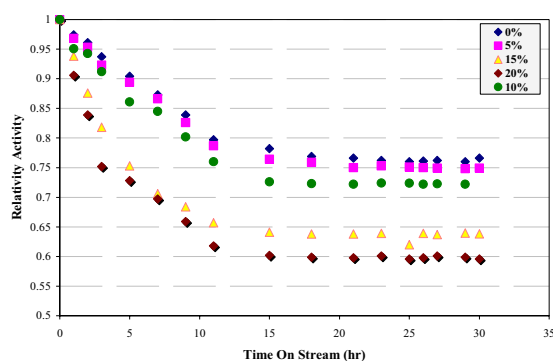
Fig.10 the effect of CO₂ on the product selectivity 240°C

activity would remain relatively unchanged.

In FT synthesis and at high CO conversions, the adsorption of CO₂ on the catalyst surface by the Lanthanum promoter is high causing a decrease in catalyst activity. Furthermore, by increasing the CO₂ partial pressure, the hydrogen concentration on the catalyst surface is reduced resulting in the oxidation of surface Cobalt and the reaction of Cobalt and Alumina [20]. However, the deactivation of alumina supported cobalt catalyst due to increasing amount of CO₂ in the feed stream is mainly due to the water-gas shift reaction. In FT synthesis the water-gas shift reaction is a reversible reaction with CO₂ as one of the products:



If the partial pressure of CO₂ increases, the reaction proceeds in the reverse direction producing water. The increase in water vapor partial pressure enhances the oxidation of cobalt as well as the interaction between cobalt and alumina. The produced cobalt aluminate reduces the catalyst activity [21], [22].

Fig.11 the effect of CO₂ on catalyst deactivation

E. CH₄ effect

To inspect the effect of CH₄ addition, the reaction was carried out at 220°C and at atmospheric pressure with H₂/CO=2 and a feed flow rate of 60 ml/min. The results are presented in Table II. It can be seen that increasing the amount of CH₄ in the feed stream did not significantly change the CO conversion and the product selectivity and CH₄ merely acts as an inert gas.

IV. CONCLUSION

The experiments conducted in this study indicated that CO conversion and the reaction rate increase with increasing temperature. Increasing the reaction temperature also leads to a decrease in the C₅⁺ selectivity and an increase in the CH₄ and C₂-C₄ selectivity. Increasing the feed flow rate resulted in an increase in the selectivity for volatile hydrocarbons and a decrease in CO conversion.

Adding small amounts of CO₂ to the feed stream did not significantly change the CO conversion or the product selectivity. With addition of 10 vol. % CO₂ and more, however, the CO conversion would decrease while the selectivity for heavy components would increase. At 220 and 240°C, addition of 20 vol. % of CO₂ to the feed stream resulted in 36.7% and 33.8% reduction in CO conversion, respectively. The C₅⁺ selectivity at 240°C were higher than those at 220°C.

If there was no CO₂ in the feed, the relative activity of the

catalyst would decrease 21.8% in the first 15 hours but with 20% CO₂ in the feed, the reduction of the relative activity was 39.8% over the same time period. The reduction of activity was only significant in the first 15 hours. Addition of CH₄ to the feed stream did not significantly change the CO conversion or the product selectivity.

REFERENCES

- [1] M.E. Dry, Catal. Today 71(2002)
- [2] A.Y. Khodakov, W. Chu, P. Fongarland, Chem. Rev. 107(2007)1692
- [3] A. Steynberg, M. Dry (Eds.), Fischer-Tropsch Technology, Stud. Surf. Sci. Catal. 152 (2004)
- [4] R.L. Espinoza, A.P. Steynberg, B. Jager, A.C. Vosloo, Appl. Catal. A 186 (1999)
- [5] J. Xiong, Y. Ding, T. Wang, L. Yan, W. Chen, H. Zhu, Y. Lu, Catal. Lett. 102(2005)
- [6] H. Ming, B.G. Baker, Appl. Catal. A: Gen. 123(1995) 23
- [7] G.Z. Bian, T. Mochizuki, N. Fujishita, H. Nomoto, M. Yamada, Energy Fuels 17 (2003)799
- [8] H. Schulz, G. Schaub, M. Claeys, T. Riedel, Appl. Catal. A 186 (1999) 215
- [9] K.W. Jun, S.J. Lee, H. Kim, M. Choi, K.W. Lee, Stud. Surf. Sci. Catal. 114 (1998) 345
- [10] T. Riedel, G. Schaub, K.W. Jun, K.W. Lee, Ind. Eng. Chem. Res. 40 (2001) 1255 J
- [11] D. Schanke, S. Vada, E.A. Blekkan, A.M. Hilmen, A. Hoff, A. Holmen, J. Catal. 156 (1995) 85
- [12] S.M.Kim, J.W.Bae, Y.J.Lee, K.W.Jun, Catalysis Communications 9 (2008) 2269
- [13] Das T., Jacobs G. Patterson P.M., Conner W. A., Li. J., Davis B.H., Fuel 82 (2003)
- [14] Hilmen A.M., Schanke D., Hanssen K.F., App. Cat. 186 (1999) 169
- [15] Kiss G., Kliewer C.E., DeMartin G.J., Culross C.C., Baumgartner J.E., J. Cat. 217 (2003) 127
- [16] Dry, M.E.; Shingles, T.; Boshoff, L.J.; Botha, C.S; J. of Catal. 17 (1970) 347
- [17] Dry, M.E.; Shingles, T.; Botha, C.S; J. of Catal. 17 (1970) 341
- [18] Uner D. O., M. Pruski, B. C. Gestein and T. S. King, J. Catal. 146 (1994) 530
- [19] Riedel. T. et al., Industrial Engineering Chemistry Research 215-227 (2001)
- [20] P. J. Van., Berge. J. Van de Loosdrecht, S. Barradas, A. M. Van der kraan, Catalysis Today, 58 (2000) 321
- [21] A. M. Hilman, D. Schanke, K. F. Hanssen, Applied catalysis A. 186 (1999)169
- [22] Christopher J. Bertole, Challes A. Mims, Gabor Kiss, J. Catal., 38 (2002)

Dr. Ali Asghar Rohani, Ph.D. Chemical Engineering, Head of Cobalt GTL Plan, Gas Division, Research institute of petroleum Industry, national Iranian Oil Company, Tehran, Iran

TABLE II
EFFECT OF CH₄ ON CO CONVERSION AND PRODUCT SELECTIVITY

CH ₄ (%) in Feed gas	N ₂ (%) in Feed gas	C ₂ -C ₄ Sel. (%)	C ₅ ⁺ Sel. (%)	CO Conversion (%)
0	20	35.486	33.102	10.378
5	15	35.834	32.865	10.318
10	10	35.208	33.242	10.56
15	5	36.16	32.724	10.435
20	0	35.364	33.343	10.337