

# EFFECT OF OPERATING CONDITIONS ON FISCHER-TROPSCH LIQUID PRODUCTS PRODUCED BY UNPROMOTED AND POTASSIUM-PROMOTED IRON CATALYST

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**Abstract**— The dependencies of Fischer-Tropsch synthesis liquid hydrocarbon product distribution on operating pressure and temperature have been studied for unpromoted and potassium-promoted iron catalyst. The study followed an experimental planning and the results were analyzed based on surface response methodology. The effects of different operating conditions on the distribution of the liquid product were compared based on number-average carbon number and distribution dispersion. Results showed that high pressures (25 to 30 atm) favor the production of heavy waxes that can be converted into liquid fuels through hydrocracking, while greater selectivity towards liquid fuels are favored by low temperature (240°C) and low pressure (20 atm). The liquid product distribution produced using potassium promoted iron catalyst presented higher number-average number of carbons, lower dispersion and lower skewness when compared to product distribution obtained with the unpromoted iron catalyst. The use of potassium as a promoter resulted in the production of longer hydrocarbon chains with higher selectivity of a specific narrow carbon number range.

**Keywords**— Fischer-Tropsch Synthesis, Liquid Fuels, Iron-based Catalyst

## I. INTRODUCTION

In recent years, the Fischer-Tropsch synthesis (FTS) has become a subject of renewed interest particularly in converting natural gas (NG) into liquid transportation fuels. This can became a major advantage when dealing with natural gas because its storage is a big logistic problem, especially regarding exploration in off-shore exploitation platforms. A palliative transportation solution, which has been in relatively widespread use for years involves the conversion of NG into liquefied natural gas (LNG). However the LNG approach has a significant drawback since it is a relatively expensive process and the storage vessels requires rigorous thermal design and construction specs due to the required low temperatures. For that reason, if the FTS process is further developed and performed efficiently, it may become an economically viable alternative for delivering natural gas across large distances.

Fischer-Tropsch synthesis (FTS) is a process that converts natural gas into liquid transportation fuels. In

this process, natural gas is converted to synthesis gas (carbon monoxide and hydrogen mixture) via steam reforming, carbon dioxide reforming, partial oxidation or catalytic partial oxidation. Syngas is then converted into hydrocarbons by the FT reaction:



Iron-based catalysts have been studied for Fischer-Tropsch synthesis (FTS) by many investigators (Raje and Davis, 1997; van Steen and Schulz, 1999; Donnelly and Satterfield, 1989; Eliason and Bartholomew, 1999), and its performance in producing liquid fuels and waxes is satisfactory. Most researches have focused on reaction conversion and overall rate of reaction (Raje and Davis, 1997; Eliason and Bartholomew, 1999). Several studies were also carried out to understand the complex kinetic mechanism and the effects of operating conditions on the distribution of the FTS product (Huff and Satterfield, 1984; Mandon and Taylor, 1981; Donnelly and Satterfield, 1989; Li *et al.* 2002; Patzlaff *et al.*, 1999; van der Laan and Beenackers, 1999; Fernandes, 2005, 2006; Fernandes and Sousa, 2006). These studies have shown that iron-based catalyst produces paraffins, especially low molecular weight paraffins (light gases, gasoline and diesel cuts) and a large quantity of olefins depending on the operating condition employed, on the catalyst and on the reactor that is used. The use of potassium-promoted catalysts also is known to improve the performance of the FT synthesis. Although iron catalysts are known to have a better performance at high pressures only few reports have addressed the Fischer-Tropsch synthesis at pressures above 20 atm (Bukur and Lang, 1999; van der Laan and Beenackers, 1999; Wang *et al.*, 2003; Farias *et al.*, 2007, 2008) and more information is still needed on the behaviour of the FTS at pressures above 20 atm. Van Berge (1997) has shown that iron-based catalysts present better performance than Co-based catalysts at high pressures (over 10 atm, preferably above 20 atm) and space velocities.

In recent studies, our group has evaluated the performance of iron-based catalysts on the production of liquid hydrocarbons, under high pressure Fischer-Tropsch synthesis. In this study we have examined the effect of a potassium-promoted and an unpromoted iron catalyst, supported on alumina, on the distribution of the liquid product of the FT reaction carried out under pressures between 20 and 30 atm.

## II. EXPERIMENTAL

### A. Catalyst Preparation

An industrial magnetite type iron catalyst with molar basis composition  $100\text{Fe}/2\text{K}/15\text{Al}_2\text{O}_3$  was obtained from FAFEM (São Paulo, Brazil). A potassium-promoted iron catalyst with a  $100\text{Fe}/20\text{K}/15\text{Al}_2\text{O}_3$  composition (molar basis) and was prepared by impregnation of the industrial catalyst with aqueous solution of  $\text{K}_2\text{CO}_3$  by incipient wetness technique in a rotary evaporator (Tecnal model TE-211, Brazil) operated at  $70^\circ\text{C}$  under 500 mmHg (vacuum maintained using a vacuum pump Tecnal model TE-058).

After impregnation, the catalyst was dried in a drying oven (Fanem model AH-T, Brazil) at  $60^\circ\text{C}$  for 24 hours and calcined in air at  $350^\circ\text{C}$  for 5 hours (heating rate of  $10^\circ\text{C}/\text{min}$  between 30 and  $350^\circ\text{C}$ ). The catalyst was analyzed for iron, potassium and aluminum by fluorescence spectroscopy.

### B. Fischer-Tropsch Reaction

The FTS was carried out in a 1 L high-pressure autoclave reactor (Parr Instruments model 4571). The reactor was fed with 10 grams of catalyst suspended in 300 grams of paraffin. The paraffin used as liquid medium consisted of linear chain paraffin with melting point between 60 and  $62^\circ\text{C}$  and was obtained from Synth (São Paulo, Brazil). Tests were carried out at pressures between 20 and 30 atm and temperatures between 240 and  $270^\circ\text{C}$ . Synthesis gas was prepared by mixing  $\text{H}_2$  and CO via two volumetric flow controllers, enabling a  $\text{H}_2:\text{CO}$  molar ratio of 1:1. The flow rate of  $\text{H}_2$  and CO was maintained at 50 NmL/min during the experiment.

The experiments were carried out in fed-batch mode with recirculation of the synthesis gas according to the scheme shown in Fig. 1. The syngas was fed to the reactor directly into the slurry phase through a feeding tube. The synthesis gas, gaseous and liquid products were allowed to circulate through a hot trap were part of the liquid product was collected. The gas phase was allowed to recycle through the slurry phase by means of a gas entrainment impeller, improving the conversion of syngas into hydrocarbons. The reaction was carried out under constant mechanical agitation (800 rpm).

Each run was carried out for 20 hours under constant pressure and temperature. The gaseous mixture exiting the reactor passed through a cold trap immersed in ice. Samples of the slurry phase, hot trap and cold trap were collected and analyzed. Only the liquid products were analyzed since they are the FTS products that have higher commercial value, and because the gaseous products are often reformed to produce syngas again.

The tests followed a  $2^2$  experimental planning with central composite. Conditions for each run are listed in Table 1. Experiments were done in duplicate and the results were based on the mean values.

### C. Data Analysis

The data at any set of process conditions were obtained during 20 hours mass balance periods when the liquid products were allowed to accumulate in the reactor.

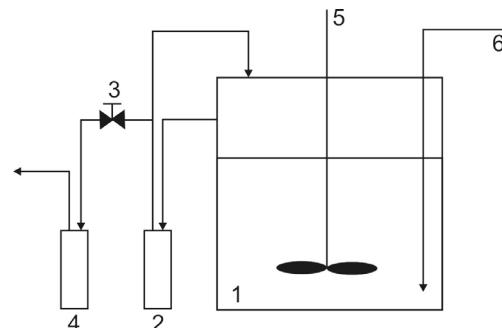


Figure 1. Schematic of the Fischer-Tropsch system. 1. reactor; 2. hot trap; 3. valve; 4. cold trap; 5. gas entrainment impeller; 6. gas inlet.

**Table 1.** Operating conditions of the experimental planning.

Run	Pressure [atm]	Temperature [ $^\circ\text{C}$ ]
1	20	240
2	20	270
3	25	255
4	30	240
5	30	270

The liquid-phase products were analyzed in a Shimadzu (Model QP5050) gas chromatograph with mass spectrum (CGMS) equipped with thermal conductivity (TCD) and flame-ionization (FID) detectors.

Temperature programming ( $30^\circ\text{C}$  to  $300^\circ\text{C}$ ) with a packed OV-5 column (30 m x 0.25 mm ID x 0.25  $\mu\text{m}$  film) allowed the identification of liquid-product Fischer-Tropsch hydrocarbons ( $\text{C}_{10}$  to  $\text{C}_{40}$ ), which were present in the hot and cold traps.

The gaseous-phase products were analyzed in a Thermo (Model Ultra) gas chromatograph. Temperature programming ( $30^\circ\text{C}$  to  $100^\circ\text{C}$ ) with a packed OV-1 column (30 m x 0.54 mm ID x 0.25  $\mu\text{m}$  film) allowed the identification of gaseous-product Fischer-Tropsch hydrocarbons ( $\text{C}_4$  to  $\text{C}_{15}$ ), which were present in the stream leaving the cold trap. A microcomputer used to perform data acquisition and process control also controlled automatic chromatograph sampling.

The gaseous mixture fed into the reactor was comprised of CO (48%),  $\text{H}_2$  (48%) and He (4% molar basis). The conversion of syngas into hydrocarbons was determined by feeding helium (inert) into the reactor and by analyzing the initial and final molar ratio between helium and carbon monoxide. The concentration of helium and carbon monoxide was analyzed in a Thermo (Model Ultra) gas chromatograph equipped with thermal conductivity detector (TCD). TCD was also used to determine the amount of  $\text{C}_1$  to  $\text{C}_6$  in the stream leaving the cold trap.

## III. RESULTS AND DISCUSSION

The full product distribution of the products obtained from the Fischer-Tropsch synthesis using the potassium promoted and unpromoted iron catalysts followed a typical Anderson-Schulz-Flory distribution (Fig. 2).

Iron catalysts form mostly straight-chain hydrocarbons. Fischer-Tropsch products of high commercial value are diesel and kerosene (jet fuel), which have

from 10 to 25 carbons ( $C_{10}$  to  $C_{25}$ ). Waxy products ( $C_{25+}$ ) have low commercial value as final products but can be cracked to produce lower molecular weight fuels such as gasoline, kerosene and diesel. As a specific chain-length is not possible to be produced the aim of this study was to find operating conditions that can produce diesel and waxy products. To assess the amount of diesel and waxy products that were produced by the reaction, the product recovered in the cold and hot traps were analyzed to understand how the operating conditions affects the production of these heavy products.

The liquid products obtained in experiments consisted mainly of n-paraffins, which were collected in the hot and cold traps. The mass of liquid product corresponded to approximately 35 to 40% of the total hydrocarbons produced by the FT reaction. The amount of olefins produced was negligible and may be related to the mode of operation of the reactor which allowed recirculation of the products and long residence time resulting on the readsorption of olefins by the catalyst and its conversion to n-paraffins due to the high concentration of hydrogen in the reactor (Kuipers *et al.*, 1995; Schulz and Claeys, 1999).

The distribution of the liquid products obtained by Fischer-Tropsch synthesis presented a log-normal shaped curve as shown in Figure 3. The same log-normal distribution was also verified by Tsubaki and Fujimoto (2000) when studying FTS liquid products. Table 2 presents the selectivity for the liquid products obtained under different operating conditions for promoted and unpromoted iron catalysts.

For the unpromoted iron catalyst, increasing temperatures increased significantly the selectivity towards heavier hydrocarbons at high pressure, while a slight change could be observed at low pressure with the shift of the main fraction of the product distribution from  $C_{20-22}$  to  $C_{23-25}$ . Comparing the mass fractions obtained at runs #1 and #2, and runs #4 and #5 (Table 2) the distribution showed a shift from  $C_{20-22}$  to  $C_{23-25}$  (at 240°C) and  $C_{26-28}$  (at 270°C) favoring the production of heavier products rather than lighter liquid products. Increasing pressures also increased the selectivity of heavy hydrocarbons when the process was carried out at 270°C. The increase observed on heavier products at higher pressures was mainly given by the higher concentration of reactants, which tend to increase the rate of the propagation reaction of the hydrocarbon chain.

For the potassium-promoted catalyst, the liquid product distribution shifted from  $C_{20-25}$  to  $C_{26-31}$  (at 20 atm) with increasing temperature. At 30 atm an increase in temperature shifted the distribution from  $C_{29-31}$  to  $C_{23-25}$  range favoring the production of lighter hydrocarbons. Higher pressures produced heavier hydrocarbons at 240°C. The conversion of syngas was  $40\% \pm 3\%$  for all runs carried out with the unpromoted and potassium-promoted catalyst.

The selectivity of  $C_{32+}$  hydrocarbons was much higher when the reaction was carried out with the potassium-promoted catalyst. Thus the use of potassium as a

promoter increased the degree of polymerization in the FTS. The higher production of heavy hydrocarbons by the potassium-promoted catalyst may be related with the in-situ reduction of iron, which occurs at 260°C and can change the overall behavior of the catalyst.

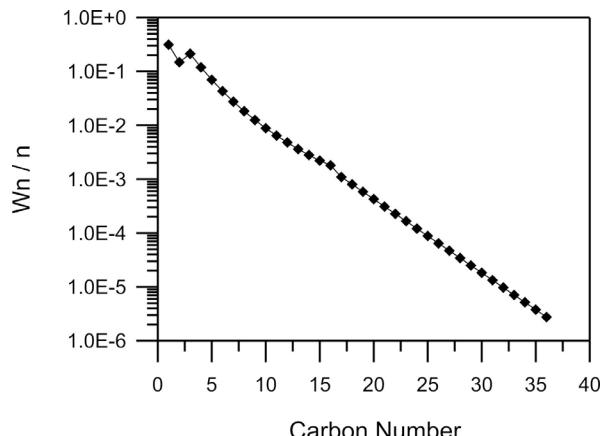
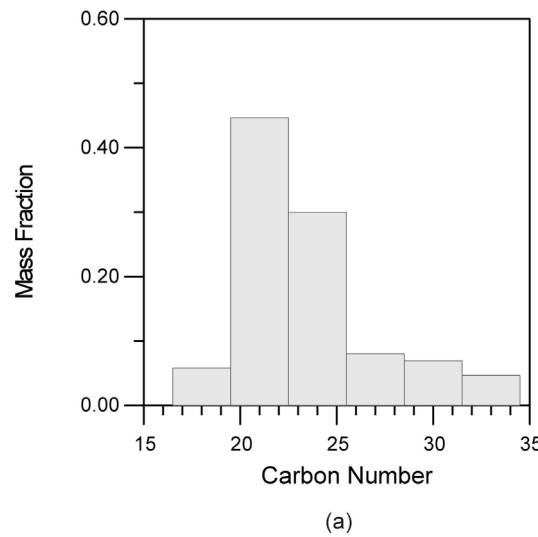
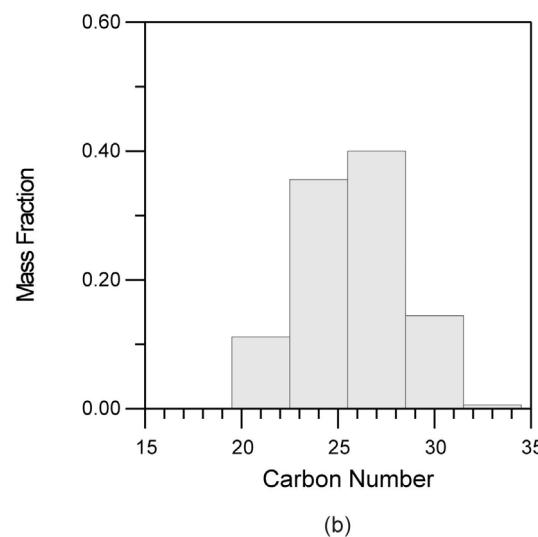


Figure 2. Distribution of the liquid product for run carried out at 240°C and 20 atm, with the potassium-promoted catalyst.



(a)



(b)

Figure 3. Distribution of the liquid product for run carried out at 240°C and 20 atm. (a) unpromoted catalyst; (b) potassium-promoted catalyst.

**Table 2.** Selectivity of liquid hydrocarbon chains produced using potassium-promoted and unpromoted iron catalyst.

Run	Hydrocarbon selectivity (mass fractions)					
	C <sub>20-</sub>	C <sub>20-C<sub>22</sub></sub>	C <sub>23-C<sub>25</sub></sub>	C <sub>26-C<sub>28</sub></sub>	C <sub>29-C<sub>31</sub></sub>	C <sub>32+</sub>
<i>Unpromoted iron catalyst</i>						
1	0.058	0.447	0.300	0.080	0.069	0.046
2	0.000	0.319	0.636	0.045	0.000	0.000
3	0.139	0.189	0.221	0.281	0.170	0.000
4	0.212	0.718	0.070	0.000	0.000	0.000
5	0.000	0.000	0.217	0.445	0.338	0.000
<i>Potassium-promoted iron catalyst</i>						
1	0.000	0.112	0.356	0.400	0.126	0.006
2	0.100	0.150	0.207	0.255	0.300	0.078
3	0.000	0.000	0.058	0.189	0.417	0.331
4	0.000	0.000	0.000	0.000	0.474	0.526
5	0.000	0.128	0.387	0.446	0.039	0.000

**Table 3.** Number-average number of carbons and distribution dispersion of liquid hydrocarbon chains produced using potassium-promoted and unpromoted iron catalyst.

Run	Number-average number of carbons	Distrib. dispersion index	Skewness index
<i>Unpromoted iron catalyst</i>			
1	23.3	1.024	1.026
2	23.3	1.003	1.003
3	24.3	1.028	1.024
4	20.1	1.008	1.008
5	27.3	1.005	1.005
<i>Potassium-promoted iron catalyst</i>			
1	25.7	1.009	1.009
2	26.7	1.018	1.017
3	30.2	1.008	1.007
4	31.9	1.003	1.003
5	25.2	1.007	1.007

The results obtained for the iron-based catalyst studied herein presented a different behavior from the results previously obtained for an iron-based catalyst supported in silica (Farias *et al.*, 2007, 2008). The increase in potassium content have increased the production of heavier hydrocarbons in both catalysts (alumina and silica supported iron-catalysts), but the behavior regarding temperature and pressure increase was different.

The effect of pressure and temperature on the distribution of the liquid product can be examined analyzing the number-average number of carbons ( $N_n$ ). The number-average number of carbons is a statistical index calculated dividing the first moment by the zeroth moment of the product distribution.

This index represents the hydrocarbon chain length where the mass fraction of the distribution is centered and can be used as a parameter to evaluate the degree of polymerization of the Fischer-Tropsch synthesis.

$$N_n = \frac{\sum n \cdot \phi_n}{\sum \phi_n} \quad (2)$$

The distribution can be further evaluated by means of the product distribution dispersion (or polydispersity) which is an index of how narrow or how broad the product distribution is. The dispersion can be calculated by:

$$Z = \frac{(\sum \phi_n) \cdot (\sum n^2 \cdot \phi_n)}{(\sum n \cdot \phi_n)^2} \quad (3)$$

Table 3 and Fig. 4 show the number-average number of carbons ( $N_n$ ) and polydispersity ( $Z$ ) for the reactions carried out with in this study. The results showed that both catalyst have produced liquid hydrocarbons with an  $N_n$  as high as 27 carbons for the unpromoted catalyst and 31 carbons for the potassium-promoted catalyst. The results showed a higher number-average number of carbons for the potassium-promoted catalyst.

The statistical t-test was carried out with the responses obtained from both catalysts and showed that the responses were statistically different at a 95% level of confidence. Thus, the use of potassium as a promoter has increased the carbon monoxide degree of polymerization. The only exception was at 270°C and 30 atm where the unpromoted iron catalyst produced an  $N_n$  higher than the potassium-promoted catalyst. Analyzing the response surface, the highest number-average number of carbons would be obtained operating the reactor at 240°C and 30 atm. Several reports (van der Lann and Beenackers, 1999; Bukur and Lang, 1999) showed that the low temperature process (240°C) has higher selectivity for heavy hydrocarbons. Our study showed that this behavior also stands for pressures above 20 atm.

Iron-based catalysts supported in silica presented high number-average number of carbons at high temperature (270°C) and high pressure (30 atm) (Farias *et al.*, 2007, 2008), while the alumina supported catalyst presented high number-average number of carbons at low temperature (240°C) and high pressure (30 atm). From an operational point of view, the use of alumina based catalyst may be an interesting option to produce liquid hydrocarbons since the synthesis may be carried out at a lower temperature. The alumina supported catalyst also presented a slightly higher number-average number of carbons (31.9) if compared to the highest number-average number of carbons produced using the silica supported catalyst (30.3). On the other hand the product distribution of the silica supported catalyst presented a broader distribution, and consequently produced a slightly higher amount of hydrocarbons with more than 32 carbons than the alumina supported cata-

lyst, behavior that is related to the larger mean pore diameter of the silica supported catalyst.

The polydispersity became lower as the number-average number of carbons increased, resulting in a narrower distribution. The polydispersity value of 1.003 obtained in Run #4 for the potassium-promoted catalyst represents a product distribution where 92.5% of the chains are within 5 carbons of distance from the number-average number of carbons. Higher dispersions (up to 1.028) were obtained with the unpromoted catalyst. Run #1 carried out with the unpromoted catalyst presented the highest dispersion index and consisted mainly of hydrocarbon chains between C<sub>18</sub> and C<sub>32</sub>. The average dispersion index was 1.014 for the unpromoted catalyst and 1.009 for the potassium-promoted catalyst. Thus, the use of potassium as a promoter might also contribute to a higher selectivity of a specific narrow range of hydrocarbons.

The results did not show significant amount of n-paraffins with more than 35 carbons which may be caused by space limitation inside the catalyst pores. This may also explain why the distribution dispersion index was lower for the highest number-average number of carbons. This hypothesis was also supported by the skewness (Sk) of the distribution which indicates if the distribution is well centered on the number-average carbon number or if the distribution is shifted to the right or left.

$$Sk = \frac{(\sum n \cdot \phi_n) \cdot (\sum n^3 \cdot \phi_n)}{(\sum n^2 \cdot \phi_n)^2} \quad (4)$$

The skewness of the distribution is presented in Table 3. For high number-average carbon number the skewness was next to unit indicating that the distribution was well centered on the average number of carbons.

The skewness of the distribution was higher when the reaction was carried out at low temperatures (240°C and 255°C). At temperature of 270°C the distribution was narrow, centered at the number-average number of carbons and presented a normal distribution. At low temperatures the distribution was broad and presented a log-normal distribution. The average skewness was 1.013 for the unpromoted catalyst and 1.008 for the potassium-promoted catalyst. Thus, the use of potassium as a promoter might shift the distribution from a log-normal shaped distribution to a normal shaped distribution enhancing the selectivity of a specific range of hydrocarbons.

## V. CONCLUSIONS

Fischer-Tropsch synthesis can be used to produce transportation fuels from natural gas and the polymerization conditions can be set to maximize the selectivity of a certain cuts, such as diesel or heavy waxy products.

The process conditions (pressure and temperature) have a complex relationship with the liquid product distribution. The results showed that the Fischer-Tropsch synthesis can be set toward a lower number-average number of carbons leading to higher selectivity of diesel

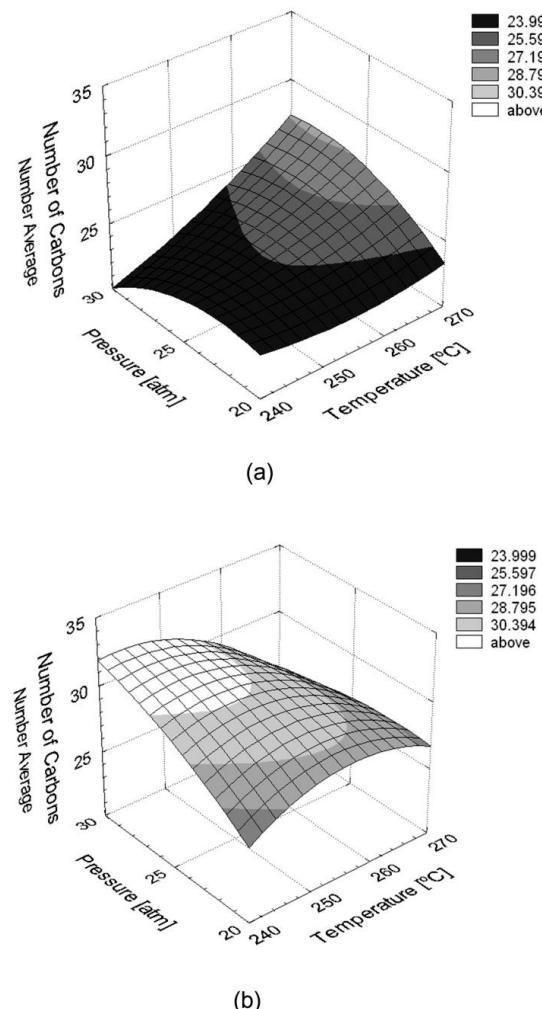


Figure 4. Number-average number of carbons obtained under different temperatures and pressures. (a) unpromoted catalyst; (b) potassium-promoted catalyst.

using the unpromoted iron catalyst and low temperature (240°C). Higher selectivity of waxy products can be obtained using a potassium-promoted iron catalyst, high pressure (30 atm) and low temperature (240°C).

The liquid Fischer-Tropsch product produced using potassium-promoted iron catalyst showed a higher number-average number of carbons, lower dispersion and lower skewness. As such the use of potassium as a promoter of the Fischer-Tropsch reaction might lead to the production of heavier hydrocarbon chains with higher selectivity of a specific narrow carbon number range.

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**NOMENCLATURE**

n	number of carbons
$N_n$	number-average number of carbons
Sk	skewness
Z	distribution dispersion
$\phi_n$	mass fraction of the hydrocarbon with n number of carbons

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