



# Parametric study of Fischer-Tropsch synthesis for the production of clean hydrocarbons in a conventional fixed bed reactor

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**Abstract**— In this paper, we present an interesting solution for the production of clean hydrocarbons from bio-syngas with less emissions of pollutants, such as sulphur. The Fischer-Tropsch (FT) synthesis was conducted over a cobalt-based catalyst in a fixed-bed reactor at different temperatures (483-513K), H<sub>2</sub>/CO molar ratios (0.5–2) and gas hourly space velocities (4000–5500 h<sup>-1</sup>), in order to find the optimal parameters that can offer the highest process efficiency. Our findings show that the temperature resulted in an increase in the syngas conversion and hydrocarbons selectivity. For a particular case, the re-absorption of ethylene on the surface of the catalyst showed a decrease in selectivity at 513K. The increase in the molar ratio improved the conversion and the products selectivity. This effect is more pronounced for methane owing to the high adsorption of H<sub>2</sub>. The decrease in the contact time between the catalyst particles and the reactants by raising the gas hourly space velocity showed a negative effect on CO and H<sub>2</sub> conversion and hydrocarbons selectivity.

**Keywords**— Fischer-Tropsch synthesis, Cobalt-based catalyst, clean hydrocarbons, bio-syngas, optimal parameters

## I. INTRODUCTION

Technology represents the main source for energy extraction, however this energy must respond to environmental considerations. Thus, using clean resources seems to be an efficient solution [1], [2]. Hence, the FT technology is set to be a vital factor in fuel production as a consequence of environmental requirements and the change of fossil energy reserves [3]. This new energy leads to the production of hydrocarbons with low concentrations of sulphur, which has a negative effect on the environment [4]. The FT synthesis produces hydrocarbons from syngas derived from the gasification technologies of coal to liquid (CTL), gas to liquid (GTL) and biomass to liquid (BTL), in the presence of gasification agents, such as air, oxygen, steam or CO<sub>2</sub> [5].

Processes like isomerisation and catalytic reforming was added in order to produce high fuel quality (high-octane index). Considering biomass as a renewable energy source [4], is likely to see in the next decade a considerable rise in BTL technology use.

In the present work, the variation of different reaction conditions is done in order to study the evolution of CO and H<sub>2</sub> conversions and products selectivity. It was found that the optimal parameters lead to higher process performance.

## II. REACTOR DESCRIPTION AND MATHEMATICAL MODEL

In our study, FT reactions take place in a packed bed reactor over cobalt-based catalyst. The fixed bed reactor is widely used due to his simplicity and its capacity of production compared to other reactors such us slurry and fluidized bed reactors [4]. The cobalt based catalyst promotes hydrogenation and deactivate less quickly than the iron ones, resulting in a higher productivity of hydrocarbons with long chain length [6]. The used dimensions of the reactor and the operating conditions are given in the table I [7]-[9].

TABLE I  
REACTOR DIMENSIONS AND OPERATING CONDITIONS

Parameter	Value
Reactor length (m)	12
Reactor diameter (m)	12.7 x 10 <sup>-3</sup>
Catalyst bed length (m)	7.0
Initial pressure (bar)	10
Initial temperature (K)	483-513
T <sub>sh</sub> (K)	539
U <sub>sh</sub> (w/m <sup>2</sup> K)	80



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Bed porosity	0.4
Density (kg/m <sup>3</sup> )	400
Particle diameter (m)	2.51 x 10 <sup>-3</sup>
Viscosity (bar/s)	0.007 x 10 <sup>-10</sup>
Gas density (kg/m <sup>3</sup> )	13.2
Gas velocity (m/s)	1

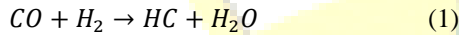
$$\beta_1 = \frac{k_G k_{IN}}{k_{P_n} + k_{O_n} \gamma_H^{-1}} \quad (15)$$

$$\beta_2 = k_{IN} \gamma_H + \frac{k_G k_{O_n}^{rev} K_{O_n}^{ad} (\sum_{n=2}^{\infty} P_{O_n})}{k_{P_n} + k_{O_n} \gamma_H^{-1}} \quad (16)$$

$$\beta_3 = k_{CO} K_{CO}^{ad} P_{CO} \quad (17)$$

Where  $R_j$  and  $n$  are the elementary reaction and the carbon number, respectively.

FT reaction consists of CO hydrogenation to hydrocarbons and water:



The kinetic model used in this study is follows:

$$R_{CH_4} = k_{CH_4} \gamma_1 \gamma_H / DEN \quad (2)$$

$$R_{C_2H_6} = k_{P_2} (A_2 \gamma_1 + B_2) \gamma_H / DEN \quad (3)$$

$$R_{P_n} = k_{P_n} \{A^{n-2} A_2 \gamma_1 + (\sum_{i=2}^n A^{n-i} B_i)\} \gamma_H / DEN \quad n \geq 3 \quad (4)$$

$$R_{C_2H_4} = (k_{O_2} (A_2 \gamma_1 + B_2) - k_{O_2}^{rev} K_{O_n}^{ad} \gamma_H P_{O_2}) / DEN \quad (5)$$

$$R_{O_n} = \left[ k_{O_n} \{A^{n-2} A_2 \gamma_1 + (\sum_{i=2}^n A^{n-i} B_i)\} - k_{O_n}^{rev} K_{O_n}^{ad} \gamma_H P_{O_n} \right] / DEN \quad n \geq 3 \quad (6)$$

Where

$$DEN = \left[ 1 + \gamma_H + \gamma_{CH_2} \left\{ \left( 1 + (\sum_{i=2}^{NP} A^{n-i} B_i) \right) \gamma_1 \right\}^2 + (\sum_{k=2}^{NP} \sum_{i=2}^k A^{n-i} B_i) \right] \quad (7)$$

$$A_2 = \frac{k_G \gamma_{CH_2}}{k_G \gamma_{CH_2} + k_{P_2} \gamma_H + k_{O_2}} \quad (8)$$

$$B_2 = \frac{k_{O_2}^{rev} K_{O_n}^{ad} \gamma_H P_{O_2}}{k_G \gamma_{CH_2} + k_{P_2} \gamma_H + k_{O_2}} \quad (9)$$

$$A_n = \frac{k_G \gamma_{CH_2}}{k_G \gamma_{CH_2} + k_{P_n} \gamma_H + k_{O_n}} \quad (10)$$

$$B_n = \frac{k_{O_2}^{rev} K_{O_n}^{ad} \gamma_H P_{O_n}}{k_G \gamma_{CH_2} + k_{P_n} \gamma_H + k_{O_n}} \quad (11)$$

$$\gamma_1 = \frac{k_{IN} \gamma_{CH_2} \gamma_H}{k_G \gamma_{CH_2} + k_{CH_4} \gamma_H} \quad (12)$$

$$\gamma_H = (K_{H_2}^{ad} P_{H_2})^{1/2} \quad (13)$$

$$\gamma_{CH_2} = \frac{-\beta_2 + \sqrt{\beta_2^2 - 4\beta_1\beta_3}}{2\beta_1} \quad (14)$$

TABLE II  
KINETIC CONSTANTS AND ACTIVATION ENERGY OF THE REACTIONS

Constant	Value	Dimension
$K_{H_2}^{ad}$	$3.91 \times 10^{-5}$	$bar^{-1}$
$k_{CO} K_{CO}^{ad}$	$5.82 \times 10^{-2}$	$mol/kg/s/bar$
$k_{IN}$	$3.73 \times 10^{-1}$	$mol/kg/s$
$k_{CH_4}$	18.9	$mol/kg/s$
$k_G^b$	$4.33 \times 10^{-1}$	$mol/kg/s$
$k_{P_2}^b$	1.46	$mol/kg/s$
$k_{P_n}$	12.1	$mol/kg/s$
$k_{O_2}^b$	$1.73 \times 10^{-1}$	$mol/kg/s$
$k_{O_2}^b$	$8.61 \times 10^{-2}$	$mol/kg/s$
$k_{O_2}^{rev} K_{O_n}^{ad}$	16.6	$mol/kg/s/bar$
$k_{O_n}^{rev} K_{O_n}^{ad}$	1.78	$mol/kg/s/bar$
$(E + \Delta H)_{CO}$	-159.8	$kJ/mol$
$E_G$	99.5	$kJ/mol$
$E_{P_2}$	168.0	$kJ/mol$
$E_{O_2}$	70.5	$kJ/mol$
$E_{O_n}$	96.7	$kJ/mol$

The variation of the conversion and the selectivity is as function of reactor length (Eq. 18 and 19).

$$\frac{dX_i}{dl} = \frac{\rho AL}{F_{CO}^0} v_{ij} R_j \quad (18)$$

$$\frac{dS_i}{dl} = \frac{\rho AL}{F_{CO}^0} v_{ij} R_j \quad (19)$$

Where

$$X_{CO} = \frac{F_{CO}^0 - F_{CO}}{F_{CO}^0} \quad (20)$$

$$X_{H_2} = \frac{F_{H_2}^0 - F_{H_2}}{F_{H_2}^0} \quad (21)$$

And



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$$S_i = \frac{F_i}{F_{CO}^0} \quad (22)$$

Eq. 23 represents the Ergun equation for pressure drop [7]:

$$\frac{dP_T}{dl} = -\frac{v}{d_p} \left( \frac{1-\varepsilon}{\varepsilon^3} \right) \left( \frac{150(1-\varepsilon)\mu}{d_p} + 1.75\rho_g v \right) \quad (23)$$

The energy balance is given by the following expression [7]:

$$\frac{dT}{dl} = \frac{\rho AL}{F_T^0 C_{pg}} \sum_{j=i}^B R_j (-\Delta H_{fj}) + \frac{L\pi D_i}{F_T^0 C_{pg}} U_{shell} (T_{shell} - T) \quad (24)$$

### III. RESULTS AND DISCUSSIONS

In order to determine the optimal operating conditions, the conversions are predicted under several operating conditions: Temperature (483-513K), gas hourly space velocity (4000-5500h<sup>-1</sup>) and the molar ratio of the feed gas H<sub>2</sub>/CO (0.5-2). The main results obtained are as follows:

#### A. H<sub>2</sub>/CO molar ratio effect

Hydrogen plays a very important role in the FT reaction, a low H<sub>2</sub> partial pressure inhibits FT reaction rate [4]. It should be noted that the conversions of CO and H<sub>2</sub> increase along the reactor. In addition, these conversions increase with increasing molar ratio (M). This effect is more pronounced for H<sub>2</sub>. For a molar ratio equal to 2, Almost, all the hydrogen was converted (conversion about 99%), while CO conversion was about 55% (figure 1 and 2).

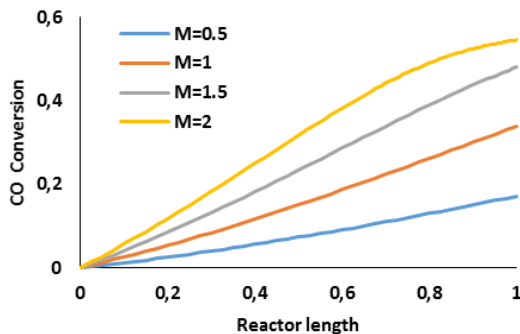


Fig. 1 (H<sub>2</sub>/CO) molar ratio effect on CO conversion. conditions: T=483K, P=10 bar, GHSV=4000 h<sup>-1</sup>.

According to the table III, the variation of the selectivity of all hydrocarbons was proportional to the molar ratio.

The increase in selectivity is more remarkable for paraffin than olefins. The high concentration of H<sub>2</sub> in the reaction

favours the production of hydrocarbons with small chain length (methane) [5].

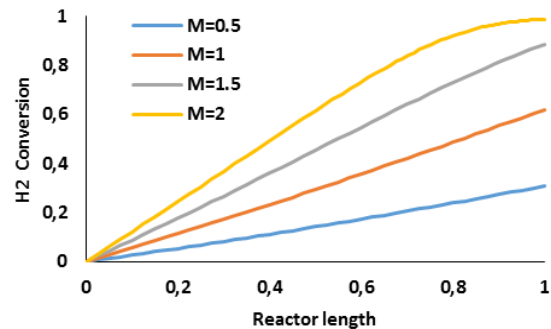


Fig. 2 (H<sub>2</sub>/CO) molar ratio effect on H<sub>2</sub> conversion. conditions: T=483K, P=10 bar, GHSV=4000 h<sup>-1</sup>.

TABLE III  
HYDROCARBONS SELECTIVITY AT DIFFERENT FEED MOLAR RATIO  
(M=H<sub>2</sub>/CO)

	Selectivity (%)			
	M=0.5	M=1	M=1.5	M=2
CH <sub>4</sub>	1,721	3,814	5,564	6,418
C <sub>2</sub> H <sub>6</sub>	0,038	0,092	0,141	0,154
C <sub>3</sub> H <sub>8</sub>	0,867	1,846	2,667	3,013
C <sub>4</sub> H <sub>10</sub>	0,742	1,519	2,165	2,407
C <sub>5</sub> H <sub>12</sub>	0,636	1,250	1,758	1,926
C <sub>2</sub> H <sub>4</sub>	0,613	0,939	1,070	1,099
C <sub>3</sub> H <sub>6</sub>	0,293	0,558	0,815	0,938
C <sub>4</sub> H <sub>8</sub>	0,251	0,462	0,679	0,791
C <sub>5</sub> H <sub>10</sub>	0,215	0,382	0,565	0,668

#### B. Gas hourly space velocity (GHSV) effect

GHSV defined as the total volumetric (NTP) feed flow rate per unit bed volume, which indicates how many reactor volumes of feed can be treated in a unit time. It represents the reverse of residence time. The rise in space velocity from 4000-5500h<sup>-1</sup> has a negative effect on CO and H<sub>2</sub> conversion (figure 3 and 4). This decrease in conversion is simply related to the lower interaction between catalyst particles and the gas molecules leading to a minimal adsorption of the reactant molecules.



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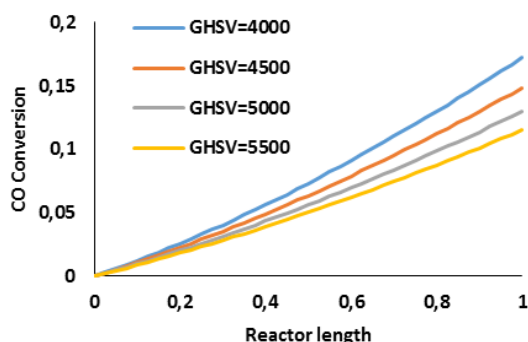


Fig. 3 GHSV effect on CO conversion. conditions: T=483K, P=10 bar, H<sub>2</sub>/CO=0.5.

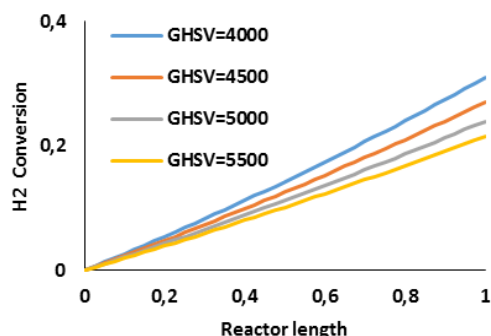


Fig. 4 GHSV effect on CO conversion. conditions: T=483K, P=10 bar, H<sub>2</sub>/CO=0.5.

This parameter affects also the selectivity of the produced hydrocarbons as shown in Table IV. It was obtained that the increase in space velocity causes a decrease in the products selectivity (olefins and paraffin).

TABLE IV  
HYDROCARBONS SELECTIVITY AT DIFFERENT GHSV

	Selectivity (%)			
	4000 h <sup>-1</sup>	4500 h <sup>-1</sup>	5000 h <sup>-1</sup>	5500 h <sup>-1</sup>
CH <sub>4</sub>	1,721	1,506	1,338	1,202
C <sub>2</sub> H <sub>6</sub>	0,038	0,031	0,026	0,023
C <sub>3</sub> H <sub>8</sub>	0,867	0,757	0,672	0,603
C <sub>4</sub> H <sub>10</sub>	0,742	0,648	0,574	0,515
C <sub>5</sub> H <sub>12</sub>	0,636	0,554	0,491	0,440
C <sub>2</sub> H <sub>4</sub>	0,613	0,547	0,491	0,445
C <sub>3</sub> H <sub>6</sub>	0,293	0,246	0,212	0,185
C <sub>4</sub> H <sub>8</sub>	0,251	0,211	0,181	0,158
C <sub>5</sub> H <sub>10</sub>	0,215	0,180	0,155	0,135

C. Temperature effect

The thermodynamic parameters related to the reaction are function on temperature. So, temperature is an important kinetic factor. Our study focuses on assessing syngas conversion and hydrocarbons selectivity at the temperature ranging from 483K to 503K. The obtained results (Figure 5 and 6) show an increase in conversions with temperature rise. For temperature equal to 513K, it was obtained conversions values for H<sub>2</sub> and CO. While for lower temperatures, there was a clear decrease in the efficiency of the process. The conversion improvement is referred to the high catalyst activity. The adsorption and the desorption properties of CO and H<sub>2</sub> on the catalyst may be changed according to the temperature.

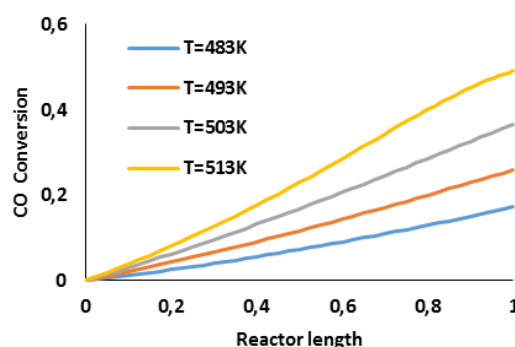


Fig. 5 Temperature effect on CO conversion. conditions: H<sub>2</sub>/CO=0.5, P=10 bar, GHSV=4000 h<sup>-1</sup>.

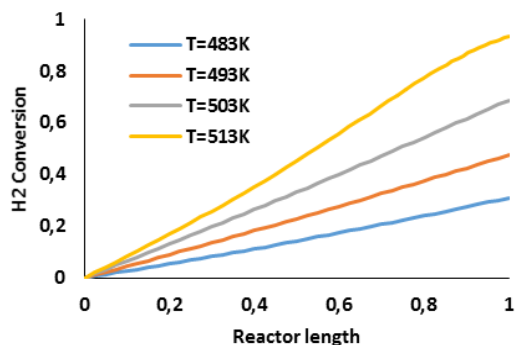


Fig. 6 Temperature effect on CO conversion. conditions: H<sub>2</sub>/CO=0.5, P=10 bar, GHSV=4000 h<sup>-1</sup>.

The selectivity of C<sub>1</sub>-C<sub>5</sub> hydrocarbons was also influenced by the operating temperature as shown in table V. The selectivity of ethylene increase from 0,613% to 0,845% when reaction temperature increasing from 483 to 503K. For a higher temperature (513K), the ethylene selectivity decrease to 0,752%. Other hydrocarbons selectivity also increases with temperature rise. This effect is more significant for propene,



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butane, pentene, and ethane. Higher temperatures cause re-adsorption of ethylene on the surface of the catalyst, in which ethylene becomes a reaction intermediate, which either can continue to grow and terminate as a longer chain olefin (propene, butane, pentene) or be terminated to n-paraffin of the same carbon number (ethane).

TABLE V  
HYDROCARBONS SELECTIVITY FOR DIFFERENT TEMPERATURES

	Selectivity (%)			
	T=483K	T=493K	T=503K	T=513K
$CH_4$	1,721	2,374	2,724	2,505
$C_2H_6$	0,038	0,114	0,275	0,499
$C_3H_8$	0,867	1,185	1,415	1,395
$C_4H_{10}$	0,742	1,015	1,266	1,357
$C_5H_{12}$	0,636	0,869	1,127	1,297
$C_2H_4$	0,613	0,831	0,845	0,752
$C_3H_6$	0,293	0,632	1,186	1,905
$C_4H_8$	0,251	0,546	1,095	2,014
$C_5H_{10}$	0,215	0,470	1,002	2,056

#### IV. CONCLUSIONS

The FT process produces a wide range of hydrocarbons from bio-syngas, including light paraffin and olefin depending on the operating parameters. It was obtained that the syngas conversion and hydrocarbons selectivity reached its maximum for higher temperature and molar ratio value. The gas hourly

space velocity shows a negative effect on the selectivity and the conversion. Reducing the residence time disadvantage the adsorption of the reactants on the catalyst surface.

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