DIESEL CONVERSION MAXIMIZATION IN A FT MULTI-BED REACTOR

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***Abstract*— Recently, modeling and simulation of the diesel production process via Fischer Tropsch (FT) have been the subject of study by several researchers. However, studies involving the optimization of FT technology are scarce, principally processes involving Fixed Bed Reactors (FBR). The present work aims to simulate and optimize a multi-tubular FT FBR in which the goal is to maximize the diesel production. In this way, the modeling, simulation and optimization of FT process were proposed. The reactor model is based on the one-dimensional pseudo-homogeneous model in which mass and energy balances were taken into account. The resultant ordinary differential equation system was solved by the use of the Adams Moulton method, while the Interior Point method was used for the optimization step. The algorithm was then implemented into the Scilab solver. Several case studies were performed, evidencing that the temperature of the cooling fluid and H_2/CO ratio fluid significantly impacts the conversion of the reaction.**

Keywords—Hydrogen, Fischer-Tropsch, Synthesis Gas.

I. INTRODUCTION

Natural gas is chemically converted through Fischer Tropsch (FT) reaction into liquid fuels. The Gas-to-Liquid (GTL) processing unit consists mainly of three basic units: (1) Reforming or synthesis gas production unit where the syngas ratio (H_2/ CO) is produced; (2) FT synthesis unit where the synthesis fuels (synfuels) are produced (3) Product upgrading and separation unit, where the hydro-treating/cracking takes place to obtain the final liquid fuels (Al-Sobhi and Elkamel 2015).

Due to environmental concerns, petroleum products have given way in the market for the development of alternative routes for the production of synthetic fuels, among them Fischer-Tropsch (FT) technology (Dunham *et al.*, 2006).

At Low-Temperature Fischer Tropsch (LTFT), between 200-240 ºC, the production of diesel is favored. On the other hand, at High-Temperature Fischer Tropsch (HTFT), 300-350 ºC, gasoline production is more favorable (Lira, 2012).

The Ficher Tropsch reaction can be written as:

$$nCO + (2n+1)H_2 \rightarrow C_nH_{2n+2} + nH_2O \quad (1)$$

For iron-based catalysts, the formation of carbon dioxide by the water-gas shift reaction is represented by Eq. (2); and methane formation is represented by Eq. (3), as described in Jess and Kern (2009):

$$CO + H_2O \rightarrow CO_2 + H_2 \quad (2)$$

$$CO + 3H_2 \rightarrow CH_4 + H_2O \quad (3)$$

In contrast to slurry phase FT reactors, the literature regarding modeling and optimization of Fischer Tropsch fixed bed reactor (FBR) is rather limited. Kinetic studies were done by Mirzaei *et al.* (2012) in which estimation of kinetic parameters were done by fitting the experimental data of the components partial pressure to the kinetic equations. Results evidenced that the optimum H_2/CO molar ratio equals to 2. Wang *et al.* (2003) used a one-dimensional heterogeneous reactor model to simulate the performance of fixed-bed FT reactors for hydrocarbon production. The resulting proposed model was capable of achieving good agreement with experimental data. However, no optimization study was proposed. Jess and Kern (2009) proposed a 1-D and 2-D model of multi-tubular reactor or FT reactions, by considering a pseudo-homogeneous model, using kinetics of two commercial iron and cobalt catalysts. The authors validated the model with experimental data, in which a good agreement was verified. Lee and Chung (2012) developed a FT-packed-bed reactor model for studying its thermal management for liquid hydrocarbon fuel production using biomass-based syngas. The authors concluded that their model could provide optimal operating conditions for attaining the maximum yield of desired products in the absence of the thermal deactivation of the catalyst. Nevertheless, although numerous case-studies have been done, the authors did not implement an optimization algorithm to investigate the best operating point. Lira (2012) proposed an analysis, simulation and optimization of the production of FT-diesel by GTL technology, for iron and cobalt catalysts, by considering one and two-dimensional analysis, using MATLAB® and HYSYS® softwares. The reactor temperature was used as the decision variable of the optimization problem, making it possible to obtain the optimal operating condition of the system, aiming to maximize the diesel.

Optimization studies were also performed by Moazami *et al.* (2017). It was used an elementary reaction mechanism. According to the authors, the results indicated that the increase of reaction temperature had positive influence on catalytic activity and its performance in terms of conversion of syngas compositions. However, increasing the temperature had also an adverse impact as it resulted in increased.

In Behroozsarand and Zamaniyan (2017) the simulation and optimization of an integrated GTL process were proposed. Five main sections of GTL process

were simulated and optimized: Synthesis gas, Amine for separating CO_2, Fischer Tropsch, Hydrocarbon separation and Water treatment units. Results revealed that the total productivity could be improved by changing the recycle ratio of light gases to the FT reactor. In the study of Martin and Grossmann (2011) the design for the optimization of FT-diesel production process from switchgrass via gasification of biomass was proposed. The authors optimized the operating conditions of the FT reactor in order to maximize the diesel production. A life cycle analysis, using simulation and optimization was proposed by Wang *et al.* (2013). Economic and environmental criteria were analyzed.

It is noteworthy that most of the works of the literature used process simulators to study aspects of GTL plant optimization. However, there are few studies involving specific optimization strategies with aid of detailed models, but the most part of studies encompasses process simulators.

This work aims to develop a mathematical model of an FT FBR (Jess and Kern, 2009) with goal of maximizing the reaction conversion and diesel production.

This paper is divided into the following steps: Topic II describes the mathematical model used to simulate and optimize the FT FBR process. In Topic III we discuss the obtained results and finally in topic VI we conclude the paper.

II. MODELLING AND OPTIMIZATION OF FT REACTOR

A. Mathematical Model

In this section, the theoretical background of mass and energy balances over the FT FBR based on the work of Jess and Kern (2009) is described. Fig. 1 illustrates the FT reactor with a cooling system. These equations can be described by Eq. (4) and Eq. (5), respectively.

$$\frac{dC_{H2}}{dz} = \frac{-\rho_b \sum r_{H2,i}}{u_s} \tag{4}$$

$$\frac{dT}{dz} = \frac{4U_{overall}(T-T_{cool})}{\rho_{mol} c_p u_s \xi} - \frac{\rho_b \sum \Delta_R H_i r_{H2,i}}{\rho_{mol} c_p u_s} \tag{5}$$

where d_R is the diameter of the multitubular reactor tube (m), z is the length of tube (m), u is the superficial gas velocity (m/s), ρ_b is the bulk density of catalyst bed (kg/m³), C_{H2} is the hydrogen concentration (mol/m³), r_{H2} is the hydrogen reaction rate per mass unit (mol.kg^{-1}.s^{-1}), T_{cool} is the cooling temperature (K), $U_{overall}$ is the overall thermal transmittance (W.m^{-2}.K^{-1}), ρ_{mol} is the molar density of gas phase (mol/m³), c_p is the heat capacity of gas phase (J.mol^{-1}.K^{-1}), ξ is the (internal) diameter of a single tube (m), T is the reactor temperature (K) and $\Delta_R H_i$ is the heat of reaction (at 1 bar, 298K) (J/mol).

The kinetics, in terms of hydrogen component, considering an iron-based catalyst, can be described by:

$$r_{H2-FT} = k_{m,FT}{}^{*} \cdot \frac{C_{H2,g}}{(1+1.6 \cdot \frac{C_{H2O,g}}{C_{CO,g}})} \tag{6}$$

$$r_{H2-S} = k_{m,S} C_{H2O,g} \tag{7}$$

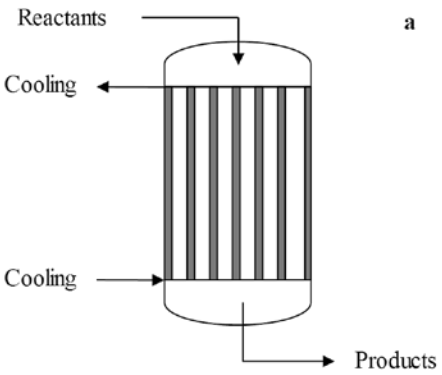

Figure 1. (a) Fischer Tropsch Fixed Bed Reactor

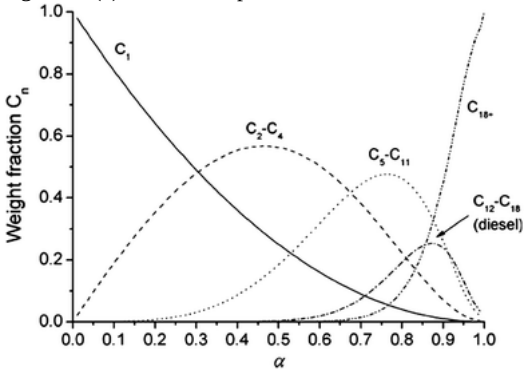

Figure 2. Anderson-Schulz-Flory distribution, showing the correlation between chain growth probability (α) and weight fraction of hydrocarbon of chain length n (Dorner *et al.*, 2010).

$$r_{H2-M} = k_{m,M} C_{H2,g} \tag{8}$$

where $k_{m,FT}{}^{*} = \eta k_{m,FT}$, with the constants and activation energies are written as:

$$k_{m,FT}{}^{*} = 5.1 \cdot \exp\left(\frac{-52000}{RT}\right) \tag{9}$$

$$k_{m,S} = 155 \cdot \exp\left(\frac{-70000}{RT}\right) \tag{10}$$

$$k_{m,M} = 27.3 \cdot \exp\left(\frac{-70000}{RT}\right) \tag{11}$$

In which R values 8.314 J·mol^{-1}.K^{-1} and T (K) is the reactor temperature. The subscripts FT, S and M denote Fischer Tropsch, Shift and Metanation reactions. In Eq. (6), the parameter η denotes the effectiveness factor resulted from the catalyst pore diffusion (Jess and Kern, 2009).

The product distribution of hydrocarbons can be described by the Anderson-Schulz-Flory (ASF) equation (Panahi *et al.* 2018):

$$y_n = (1-\alpha)\alpha^{(n-1)}, n \geq 2 \tag{12}$$

where y_n represents the mole fraction of a hydrocarbon with chain length n and the growth probability factor, α which does not depend on n. All the components lighter than the carbon number 21 were modeled as individual components, while the carbon number components between 21-30 were aggregated into a component designated C21+. A constant α between 0.8-0.9 is frequently proposed in the literature at typical operat-

ing conditions of a low temperature FT reactor. The Fig. 2 represents the hydrocarbon distribution according to the ASF equation.

It is possible to observe in Fig. 2 that the parameter α can control the weight fraction of diesel.

B. Numerical Optimization

(i) – Maximization of CO conversion

In order to optimize the FT reactor, the objective function was written as the CO concentration. The differential equation that describes the evolution of the CO concentration along the FT reactor can be written as:

Table 1. Parameters of the FT reactor (Jess and Kern (2009).

Parameter	Value
Feed (%)	66.6 [H_2] 33.4 [CO]
ρ_{mol} (mol/m^3)	563 (total)
$\Delta_R H^0{}_{298}$ (J/mol)	$\Delta_R H_{FT} = 152.10$ $\Delta_R H_{SHIFT} = -41 \cdot 10^3$ $\Delta_R H_{Methanation} = -206 \cdot 10^3$
c_p (J/mol$^{-1} \cdot$K^{-1})	30
$U_{overall}$ (W/m$^{-2} \cdot$K^{-1})	364
T_{in} (°C)	224
u(m/s)	0.55
ρ_b (kg/m^3)	790
ξ (m)	0.046
z (m)	12

$$\frac{dCco}{dz} = -\frac{\rho_b}{u_s}\left(\frac{1}{3}r_{H2-M} + r_{H2-S} + \frac{1}{2.1}r_{H2-FT}\right) \quad (13)$$

Thus, the optimization problem can be formulated according to the following equations:

$$min\ _{T_{cool}}\ \mathcal{L} = Cco|_{z=12m} \quad (14)$$

subject to:

$$T(z) \leq 248\ ℃ \quad (15)$$

$$200\ ℃ \leq T_{cool} \leq 260\ ℃ \quad (16)$$

In the Eq. (16), the function $\mathcal{L}$ represents the objective function to be minimized. As observed, the goal of the optimization is minimizing the CO concentration (in mol/m^3) at the reactor exit (with $z = 12$ m). Eq. (15) and (16) denote the constraints of the optimization. In addition to Eq. (15) and (16) the system of ordinary differential equations, represented by Eq. (6), (7) and (13) must also be satisfied at each optimization iteration.

Table 1 lists the parameters used to simulate and optimize the FT reactor.

The CO conversion was calculated according to the Eq. (17):

$$x_{CO}(\%) = \left(\frac{c_{CO_{in}} - c_{CO_{out}}}{c_{CO_{in}}}\right) \cdot 100\ \% \quad (17)$$

where $c_{CO_{in}}$ is the molar concentration of CO at the reactor entrance and $c_{CO_{out}}$ is the molar concentration at the reactor exit.

(ii)– Maximization of Diesel production

The optimization was also performed by considering the parameter α as decision variable to maximize the molar flow of diesel. In this way, the optimization problem can be written as:

$$max\ _{T_{cool},\alpha}\ \mathcal{L} = \dot{n}_{Diesel} \quad (18)$$

subject to:

$$T(z) \leq 250\ ℃ \quad (19)$$

$$200\ ℃ \leq T_{cool} \leq 260\ ℃ \quad (20)$$

$$0.7 \leq \alpha \leq 1 \quad (15)$$

where $\dot{n}_{Diesel}$ denotes the molar flow of diesel.

C. Methodology

The work is divided in two parts: (i) analysis of the model through the computational simulation performed and (ii) optimization of the FT reactor. The resulting mass and energy balance model coupled to the reaction kinetics (Eqs. 4-11) results in a system of ordinary differential equations (ODEs). For solving the ODE system the open source Scilab® (Scilab Enterprises 2012) software was used. The Adams Molton method (Biegler, 2010) was used for solving the ODE system. For optimization, the interior point method (*fmincon subroutine*) (Biegler 2010) was used. The algorithm settings are listed in Table 2.

Table 2. Parameters of the integration and optimization algorithms.

NLP solver	Interior point (fmincon)
Integrator solver	Adams Molton (Biegler 2010)
ϕ_r	10^{-5}
ϕ_A	10^{-5}
ϵ_{fun}	10^{-4}
ϵ_{con}	10^{-4}
ϵ_x	10^{-4}

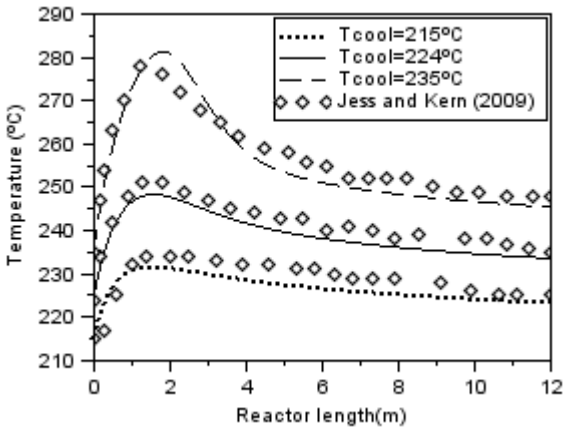

Figure 3. Influence of cooling temperature on the reactor temperature profiles along the reactor length (for u = 0.55 m/s).

In Table 2, ϕ_r denotes the relative tolerance of the ODE integrator, ϕ_A is the absolute tolerance, ϕ_{fun} is the tolerance of objective function, ϕ_{con} is the tolerance of the constraints and ϕ_x denotes the tolerances related to the state variables (Biegler 2010).

III. RESULTS AND DISCUSSION

A. Simulation of FT Reactor

In order to compare reactor temperature profiles with results obtained by Jess and Kern (2009), the temperature profile (in ° C) along the reactor length (in m) was evaluated. For this study, the temperature profile was analyzed for three different temperature values of the cooling fluid. In all cases, an operating velocity of 0.55 m/s was considered. The results can be seen in Fig. 3.

Figure 3 shows the reactor temperature profile for the cooling fluid with temperatures of 215 °C, 224 °C and 235 °C. It can be seen that, for all cases, at the entrance of the reactor, the temperature tends to increase, reaching a maximum peak before half the reactor length followed by a temperature decrease up to the end of the reactor. This temperature peak occurs due to the exothermic characteristic of the reaction. In addition, it is noted that the temperature trajectories are relatively close to the profiles obtained by Jess and Kern (2009). Another important result of Fig. 3 is that the reactor temperature may exceed the maximum catalyst deactivation temperature, which according to Jess and Kern (2009) is about 250 °C (considering an iron catalyst). In this way, it is possible to predict that the temperature of the cooling fluid must be restricted in order to avoid overheating of the reactor. These results indicate that the implementation of the reactor model into Scilab presents satisfactory results when compared to the reference literature.

The variation of the molar concentration (for $T_{cool} = 224$ ℃) of H_2, CO and H_2O along the reactor length is shown in Fig. 4. It can be noted that the concentration of H_2 and CO decreases as the reaction takes place inside the reactor, as expected.

The concentration of the main hydrocarbons is showed in Fig. 5. We can observe that the molar concentration of all species grows along the reactor. However, the concentration of naphtha presents the highest value.

Table 3 summarizes the values of the conversions obtained and also of the outlet temperatures for different temperature values of the cooling fluid. According to the results, the conversion of the reaction increases as the cooling temperature increases. Also, the maximum conversion occurs for T_{cool} equals to 235 ℃.

According to the results of Table 3, we can verify that the cooling temperature causes a significant variation on the reaction conversion. This indicates that such a variable is an important decision variable to maximize the conversion.

Table 4 shows the influence of gas velocity on conversion. It can be noted that the conversion is lower for higher gas velocities. It may be explained by the fact that the residence time is lower at higher velocities and consequently the system has lower time to react. These results indicate that the correlation between the conversion and the temperature of the cooling fluid is different for each gas velocity. This implies that, the optimal point may vary for different operating points.

The hydrocarbon distribution will be discussed in the next section.

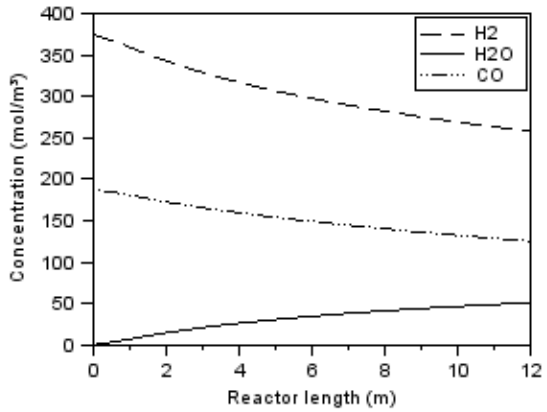

Figure 4. Molar concentrations of CO, H_2, and H_2O along the reactor length ($T_{cool} = 224$ ℃).

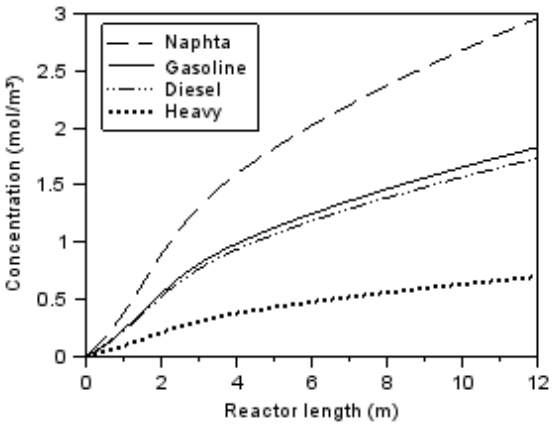

Figure 5. Distribution of the hydrocarbons along the reactor length.

Table 3. Influence of cooling temperature on CO-conversion, y iron-based catalyst (for $u = 0.55$ m/s)

Parameter	Value		
T_{cool} (℃)	215	224	235
u (m/s)	0.55	0.55	0.55
x_{CO}(%)	25.6	32.4	45
x_{CO}(%) (Jess and Kern, 2009)	25	32	42

Table 4. Influence of gas velocity on CO-conversion (for $T_{cool} = 224$ ℃)

Parameter	Value				
u (m/s)	0.100	0.200	0.300	0.400	0.550
T_{cool} (℃)	224	224	224	224	224
T_{out} (℃)	227	228	230	231	233
x_{CO}(%)	78.11	6202.	49.21	41.03	33.06

Table 5. Optimization results for different gas velocities.

Parameter	Value				
u (m/s)	0.100	0.200	0.280	0.400	0.550
T_{cool} (℃)	224.88	224.88	224.88	224.88	224.88
T_{max}(℃)	250	250	250	250	250
x_{CO}(%)	79.28	63.13	49.78	41.72	34.04

B. Optimization of FT Reactor

The FT reactor optimization was performed by considering maximization of diesel conversion: (i) different gas velocities and (ii) different H_2/CO ratios and (iii) maximization of diesel production.

(i) Case-I-Optimization with different gas velocities

Firstly, the optimization was performed at different gas velocities, with the objective of evaluating the variation of the optimal point under different conditions. For each case, the cooling temperature was used as the decision variable of the optimization problem. The results are summarized in Table 5.

As observed in the Table 5, for lower velocities the reaction conversions is greater. This result can be explained by the decrease of the residence time with the increase of the velocity, as expected. In addition, it may be noted that the temperature of the refrigerant remained constant, equals to 224.88 °C, for all cases, which can be explained by the fact that the maximum allowable temperature of 248 °C restricts the heating of the reactor for all cases. In this case, it can be noted that the algorithm had few degree of freedom to optimize the reactor. For example, for the base case (with $u = 0.55\, m/s$), it was possible to increase the conversion from 33.06 % (base case) to 34.04 %.

The optimum temperature profiles can be seen in Fig. 6 where we can observe that the maximum temperature constraint of 248 °C was reached. Visibly, we can see that the profile is shifted to the right as the speed increases.

(ii) Case-II-Optimization with different H_2/CO ratios

The previous study showed that the conversion changes naturally with the gas velocity. In that case, there was not degree freedom to change the temperature of the cooling fluid, because the maximum temperature of the reactor reached the limit of 250 °C for all cases.

In this section, the optimization of the reactor was also performed for different H_2/CO ratios: 0.66, 1, 4, 1.5 and 2. Table 6 shows the results of this study. It is possible to verify that the conversion decreases with the increase of H_2/CO ratio, reaching a minimum value equals to 18.25 % for the ratio of 0.66. On the other hand, for the ratio of 4, the conversion was equal to 53.63 %. However, since the H_2/CO ratio at the reactor inlet is not constant, the conversion does not reflect the diesel production. Notice that the diesel production (in mol/h) decreased due to the lower availability of CO at the entrance of the reactor. Thus, the point of maximum conversion of CO does not correspond to the point of maximum diesel production. For example, we can observe that the maximum diesel production occurs for $H_2/CO = 2$, in which the molar flowrate is equal to 26132 mol/h.

(iii) Case-III - Maximization of diesel production

The optimization of biodiesel production was carried out according to the mathematical formulation presented in Section 2. The optimization was performed according to the mathematical formulation presented in Section 2 (Case-II). Figure 7 shows the production of diesel as a function of α, for different values of H_2/CO. It is possible to observe that the maximum production of diesel is around $\alpha = 0.94$ for the different H_2/CO ratios. It could be observed that after the optimization the maximum production of diesel in the ratio of 2 was 27957 mol/h. These results are in accordance with the ASF equation (Fig. 2) which shows that there is an optimal diesel production region.

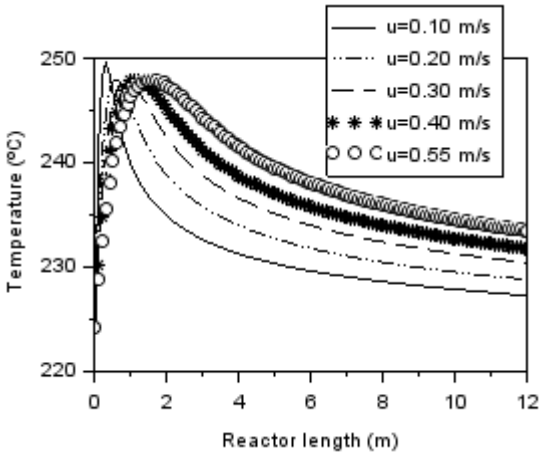

Figure 6. Temperature profiles for different gas velocities.

Table 6. Optimization results for different H_2/CO ratios ($u = 0.55\, m/s$ and $\alpha = 0.85$).

Parameter	**Value**				
H_2/CO	4	2	1.5	1	0.66
T_{cool} (℃)	221.29	224.87	227.03	234.25	242.74
x_{CO}(%)	53.63	34.04	27.65	20.16	18.25
Diesel (mol/h)	24686	26132	25457	23199	19868

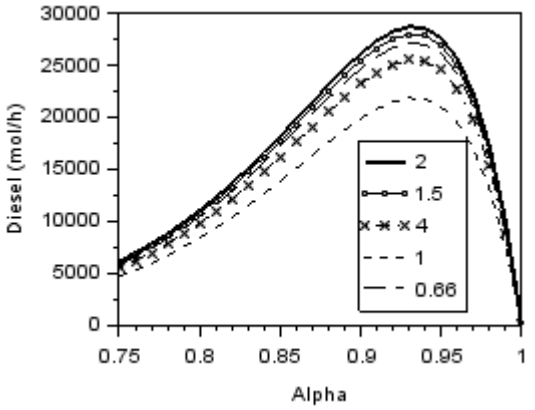

Figure 7. Diesel production vs. α.

IV. CONCLUSIONS

In this work the simulation and optimization of a Fischer Tropsch Reactor was proposed. The optimization of the reactor was performed in the Scilab simulator, by the use of the 1-D model based on mass and energy balances. First, the results of the model were compared with experimental data taken from literature. The results evidenced that the CO conversion of 32.46 % could be obtained, resulting in a deviation of 1.4 %. In the sequence, two optimization studies were pro-

posed. In the first one the cooling temperature was changed to maximize the CO conversion. Results evidenced that the conversion could be slightly maximized to 33.06 %. However, the maximum temperature constraint was reached, avoiding the optimizer to obtain a higher conversion. In the second study, the diesel production was maximized by changing the cooling temperature and α parameter. The results evidenced that the maximum diesel production of 27957 mol/h could be obtained with H_2/CO equals to 2 and α equals to 0.94. It also could be observed that the diesel production is accordance to the ASF equation, indicating that the model is suitable for the prediction of the reactor performance.

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