Modeling of the dynamic behaviour of Fischer-Tropsch fixed-bed reactors: a pseudohomogeneous approach

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Abstract

This work aims to model and evaluate the dynamic behaviour of a conceptual reactor for Fischer-Tropsch synthesis based on a first principle model using classical mass and energy conservation equations. The system was designed to produce hydrocarbons within the commercial fuel ranges such as gasoline and aviation diesel. The model was coded in Aspen Custom Modeler® v12 and component properties as well as the Soave-Redlich-Kwong equation of state were embedded in the model through the connection with Aspen Properties® v12 software or by direct implementation of literature correlations. Upon achieving a stable numerical solution for different operating conditions, a sensitivity analysis was conducted by varying the flow rate, temperature, and composition at the system’s inlet in order to evaluate the impact of these variables on the dynamic behaviour of the reactor and the yield of hydrocarbons in the desired range. It was observed that the system reaches steady state within short times, of approximately one minute for most tested cases. Furthermore, it was noted that, among all evaluated scenarios, a slight increase in the system temperature would allow for a CO conversion of 84.22% (higher than the 72.87% in the base case) with 48.25% selectivity for hydrocarbons in the C2-C7 range and 24.27% in the C8-C16 range, which could then be blended in order to produce commercial fuels.

**Keywords**: Fischer-Tropsch, Fixed-bed, Mathematical Modeling, Biofuels, Dynamic Model

* 1. Introduction

Despite extensive efforts to diminish greenhouse gases emissions, global demand for petroleum continues to rise. For instance, in 2017, daily production exceeded 90 million barrels, from which 85% were used to manufacture different fuels types accountable for emitting not only carbon dioxide, but also sulfur based and oxygenated organic compounds (Mahmoudi et al., 2017). Within this scenario, the Fischer-Tropsch (FT) process emerges as a technology not only proven to efficiently convert greenhouse gases (CO2 or CO) into usable fuels, but it is already implemented in industrial scale. Such technology makes it is possible to synthesize a wide range of hydrocarbons suitable for blending into gasoline and/or sustainable aviation fuels (SAFs) (Méndez et al., 2017). However, it is worth noting that, in spite of the great benefits FT reaction is able to provide, it also faces several obstacles, such as unknown kinetic mechanisms, unpredictable nature of product distribution and the high reaction exothermicity, which can lead to the formation of hot-stops in the reaction system.

As a result of the above-mentioned drawbacks, it is thus imperative that the process available technologies are refined, in an effort to facilitate its implementation on a larger scale and to avoid operational problems. Mathematical models are a useful tool due to its capacity of describing, through constitutive equations, the characteristic phenomena occurring in a given system, allowing a deep understanding of its performance and also makes room for optimization studies. Nevertheless, few studies have been published regarding the dynamics of a FT reactor (Sauerhöfer-Rodrigo et al., 2023). To fill this gap, the present study focuses on modeling the dynamic behavior of a fixed-bed FT reactor by means of a one-dimensional pseudohomogeneous approach in different operating conditions. Additionally, the proposed model incorporates several enhancements. The proposed model incorporates enhancements, such as: 1. Using the Soave-Redlich-Kwong Equation of State to represent the system non-idealities; 2. The model encompasses 42 different substances, with their properties directly computed from Aspen Properties® interface. This modeling strategy not only enhances the realism of the reactor’s behavior but also facilitates the computation of the properties involved.  The sensitivity analysis was conducted to evaluate the effects of inlet composition, temperature and molar flow-rate according to available literature data, which reflects the industrial operating conditions of such reactors (Espinoza et al., 1999; Lee & Chung, 2012; Jess & Kern, 2009). The results underscored the significant influence of these operating variables in the stabilization of a stationary regime and yield of higher chain hydrocarbons.

* 1. Methods and Modeling

The conceptual model proposed in this study encompasses a tubular arrangement, measuring 12 meters in length and 4.6 centimeters in inner diameter, within a multitubular fixed-bed reactor designed for Fischer-Tropsch synthesis. It utilizes spherical particles of Co-Al2O3 catalyst with 3 mm diameter. The reactor has an outer cooling mechanism, consisting of boiling water at a temperature 5 to 10 °C lower in respect to that of the incoming syngas in order to avoid thermal runaways. Moreover, due to the intrinsic complexity of such process, the following considerations were made: 1. Dynamic operation; 2. One-dimensional pseudohomogeneous model; 3. Solid-gas model (as it was observed that over 99% of the system exists in vapor phase); 4. No resistance to thermal convection at the external tube wall; 5. Formation of alcohols or aromatics was not considered; 6. Reaction enthalpy and bed porosity remain constant alongside the reactor length; 7. Paraffins and olefins formation is considered up to a chain length of 20 carbons. As a result, the constitutive equations describing this model are represented in Eqs. (1) to (3)with initial and boundary conditions included in Table 1.

|  |  |
| --- | --- |
|   | (1) |
|  | (2) |
|  | (3) |

Where ε is the bed porosity (Benyahia and O’Neill, 2005), Ci is the component concentration (mol/m3), us is the fluid superficial velocity (m/s), ρb is the bulk density (kg/m³), ri is the component reaction rate (mol/kg.s), ρf is the fluid density (kmol/m3), ρp is the catalyst density (kg/m3) (Wang et al., 2016), cpf is the fluid heat capacity (kJ/kmol.K), cps is the solid heat capacity (kJ/kg.K) (Wang et al., 2016), T is the temperature (K), Uwall is the global heat transfer coefficient evaluated at the wall (kJ/m².K) and its calculation procedure has been reported in extensive detail by Rafiq et al (2011), Twall is the temperature at the tube wall, ΔHrxn is the reaction enthalpy (kJ/mol) (Méndez et al., 2017), P is the pressure (Pa), dp is the catalyst particle diameter and µm is the fluid viscosity (Pa.s).

Table 1. Initial and boundary conditions for the set of differential equations.

|  |  |
| --- | --- |
| Condition | Variables |
| $$t=0, 0<z\leq L$$ | $$C\_{i}=0$$ | $$T=25 °C$$ | $$P=P\_{in}$$ |
| $$t>0, z=0$$ | $$C\_{i}=C\_{i,in}$$ | $$T=T\_{in}$$ | $$P=P\_{in}$$ |

The reaction rate expression is obtained according to Eq. (4).

|  |  |  |
| --- | --- | --- |
|  |  | (4) |

Where νi is the component’s stoichiometric coefficient, Si is the component’s selectivity following the Anderson-Shulz-Flory distribution (Förtsch et al., 2015) by means of a variable chain growth probability factor (Vervloet et al., 2012), φi is the distribution factor for the Olefin/Paraffin ratio (Pandey et al., 2020) and rFT, denoting the reaction kinetics, is related to the commercial Co-Al2O3 catalyst and have been obtained from Kaiser et al. (2014) comprehensive study.

In addition, the remaining properties concerning the system's components were computed using the databases within the Aspen Properties® v12 software, employing the Soave-Redlich-Kwong equation of state (Karimi et al., 2012). The resulting system of differential equations was subsequently implemented as a model in Aspen Custom Modeler® v12 software. The solution was obtained by employing the lines method, using backward finite differentiation for discretizing the axial domain in 50 slices of 0.24 m each and Implicit Euler as the integration method for the time derivatives up to t = 300 s and variable step size.

In order to test the developed model, a sensitivity analysis varying syngas inlet molar flow-rate, temperature and syngas composition was conducted in order to evaluate how long the system would take to achieve steady-state, CO conversion and selectivity towards different chain length hydrocarbons. Table 2 presents an overview of both the base case and the varied conditions examined, which further allowed to analyze alterations and deviations from the base case scenario clarifying how the operational variables impact the system behavior.

* 1. Results and discussion

Modeling a dynamic system that represents the Fischer-Tropsch process has proven to be a complex task, despite the usage of simplifying assumptions. The numerical initialization is highly sensitive to initial conditions, given the nonlinearities inherent not only in the overall constitutive equations of the model but also in the calculations of the system's parameters and properties.

Table 2. Conditions tested in the sensitivity analysis.

|  |  |  |  |
| --- | --- | --- | --- |
| Case | Inlet Temperature (°C) | Syngas inlet flow-rate (mol/s) | Inlet H2/CO Ratio |
| Base | 210 | 0.5 | 2:1 |
| 1 | 205 | 0.5 | 2:1 |
| 2 | 215 | 0.5 | 2:1 |
| 3 | 210 | 0.25 | 2:1 |
| 4 | 210 | 1 | 2:1 |
| 5 | 210 | 0.5 | 1:1 |
| 6 | 210 | 0.5 | 3:1 |

Furhermore, due to the high exothermicity of the reaction, operating at wall temperatures lower than those of the syngas is imperative to prevent thermal runaways, which excessively raise the fluid temperature and cause numerical instabilities in the final solution of the model. Figure 1 shows the variations in the profiles of the base case for the CO flow-rate, C5+ hydrocarbons flow-rate and temperature in respect with the reactor length considering four different times. Specifically for this case, steady-state operation was achieved at 44 s.



Figure 1. Simulated profiles for the base scenario considering four different times.

It can be noted that the system behaves as it would be expected. In the initial seconds, while the temperature is low and still stabilizing, no reaction is observed in the system, only the passage of CO through the tube. The first product fractions alongside the axial length are observed after the bed reaches approximately 180 °C. The reactor then continues to heat, not only due to the energy transfer between the wall and the bed but also because of the heat released by the reaction, until it is thermally stable. Eventually, with the interior temperature stabilized, the system evolves for a few more seconds until it reaches steady-state, with the flow rates of reactants and products stabilizing along the reactor. Table 3 summarizes the final results obtained during the sensitivity analysis. The ‘SS’, ‘XCO’ and ‘S’ abbreviatures address the time required for the system to reach the steady-state operation, CO conversion and product selectivity for the specified hydrocarbon chain length, respectively.

Table 3. Overall results obtained in the sensitivity analysis.

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Case | SS (s) | XCO (%) | S-C1 (%) | S-C2-C7 (%) | S-C8-C16 (%) | S-C17+ (%) |
| Base | 44 | 72.87% | 8.26% | 35.91% | 26.87% | 28.96% |
| 1 | 45 | 57.45% | 5.20% | 24.97% | 23.10% | 46.73% |
| 2 | 94 | 84.22% | 13.56% | 48.25% | 24.27% | 13.91% |
| 3 | 120 | 86.19% | 6.27% | 28.60% | 23.95% | 41.18% |
| 4 | 35 | 42.76% | 7.83% | 34.72% | 26.95% | 30.50% |
| 5 | 43 | 26.09% | 0.71% | 3.97% | 5.09% | 90.23% |
| 6 | 137 | 99.73% | 45.67% | 49.06% | 5.01% | 0.25% |

The system takes an average of 74 seconds to reach steady-state operation, with 35 seconds as the minimum time and 137 seconds as the maximum. The obtained results align with what would be theoretically expected from the system, as in case 4, for instance, a great impact was assessed from a flow rate twice as high compared to the base case. The increased fluid spatial velocity caused it to traverse the reactor length more rapidly, resulting in a direct negative impact on CO conversion. For the 6th case, a notable observation is the extended duration required to attain the steady-state condition. This prolonged period correlates with a heightened CO conversion, consequently amplifying the thermal effects within the system due to the escalated heat release from the reaction, thereby prolonging temperature stabilization.

Other evaluated cases also align with theoretical expectations. The temperature increase demonstrated the capability to rise CO conversion. However, at the same time, it reduced the selectivity towards larger hydrocarbon chains, showcasing a disadvantage to processes aiming, for example, to produce aviation kerosene (which encompasses hydrocarbons with chains with more than 8 carbons in it). The syngas ratio also yielded significant impacts, especially towards products selectivities. A higher ratio of H2/CO has been showed to be capable of achieving higher selectivities solely for lighter hydrocarbons, jeopardizing the production of higher chain compounds. Finally, the scenario 2 was considered to be the best, regardless of the higher required time to reach its equilibrium or the slightly lower selectivities towards higher chain hydrocarbons, the operation condition was able to convert the most out of CO and had the highest overall yield of hydrocarbons that could be blended together into fuels.

* 1. Conclusions

A dynamic model of a fixed-bed reactor for Fischer-Tropsch synthesis was developed and its behavior studied. Employing mass and energy balances and utilizing the Ergun Equation to assess pressure drop in the bed, not only conversions and selectivities were unveiled but also the theoretical time for the system to reach steady-state was evaluated. In general terms, the system exhibited short times to achieve equilibrium, with an average value close to one minute. Furthermore, it was observed that reductions in inlet flow rates and the increment in inlet temperature or H2/CO ratio led to longer times required for the system’s stabilization. Among the evaluated conditions, the temperature increase tested in case 2 yielded the most favorable results for hydrocarbon yields with chain lengths suitable for blending into commercial fuels.

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