

Biosyngas Conversion by Fischer – Tropsch Synthesis: Experimental Results and Multi-scale Simulation of a PBR with High Fe Loaded Supported Catalysts

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Bio-syngas, i.e. the syngas mixture produced from biomass, is mainly characterized from a H₂/CO molar ratio in the range 1.0-1.5, different from those of traditional syngas equal to 2. By feeding directly this mixture in a catalytic reactor for Fischer-Tropsch synthesis, iron based catalysts are more suitable with respect to the cobalt-based one. These catalysts are used industrially in their massive form. The possibility to use supported Fe-based catalysts are recently deeply considered in order to improve the surface area and the mechanical stability of the samples. In particular high Fe loaded supported catalysts are required to achieve satisfactory performance. Iron-based catalysts supported on silica for CO hydrogenation with 30%wt of metal have been prepared, characterized by BET, SEM, TEM, TPR, XRD and tested at different temperature and H₂/CO ratio in a FT laboratory plant using a Packed Bed Reactor. On the basis of the collected data, a multi-scale simulation of the FT synthesis reactor has been developed considering that on the catalyst surface the reaction both of FT and Water Gas Shift are simultaneously activated.

The experimental results demonstrated that by increasing the inlet H₂/CO ratio, the CO conversion can be increased while preserving the products selectivity and confirm that FT are suitable also for low H₂/CO ratio; furthermore the model elaborated agree with the experimental data obtained.

1. Introduction

Fischer Tropsch (FT) is an industrial process that converts syngas (H₂+CO), in hydrocarbons in the range C₁ to C₁₀₀. FT is a particularly complex system, in which a number of different reactions are combined to a unique mechanism: irreversible Fischer Tropsch reactions produce hydrocarbons and some equilibria reactions between CO, CO₂, CH₄ and C, such as the Water Gas Shift (WGS) reaction and the Boudouard equilibrium, are present too. Nevertheless, it is possible to suppose that FT can be simplified as a combination of the FT reactions and the WGS reaction (Van Der Laan et al., 1999). Hydrocarbons are primary products of FT reaction, and CO₂ can only be produced by WGS reaction, a reversible parallel-consecutive reaction with respect to CO (Van Der Laan et al., 2000).

As reported in the Annual Energy Outlook 2013, the aggregate fossil fuels share of total energy use falls from 82 % in 2011 to 78 % in 2040, while renewable use grows rapidly and the renewable share of total energy use grows from 9 % in 2011 to 13 percent in 2040; biofuels, including biodiesel blended into diesel, E85, and ethanol blended into motor gasoline (up to 15 %), account for 6 % of all petroleum and other liquids consumption by energy content in 2040 and CTL (coal to liquid)/GTL (gas to liquid) together supply 0.3 million barrels per day of nonpetroleum liquids.

In the BTL (Biomass To Liquids)-FT process, biomass, such as woodchips and straw stalk, is firstly converted into biomass-derived syngas (bio-syngas) by gasification. FT synthesis is at the heart of the BTL process. Bio-syngas, i.e. the syngas mixture produced from biomass, is mainly characterized from a H₂/CO molar ratio in the range 0.8-1.5, different from those of traditional syngas equal to 2. By feeding

directly this mixture in a catalytic reactor for FT synthesis, iron based catalysts are more suitable with respect to the cobalt-based one (Van Steen et al., 2008) because the iron is a metal catalytically active not only for FT but also for WGS reaction too. Renewable fuels from BTL-FT are usually much cleaner and environmentally friendly, and they contain little or even no sulfur and other contaminant compounds.

Bio-syngas resulting from biomass gasification contains CO, H₂, CO₂, CH₄, and N₂ in various proportions (Klass, 1998; Bridgewater, 1984). Then, a cleaning process is applied to remove impurities from the bio-syngas to produce clean bio-syngas which meets the FT synthesis requirements. Cleaned bio-syngas is then conducted into a FT catalytic reactor to produce green gasoline, diesel and other clean biofuels. Supported Fe-based catalysts have several advantages (greater surface area, better dispersion of the heat developed by the reaction and better mechanical resistance) compared to massive iron catalysts adopted in the current FT industrial plants. The main drawback of this kind of catalysts is represented by their lower activity respect the massive-ones. For this reason high loading of active metal on the support are required. In particular, in previously papers (Pirola et al., 2009) a detailed research activity has been reported concerning the optimized quantity of iron and promoters (K and Cu) on silica supported catalysts (Pirola et al., 2009). The best metals quantity identified were 30 wt% of Fe promoted with K (2.0 wt%), to improve the CO adsorption (Van Der Laan et al., 1999) and Cu (3.75 wt%) which promotes the reduction of iron oxide phases: from hematite (Fe₂O₃) to magnetite (Fe₃O₄), and then from magnetite to iron metal or iron carbide (Pour et al., 2010), that are the active species for FT reaction.

This catalysts has been characterized with several techniques (BET, TEM, SEM, TPR, XRD) and tested in a suitable FT laboratory plant in a Packed Bed Reactor (PBR) at different temperature in the range of 220-260 °C at 2.0 MPa and at different H₂/CO ratio (2; 1,5; 1,0) in order to simulate different bio-syngas compositions.

On the basis of the collected data, a rigorous multi-scale simulation of the FT synthesis reactor has been developed for different purposes: (i) to support the experimentations and their planning; (ii) to predict the reactor yield and conversion; (iii) to predict and optimize the performance of the reactor system with different operating conditions; and (iv) to calculate novel reliable kinetic parameters based on the experimental data fitting by means of model-based nonlinear regression techniques. The model consider the simultaneously activity both of FT and WGS reaction on the catalyst surface.

2. Experimental

In this paper, all the percentages concerning the catalysts composition are on a weight basis, while the percentages concerning the CO conversion, the products selectivity and the hydrocarbons yield are on a molar basis. The catalysts are named as Fe₃₀K₂Cu_{3,75} which each number is respectively, the wt% of Fe, K and Cu in the catalyst.

2.1 Catalyst preparation and characterization

All catalysts have been prepared according to the traditional impregnation method, always using the same kind of commercially available silica support (Fluka, BET surface area 520 m²g⁻¹, pore volume: 1.22 mLg⁻¹ and average pore diameter: 8.7 nm). The support, after heating treatment in air at 120 °C for 12 h, has been wetness impregnated with an aqueous solution of Fe(NO₃)₃•9H₂O (Riedel de Haen product) and KNO₃ (Merk product) along with Cu(CH₃COO)₂•H₂O (Fluka product), and then put into a vacuum oven at 40 °C at 36 rpm for 24 h. The samples have been heated in air at 100 °C for 12 h and at 500 °C for 4 h.

The surface area of all catalysts has been determined by conventional N₂ absorption at 77 K (BET method) using a Sorptometer 1042 instrument (Costech). Before the analysis, the catalyst samples have been heated at 120 °C for 12 h, and then pre-treated at 200 °C in a nitrogen flux. SEM images have been obtained using an electron microscopy Philips XL-30CP with RBS detector of backscattered electrons. Conventional temperature-programmed reduction experiments (TPR) have been performed on the calcined iron catalysts using a Thermoquest Mod. TPR/D/O 1100 instrument. The samples have been initially pre-treated in a flow of argon at 200 °C for 0.5 h. After being cooled to 50 °C, the H₂/Ar (5.1% v/v) reducing mixture flowed through the sample at 30 mLmin⁻¹ and the temperature has been increased from 50 to 900 °C at a constant rate of 8 °C min⁻¹. The X-ray powder diffraction (XRD) patterns were taken with a computerized Philips PW1710 diffractometer using the CuKα radiation, operating at 40 kV and 20 mA, step scan 1°min⁻¹ and 1 s counting time in the 2-40° 2θ range at room temperature.

2.2 Apparatus for FT runs

Fischer-Tropsch reaction tests have been carried out in a fixed bed tubular reactor, using 1 g of fresh catalyst mixed with 1 g of diluting material (α-Al₂O₃, Fluka). This diluting material must be inert for FT and acts as a good thermal conductor to control the process temperature; the chosen catalyst/diluting material ratio was particularly optimized for the used experimental set-up (Bianchi et al., 2006). All the catalysts

have been initially activated in situ in flow of H_2/CO (ratio of 2/1, 46.8 mL min^{-1} at $350 \text{ }^\circ\text{C}$, 0.4 MPa for 4 h). The catalysts have been tested in a flow of syngas with H_2/CO (ratio of 2/1; 1,5/1; 1/1; flow = $46.8 \text{ NmL min}^{-1}$) using nitrogen as internal analytical standard (flow = 5.0 NmL min^{-1}) at 2.0 MPa and different temperature in the range $220\text{--}260 \text{ }^\circ\text{C}$, for 90 h. Analysis of the gas-phase products (the fraction $\text{C}_1\text{--}\text{C}_6$ not condensed in the cold trap) have been performed with an on-line micro-gaschromatograph (Agilent 3000A) equipped with two different columns: the first, a molsieves module, by which it is possible to separate CO , N_2 and CH_4 with a column temperature of $100 \text{ }^\circ\text{C}$, the second, a OV-1 module (filled with polydimethylsiloxilane), by which it is possible to separate CO_2 and all the hydrocarbons in the range $\text{C}_2\text{--}\text{C}_6$ with a column temperature of $45 \text{ }^\circ\text{C}$. In this instrument the gas sample is split into the two modules and then analyzed at the same time. Measurements have been carried out every 120 min during the reaction. Liquid products have been collected, during the complete reaction cycle (90 h), in a trap ($V = 400 \text{ mL}$), operating at $5 \text{ }^\circ\text{C}$ and at the same pressure of the reactor (2.0 MPa), then analyzed by a gas chromatograph (Fisons—8000 series) equipped with a Porapack-Q columns (this being able to separate $\text{C}_7\text{--}\text{C}_{30}$ hydrocarbon fraction). The column temperature has been maintained at 60°C for 1 min and then heated up to $300 \text{ }^\circ\text{C}$ at $8 \text{ }^\circ\text{C min}^{-1}$. The aqueous phase collected in the cold trap has been analyzed by a TOC (Shimadzu 5000A) to identify the quantity of carbonaceous species dissolved in water. Using all the collected data, a mass molar balance resulted with a maximum error of $\pm 5\%$ moles, for each run.

3. Results

3.1 Catalyst characterization

All the characterization analyses have been performed on fresh catalysts, after the calcination step and before the activation treatment of the FT runs.

The surface area determined by BET on the catalyst $\text{Fe}_{30}\text{K}_2\text{Cu}_{3,75}$ was $160 \pm 0,5 \text{ m}^2\text{g}^{-1}$. The difference with respect to the bare support, having a surface area of $520 \text{ m}^2\text{g}^{-1}$ is due to the diluting effect of the metals. TPR profiles for the same sample is reported in Figure 1:

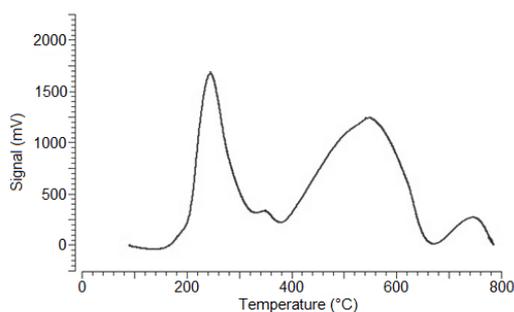


Figure 1: TPR analysis for the catalyst $\text{Fe}_{30}\text{K}_2\text{Cu}_{3,75}$

For the supported iron-based catalysts, two stages of the iron phase transformation could be identified, starting from the metal oxide: hematite (Fe_2O_3) to magnetite (Fe_3O_4) and then magnetite to metallic iron ($\alpha\text{-Fe}$). The second and the third peak at $550\text{--}750 \text{ }^\circ\text{C}$ can be associated at the transition $\text{Fe}_3\text{O}_4 \rightarrow \alpha\text{Fe}$.

In Figure 2 is shown the XRD diffractogram of the Fe-based catalyst.

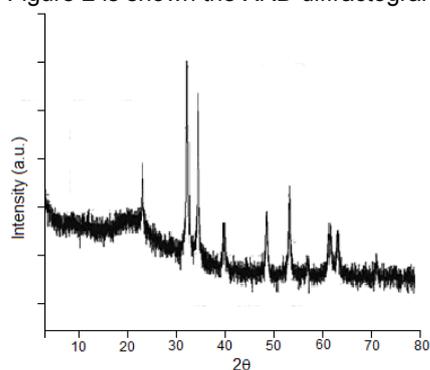


Figure 2: XRD analysis for the catalyst $\text{Fe}_{30}\text{K}_2\text{Cu}_{3,75}$

The XRD analysis showed that the iron, before reductive activation, which is carried out directly in the reactor before the start of the test of reactivity, is present in its oxidized phase of hematite ($\alpha\text{-Fe}_2\text{O}_3$). In the sample was found in fact to have the following diffraction peaks related to 2θ : 33° , 35° , 41° , 50° , 54° , 62° , 64° . They are indicative of the presence of the phase hematite ($\alpha\text{-Fe}_2\text{O}_3$).

The SEM and TEM analysis (Figures 3 and 4) allows to evaluate the morphology and distribution of the metal, showing the existence of a close dependence between the distribution of the metal and the method of preparation used during the synthesis of the catalyst. Using the impregnation method, the sample shows aggregates of spherical iron particles uniformly distributed on the grain.

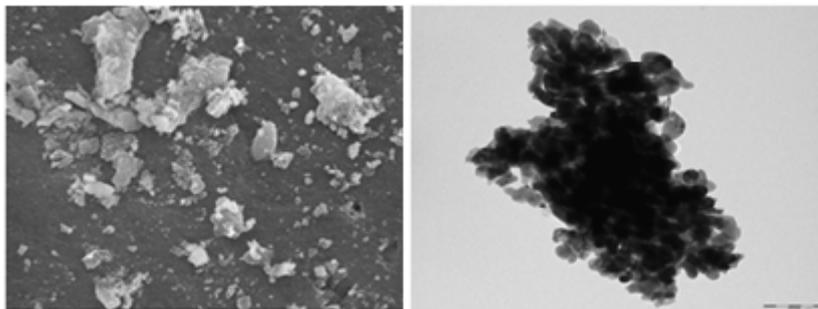


Figure 3: SEM analysis for the catalyst $\text{Fe}_{30}\text{K}_2\text{Cu}_{3.75}$ Figure 4: TEM analysis for the catalyst $\text{Fe}_{30}\text{K}_2\text{Cu}_{3.75}$

3.2 FT results

The results are hereby presented in term of CO conversion and selectivity toward CO_2 , CH_4 , light hydrocarbons ($<C_7$ having less than 7 carbon atoms) and heavy hydrocarbons ($>C_7$: having more than 7 carbon atoms). Furthermore, the combination of the results of both the CO conversion and products selectivity is taken into account calculating the total yield to C_{2+} hydrocarbons, i.e., not considering methane and carbon dioxide since they are usually regarded as undesired products in the FT process. The FT data have been collected when the reaction reached the stationary state (i.e., constant values of CO conversion and products selectivity), about 24 h after the run start. After this initial step, both conversion and selectivity remained steady, suggesting good catalysts stability for the whole duration of each single run (90 h).

In Table 1 are reported the results in function of the temperature and the H_2/CO ratio.

Table 1: FT results for the sample $\text{Fe}_{30}\text{K}_2\text{Cu}_{3.75}$

| H_2/CO | T($^\circ\text{C}$) | CO conv % | C_{2+} yield | Selectivity | | | |
|------------------------|-----------------------|--------------|----------------|---------------|---------------|--------|--------|
| | | | | CO_2 | CH_4 | $<C_7$ | $>C_7$ |
| 2/1 | 220 | 8.5 | 6.9 | 11 | 8 | 22 | 59 |
| 2/1 | 235 | 21.1 | 17.5 | 11 | 6 | 20 | 63 |
| 2/1 | 250 | 49.8 | 39.3 | 16 | 5 | 19 | 60 |
| 2/1 | 260 | 56.7 | 42.5 | 19 | 6 | 20 | 55 |
| 1.5/1 | 250 | 38.8 | 29.9 | 18 | 5 | 17 | 60 |
| 1.5/1 | 260 | 46.3 | 33.8 | 22 | 5 | 17 | 56 |
| 1/1 | 250 | 23 | 18.2 | 17 | 4 | 16 | 63 |
| 1/1 | 260 | 38.9 | 27.2 | 26 | 4 | 16 | 54 |

The CO conversion (%) increases with temperature and with increasing H_2/CO ratio used in the feed and that results are confirmed by previous work (Pirola et al., 2009) and the general state of the art in iron based catalysts for FT process (Abello et al., 2011). At the same temperature and at different H_2/CO ratio the selectivity towards the reaction products remain largely unchanged. The H_2/CO ratio is a very important parameter as regards the FT synthesis because the bio-syngas obtainable from biomass has a ratio between hydrogen and carbon monoxide of about 1. The tests performed kinetics show an increase of the conversion (%) of CO increasing the H_2/CO ratio, this is because increasing it up to the value of 2 is reached the ideal ratio expected from the stoichiometry of the reaction, the selectivity towards the products being unchanged at different ratios of reagents used and the C_{2+} yield increases with the fed ratio.

3.3 Kinetic model

The model, based on experimental data, at different temperatures and different H_2/CO ratios allows to obtain and simulate the performance of these types of catalysts at temperatures and different H_2/CO ratios feeding.

The modeling work has not been limited to the laboratory scale, since it is possible to "predict" the trend of reaction kinetics using these types of catalysts in reactors with much greater volumes and integrated in an entire industrial process such as the use of biosyngas for FT synthesis obtained from biomass.

The model is based on the fact that both FT reaction and WGS reaction are active on the catalyst, therefore the rate constants of both reactions called k_{FT} (kinetics constant of FT reaction) and k_{WGS} (kinetic constant of WGS reaction) can be regressed.

The following Eqs. (1) and (2) that express the speed of the two reactions are (Zimmerman et al., 1990):

$$r_{FT} = k_{FT} \frac{P_{CO} P_{H_2}}{P_{CO} + a_{FT} P_{H_2O} + b_{FT} P_{CO_2}} \quad k_{FT} = \left[\frac{\text{mol}}{\text{Kg}_{\text{cat}} \cdot \text{Pa} \cdot \text{s}} \right] \quad (1)$$

$$r_{WGS} = k_{WGS} \frac{P_{CO} P_{H_2O} - P_{H_2} P_{CO_2} / K_p}{P_{CO} + a_{WGS} P_{H_2O} + b_{WGS} P_{CO_2}} \quad k_{WGS} = \left[\frac{\text{mol}}{\text{Kg}_{\text{cat}} \cdot \text{Pa} \cdot \text{s}} \right] \quad (2)$$

The reaction rate, in both cases, is a function of the partial pressures of the reactants (CO, H₂, H₂O and CO₂) and K_p calculated from the experimental data, and of the regressed constants ($k_{0,i}$, $a_{FT/WGS}$, $b_{FT/WGS}$). The equilibrium constant K_p expressed as Eq (3):

$$K_p = e^{\left(\frac{4578}{T} - 4.33\right)} \quad (3)$$

The parameter values $k_{0,i}$ were obtained with a regression, using MATLAB software using the original coefficients $k_{0,FT}$, $k_{0,WGS}$, a_{FT} , a_{WGS} , b_{FT} , b_{WGS} , as values of the first attempt. (Rafiee, 2012). The software allows the regression of the parameters $k_{0,FT}$, $k_{0,WGS}$, a_{FT} , a_{WGS} , b_{FT} and b_{WGS} , by setting an objective function that must be minimized as much as possible up to a tolerance of 10^{-6} (basis MATLAB tolerance), Eq. (4):

$$F_{obj} = \sum_{j=1}^N (X_{i, \text{spere}} - X_{i, \text{model}})^2 \quad (4)$$

In Table 2 below are reported the regressed constants from the kinetic model elaborated.

Table 2: FT and WGS constants regressed from the kinetic model.

| k°_{FT} | k°_{WGS} | a_{FT} | a_{WGS} | b_{FT} | b_{WGS} |
|------------------|-------------------|----------|-----------|----------|-----------|
| 9,6 | $9,31 \cdot 10^6$ | 4,71 | 24,47 | 0,32 | 0 |

In Figure 4 the comparison between the experimental data and the data given by the model in a kinetic run at T = 260 °C and H₂/CO = 2/1 is reported, as example:

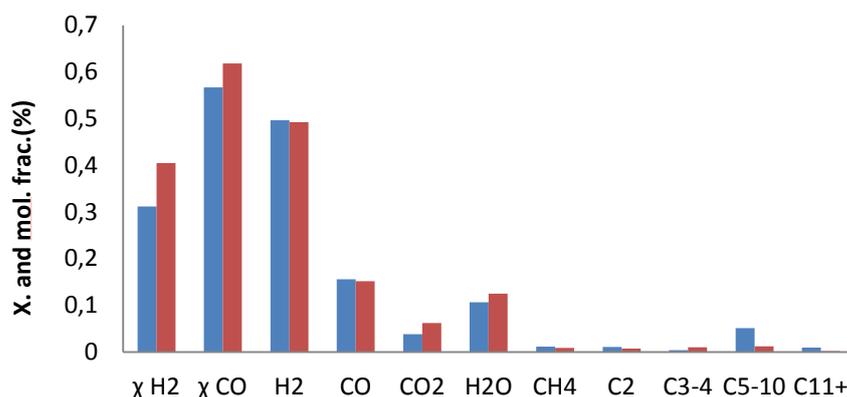


Figure 4: comparison between experimental data and model data

In the first two columns are reported the hydrogen and carbon monoxide conversion and in the other columns the molar fraction of the main products and the lump C₃₋₄ C₅₋₁₀ and C₁₁₊.

4. Conclusions

Fe₃₀K₂Cu_{3,75} catalyst presents good results with different H₂/CO ratio. Using ratios less than two the catalyst present a gradual drop of CO conversion from 49,8% to 23% at 250°C. The selectivity towards the

products remain substantially unchanged at constant temperature, about 60% to heavy products and 19% to light products at 250°C and $H_2/CO = 2/1$; the selectivity to heavy products decreases with increasing the reaction temperature and the developed model shows a good agreement with the experimental data.

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