

Microwave Assisted Fischer - Tropsch Synthesis at a Atmospheric Pressure

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The purpose of this study was to test the efficiency of the microwave activation of a Fischer-Tropsch used catalyst under atmospheric pressure. Experiments were carried out on a cobalt, manganese, calcium catalyst on a 10:1:1 molar ratio that was impregnated on a AISBA-15 support. The amount of metal impregnated was equivalent to 20% of the supports mass. Experiments were carried out both with conventional as well as microwave heating. In order to compare the efficiency of both types of heating, the product compositions were determined at 110, 140, 170, 190, 200, 225, 250 °C. At each temperature 4:1, 2:1, 1.25:1 H₂:CO molar ratios were tested. The microwave assisted Fischer-Tropsch reaction allows the use of lower temperatures, as well as larger CO conversion values with better yields especially in methane.

Keywords: Fischer-Tropsch, Catalyst, Microwaves, Cobalt

The Fischer-Tropsch (F-T) process is used to synthesize fuels from syn gas. The product distribution for this process can be predicted with the Anderson-Schulz-Flory (ASF) formula [1]. The ASF distribution is a mathematical model (equation 1) that was proposed to predict the formation of hydrocarbons in the process. By obtaining the chain growth parameter, α , one can predict the amount of a certain hydrocarbon (w_n) formed.

$$w_n = n \cdot \alpha^{(n-1)} \cdot (-\alpha)^2 \quad (1)$$

where:

- w_n , fraction of hydrocarbon of length n formed
- n , the number of carbon atoms in a hydrocarbon
- α , the chain growth parameter

This growth parameter can be controlled by temperature, pressure, H₂: CO ratio and the catalyst type [2]. High temperatures and pressures lead to longer hydrocarbon chains and higher yields in oxygenate compounds [3], whereas lower pressure favours shorter hydrocarbons formation [4]. The most used catalysts in this process are Fe, Co, Ru metals as active phase [5-7]. Iron generally has optimal operation temperatures of 300- 350°C and usually results short chain hydrocarbons [5]. Cobalt-based catalysts can be operated at lower temperatures (200-250°C), but lead to longer, diesel range (C₁₂-C₂₅) hydrocarbons [6]. Ruthenium has advantages in obtaining shorter hydrocarbons that can be obtained at lower temperatures (200-250°C), but is very expensive catalyst and is difficult to implement on the industrial scale [7]. F-T catalysts can be a self-supported metal or a supported catalyst where fine metallic particles are dispersed on a porous support, both types of catalysts being obtained by reduction of the corresponding metal oxides. In the case of self-supported metallic catalysts, higher metallic active site density is exhibited than in the case of supported catalysts. An increased active sites density favours an accelerated carburization of the metal surface and a premature deactivation of catalyst. In a supported catalyst, the metallic active sites are more dispersed and the hydrocarbon formation is favoured over resulting of metallic carbide [8]. Another parameter that can affect the reaction products consists in the amount of hydrogen used, which is expressed in the H₂: CO ratio. Generally, a higher ratio, would result in a higher probability to obtain short saturated

hydrocarbons [9]. Using for example low pressure, mild temperature and a high amount of hydrogen would eventually result in a high yield of methane. The necessary heat required for the process can be achieved by conventional or microwave heating. In recent studies microwave heating has gained considerable attention and is being used more and more due to a more efficient heat transfer [10]. In a microwave system, the sample heating is mostly dependent on its dielectric properties, that contribute to the microwave energy absorption [11-13]. The current work is focused on microwave assisted Fischer-Tropsch synthesis at low pressure for the following reasons: (i). low pressure favours the formation of short chain compounds (methane, C₂-C₄ hydrocarbons, both saturated and non-saturated); (ii). microwaves yield better results at lower temperatures which, can result in the use of less energy than conventional processes; (iii) mild conditions on the F-T process would result in a safer process operation and lower impact on the environment.

Experimental part

Catalyst preparation

The catalyst used for this work consisted on an AISBA-15 support which was impregnated with a mixture of Co, Mn and Ca nitrates at a molar ratio of 10:1:1. The total amount of metal load onto the support was 20% (wt.).

In order to synthesize the support, 5.7 g of Pluronic P123, used as template agent, was dissolved in 180 mL of distilled water along with 2.0025 g of Al₂(SO₄)₃ x 18H₂O that was used as the source for aluminium. The mixture was stirred at room temperature for 24 h, under magnetic stirring and then 13.275 mL of tetraethyl orthosilicate were added. The reaction mixture was aged at 40°C for 24 h and then hydrothermally treated at 100°C for 48 h at auto generated pressure. The formed solid was filtered off, intensively washed with water and ethanol and dried at room temperature. For removal of structure directing agent, a calcination step at 550°C for 5 h was performed.

The prepared support was impregnated with a solution of Co, Mn, Ca nitrates which were computed according to the metal quantity that would remain deposited on the supports after calcination and activation. The support was outgassed in vacuum and then impregnated with the metal

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nitrate solution. After complete removal of water, the impregnated support was calcined at 400°C for 4 h.

Catalytic tests

Both conventional and MW heating were used in the catalytic tests. The catalyst was placed inside a quartz tube with an external diameter of 13 mm and a wall thickness of 2 mm. 1 g catalyst was placed inside the reactor along with 2 g of SiC. The purpose of the addition of silicon carbide is to improve absorbance of MW at the catalytic level. Catalytic tests were performed at different H_2 : CO molar ratios and temperatures at atmospheric pressure and a H_2 : CO flowrate of 25 mL/min, which was the equivalent of $0.1s^{-1}$ gas hourly space velocity. The catalyst activation was performed at 400°C in 80 mL/min flow rate of hydrogen and nitrogen mixture of 1:1 molar ratio.

Equipment

The syn gas for the F-T reaction was provided by a hydrogen gas cylinder (2) and a carbon monoxide gas cylinder (3), both supplied by Linde. The gas flow-rate was controlled with two mass-flow controllers (6), which were calibrated for hydrogen and carbon monoxide. The pressure drop in the reactor was monitored with two manometers (7) located before and after the reactor (8). The reactor consisted in a quartz tube, which contained the catalyst bed (9) that was fixed with glass wool. It was heated either in a conventional way by a tubular furnace controlled with a thermocouple or in MW field where the temperature in the reactor was controlled by an IR sensor (11) connected to the microwave control unit (12) able to change the power of a microwave generator connected to a monomode type magnetron (10). Any resulting liquid hydrocarbons or water were collected in a catch pot (13). The resulting gases were analysed via Gas Chromatography (GC) (15).

The gas chromatograph used to detect the product composition was a Buck 910 GC equipped with a 1 mL sampling loop, 1 column packed with type 10X molecular

sieves which separated the carbon oxides and methane from the mixture and another 65 mm silicagel packed column, which separated the hydrocarbons. The compounds were detected via a Flame Ionization Detector (FID) provided with a methanizer to increase the sensibility for carbon oxides.

The monomode microwave unit is described in figure 2. The microwave generator (1) transmits the power through the waveguide (2) which is monitored by a reflectometer (3) that is in turn connected to a power meter that measures the forwarded and reflected power in the waveguide. The MW radiation can be controlled with 3-stub tuner (4) and a cooling pad or loading piston (7). Temperature in the reactor is monitored with the IR sensor (8). The use of an Infra-Red (IR) sensor is a non-invasive method and can deliver accurate readings if calibrated. For calibration, a fiber optic sensor was mounted in the middle of the catalyst bed and its recorded temperature were compared with the IR sensor readings.

Results and discussions

Experiments were performed in a step by step increase in temperature with both conventional and microwave heating. The microwave experiments were carried out until the temperature at which the yields were at least equal in value with the data obtained in conventional heating. CO conversion and reaction product yields were determined with equation 2.

$$yield = \frac{CO\ conversion \times selectivity}{100} \quad (2)$$

The catalytic tests were carried out at 110, 140, 170, 190, 200, 225 and 250 °C in conventional heating, whereas microwave experiments were performed at 110, 140, 170, 190°C. The CO : H_2 ratios were varied starting from 1 : 4, to 1 : 2, and 1 : 1.25.

In figures 3-7, the purpose of the continuous line is for suggesting the trend of the data.

A higher amount of hydrogen in the feed gas led to a higher CO conversion, resulting that the reaction process

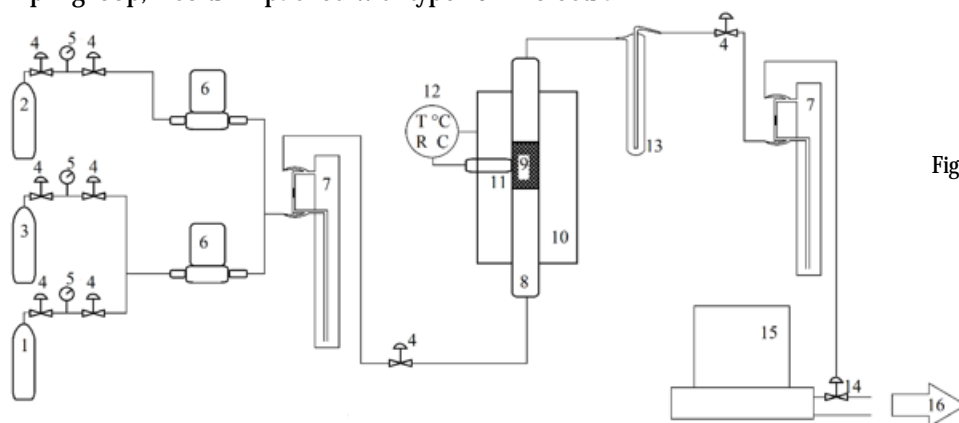


Fig. 1. Experimental set-up of the F-T process

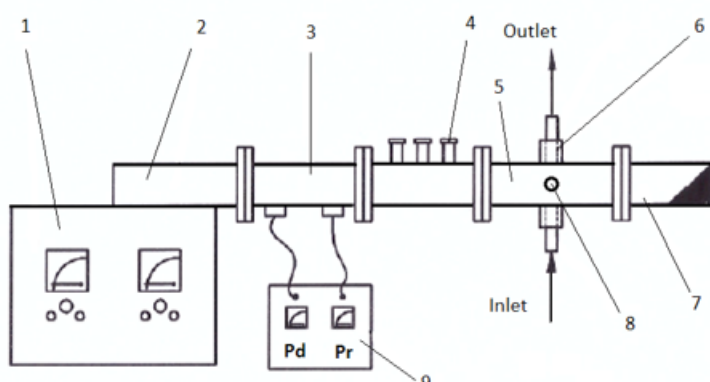


Fig. 2. Monomode Microwave Unit

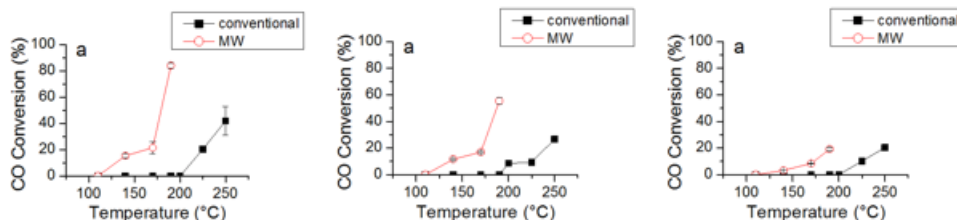


Fig. 3. Conversions at $H_2 : CO$ ratios of 4 : 1 (a), 2 : 1 (b), 1.25 : 1 (c)

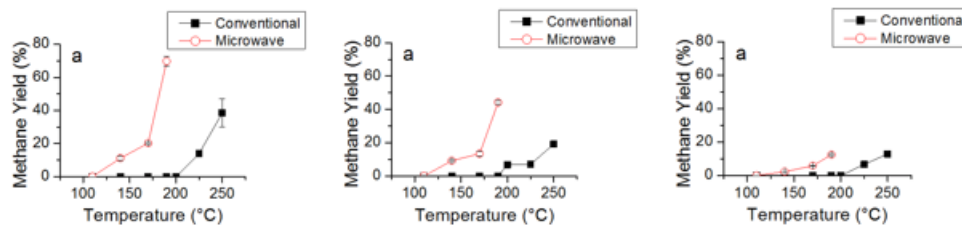


Fig. 4. Yield in methane at a $H_2 : CO$ ratio of 4 : 1 (a), 2 : 1 (b) and 1.25 : 1 (c)

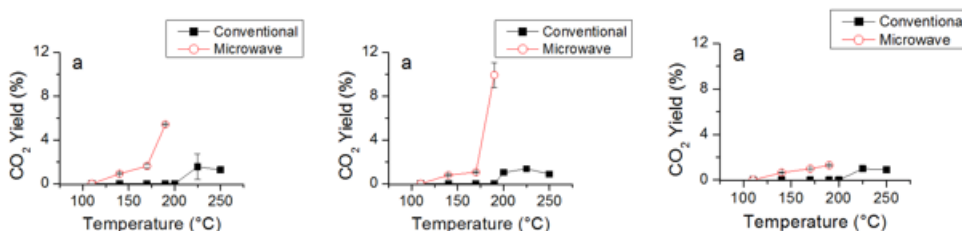


Fig. 5. Yield in CO_2 at a $H_2 : CO$ ratio of 4 : 1 (a), 2 : 1 (b) and 1.25 : 1 (c)

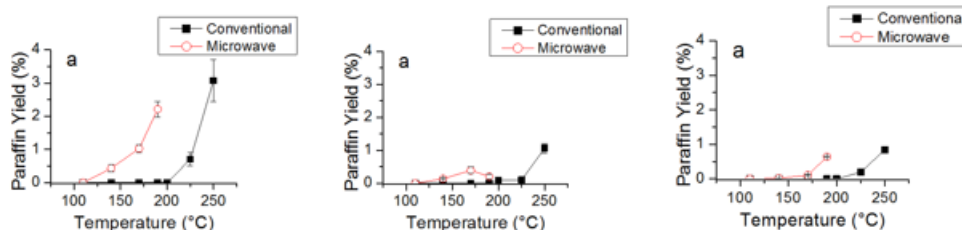


Fig. 6. Yield in paraffins (C_2-C_4) at a $H_2 : CO$ ratio of 4 : 1 (a), 2 : 1 (b), 1.25 : 1 (c)

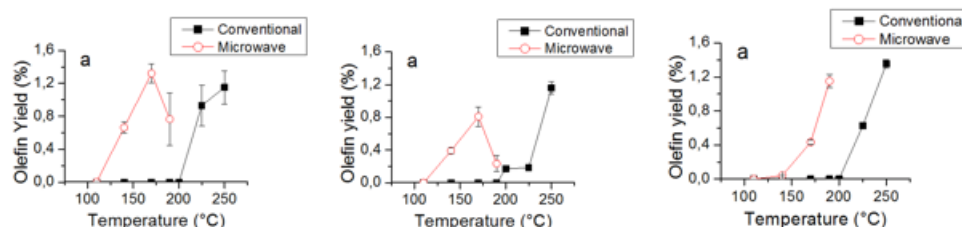


Fig. 7. Yield in olefins (C_2-C_4) at a $H_2 : CO$ ratio of 4 : 1 (a), 2 : 1 (b), 1.25 : 1 (c)

had a better performance. The microwave activation of catalyst allows higher CO conversion at lower temperatures than the conventional heating process.

The use of a high $H_2 : CO$ ratio resulted in high methane yield as can be seen in figure 4a. The overall yield for methane in MW heating tends to be significantly better than in the case of conventional heating. Furthermore, superior yields for methane were obtained at lower temperatures in MW field. In both figure 4a and figure 4b, the yields for methane in MW field were of 70% for a 4 : 1 $H_2 : CO$ ratio at 190°C when compared to the maximum of 40% obtained by conventional heating at 250°C. Lowering the ratio $H_2 : CO$ used in the reaction also led to a lower yield for methane.

Carbon dioxide formation was favoured by high temperatures. Regarding MW activation of the catalyst, higher yields in CO_2 are obtained especially at higher $H_2 : CO$ ratios. This aspect could be a limitation to MW activation of the catalyst.

The overall yields for paraffins (C_2-C_4) were low with the highest values being obtained at 4 : 1 $H_2 : CO$ ratio.

Similar to paraffin yields, olefins were obtained in low amounts, but a slight increase in yields can be observed in figure 7c due to a lower ratio of $H_2 : CO$ used in the reaction.

Conclusions

A 10 : 1 : 1 molar ratio Co : Mn : Ca (20% wt) supported catalyst on AISBA-15 was tested in the Fischer-Tropsch process under atmospheric pressure. The experiments were carried out under conventional and microwave heating, and the temperatures were chosen in order to obtain comparable results for the CO conversion, as well as the product yields. Thus, temperatures of 110, 140, 170, 190°C and temperatures of 200, 225, and 250°C were used for the microwave heating and conventional heating, respectively. For each temperature, experiments were carried out at different $H_2 : CO$ ratios of 4 : 1, 2 : 1 and 1.25 : 1.

In the experimental conditions (at atmospheric pressure and a gas hourly space velocity of $0.1 s^{-1}$) the main reaction product was CH_4 , along with very small amounts of C_2 C_4 saturated and unsaturated hydrocarbons.

The microwave catalyst heating allowed the use of much lower reaction temperatures in the F-T process (170-190°C) than in the conventional one (225-250°C), as well as higher CO conversions (two times higher), especially at high H₂:CO ratios.

The low temperature required (170 °C) at atmospheric pressure, along with a 4 : 1 H₂ : CO ratio suggests the possibility to use this non-conventional heating method as milder methanation process than the classical Sabatier method, which implies a nickel catalyst and a temperature of 400 °C.

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