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Optimisation of Fischer-Tropsch Unit

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OPTIMALIZACE FISCHER-TROPSCH jednotky

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katalyzátory kobalt

Abstract

The goal of this work was to investigate Fischer Tropsch Micro Catalyst (MCB) (Vinci Technologies, France) operation and the Fischer-Tropsch Synthesis (FTS) process with a cobalt catalyst that was carried out in it. To provide this, the MCB unit was run and tested considering all its elements and software functionality. Moreover, a wide range of FTS experiments was carried out to investigate the process conversion rate and selectivity considering given conditions, i.e. temperature and pressure.

Keywords: cobalt-based catalyst, Fischer-Tropsch synthesis, conversion rate, selectivity

Abstrakt

Cílem této práce bylo optimalizovat provoz Fischer Tropsch Micro Catalyst (MCB) (Vinci Technologies, Francie) jednotky a proces Fischer-Tropsch syntézy (FTS) použitím kobaltového katalyzátoru. Za tímto účelem byla jednotka MCB provozována a testována s ohledem na všechny její prvky a softwarovou funkčnost. Kromě toho bylo provedeno široké spektrum experimentů FTS, aby se zjistila rychlost a selektivita přeměny procesu s ohledem na experimentální podmínky, tj. teplotu a tlak.

Klíčová slova: kobaltový katalyzátor, Fischer-Tropsch syntéza, rychlost konverze, selektivita

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1. Introduction

The Fischer-Tropsch synthesis (FTS) is a process developed in 1930 in Germany and connected with a coal utilization. The goal of this technology is to produce hydrocarbons from a synthetic gas (a mixture of carbon monoxide and hydrogen). The hydrocarbon products are mainly liquid, but some of them might be solid or gaseous. The state of the products, as well as their chemical composition depends on the synthesis conditions. These products include light hydrocarbons (C1 and C2), olefins, LPG (C3-C4), naphtha (C5-C11), diesel (C12-C20) and wax (>C20) [1] fractions, however the amount of the given products changes in favour of lighter compounds with the increase of process temperature. Considering that, a High Temperature Fischer Tropsch (HTFT) and a Low Temperature Fischer Tropsch (LTFT) might be distinguished [2]. The LTFT is used mainly to produce waxes and paraffin that might be used for purpose of liquid fuels or speciality waxes. The HTFT is used mainly to produce methane, gasoline and diesel compounds and olefins, with the latter one being used mainly in polymers production. Beside hydrocarbon products, due to the presence of water, some alcohols might be included in the products stream, especially with iron catalyst [1,3]. As the main feedstock for synthetic gas production coal and methane are used.

2. Experiment

The Fischer-Tropsch Micro Catalyst Bed unit (FTMCB) unit is shown in Figure 1.

Figure 1: The Micro Catalyst Bed unit

It consists of the main following elements: nitrogen, hydrogen and carbon monoxide Flow Indicator Controller (FIC) (1.1-1.3), pre-heater (2), reactor (3), wax separation module (4), gas/liquid separation module (5), safety valve (6), Pressure Indicator Controller (PIC) (7), expansion tank (8) and gas flow meter (Definer 220, MesaLabs) (9). The temperature of the pre-heater, reactor, wax separation module and gas/liquid separation module can be controlled by means of the MCB unit software (Figure 2). Besides temperature, the software allows to control gas flow rates and pressure in the reactor. Additional equipment that was used during the tests includes: electronic leak detector (Restek), CO detector (J.T.O. Systems) and gas analyzer (GAS 3000P, Pollutek) used to measure concentration of H_2, CO, CO_2, CH_4, N_2 and C_xH_y.

3. Results and discussions

Figures 2-5 below presents results from the F-T synthesis experiments. The figure show conversion/selectivity and carbon streams. The carbon stream reflects the amount of carbon that was consisted in given reagent, i.e. carbon monoxide, carbon dioxide, methane and others. The “others” refers to all the carbon that was not included in carbon oxides or methane, thus, it was calculated as a difference between the initial carbon stream (initial CO) and the carbon stream included in synthesis products (carbon dioxide, methane and untreated carbon monoxide).

Figure 2: Carbon distribution in reagent streams (15 bar)

Figure 3: CO conversion and CO2, CH4 selectivity (15 bar)

Figure 4: Carbon distribution in reagent streams (25 bar)

Figure 5: CO conversion and CO_2, CH_4 selectivity (25 bar)

It is important to mention, that the Figures 2-5 show only a part of the temperature profile. The figures show only the period when the temperature was quite stable. This means, that the temperature in the reactor was close to the one that was set. After exceeding this temperature, the reactor was overheated and the temperature increased severely by 30-50°C. This phenomenon, caused by the exothermal of the FT process, is unwanted since high temperature results in production of mainly CO_2 and CH_4 – products of low value. This phenomenon will be discussed in more detail in further part of the report. The FTS reaction rate can be associated with CO conversion – the higher it is, the greater amounts of products should be obtained. At the same time, it is important that these products are not CO_2, neither CH_4 since they are the least valuable. Thus, the C_{other} parameter is of great importance, since it somehow refers to the amount of other carbon compound (like paraffin, olefins and alcohols).

As one can see, Presented Figures (2-5) show that in most of the cases, considering the best results, the pressure of the process didn't influence much. No matter wat pressure was applied, 15, or 25 bars, the $CO_{conversion}$ and C_{other} were similar. It is important to point out that this phenomenon refers to the test with reused catalyst. In that case, the $CO_{conversion}$ was 25-30% and C_{other} around 0.7-1.0 g/h. It is important to notice, that while the carbon conversion is almost of the same rate, the products distribution might be different. In other words, the pressure may influence the product composition. In carried out research, all the products were gathered in one tank. To check, if the pressure really affects product distribution, additional tests should be done with collecting samples into different tank for each pressure regime. The second important result, that might be derived from Figures 2-5, is that the factor that truly affected the process rate was the catalyst. As it can be seen, with a fresh catalyst (catalyst that was completely new and only activated) the temperature in which the process parameters are the best is around 300°C. In case of reused catalyst (the one that was used in more than one test) this temperature is much lower – c.a. 250-280°C. Moreover, in case of fresh catalyst, due to higher temperature, the $CO_{conversion}$ was a bit higher, but at the same time, the amount of CH_4 and CO_2 was also higher. It is well known that the higher temperature results in higher concentrations of CO_2 and CH_4 [3]. Additionally, experiments in which the activation was carried out at elevated pressure and extended time shown the worst results. In case of a fresh activated catalyst, the temperature of the process could be as high as 350°C and no overheating occurred. In such a temperature, the conversion was almost 50% but the main products were CH_4 and CO_2. Even if the catalyst was reused, no matter if it was or wasn't activated, the temperature profile was

still significantly higher when compared to other experiments. Theses result suggest, that the structure of the cobalt catalyst may somehow change during the FTS and activation process. It is possible, that during FTS process, with elevated temperature the catalyst surface structure and pore distribution may increases somehow (for instance, due to crumbling). As a result, the fallowing processes are carried out more efficiently. On the other hand, if the temperature and pressure are high for a sufficient period of time (like during the prolonged activation), the catalyst structure might have collapsed or sintered and reduce its surface and pore structure. In consequence, the FTS in less efficient. It is also possible, that some chemical reactions taking place at the catalyst surface during the FTS process may somehow affect the catalyst performance. To make sure of it, some deeper insight of the fresh, activated and used catalyst should be given. It should involve surface and pore distribution measurement as well as some microscope analyses.

4. Conclusions

The paper presents result from the experiments considering Fischer-Tropsch synthesis with a use of Micro Catalyst Bed and cobalt catalyst. The test showed that the set-up can be successfully used to produce liquid fraction consisting organic compounds. These compounds are mainly alcohols and paraffins. The best conditions, resulting in the greatest output of heavier organic products, are c.a. 260°C and 15-25 bars. These method was used to extend the techniques employed so far to model dangerous properties of complex chemical mixtures. The products of FTS enabled the investigation of the explosion characteristics. The values of explosion characteristics are used to describe the effect of complicated mixtures on a deflagration process as well as to rate the effects of an explosion. Combining the FTS unit and explosion vessels offer great possibilities for experimental orientated application research.

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