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INITIAL PROCESS AND SYNTHESIS GAS CONVERSION IN FISCHER-TROPSCH FUSION REACTION

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Abstract

We performed a series of Fischer-Tropsch (FT) reaction experiments in a bulk reactor on Al_2O_3 *supported cobalt catalyst . The batch experiment was started while the low-pressure reactor (PBFR) was operating at steady state. The reaction conditions used were typical low-temperature Fischer-Tropsch synthesis (FTS) for cobalt catalyst, reaction temperature 210* ^{o} *C, initial pressure 20 bar(g) and* $H_2/CO = 2$ *in the feed. For batch experiments, we varied the duration of the batch reaction between 20 minutes and 2.5 hours. We monitored the conversion for each reaction duration and compared the reaction rates with those obtained in PBFR mode. The product distribution for C1-C9 showed an increasing trend with increasing carbon number, The pressure in the reactor was monitored during the reaction and a comparison of the pressure readings with the predicted pressure showed that most of the water produced was in the liquid phase in the reactor.*

Keywords

PBFR reactor, Fischer-Tropsch synthesis, CO conversion, H_2 *conversion .*

Introduction: Fischer-Tropsch synthesis (FTS) is a catalyzed chemical reaction in which synthesis gas (syngas), a mixture of carbon monoxide (CO) and hydrogen (H2), is converted to paraffins, olefins, and oxygenates [1-7]. The FT reaction for paraffins can be written as:

$$nCO + (2n+1)H_2 \text{ « } C_nH_{2n+2} + nH_2O$$

generally assumed that at low temperature (Co catalyst: 210-230 ^{o} C, Fe catalyst: 230-250 ^{o} C) FTS is controlled kinetically rather than thermodynamically, because the thermodynamic equilibrium constant is high. Under suitable reaction conditions, the degree of conversion of the reactant can be almost complete. Since Franz Fischer discovered this type of synthesis, a large amount of research has been devoted to the kinetics of FTS on the rate of consumption of reactants and the formation of products using cobalt and iron catalysts low-temperature FTS are usually performed in a fixed-bed or slag-bed reactor. Researchers rarely use a bulk reactor with a gas–solid reaction regime to evaluate a catalyst or study the mechanism of FTS, but we suggest that it may be useful in investigating FTS. The reasons are that it can create a uniform reactive distribution medium for all catalyst granules in the reactor and eliminate the effect of medium (long chain) paraffins used in suspended bed mode.

Also, while batch reactors (PBFRs) operate in a steady state in most cases, a batch reactor operates in an unsteady state, and the reactor pressure and the partial pressures of the reactants and products vary depending on the rate of change. reaction. This gives us additional information to help us understand the behavior of the FT reaction.

Experience: The FT experiments were performed in a tank reactor in batch mode in a gas-solid system with adequate mixing. Batch experiments were performed with reaction durations ranging from 20 minutes to 2.5 hours. Our goal was to study the conversion and reaction rates of reactants, selectivity and distribution of products.

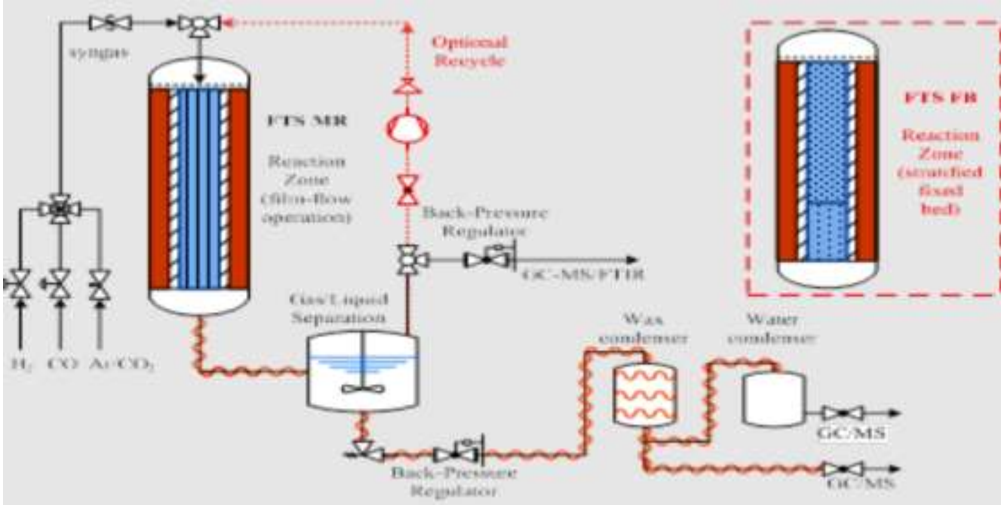

Figure 1: *Experimental microreactor setup for FTS testing.*

Experiments were performed in a 100 mL PBFR in a gas–solid system without any solvent addition. Residence time distribution (RTD) experiments have shown that gaseous materials can be well mixed. The reactor was operated in PBFR mode and later in bulk mode. Premixed syngas (10% N_2/30% CO/60% H_2) was fed into the reactor at 20 bar(g) and the flow rate was controlled by the Flow Controller. The product was poured from the bottom of the tank to completely remove all contents, including liquid phase products, from the reactor. To avoid product condensation in the outlet lines, these lines were heated to 180 o C to two product traps maintained at reactor pressure and 150 o C and 30 ^{o} C, respectively, to collect wax and liquid products .

A supported cobalt catalyst (28.6 m2/g, average pore diameter 35.8 nm) containing 10% Co/90% Al $_2$ O 3 was used in the experiments. Al_2O_3 was mixed with distilled water in a 1:1 ratio to make a paste, which was dried at 120 ° C for two hours, calcined at 400 ° C for six hours, and then cooled overnight 2 at ambient pressure . The gas space velocity was based on the wax mass of the unreduced catalyst. The temperature was raised from room temperature to 120 ° C, first at a ramp rate of 60 os-1 and held for two hours before increasing to 280 o C at the same ramp rate, and held at this temperature for 24 hours. After recovery, the reactor was cooled below 100 ° C. The feed gas was switched from H 2 used for reduction to syngas. The reactor pressure was stabilized at 20 bar (g) by a back pressure regulator and the feed flow rate was kept constant by a mass flow regulator. The temperatures used in the experiments were 190 ° C and 210 o C. The initial stirring speed inside the reactor was set at 100 rpm.

The performance of FTS differs from that of a catalyst coated with and coated with liquid phase products. To establish the same starting point for batch operations lasting different periods, we operated the reactor in PBFR mode until steady state before starting each batch operation. The process was carried out as a cyclic sequence: using the PBFR operation mode until steady state , then batch operation for a certain period of reaction and sampling, and then restarting the PBFR operation until steady state was reached. the next batch operation is scheduled for a different period. We started the batch operation by isolating the reactor by closing the inlet and outlet valves and simultaneously starting the time recording. After the specified duration of the batch operation (20 min, 40 min, 1 h, etc.) was completed, the sample was collected and analyzed. During sampling, we completely flushed its sampling ring with the sample from the reactor to ensure the accuracy of the experiment. All materials in the reactor, including light and heavy hydrocarbons, were to be collected and sent. However, since long-chain hydrocarbons are in the liquid phase, we were not sure that online gas chromatography would analyze them effectively. Therefore, the information we present in this article only applies to short-chain hydrocarbons. After the sample was subjected to gas chromatography, we set the reactor to the original PBFR mode under the same operating conditions as before. After about 24 hours, steady state was again achieved and we started the next batch mode operation.

Result: Figures 2 and 3 depict the conversion of reactants for different reaction cycles used in batch experiments. Indicates the end of PBFR mode operation and the beginning of bulk mode operation for the reactor. The shape of the conversion curves was logarithmic, and the maximum conversion for CO and H_2 was found to be around 98.5%. None of the reagents achieved 100% conversion.

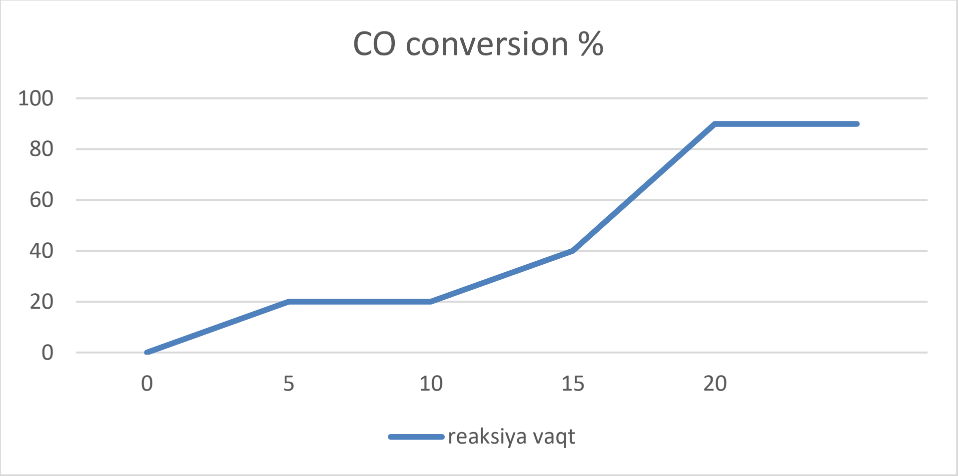

Figure 2. CO conversion for different reaction durations

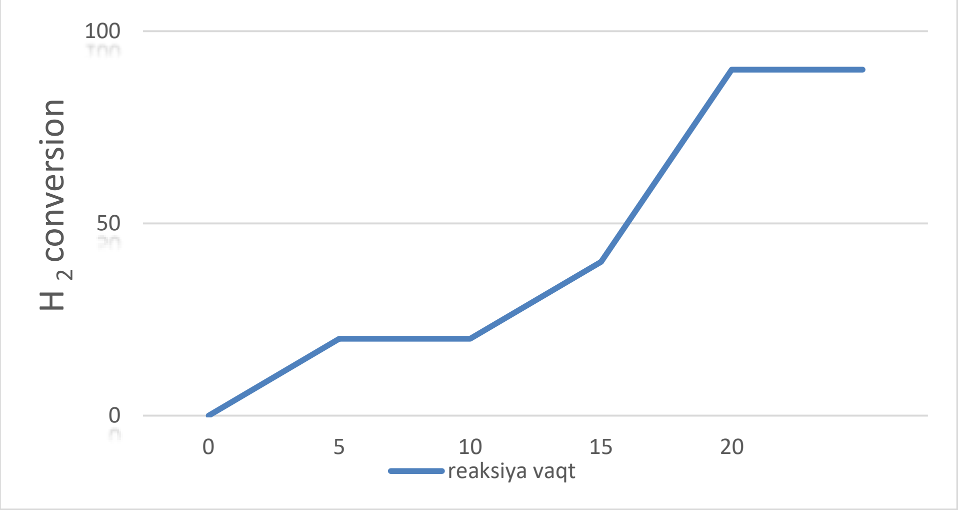

Figure 3. H_2 conversion for different reaction durations

In batch mode, the reaction rate is the average reaction rate over time by calculating the difference of reactants remaining at two time points. The operating conditions for the PBFR and batch experiments were identical in all respects except for one aspect: no feed or products were withdrawn during the batch operation. We believe that the change in reaction rate with time in the PBFR regime is due to the altered mass transfer caused by the accumulation of liquid product in the catalyst. When we switched the reactor from PBFR to batch, the reaction rate was around 3 mol/s CO, while the average CO reaction rate in the first 20 min of the batch increased to 3.4. 10, 5 mol/s CO. The reaction rate then decreases with increasing duration as the reactants in the reactor decrease (shown as CO conversion rate in the figure).

A decrease in the reaction rate in proportion to the decrease in the concentration of reactants in the reactor is understandable from a kinetic point of view, since the reaction rate can depend on the concentration of reactants in the reactor. However, when we switch the operating mode from PBFR to batch, it is more difficult to explain the jump of the reaction rate by about 70%, because the average concentration of reactants in the first 20 minutes of the reaction duration is slightly lower than that. In PBFR mode. Note that the catalyst was prepared as the reactor operated in PBFR mode for over a week before switching to batch operations and was at steady state. Thus, a sudden change in catalyst properties was not expected at the start of batch operation, so the jump in reaction rate was unlikely to be caused by a change in catalyst properties.

In continuous experiments, the analysis of medium and long chain hydrocarbons is usually performed on products collected in product brines. This is a lengthy process in a mass balance because it takes time to collect enough product for analysis. In our experiments, due to the limited amount of reactant in the reactor, the amount of liquid phase product formed in batch mode was insufficient for collection and analysis. The sampling process sent all hydrocarbons to gas chromatography without any separation to ensure that at least all light hydrocarbons were presented to the analysis equipment. Therefore, the product breakdown below represents only short-chain hydrocarbons (C1-C9). Although the full spectrum of product distributions is not available, the results for light ones are clear enough to show the characteristics of the product distribution of FTS in a batch reactor.

Water is the main product of FTS and its effect on catalyst performance has been widely studied by researchers. They reported that water has both positive and negative effects on the FTSreaction rate . The produced water deactivates the catalyst by oxidizing the active sites, which are actually the reduced metal. If the support is sensitive to high temperature water, it can change the stability of the support structure . In addition to its effect on the catalyst itself, water also has a potential effect on FTS from a reaction engineering perspective, as it affects the mass and heat transfer in the reaction system depending on whether it is in the liquid or gas phase. Water is usually assumed to be in the gas phase under FTSreaction conditions because its boiling point at operating pressure is lower than operating temperature.

Conclusion: The FTS reaction was carried out in a batch reactor with Al_2O_3 supported cobalt catalyst. To avoid any disruption and depletion of materials as a result of sampling from the reactor, we separately performed a series of operations over the duration of the reaction; PBFR is started after steady state in operation mode. This ensured that the starting point of each batch operation was the same. The duration of the reaction varies from 20 minutes to 2.5 hours. During each of them, we investigated the conversion, reaction rate, product selectivity and distribution, and the product water phase. When the reaction duration was long enough, 90.5% was achieved, but complete conversion of the reactants was not achieved, indicating a thermodynamic limitation. When the reactor was switched from PBFR mode to bulk mode, a jump in reaction rate was observed with a 70% increase, all other operating conditions being the same.

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