Transient operation of Fischer-Tropsch synthesis reactor with H₂/CO₂ – Catalyst behavior and reaction kinetics

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Introduction: Electricity-to-fuel as future storage technology for excess electricity

Large-scale catalytic reactors in chemical industry are, in general, operated under steady state conditions. However, in some cases, transient operation of catalytic reactors could lead to benefits for the overall process. The conversion of electricity into fuels (chemical energy carriers, e.g. hydrocarbon synfuels) is a potential storage technology that may become interesting if electricity from renewable intermittent sources (wind/solar) covers a high percentage of electricity demand [1]. Storage of H₂ facilitates continuous operation of the catalytic synthesis process. Motivation to operate the reactor under transient conditions may be a reduction of H₂ storage size and consequently of required investment [2].

Fischer-Tropsch (FT) synthesis with H₂/CO, was selected as an example fuel-related reaction. The production of gaseous hydrocarbons via FT synthesis is described as a two-step catalytic reaction (eqs. 1, 2) with CO as intermediate product. Iron-based catalyst is the catalyst of choice due to its activity for both reactions.

\[ \text{CO-Shift: } n \text{ CO}_2 + n \text{ H}_2 \xrightarrow{\text{cat}} n \text{ CO} + n \text{ H}_2\text{O} \]  

\[ \text{Fischer-Tropsch: } n \text{ CO} + 2(n-1) \text{ H}_2 \xrightarrow{\text{cat}} n \text{ CH}_{2n-2} + n \text{ H}_2\text{O} \quad n=1-5 \]  

The aim of the present study is to analyze the behavior of iron catalyst under transient operation conditions and to demonstrate the importance of reaction kinetics in the design of a catalytic fixed-bed reactor for transient operation. The approach followed is a combination of experimental work and mathematical modeling studies.

Approach: Experiments in lab-scale set up and mathematical modeling studies

Experiments under steady state conditions with the 100g Fe/2g K were carried out in advance [3] to identify the stable and accessible operation window to determine kinetic parameters (i.e. temperature, pressure, residence time, (H₂/CO₂))n, in a fixed bed reactor with 1.5 g of catalyst). Kinetic equations are considered as shown in equations (3) and (4). The catalyst behavior was studied under transient conditions using three different methodologies: a) step-change experiments combined with mathematical modeling of the lab-scale setup to separate effects of the peripheral equipment (Figure 1), b) periodic changes in inlet concentration to study characteristic times of potential catalyst changes, and c) in-situ experiments with X-Ray diffractometry (XRD) and magnetometer measurements under reaction conditions.

\[ r_{\text{CO}_2}\text{-\text{H}_2} = k_{\text{CO}_2}\text{-\text{H}_2} \frac{p_{\text{CO}_2} \cdot p_{\text{H}_2} \cdot p_{\text{H}_2\text{O}}}{p_{\text{H}_2} + \beta_{p_{\text{H}_2}}p_{\text{H}_2} + \beta_{p_{\text{H}_2\text{O}}}p_{\text{H}_2\text{O}}} \]  

\[ r_{\text{CO}} = k_{\text{CO}} \frac{p_{\text{CO}} \cdot p_{\text{H}_2\text{O}}}{p_{\text{CO}} + \beta_{p_{\text{CO}}}p_{\text{CO}} + \beta_{p_{\text{H}_2\text{O}}}p_{\text{H}_2\text{O}}} \]  

Results and discussion

The three methods indicate that according to the catalyst activity, the selected iron catalyst seems not be a limiting factor for transient operation as long as the range of stable steady state conditions is not exceeded. Steady state kinetics can describe the transient operation of the catalyst in the lab-scale reactor (in the range of operation conditions for which the steady state kinetics were determined). This is consistent with a catalyst characteristic time \(t_{\text{cat}} < 20 \text{ s}\) obtained from periodic experiments, which indicates that the catalyst activity operates most of the time under steady state conditions. The combination of experimental work and mathematical modelling (e.g. Fig 1) is in this case a powerful tool that allows the analysis of the catalytic reactor with its periphery under dynamic conditions.

Design of catalytic reactors able to operate under varying load conditions requires that conversion and selectivity meet specifications for each operation load. Often, this implies an increase in reactor size and/or periphery compared to steady-state operation. The increase of complexity due to transient operation can be roughly estimated based on the inhibition term of the reaction rate. In the case of FT with H₂/CO₂ (eqs. 1, 2), high conversion cannot be reached due to the strong inhibition of H₂O and catalyst deactivation. Consequently, a reactor with H₂O separation and recycle of reactants is proposed for transient operation [2]. The influence of the inhibition parameters on the design of the catalytic reactor is calculated using a one- and two-dimensional mathematical models of a non-adiabatic fixed bed reactor.

Significance

This work contributes to an assessment of the potential use of chemical reactors as flexibilization units in a future situation with a high contribution of renewable energies to electricity production. In addition, catalytic effects in a novel CO₂ hydrogenation concept to gaseous hydrocarbons are discussed in detail.

References

