Forced Periodic Operations of Millimetre-Scale Fixed-Bed Reactors for Fischer-Tropsch Synthesis

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Highlights

- Forced period operation is applied to unconventional millimeter-scale fixed bed reactor
- Fischer-Tropsch reaction kinetics offer opportunities for periodic operation
- Maximal C_{5+} productivity realized with modulation of inlet CO pressure and coolant T
- Dynamic optimization is used to obtain optimal frequencies, phase shift and amplitudes

1. Introduction

Fischer-Tropsch synthesis (FTS) is an exothermic multiphase catalytic reaction for conversion of carbon-monoxide and hydrogen into a wide array of hydrocarbon products, primarily n-alkanes and 1-alkenes. FTS is commercially used as a key part of gas-, biomass- and coal-to-liquid processes for production of value added liquid fuels and chemicals. Millimetre-scale multitubular fixed bed FTS reactors offer advantages over conventional scale systems, as they can provide better control of temperature and products selectivity [1,2]. Forced periodic operation (FPO) of chemical reactors is an intensification method in which one or more reactor input variables are deliberately perturbed in a periodic manner, in order to achieve superior performance in terms of productivity or/and selectivity in comparison to the conventional steady-state operation. The basis for enhancement is associated to specific nonlinearity of a system. In this numerical investigation, forced periodic operation is applied to an optimized milli-scale fixed bed reactor (FBR), to examine the potential improvement and to determine the input variables and conditions that lead to maximal productivity of the higher hydrocarbon products (C_{5+}).

2. Methods

A pseudo-homogenous model that includes detailed reaction kinetics [3] is used for this dynamic optimization study. The model is derived by reducing a more detailed heterogeneous model (gas-liquid-solid phase), which has been previously developed [4]. Optimal design and process conditions in steady-state, which served as a reference point, are obtained through a rigorous NLP optimization, using the detailed heterogeneous model. Simulation results obtained with the detailed and the reduced model of the optimized milli- FBR show very good agreement, and thus the simpler pseudo-homogenous model is chosen for further numerical investigation.

The forced periodic operation analysis is performed in a stepwise procedure:

1. *Reaction rates screening*. Dynamic optimization, using only the reaction kinetic model, is carried out to screen the possibilities for improvement. The objective function is defined as the relative difference of the C_{5+} reaction rate between the time-averaged value during the periodic operation and the steady-state value. Partial pressures of the reactants (CO and H_2), reactants molar ratio (H_2/CO) and temperature are varied as sinusoidal waves around their steady-state values at inlet conditions.
2. *Reactor FPO simulations*. Dynamic simulations of the reactor under forced periodic operations are performed, taking into account the results from the first step (screening). The objective is to test the initial result in the mili-scale reactor environment, and to adjust the operating windows, i.e. variables and ranges of amplitudes and frequencies.

3. *Reactor FPO optimization.* Dynamic optimization of forced periodic operations for the milli-scale FBR is carried out in order to obtain optimal amplitudes, frequencies and phase shift and to determine the scale of the enhancement obtained by periodic modulations of the input variables selected in the previous steps. The objective function, i.e. the improvement criterion, is the relative difference of the C_{5+} molar productivity corresponding to the forced periodic operation (the time-averaged value) and the optimized steady-state value.

3. Results and discussion

The first step – reaction rate screening, demonstrates that there is a high potential for improvement by utilizing FPO, in comparison to the steady-state operation. The largest enhancement is achieved when partial pressure of CO and temperature are varied simultaneously. The screening shows that for high amplitudes of sinusoidal changes (≈90%), the relative change of the C_{5+} reaction rates (FPO vs. steady-state) is over 300%. However, for lower amplitudes (≈20%), the difference sharply drops to 29%. The second largest improvement is obtained with variation of the partial pressure of CO (90% for high amplitudes and 2.4% for low). Variation of the temperature results in modest improvement, while the periodic change of H_2/CO makes practically no difference. The main reason for enhancement of the C_{5+} reaction rates is due to the negative reaction order with respect to CO.

The reactor FPO simulations show that higher amplitudes cannot be achieved in the reactor, and thus the initial ranges had to be narrowed. Simulation results point out that the inlet coolant temperature is the input variable to be perturbed, since the milli-scale FBR is almost insensitive to change of the feed temperature. The dynamic optimization of the milli-FBR forced period operation confirmed that enhancement is noticeable, although the time-averaged C_{5+} productivity is increased moderately (less than reaction rates). Simultaneous modulation of the inlet CO partial pressure and inlet coolant temperature, with an appropriate phase shift, results in the highest gain. It was shown that the input amplitudes should be as high as possible, while there are regions of optimality for the modulation frequency and the phase shift between the two inputs.

4. Conclusions

This numerical study demonstrated that intensified and optimized millimeter-scale fixed bed reactors for Fischer-Tropsch synthesis can be further improved by operating them in forced periodic conditions. The scale of enhancement largely depends on the values of the amplitudes of the input periodic changes that can be applied. The maximal gain in C_{5+} productivity with the FPO, in comparison to the steady-state operation, is achieved with simultaneous modulation of the inlet CO partial pressure and inlet coolant temperature. Since the FPO is a technically demanding operation, the results of this study are valuable for further investigations and potential development. The presented methodology for forced periodic operation analysis may be applied to other reaction systems.

References

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Keywords
Forced periodic operation; Fischer-Tropsch synthesis; Fixed bed reactors; Dynamic optimization