On the Equivalence of Kinetic Data Obtained in Fixed-Bed and Slurry Reactors in the Fischer-Tropsch Synthesis

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Introduction

Both fixed-bed and slurry reactor configurations have been proposed for the low temperature (200-240°C) Fischer-Tropsch Synthesis (FTS) with cobalt-based catalysts. Multitubular Fixed Bed Reactors (FBR) were used largely in the first FT industrial processes but, in the last years, have been progressively substituted by Slurry Reactors (SR), which are less expensive and almost isothermal, allow easier catalyst make-up, and reduce mass transfer limitations. At the lab scale, both FBR and SR are employed widely for catalyst screening, reactivity tests, and kinetic studies of the FTS. FBR are particularly appropriate for this work, because they are easily operated at this scale. However, they may suffer from temperature gradients inside the catalyst bed and difficulties in the temperature control, which make them inadequate for studies at typical industrial process conditions (high CO conversion). On the other hand, SR allow to work at these conditions, but are characterized by long transients in the liquid products renewal upon start-up and during changes of the operating conditions, so that data collection is extremely time-consuming [1].
The goal of this work is to show that kinetic data collected in fixed bed reactors can be adopted successfully to describe the behavior of slurry reactors. For this purpose a comparative kinetic analysis has been carried-out in our labs on both a slurry and a fixed-bed reactor using the same Co-based FT catalyst, working at suitable process conditions (CO conversion lower than 40% for the FBR and 70% for the SR). Lumped kinetic models of CO conversion have been fitted to data from both reactors, and the resulting kinetic parameter estimates have been compared. A second, more extensive comparison has involved developing a complete mechanistic kinetic model based on the FB experimental data and validating it with the experimental data obtained in the SR at typical process conditions.

Materials and Methods

The catalytic activity tests hereby illustrated were carried out in two similar lab-scale set-ups, based on a fixed bed tubular reactor with 0.5″ I.D. and a 0.5 L slurry autoclave, respectively, utilizing a 15% w/w Co/Al_2O_3 catalyst. The process conditions were varied within a range relevant to industrial operation (T=210-240°C; P=8-20 bar; H_2/CO feed molar ratio=1.5-2.3; $GHSV_{FBR}$=4-7 $dm^3(STP)\cdot h^{-1}\cdot g_{cat}^{-1}$; $GHSV_{SR}$=1.2-3 $dm^3(STP)\cdot h^{-1}\cdot g_{cat}^{-1}$. During each experiment, both the CO conversion and the reaction selectivity were monitored by full analysis of the product distribution up to C_{49}, until steady state conditions were reached. Mass transfer limitations were ruled out by dedicated diagnostic experiments in both reactors. Further experimental details can be found in a previous work [2].

Results and Discussion

The effect of the operating conditions on the CO conversion and selectivity to the various products was first investigated. Very similar effects of the process variables on the catalyst performances were observed in both reactor configurations. In particular, CO conversion data (32 experimental tests in the case of SR and 46 for the FBR) were fitted by means of three different kinetic models: Power Law, Yates-Satterfield [3] and Sarup-Wojciechowski [4]. The isothermal homogeneous models adopted for the lab-scale reactors were a Continuous Stirred Tank (CST) in the case of the slurry unit and a Plug Flow (PF) for the fixed-bed unit. A good agreement was found between the two sets of kinetic parameter estimates obtained for the two adopted reactors, confirming similar activities of the two lab-scale units and indicating that both of them are suitable for collecting representative kinetic data. A complete kinetic model [5] based on a detailed reaction mechanism was also developed on the basis of the data collected in the FBR. An elementary rate law was assigned to each step included in the reaction scheme and the related kinetic parameters were estimated by multi-response non-linear regression. The obtained model predicted well both the CO conversion and the observed product distribution up to carbon number 49, in terms of total hydrocarbons, paraffins and olefins for all the experimental conditions considered in this study. The kinetic model, developed in the case of the FBR, was also validated by simulating the data set collected in the slurry reactor, resulting in a good match. Only slight modifications to the kinetic parameters were necessary, in fact, to fit the data collected in this reactor at the highest CO conversions, i.e. in conditions more similar to those adopted in industrial FT plants.

Significance

The comparative study carried out in this work demonstrated equivalence between the kinetics obtained from the slurry and from the fixed bed units. This suggests that is possible to develop a FT kinetic model valid for an industrial SR on the basis of data more easily and rapidly available from a lab-scale FBR.

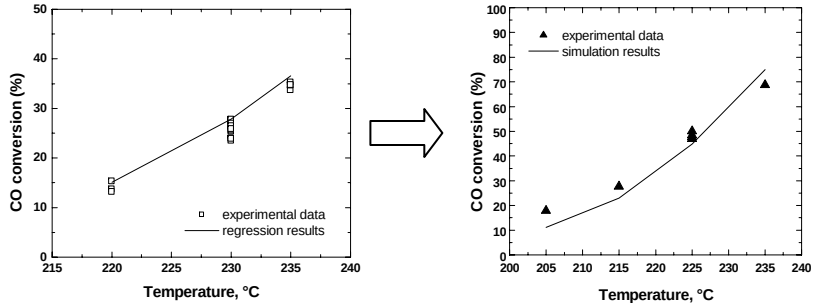

Figure 1. Experimental and calculated effect of the temperature on CO conversion for both the fixed bed and the slurry reactor.

References

1. D. Pinna, E. Tronconi, L. Lietti, R. Zennaro, P. Forzatti, *J. Catal.* 214, 251 (2003).
2. C.G. Visconti, L. Lietti, P. Forzatti, R. Zennaro, *Appl. Cat. A: General* 330, 49 (2007).
3. I.C. Yates, C.N. Satterfield, *Energy Fuels* 6, 168 (1991)
4. B. Sarup, B.W. Wojciechowski, *Can. J. Chem. Eng.* 67, 62 (1989
5. C.G. Visconti, E. Tronconi, L. Lietti, R. Zennaro, P. Forzatti, *Chem. Eng. Sci.* 62, 5338 (2007).