Operating Strategies for Fischer-Tropsch Reactors: A Model-Directed Study

Hyun-Seob Song**, Doraiswami Ramkrishna[†], Sinh Trinh* and Harold Wright*

School of Chemical Engineering, Purdue University, West Lafayette, IN 47907, USA
*Conoco Inc., Ponca City, OK 74602, USA
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Abstract−A comprehensive parametric study for a Fischer-Tropsch (FT) synthesis process has been conducted to investigate the relation between process parameters and reactor characteristics such as conversion, selectivity, multiplicity, and stability. A flexible model was employed for this purpose, featuring the dependence of Anderson-Shultz-Flory (ASF) factor on composition and temperature. All variable process parameters in industrial FT reactors were subject to variation, including reaction temperature, reactor pressure, feed ratio, inlet mass flux, feed temperature, heat transfer coefficient, catalyst concentration, catalyst activity, etc. While typical trade-off was encountered in most cases, i.e., the change of a parameter in one direction enhances one aspect but deteriorating another, the change of feed conditions gave some promising results. It has been found that decreasing the feed rate (or increasing the residence time) and/or lowering the feed concentration can successfully enhance the conversion up to more than 90% for our specific case, without hurting the product selectivity as well as effectively condense the region of multiple steady states. The benefits and limitations accompanied with the variation of the parameters were discussed in detail and a rational start-up strategy was proposed based on the preceding results. It is shown that the decrease of inlet mass flux (say, 85% decrease of the feed rate or 60% decrease of the feed concentration from the nominal condition chosen here) or the decrease of H_2/CO ratio (specifically, below about 0.25), or their combination can eliminate multiple steady states. The resulting unique relation between temperature and manipulated variable (i.e., coolant flow rate) appears to assure a safe arrival at the target condition at the start-up stage.

Key words: Fischer-Tropsch (FT) Synthesis, Multiplicity, Stability, Conversion, Selectivity, Start-up Strategy

INTRODUCTION

Fischer-Tropsch (FT) synthesis provides a promising route for the transformation of syngas (i.e., a mixture of hydrogen and carbon monoxide) produced from natural gas to high quality liquid fuels or valuable petrochemicals.[1] The importance of FT is increasing not only from the expectation that natural gas would eventually exceed oil as a main resource of fossil fuel in the near future considering the current trends, but also from the economic incentive in the rising demands of the middle distillate transportation fuels [Sie, 1998]. Owing to the strong exothermicity of FT synthesis, the control of temperature within the reactor is one of the most important issues for a safe and stable operation. In this regard, the industrial preference of bubble column slurry reactors to fixed bed reactors is understandable considering its higher heat transfer characteristics. For the fundamental studies of FT slurry processing, stirred tank slurry reactors, instead of bubble column reactors, are often employed in lab-scale experiments. The necessity of considering complex hydrodynamic effect of bubble, liquid, and catalyst particles

on chemical reactions and heat and mass transfer reasonably disappears under stirred tank configurations where uniform distributions of temperature, species concentration, and catalyst particles can be realized.

A safe operation is often threatened by complex nonlinear characteristics inherent in FT synthesis. Multiple steady states are likely to exist in a wide range of operating conditions normally employed for FT synthesis even in stirred tank reactors [Bhattacharjee et al., 1986; Shah et al., 1990; Song et al., 2003a], not only in bubble column reactors [Song et al., 2003b]. Undesirable runaway behavior by ignition [Bhattacharjee et al., 1986; Shah et al., 1990] or other reasons as provided by Song et al. [2003a] might take place during operation if the operating state is not carefully chosen in view of the multiplicity feature of FT reactors. It is of paramount importance to address the issue of whether or not there exists an achievable parameter space providing better selective conversion without sacrificing safe operability. Such knowledge would also be essential for developing an appropriate start-up strategy towards establishing a safe operating state and suitable control parameter settings.

It is an important aspect of FT synthesis to identify an operating range under which both the conversion and the product selectivity are enhanced. In many cases, the desirable products of FT processes are heavy hydrocarbon waxes from which the middle distillate transportation fuels can be obtained. There have been some interesting attempts to increase the efficacy of FT synthesis processes via periodic operation [Barshad and Gulari, 1986; Adesina et al., 1995]. When the steady state mode suffers from low reaction rate, poor selectivity, or both, cyclic forcing in feed composition might present interesting alternatives for solution. However, when multi-

ple steady states exist, safe periodic operation of the reactor requires exacting information on both process steady states and dynamics that is usually not available. Besides the conversion and selectivity issues, we explore the effects of various processing conditions on the operability (i.e., safely away from the hazards of multiplicity and stability). In order to obtain more realistic results on steady state multiplicity, the model employed here included the energy balance around the cooler, often neglected in other modeling works. This seems necessary because the inclusion of the cooler's energy balance leads to significantly different multiplicity features [Russo and Bequette, 1995; Song et al., 2003a]. Further, the dependence of Anderson-Schultz-Flory (ASF) factor on operating conditions has been considered, which can be used as a measure of product selectivity. Although the temperature dependence of ASF factor is simply described by a linear equation based on experimental data available in the literature, it gives a reasonable prediction on the product selectivity of our FT system.

The processing conditions considered to vary in this study include temperature, pressure, feed conditions (i.e., inlet mass flux, feed temperature, and H_2/CO ratio), St_H (i.e., heat transfer area of cooler and/or heat transfer coefficient), and Da (i.e., catalyst loading and/or catalyst activity), which can readily change in industrial FT reactors. Changes of such parameters often lead to conflicting results. For instance, although an increase of a certain parameter enhances the conversion, it may make more serious undesirable multiplicity problem or deteriorate selectivity, or both. The advantages and limitations in varying parameters are discussed in detail later, by which reasonable criteria for the modification of FT processes could be provided. From the results of the multiplicity changes by parameter variation, it was also possible to evolve a rational start-up strategy, which is another significant accomplishment of this study. As will be clear later, decreasing the feed flux and/or lowering H_2/CO ratio in feed gas can give rise to a monotonic temperature curve, avoiding difficulty in arriving at the target condition.

MATHEMATICAL MODEL

The reactor model is constructed based on the following assumptions: (i) the mass transfer resistance between liquid and catalyst particles is neglected, by which only two phases of gas and slurry phase are considered in mass balances, (ii) the gas and slurry phases are both well mixed, (iii) the catalyst particles are uniformly distributed in the reactor, (iv) the temperature is constant throughout the reactor, (v) the coolant is well-mixed so that its temperature is regarded as constant, (vi) there is no recycling of slurry phase. Under these assumptions, the resulting mass and heat balances at steady state are written in dimensionless form as follows:

Mass balance of species j in gas phase:

$$q_{G,0}\phi_{Gj,0} - q_G\phi_{Gj} - St_j(\phi_{Gj} - \phi_{Lj}) = 0 \quad (j=1, \ldots, ns) \tag{1}$$

Mass balance of species j in liquid phase:

$$St_j(\phi_{Gj} - \phi_{Lj}) + \nu_j Da\psi = 0 \quad (j=1, \ldots, ns) \tag{2}$$

Overall mass balance in gas phase:

$$\left(q_{G,0}\sum_{j=1}^{ns}\phi_{Gj,0} - q_G\tilde{P}/\theta\right) - \sum_{j=1}^{ns}St_j(\phi_{Gj} - \phi_{Lj}) = 0 \tag{3}$$

Energy balance around the reactor:

$$(q_{G,0}\Omega_{G,0}\theta_{G,0} - q_G\Omega_G\theta) - St_H(\theta - \theta_C) + Da\psi Be_R = 0 \tag{4}$$

Energy balance around the cooler:

$$\delta q_C(\Omega_{C,0}\theta_{C,0} - \Omega_C\theta_C) + St_H(\theta - \theta_C) = 0 \tag{5}$$

where 'ns' denotes the number of chemical species and the subscriptions G, L and C indicate the gas, the liquid, and the cooler, respectively and the subscript '0' signifies the inlet condition. The definitions of the dimensionless parameters and variables are given in Table 1 with the nominal values taken as a test condition in this study. A consideration of detailed fluid motion within the reactor is not necessary here dealing with the stirred tank where the perfect mixing is readily achieved unlike the bubble columns.

Table 1. Definition of dimensionless variables and their nominal values

$$\phi_{Gj,0} = \frac{C_{Gj,0}}{C_{Ref}}, \quad \phi_{Gj} = \frac{C_{Gj}}{C_{Ref}}, \quad q_G = \frac{Q_G}{Q_{Ref}}, \quad \theta_{G,0} = \frac{T_{G,0}}{T_{Ref}}, \quad \theta = \frac{T}{T_{Ref}}, \quad \theta_C = \frac{T_C}{T_{Ref}},$$

$$\tilde{P} = \frac{P}{C_{Ref}RT_{Ref}}, \quad \Omega_{G,0} = \frac{\rho_{G,0}C_{pG,0}}{\rho_L C_{pL}}, \quad \Omega_G = \frac{\rho_G C_{pG}}{\rho_L C_{pL}}, \quad \Omega_{C,0} = \frac{\rho_{C,0}C_{pC,0}}{\rho_L C_{pL}}, \quad \Omega_C = \frac{\rho_C C_{pC}}{\rho_L C_{pL}},$$

$$St_j = \frac{(k_L a)_j}{He_j Q_{Ref}/V}, \quad St_H = \frac{h_C a_C}{\rho_L C_{pL}Q_{Ref}/V}, \quad Be_R = \frac{(-\Delta H_R)C_{Ref}}{\rho_L C_{pL}T_{Ref}}, \quad \gamma = \frac{E}{RT_{Ref}},$$

$$Da = \frac{w(1-\varepsilon_G)a_{cat}k(T_{Ref})/He_1}{Q_{Ref}/V}, \quad \psi = \exp\left[-\gamma\left(\frac{1}{\theta}-1\right)\right]\frac{\phi_{L,1}^2\phi_{L,2}}{\phi_{L,1}\phi_{L,2} + \tilde{K}\phi_{L,4}},$$

$$\tilde{K} = K\frac{He_1 He_2}{C_{Ref}He_4}, \quad \delta = \frac{V}{V_C}$$

Feed conditions	$\phi_{G1,0} = \phi_{G,0}\dfrac{FR}{1+FR}$, $\phi_{G2,0} = \phi_{G,0}\dfrac{1}{1+FR}$, $FR = 2$,	
	$\phi_{G3,0} = 0$, $\phi_{G4,0} = 0$, $\theta_{G,0} = 0.6928$, $q_{G,0} = 1$	
Stanton numbers for heat and mass transfer	$St_H = 0.38$, $St_1 = 5.3423$, $St_2 = 7.5196$, $St_3 = 3.8956$, $St_4 = 37.761$	
Reaction parameters	$Da = 0.01225$, $Be_R = 0.3021$, $\gamma = 27.657$, $\tilde{K} = 0.12067$	
Pressure & temperature	$\tilde{P} = 1.0392$, $\theta = 1.1772$	
Others	$\Omega_{G,0} = 0.0097$, $\Omega_G = 0.0057$, $\Omega_{C,0} = \Omega_C = 0.000934$, $\delta = 20$	

FT synthesis is commonly conducted on iron- or cobalt-based catalysts with or without the presence of metal promoters. Cobalt-based catalysts have been employed in this study because they desirably generate higher molecular weight hydrocarbons as well as deactivate much less in comparison with iron-based catalysts [Maretto and Krishna, 1999]. FT synthesis is recognized as a complex polymerization reaction with a sequence of adsorption, initiation, growth, termination, desorption, readsorption and further reaction [Adesina, 1996]. In order to precisely describe the FT synthesis, it is required not only that all the reactants, intermediates and main- and by-products participating in the sequential reaction steps be incorporated into the model, but also that the accurate kinetic parameters be given. Considering the purpose of this study, it is also necessary that the reaction rates be a function of the operating conditions such as temperature and pressure. Although it was difficult, unfortunately, to find a comprehensive FT synthesis model capable of simulating the reactor behavior over a range of operating conditions we are interested in here, the inclusion of the realistic reaction mechanisms is indispensable whenever it is possible.

With the foregoing statements, we employed a rather simple but practical reaction model as follows:

$$(-v_1)H_2 + (-v_2)CO \rightarrow v_3 C_n H_m + v_4 H_2 O \qquad (6)$$

Since it is well known that the water-gas shift reaction is inactive over cobalt-based catalysts, it suffices to consider the main FT synthesis reaction only as above. Despite the apparent simplicity of Eq. (6), we will explain presently how the product selectivity and subsequently the distribution of the polymer products can be described using the ASF factor. Among the reaction kinetic equations for cobalt-based FT reactions available in the literature, it is reported that the one suggested by Withers et al. [1990] performs the best [Kirillov et al., 1999]:

$$R = \left(\frac{v_2}{v_1 + v_2}\right) \frac{kC_1^2 C_2}{C_1^2 C_2 + KC_4} \qquad (7)$$

where the reaction rate R denotes the consumption rate of carbon monoxide per unit mass of catalysts. Hereafter, the subscripts 1, 2, 3, and 4 denote hydrogen, carbon monoxide, hydrocarbon, and water respectively. The stoichiometric coefficients (v) and the average carbon (n) and hydrogen numbers (m) of the obtained hydrocarbon products in Eq. (6) are expressed as functions of the two parameters α and β [Stern et al., 1985], i.e.,

$$v_1 = -[2+(1-\alpha)^2+\beta\alpha(1-\alpha)]; \; v_2 = -1; \; v_3 = 1-\alpha; \; v_4 = -v_2 \qquad (8)$$

$$n = (1-\alpha)^{-1}; \; m = 2[(1-\alpha)^{-1}+(1-\alpha)+\beta\alpha] \qquad (9)$$

The parameter β indicates the paraffin fraction in the reaction products and the parameter α indicates the chain growth factor or ASF factor. These two parameters not only determine the stoichiometric coefficient of the FT reaction mechanism, but also describe the distribution and selectivity of the hydrocarbon products. While the value of β has been assumed constant, i.e., 0.85 in this study, which indicates that 85% of the products are paraffins and the rest of them are olefins, we have tried to consider the dependence of α on the reaction conditions as much as possible. Unfortunately, there has not been established yet a generally acceptable function for the α correlation with operating conditions in the literature. Yermakova

and Anikeev [2000] suggested the following empirical relation between α and the compositions of H_2 and CO after testing several different equation forms:

$$\alpha = A\frac{y_{CO}}{y_{H_2} + y_{CO}} + B \qquad (10)$$

where y_{H_2} and y_{CO} indicate the mole fraction of hydrogen and carbon monoxide in the gas phase, respectively. The parameters A and B in Eq. (10) are adjusted as A=0.2332±0.0740 and B=0.6330±0.0420 to fit their experimental data over an alumina-supported *cobalt* catalyst promoted with zirconium. This equation, however, does not include the explicit dependence of α on the reaction temperature. Lox and Froment [1993] proposed a as a function of temperature and reaction mixture composition for an *iron* catalyst as follows:

$$\alpha = \frac{k_1(T)p_{CO}}{k_1(T)p_{CO} + k_2(T)p_{H_2} + k_3(T)} \qquad (11)$$

where p_{H_2} and p_{CO} denote the partial pressure of hydrogen and carbon monoxide in the gas phase and the parameters k_1 to k_3 are given as functions of temperature. Although Eq. (11) is more general than Eq. (10) in that the former can account for the temperature dependences of α, it is uncertain whether it could be applied to our system based on a *cobalt* catalyst. Instead of using Eq. (11), we modify Yermakova and Anikeev's model above to incorporate the temperature dependence as follows:

$$\alpha = \left(A\frac{y_{CO}}{y_{H_2} + y_{CO}} + B\right)[1 - 0.0039(T - 533)] \qquad (12)$$

Eq. (12) is immediately reduced to Eq. (10) by setting T=533 K at which Eq. (10) is derived. The usage of this equation is limited to the range of the operating conditions rendering $0 \leq \alpha \leq 1$. The slope of temperature dependence (i.e., −0.0039 in Eq. (12)) was obtained by fitting Eq. (12) to various experimental data summarized in Fig. 13 of a recent paper by Van Der Laan and Beenackers [1999].

Fig. 1 compares Eq. (12) suggested in this study with Eq. (11) developed by Lox and Froment with respect to its temperature dependence. Both curves in Fig. 1 are drawn based on the nominal condition given in Table 1. As expected, it seems that Eq. (12) is
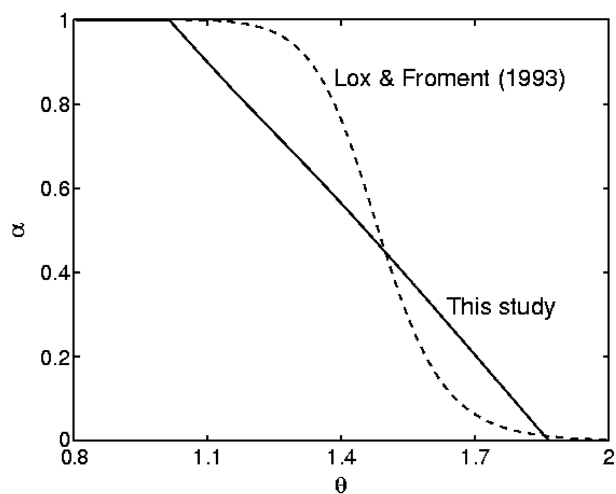

Fig. 1. Comparison of chain growth probability factors as a function of temperature.

more appropriate for cobalt-based systems being considered here than Eq. (11) in the following two ways. First, Eq. (11) shows a rapid drop relative to Eq. (12), contrary to the rather gradual decrease of the experimental data with temperature [Van Der Vaan and Been-ackers, 1999]. Second, the prediction of α by Eq. (11) is much higher than the experimental data obtained in our FT system. In the experimental data used in our work, the value of α was reported between 0.8 to 0.85 at θ=1.1772, which is in a good agreement with the prediction by Eq. (12) as shown in Fig. 1.

RESULTS AND DISCUSSION

Based on the model developed above, the effects of various processing conditions on FT reactors are investigated in regard to multiplicity, stability, conversion and selectivity. A brief explanation is given here on how to measure or quantify such criteria. First, it is straightforward to identify the multiplicity from the shape of the reaction temperature curve plotted against the coolant temperature. Second, the open-loop stability is investigated along the tempera-

ture curve based on the linear stability analysis. Third, the conversion of species j is easily calculated by the following equation:

$$\xi_j = 1 - \frac{q_G \phi_{Gj}}{q_{G,0} \phi_{Gj,0}} \qquad (13)$$

where species j can be H_2, CO or syngas (H_2+CO). Finally, the product selectivity is quantified by α value, which is a convenient measure for the distribution and the average chain length of the obtained products. For the case when heavy hydrocarbon waxes are considered as the desired products, we might simply regard that higher α values provide for better product selectivity.

1. Temperature and Pressure

An inverse-S-shaped temperature curve is obtained by solving the model equations given by Eqs. (1) to (5) based on the test condition given in Table 1 (Fig. 2(a)). The dashed and the solid lines indicate the unstable and the stable steady-state solutions, respectively. The nominal operating temperature of our lab-scale FT reactor is around 1.1772 on the unstable intermediate branch as marked by open circle. It is clear that, in order for the operating state to be stable, the reaction temperature should be set higher than 1.2 or less
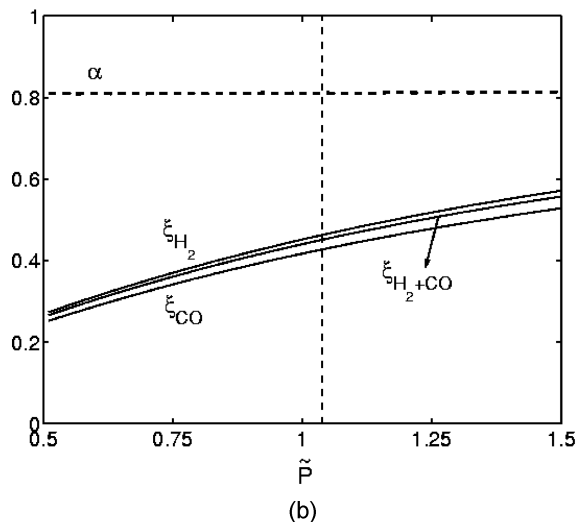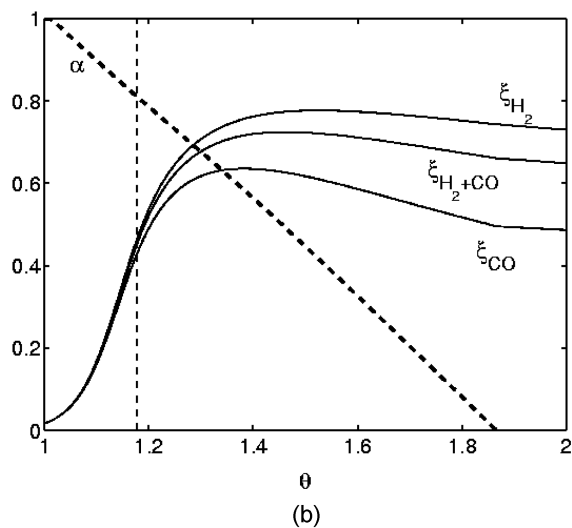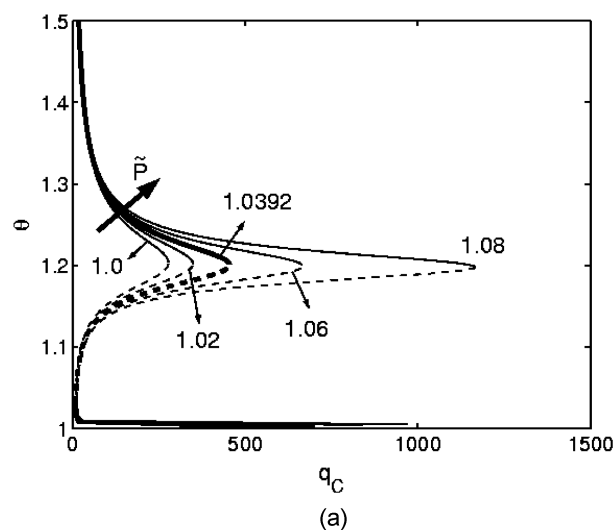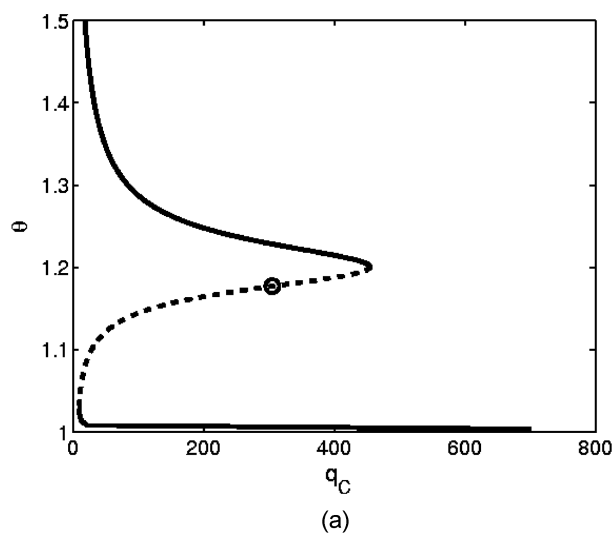

Fig. 2. (a) Inverse-S-shaped temperature profile calculated at the test condition given by Table 1 and (b) effect of temperature on conversion and ASF factor.

Fig. 3. Effect of pressure on (a) multiplicity and stability and (b) conversion and ASF factor.

than 1.03, but such a simple remedy would not be allowed here considering the reactor performance. Fig. 2(b) illustrates the effects of temperature on the conversion and the selectivity. The test condition (i.e., $\theta = 1.1772$) is represented by the vertical dashed line where the conversions of hydrogen (ξ_{H_2}), carbon monoxide (ξ_{CO}), and syngas (ξ_{CO+H_2}) are between 0.4 to 0.5 and the ASF factor is around 0.8. The conversion is enhanced with temperature although it slightly drops after a certain temperature. It is undesirable to increase the temperature for improving the conversion because it would cause the ASF factor to decrease, diminishing the product selectivity.

In Fig. 3(a), the effects of pressure on multiplicity and stability are shown. As pressure increases, the range of coolant flow rates for which multiple steady states exist is expanded. It implies that at higher pressure, control action should be more aggressive to maintain a safe operation. Interestingly, quenching points (or right turning points) move sensitively to the pressure change while ignition points (or left turning points) almost remain unchanged. From Fig. 3(b), it seems that the increase of pressure can enhance the conversion without affecting the product quality. In general, it is known that the increase of pressure results in a shift toward heavier prod-
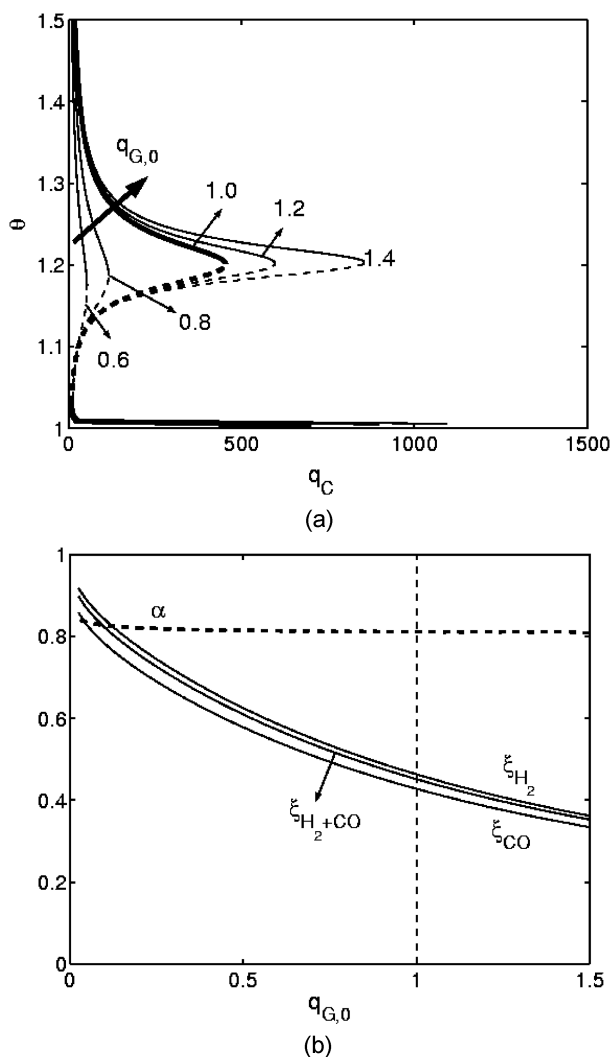

(a)

(b)

Fig. 4. Effect of feed mass flux on (a) multiplicity and stability and (b) conversion and ASF factor.
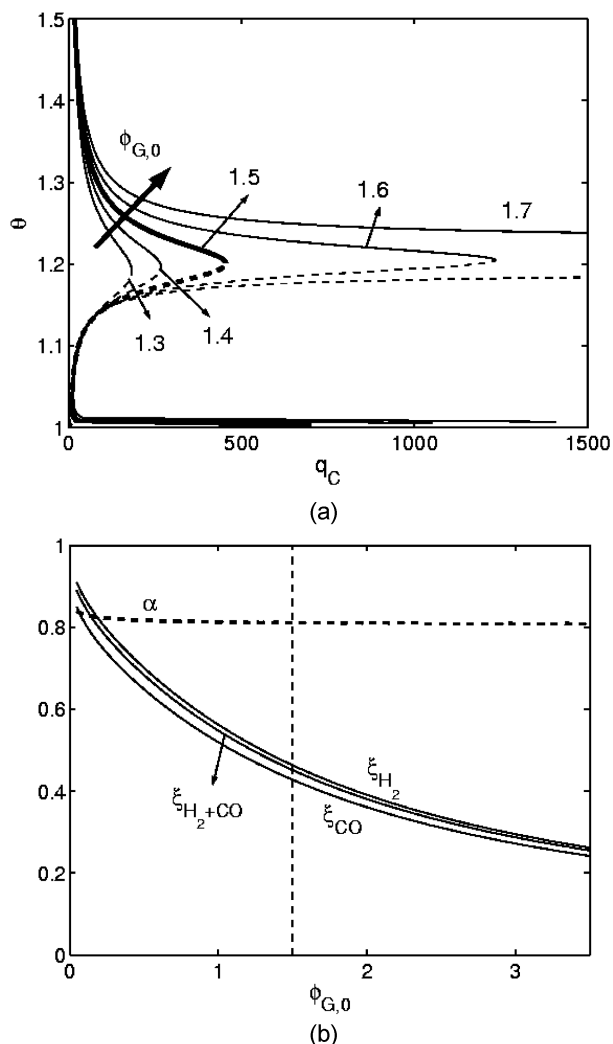
(a)

(b)

Fig. 5. Effect of total feed concentration on (a) multiplicity and stability and (b) conversion and ASF factor.

ucts [Van Der Vaan and Beenackers, 1999], but clearly this effect is not noticeable in Fig. 3(b). This is because of the limitation of Eq. (12) in our model, which accounts only for dependence of conversion on compositions and temperature, but not explicitly on pressure.

2. Feed Conditions

Feed conditions might readily be varied in the operation of FT reactors. The effects of feed rate and feed gas concentration are shown separately here in Figs. 4 and 5 because the former affects the energy balance of the reactor while the latter does not. However, since these two variables define together the mass flux of syngas at inlet, they have qualitatively similar effects on the operability as well as the performance (i.e., conversion and selectivity). Increasing feed rate and/or feed concentration results in the expansion of the multiplicity region as in the case of pressure. The selectivity seems to slightly drop as feed mass flux increases from Figs. 4(b) and 5(b), although no clear relation between feed flux and ASF factor has been reported. It should be noted that conversion can be significantly increased up to more than 90% by lowering the feed mass flux without seemingly hurting the product selectivity. Considering the fact
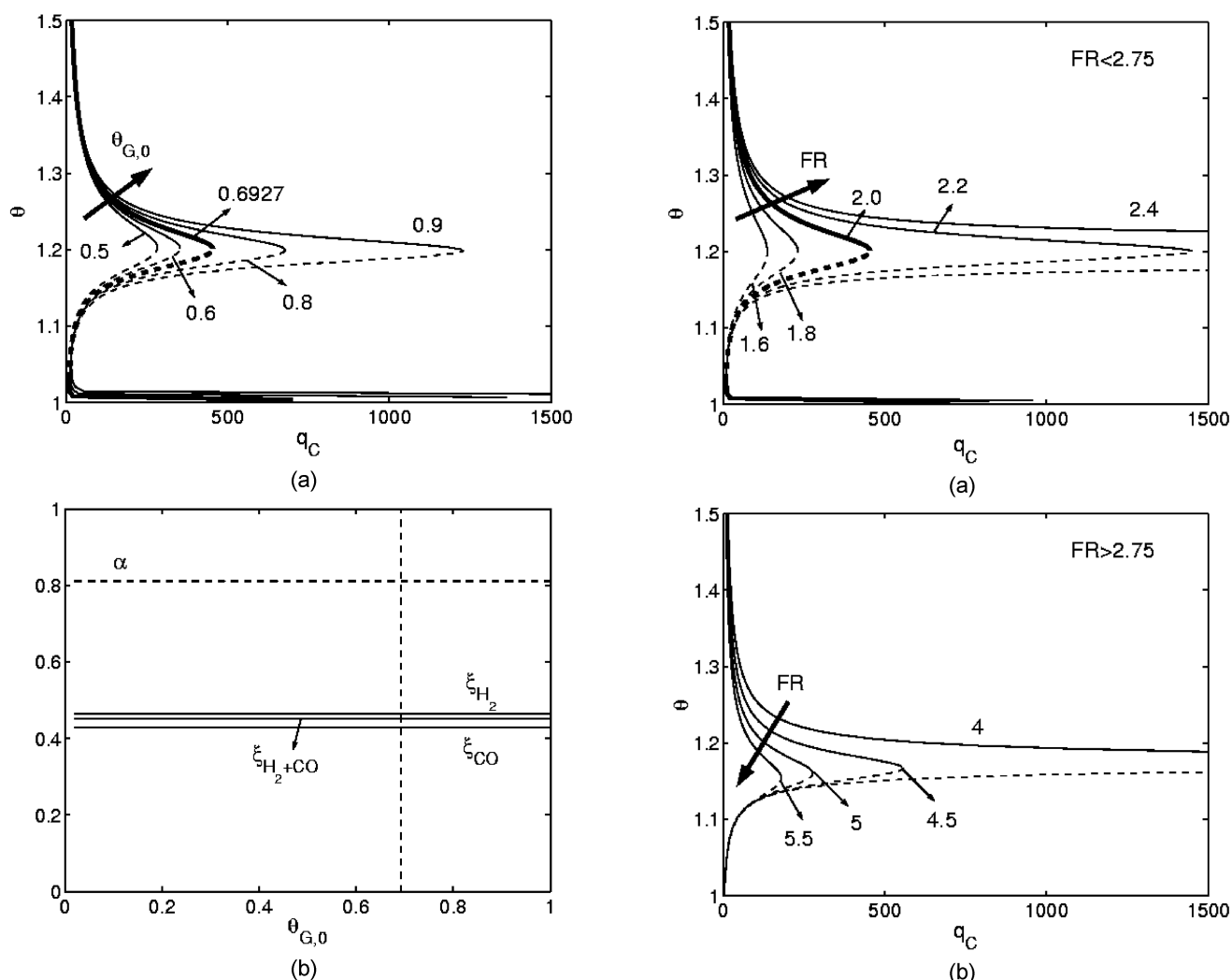
Fig. 6. Effect of feed gas temperature on (a) multiplicity and stability and (b) conversion and ASF factor.

that the operating region where multiple steady states exist becomes smaller by decreasing the feed mass flux as observed above, we might suggest that the variation of feed mass flux can be considered one of the most effective approaches for improving the performance of FT synthesis reactors. It might be possible that the decrease of feed flow rate and/or feed concentration drop the production rate to some extent despite the conversion is proportionally elevated. However, such a defect can be compensated, if necessary, by enlarging the reactor volume.

Fig. 6(a) shows the effect of feed temperature on the operability. As with the gas feed rate, the decrease of feed gas temperature contracts the region of multiplicity, while the conversion and the selectivity are unaffected (Fig. 6(b)). The latter is explained by the fact that the feed temperature has nothing to do with the actual reaction occurring within the reactor as long as the reaction temperature is perfectly maintained by adjusting the coolant flow rate, as is assumed here. The increase of the feed temperature might give a significant effect on the conversion and selectivity if a reaction between the reactants is initiated by preheating before being fed to the reactor, which is, however, not the case for this study.
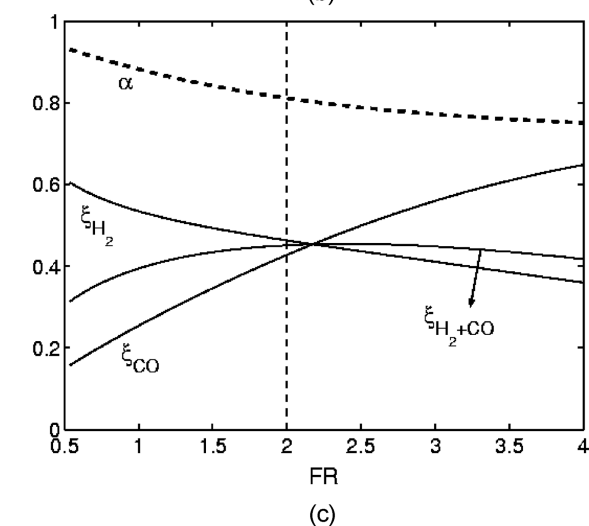

Fig. 7. Effect of feed ratio on (a) multiplicity and stability and (b) conversion and ASF factor.

Feed ratio (FR), i.e., molar ratio of H_2 and CO is an important factor affecting the operability and the performance of FT reactors. In Fig. 7, it is shown that the multiplicity region becomes contracted as feed ratio deviates from a certain value (=2.75 in this calcula-

tion). In other words, the region of multiplicity expands as the feed ratio increases to 2.75 (Fig. 7(a)); further increase in the feed ratio reduces the multiplicity region (Fig. 7(b)). This is probably due to the diluting effect of excess gas when the feed ratio is too low or too high. The effect of feed ratio on the conversion is more interesting (Fig. 7(c)). As feed ratio increases, i.e., the amount of H_2 is relatively larger than CO with the total gas amount fixed, the conversion of H_2 (CO) is monotonically decreased (increased) while syngas (H_2+CO) shows a maximum conversion when feed ratio is around 2.39. It is not surprising that these three conversion curves exactly intersect at one point (which does not necessarily correspond to the feed ratio at maximum ξ_{H_2+CO}) since when the feed ratio exactly matches the stoichiometric value, the conversions of H_2, CO and H_2+CO become the same regardless of the extent of reaction. The decrease of the ASF factor with feed ratio, which is consistent with experimental data reported in the literature [Van Der Vaan and Beenackers, 1999].

3. St_H and Da

From the definition of the dimensionless groups given in Table 1, St_H can be conveniently interpreted as a measure for the heat re-
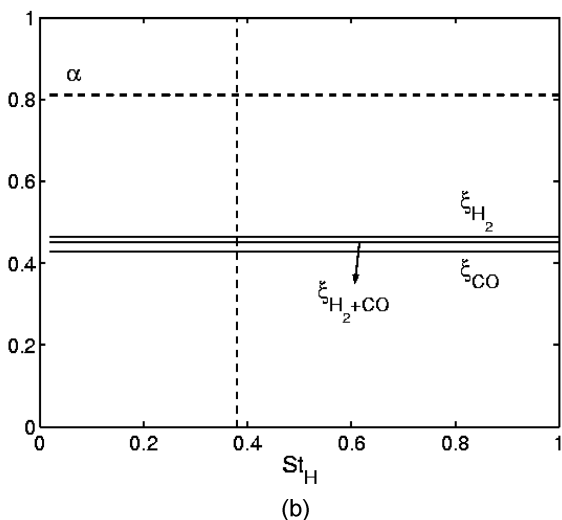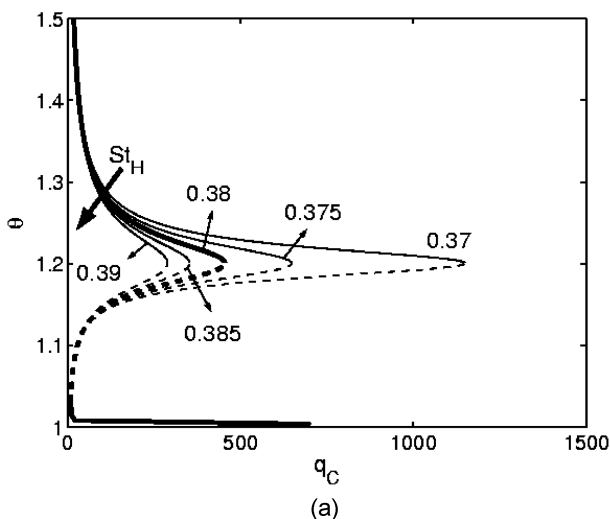

(a)

(b)

Fig. 8. Effect of St_H on (a) multiplicity and stability and (b) conversion and ASF factor.
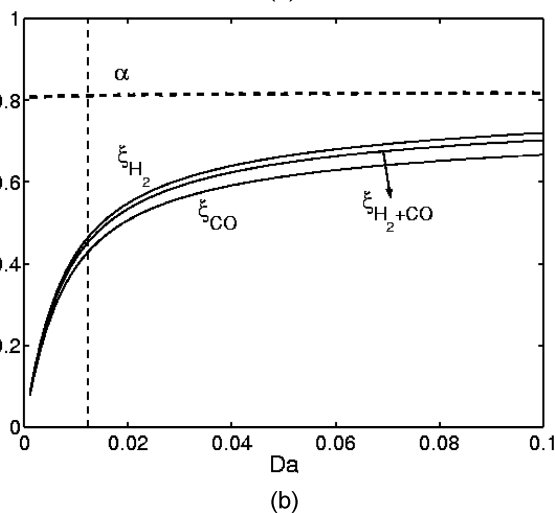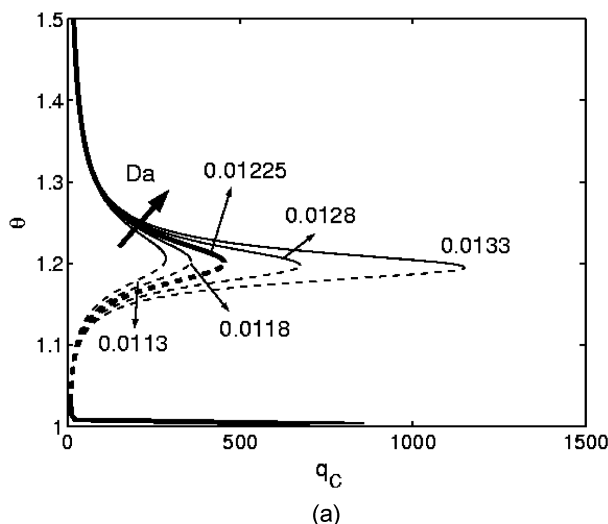

(a)

(b)

Fig. 9. Effect of Da on (a) multiplicity and stability and (b) conversion and ASF factor.

moval capability of the cooler (heat transfer area or heat transfer coefficient) if the other parameters are fixed. As shown in Fig. 8(a), high St_H leads to an improvement in reactor operability because a mild control action (i.e., a slight change of coolant flow rate) would be enough to control the reaction temperature if the heat transfer area or coefficient of cooler is sufficiently large. As with the change of feed temperature, the conversion and the selectivity are not affected by St_H variation (Fig. 8(b)).

Fig. 9 shows the effect of variation of Da which signifies the catalysts activity or the catalyst loading in slurry phase from the definition given in Table 1. Although a higher value of Da enhances conversion (Fig. 9(b)), it has two disadvantages. The first arises from the practical limitation on catalyst loading for maintaining the fluidity of slurry reactors and the second from diminishing the operability by expanding the region of multiple steady states (Fig. 9(a)). The effect of Da on the selectivity looks negligible in Fig. 9(b).

4. Summary

The effects of parameters investigated hitherto are summarized in Table 2. The direction of the arrows (up or down) in Table 2 indicates the recommended parameter changes for improving the operability, conversion and selectivity of FT reactors around the stan-

Table 2. Recommended parameter changes to improve the operability, the syngas conversion, and the product selectivity

	θ	$\bar{P}$	$q_{G,0}$ & $\phi_{G,0}$	$\theta_{G,0}$	Feed ratio (FR)	St_H	Da
Operability	Upper or lower branch	↓	↓	↓	↓ (FR<2.75) ↑ (FR>2.75)	↑	↓
Conversion (H_2+CO)	↑	↑	↓	-	Around 2.39	-	↑
Selectivity	↓	-	-	-	↓	-	-

dard condition. As shown in the results obtained so far, 'trade-off' is observed between the conversion and the selectivity, or between the operability and the conversion when a processing condition is changed. The increase of reaction temperature, for example, enhances conversion, but deteriorates selectivity (i.e., lowers the value of ASF factor). As another example, increase of pressure can improve conversion without hurting the selectivity but has an unfavorable effect on the operability. A similar conflicting effect is also found in the case of Da variation.

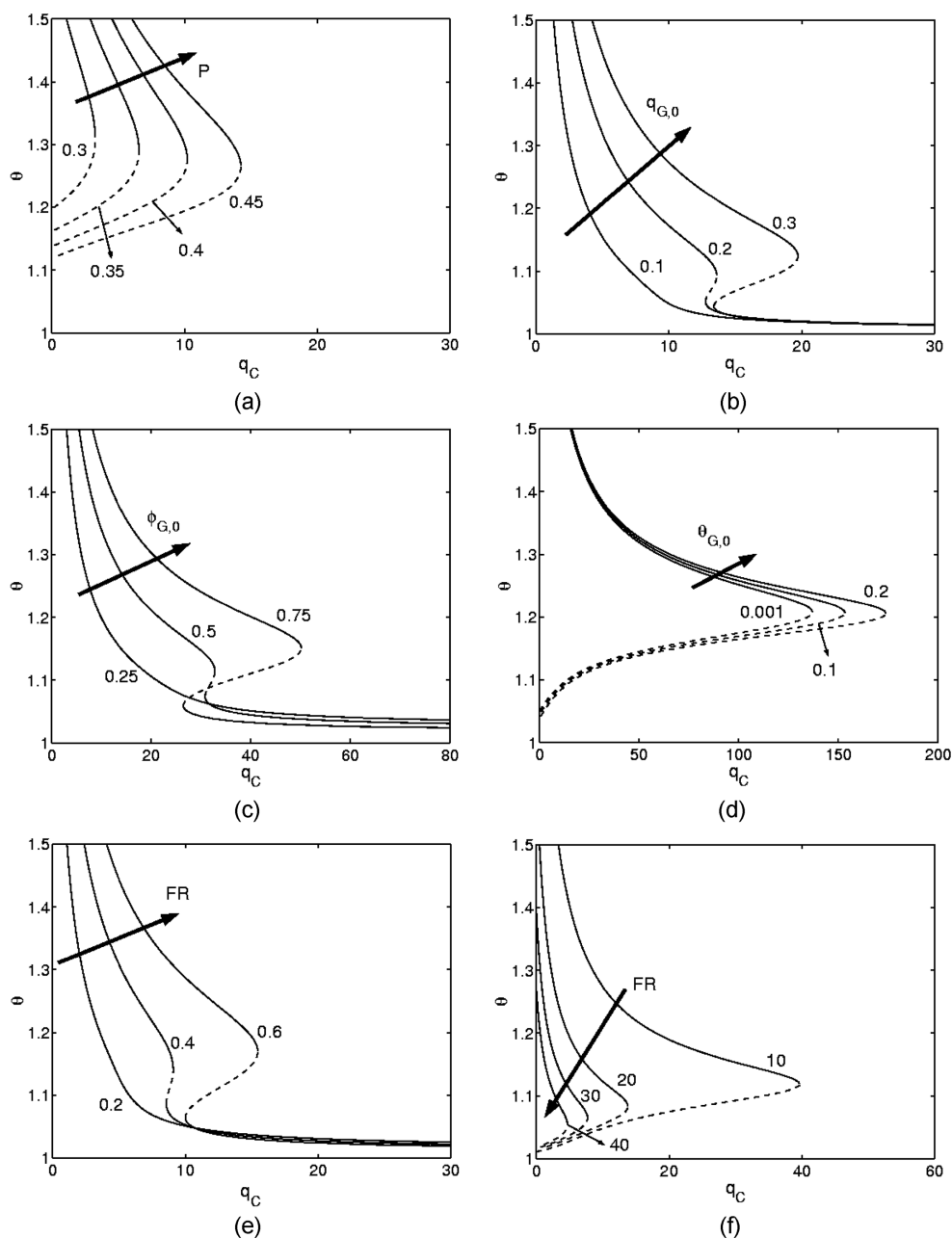The feed ratio may be set substantially low for obtaining better

Fig. 10. Effect of parameter variations on sigmoidal temperature curves: (a) pressure, (b) feed mass flux, (c) total feed concentration, (d) feed gas temperature, (e) feed ratio with CO excessive, and (f) feed ratio with H_2 excessive.

operability and selectivity, however, its value should be set around the stoichiometric ratio to avoid wasting an excessive amount of gas. Although the decrease of feed gas temperature or the increase of St_H may provide a better operating environment, varying such parameters is not effective for controlling conversion and selectivity. While it may appear that the decrease of inlet mass flux (i.e., feed rate and/or feed gas concentration) is the most effective way for improving both operability and performance, it must be weighed relative to the loss of production rate or to the increase in capital cost for a larger reactor volume to maintain a fixed productivity.

START-UP STRATEGY

It is often difficult to arrive at the desired operating state starting from an initial condition, especially when there exist multiple steady states and the target condition is on the unstable intermediate branch. This difficulty in the reactor start-up can be avoided hopefully if we could somehow iron out an inverse-S-shaped temperature curve to be a unique function of the coolant flow rate q_C. The results of Figs. 3 to 9 and Table 2 suggest there are many possible ways for eliminating multiple steady states, for example, decreasing the pressure, lowering the feed gas temperature, etc. Fig. 10 shows, however, that only a few parameters are effective in eliminating the multiple steady states.

As the pressure decreases, temperature curves move towards the infeasible region (i.e., the region $q_C<0$) such that a part of inverse-S-shaped temperature curve vanishes out of the feasible region, but multiple steady states never die out (Fig. 10(a)). Fig. 10(d) shows that cooling down the feed gas temperature is not an effective way either for removing the multiplicity. On the other hand, decreasing feed mass flux (i.e., $q_{G,0}$ and/or $\phi_{G,0}$) can successfully eliminate multiple steady states as shown in Figs. 10(b) and 10(c). To be more specific, $q_{G,0}$ should be lowered at least by 85% while $\phi_{G,0}$ by 60% from the reference condition set in this study to assure a unique relation between the reaction temperature and the coolant flow rate. Fig. 10(e) shows that multiplicity can also be eliminated by setting FR far away from the stoichiometric ratio of H_2 and CO (i.e., 2.75 here as shown in Fig. 7(c)) although increasing the feed ratio fails to result in a unique solution in the specific case considered in this study (Fig. 10(f)). Decreasing the feed ratio below about 0.25 (i.e., excessively CO-rich syngas) is necessary to completely remove the multiple steady states out of the feasible region.

Based on the above observations, it seems that a rational start-up strategy could be suggested in a rather simple way. First, it would be better to keep the low feed mass flux (e.g., $q_{G,0}$=0.1 or $\phi_{G,0}$=0.25) or the low H_2/CO ratio (e.g., a certain value less than 0.25) for providing a safe condition where a unique relation the reaction temperature and the manipulated variable is assured. Under this favorable environment, the target temperature could be arrived without difficulty by manually or automatically controlling the coolant flow rate. After making sure that the steady state is realized at this temporary condition, we may gradually increase the feed mass flux or feed ratio towards the nominal values set in advance. It would be important to make the controller keep the reaction temperature as close as possible to the set point during this drift. Abrupt change of such variables to the final conditions should be avoided for the reaction temperature not to deviate far away from the set point. Elimi-

nation of multiple steady states could be more effectively achieved by the combination of the adjustments of feed flux and feed ratio, but it would be reasonable to select the most easy-to-implement variable from a practical and technical point of view in order to achieve a safe start-up in an effective manner.

CONCLUDING REMARKS

The effects of parameter variations in a FT stirred tank slurry reactor have been thoroughly investigated. A special concern was placed on the identification of favorable operating conditions with respect to multiplicity, stability, conversion and selectivity. More often than not, a simple change of one parameter might not be effective in solving such a multiple-objective problem because of its conflicting nature. Under this situation, it is important to properly set the priority among those criteria, which will depend on a specific condition of FT reactors, since modification of the processing conditions will be made according to the order of importance. Through a comprehensive parametric study conducted here, we could provide a reasonable guide for the direction of the parameter variation. It is admitted that the interpretation made in this work would be valid only in a local sense because our calculation is based on the specific test condition. Furthermore, the criticism often arises that a model is deficient in many ways in representing the reality of a complex process such as FT synthesis. Several assumptions are made the reality of which is suspect and researchers have sought to incorporate more complexities into the model. The price of such complexity is the difficulty with which computation, if at all possible, can be made to extract the effect of parametric variations as conducted in this study. Of course, in the absence of any guidance from models, process strategies are often arrived at by conservative trial-and-error initiatives based on good engineering intuition. The role of such simplified models, as is developed in this work, cannot be overemphasized in providing the conceptual framework required for such trial-and-error ventures. Hence, the results obtained in this study must be viewed as being practically significant for improving operability, enhancing performance, and developing a safe start-up strategy of FT reactors.

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NOMENCLATURE

a_{cat} : catalyst activity
C_j : molar concentration of chemical species
C_p : heat capacity
E   : activation energy
FR   : feed ratio, i.e., molar ratio of H_2 to CO
$h_C a_C$: heat transfer coefficient per unit volume
He   : Henry's constant
$(-\Delta H_R)$: heat of reaction
K   : equilibrium constant
$k_L a$: mass transfer coefficient per unit volume
P   : reactor pressure

Q$_G$: volume flow rate of gas phase
R : universal gas constant
t : time
T : temperature
U : velocity
V : reactor volume
V$_C$: cooler volume
w : catalyst loading in slurry phase
y : mole fraction in gas phase
ε : holdup ratio
ρ : density

Subscripts

0 : inlet condition
C : cooler
G : gas phase
L : liquid phase

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