APPENDIX

"Modeling of Non-Isothermal F-T Slurry Reactors"

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SUMMARY

The analysis of a non-isothermal slurry reactor used for Fischer-Tropsch synthesis is presented in this report. First, the development of the model is analyzed and then, the evaluation of the parameter values is discussed. Finally, the analysis of the results is presented.

The occurrence of multiple steady states at current conditions of operation is shown in this work. The system is properly characterized by a fixed set of parameters. The results are presented in plots of pressure vs. liquid phase residence time, and the most common conditions of operation in commercial units are conveniently marked in the figures. This multiplicity phenomenon is sensitive to various parameters, especially to heat removal, inlet temperature, pressure, mass transfer coefficients and water content in the slurry phase.

From the results that are presented here, safe conditions of operation can be determined in order to avoid any chance of multiplicity when operating these reactors. The results are for a limiting case of complete mixing in both phases, a condition which is not always met in bubble column slurry reactors.

INTRODUCTION

The slurry phase F-T process has been a subject of a number of investigations during the past five years. This process mode permits the direct conversion of low H_2/CO synthesis gases as generated from advanced gasifiers. The reported literature has been focused on either evaluation of detailed reaction kinetics or on the operation of isothermal bubble column slurry reactors. (Huff and Satterfield (1984), Nettelhoff et al. (1985), Deckwer et al. (1986)).

Bubble column slurry reactors have been modeled extensively, mainly in the isothermal regime. The kind of mixing prevailing in both phases and the mass transfer coefficients play a major role on the final result. More recently (Stern et al. (1985), Bukur and Zimmerman (1987)) have introduced the coupling of the FTS reaction with the WGS reaction. This is important for the cases where the catalyst used for FTS show some degree of activity towards WGS reaction.

The exothermicity of the FTS process requires the control of the reactor temperature . Only Deckwer et al. (1982) has considered the coupled problem of heat and mass transfer in a bubble column slurry reactor for FTS. The objective of this work is to present an analysis of multiple steady states that can be observed in a stirred tank non-isothermal slurry reactor for FTS. In particular, the present analysis delineates the conditions under which multiple steady states are possible in FTS slurry reactor.

Several workers have studied steady state multiplicity in gas-liquid CSTRs (Raghuram and Shah (1977), Raghuram et al. (1979), Singh et al. (1982), Shaikh and Varma (1984)). In the case of the FTS, two main reactions are assumed to occur: Fischer-Tropsch reaction and water-gas shift reaction. The mass transfer across the gas-liquid interface is assumed to be dependent upon reaction conditions. The reactions are assumed to occur in bulk liquid. Both adiabatic and non-adiabatic conditions are evaluated. The practical implications of the results are briefly discussed.

DEVELOPMENT OF THE MODEL

Dimensional equations:

The gas phase mass balance for each species can be written as:

$$F_G^o\, C_{i,G}^o - F_G\, C_{i,G} - (k_L a)_i\, V_L\, (C_{i,L}^* - C_{i,L}) = 0 \qquad (1)$$

for $i = 1, 2, 3, 4, 5$

being $(k_L a)_i$ the mass transfer coefficient associated with V_L (Karandikar et al., 1987). Other authors present $(k_L a)_i$ associated with the volume of the reactor.

Eq. (1) is made non-dimensional, defining:

$$\alpha = \frac{F_G}{F_G^o} \qquad (2)$$

$$y_i = \frac{C_{i,G}}{C_{1,G}^o} \qquad (3)$$

$$x_i = \frac{C_{i,L}\, m_i}{C_{1,G}^o} \qquad (4)$$

$$\beta_{i,G} = \frac{(k_L a)_i}{m_i}\, \frac{F_L^o}{F_G^o}\, \frac{V_L}{V_R}\, \tau_L \qquad (5)$$

$$\tau_L = \frac{V_R}{F_L^o} \qquad (6)$$

and recalling,

$$C_{i,L}^* = \frac{C_{i,G}}{m_i} \qquad (7)$$

then:

$$y_i^o - \alpha y_i - \beta_{i,G}\, (y_i - x_i) = 0 \qquad \text{for } i = 1, 2, 3, 4, 5 \qquad (8)$$

In addition, the total mass balance for the gas phase is:

$$y_G - \alpha y_G - \sum_{i=1}^{5} \beta_{i,G} \; (y_i - x_i) = 0 \tag{9}$$

where $$y_G^o = \sum_{i=1}^{5} y_i^o \tag{10}$$

$$y_G = \sum_{i=1}^{5} y_i \tag{11}$$

being $$C_G = \frac{P}{RT} \tag{12}$$

The latter equation can be used to define,

$$\gamma = \frac{P}{R \, C_{1,G}^o \; T} \tag{13}$$

so that with $\theta = T/T^o$ (14)

$$y_G = \gamma/\theta \tag{15}$$

The liquid phase mass balance for each species can be written as:

$$F_L^o \; C_{i,L}^o - F_L \, C_{i,L} + (k_L a)_i \; V_L \, (C_{i,L}^{*} - C_{i,L}) + C_c \, V_L \, \nu_{ij} \, r_j = 0 \tag{16}$$

It can be made dimensionless by defining

$$\beta_{i,L} = (k_L a)_i \; \frac{V_L}{V_R} \; \tau_L \tag{17}$$

$$Da_L = \frac{C_c \; b_{10}}{2 + \frac{n}{2}} \; \tau_L \tag{18}$$

$$Da_L^{\bullet} = C_c \; k_{WGS}^{-} \; C_{1,G}^o \; \tau_L \tag{19}$$

$$d_1 = \frac{\exp(-E'_{FTS}/\theta)\; x_1^2\; x_2}{x_1\, x_2 + b'_2 \exp(g'/\theta)\, \dfrac{m_1\, m_2}{m_3}\; x_3} \tag{20}$$

$$d_2 = \exp(-E'_{WGS}/\theta) \cdot \left(x_2 x_3 - \frac{x_1\;\, x_4}{a_e \exp(b'_e/\theta)\, \dfrac{m_1\, m_4}{m_2\, m_3}} \right) \tag{21}$$

$$E'_{FTS} = E_{FTS}/RT^{o} \tag{22}$$

$$E'_{WGS} = E_{WGS}/RT^{o} \tag{23}$$

$$q' = q_{ads}/RT^{o} \tag{24}$$

$$b'_2 = b_{20}/C^{o}_{1,G} \tag{25}$$

$$b'_e = b_e/T^{o} \tag{26}$$

Finally, the liquid-phase mass balance for each component is:

$$x_i^{o} - x_i\, \frac{F_L}{F_L^{o}} + \beta_{i,L}\,(y_i - x_i) + \nu_{i1}\, Da_L\, \frac{m_i}{m_1}\, \frac{V_L}{V_R}\; d_1 \; +$$

$$\nu_{i2}\; Da'_L\; \frac{m_i}{m_2\;\, m_3}\; \frac{V_L}{V_R}\; d_2 = 0$$

$$\text{for } i = 1, 2, 3, 4, 5 \tag{27}$$

We have used to model the reaction terms the following reaction scheme:

- Fischer-Tropsch

$$CO + (1 + n/2)\, H_2 = (-CH_n-) + H_2O$$

$$r_{FTS} = \frac{b_1\, C_{H2}^2\;\, C_{CO}}{C_{H2}\;\, C_{CO} \;+\; b_2\;\, C_{H_2O}} \tag{28}$$

with

$$b_1 = \left(2 + \frac{n}{2}\right)^{-1}\; b_{10}\; \exp(-E_{FTS}/RT) \tag{29}$$

$$b_2 = b_{20} \exp(q_{ads}/RT) \tag{30}$$

- Water-Gas Shift

$$CO + H_2O = CO_2 + H_2$$

$$r_{WGS} = k_{WGS} (C_{CO} \; C_{H_2O} - K^{-1} C_{CO_2} C_{H_2}) \tag{31}$$

with

$$k_{WGS} = k_{WGS}^{\infty} \exp(-E_{WGS}/RT) \tag{32}$$

$$K = a_e \exp(be/T) \tag{33}$$

Eq. (28) has been proposed by Huff and Satterfield (1984). They investigated the FTS in the slurry phase by employing a reduced fused magnetite catalyst - a conventional catalyst for ammonia synthesis. These authors report that their comprehensive rate data covering a wide range of experimental conditions can be described excellently by the proposed equation. Nettelhoff et al. (1985) studied the FTS in the slurry phase on a precipitated Fe catalyst and a fused magnetite catalyst as well. In the case of the unpromoted precipitated catalyst, rate inhibition by product water probably due to competitive adsorption was observed. The authors did not conclude on any comprehensive rate equation, but some kind of equation like eq. (28) was good in many cases. At low H_2/CO inlet ratio, the water concentration was low and one inhibition by water could not be observed. Instead, the rate data indicated that weak adsorption of CO_2 may take place an thus the reaction rate decreases.

Deckwer et al. (1986) found that their experimental results were adequately correlated by eq. (28) in the presence of water. On the whole, the analysis of the water inhibited rates measured in their study at $H_2/CO \leq 0.8$ confirms the results and conclusions reported by Huff and Satterfield (1984).

Both works arrive at similar values for the kinetic parameters with different catalysts.

The water-gas shift reaction has been studied by Moe (1962) and Newsome (1980). Thermodynamics and kinetic parameters have been taken from their works.

The energy balance for the system is:

$$
\begin{aligned}
&(F_L C_{P_L} \rho_L + F_G C_{P_G} \rho_G) T - (F_L^o C_{P_L} \rho_L^o + F_G^o C_{P_G} \rho_G^o) T^o = \\
&[r_{FTS} (-\Delta H^R_{FTS}) + r_{WGS} (-\Delta H^R_{WGS})] C_c V_L + \\
&\sum_{i=1}^{5} [(k_L a)_i (C^*_{i,L} - C_{i,L}) \; (-\Delta H_{s_i}) V_L] + \\
&\sum_{i=1}^{5} [\nu_{i1} r_{FTS} + \nu_{i2} r_{WGS}] V_L (-\Delta H_{s_i}) C_c \qquad (34)
\end{aligned}
$$

It can be written in dimensionless form by defining:

$$\eta_1 = -\Delta H^R_{FTS} \cdot \frac{\dfrac{F_L^o}{F_G^o} C^o_{1,G}}{\left(\dfrac{F_L^o}{F_G^o} C_{P_L} \rho_L^o + C_{P_G} \rho_G^o\right) T^o} \qquad (35)$$

$$\eta_2 = -\Delta H^R_{WGS} \frac{\dfrac{F_L^o}{F_G^o} C^o_{1,G}}{\left(\dfrac{F_L^o}{F_G^o} C_{P_L} \rho_L^o + C_{P_G} \rho_G^o\right) T^o} \qquad (36)$$

$$\zeta_i = -\Delta H_{si} \frac{\frac{F_L^o}{F_G^o} C_{1,G}^o}{\left(\frac{F_L^o}{F_G^o} C_{P_L} \rho_L^o + C_{P_G} \rho_G^o \right) T^o} \tag{37}$$

$$K = \frac{UA}{\left[\frac{F_L^o}{F_G^o} C_{P_L} \rho_L^o + C_{PG} \rho_G^o \right] F_G^o} \tag{38}$$

$$\theta_W = T_W / T^o \tag{39}$$

Then we finally have:

$$\theta - 1 + \kappa(\theta - \theta_w) =$$

$$\frac{Da_L}{m_1} \frac{V_L}{V_R} d_1 \eta_1 + \frac{D\dot{a}_L}{m_2 m_3} \frac{V_L}{V_R} d_2 \eta_2 +$$

$$\sum_{i=1}^{5} \beta_{i,L} (y_i - x_i) \zeta_i / m_i + \sum_{i=1}^{5} v_{i1} \frac{Da_L}{m_1} \frac{V_L}{V_R} d_1 \zeta_i +$$

$$\sum_{i=1}^{5} v_{i2} \frac{D\dot{a}_L}{m_2 m_3} \frac{V_L}{V_R} d_2 \zeta_i \tag{40}$$

In arriving at eq. (40) it has been assumed that $F_L C_{P_L} \rho_L + F_G C_{P_G} \rho_G$ is approximately constant.

In summary, the system is described by eqs. (8), (9), (27) and (40).

DEVELOPMENT OF THE MODEL

Most of the parameters needed for the evaluation of the dimensionless parameters are presented in Tables 1 and 2. However, some of them need some further computation to arrive at their final values.

The heat capacities are considered to be constant throughout of the analysis. This implies that the heats of reaction are also constant. The values for the heat capacities of the three different phases have been evaluated separately. The heat capacity of the FT liquid was calculated considering an average molecular weight of 366 g-mol (Karandikar et al., 1987) and using the Chueh-Swanson method (Reid et al., 1986). The heat capacity of the gas phase was estimated by assuming ideal-gas state (Smith, 1987) and an average molecular weight of 28 g-mol. As the composition of the gas phase changes during the course of reaction one would expect it to change too, but it is assumed that this change is negligible. The solid heat capacity was estimated by using data from Perry and Green (1984), and considering the solid to be made out of Fe and K.

The density of the hydrocarbon media, ρ_H, was taken from Karandikar et al. (1987):

$$\rho_H = 1028 - 0.67\,T \tag{41}$$

These authors reported this value for the heavy fraction Fischer-Tropsch liquid they used in their experiments. The gas phase density was calculated assuming ideal-gas state,

$$\rho_G = \frac{P}{RT} \sum_{i=1}^{5} \frac{MW_i\, y_i}{\sum_{j=1}^{5} y_j} \qquad \text{for } i = 1, 2, 3, 4, 5 \quad j = 1, 2, 3, 4, 5 \tag{42}$$

This implies that no inert gas species was considered in this work. However, the only place where the gas phase density is employed along this work is eq. (47, for the computation of F_L/F_L^o, and it has no major impact on the final result.

The slurry density and heat capacity were calculated according to the same procedure employed by Deckwer et al., (1982). We fixed the solid weight fraction, W_C, which can be related to the catalyst concentration, C_C, as

$$W_c = \frac{C_c}{\rho_H \left[1 + \frac{C_c}{\rho_H \rho_c} (\rho_c - \rho_H) \right]} \tag{43}$$

From eq. (43) we can get C_C, a parameter that is needed in the model. The volume fraction of the catalyst in the slurry is:

$$\upsilon_{cat} = \frac{\rho_H W_c}{\rho_c - W_c (\rho_c - \rho_H)} \tag{44}$$

so that the density and heat capacity of the suspension can be calculated as:

$$\rho_L = \upsilon_{cat} \rho_c + (1 - \upsilon_{cat}) \rho_H \tag{45}$$

$$C_{P_L} = W_c C_{P_c} + (1 - W_c) C_{P_H} \tag{46}$$

The reactor was assumed to be operating at steady state, so that mass conservation for the entire system provides an expression for F_L/F_L^o,

$$\frac{F_L}{F_L^o} = \frac{\rho_L^o}{\rho_L} + \frac{\rho_G^o}{\rho_L} \frac{F_G^o}{F_L^o} - \alpha \frac{F_G^o}{F_L^o} \frac{\rho_G}{\rho_L} \tag{47}$$

The V_L/V_R ratio can be related to the reference value $(V_L/V_R)^o$ at inlet temperature through:

$$\frac{V_L}{V_R} = \frac{\rho_L^o}{\rho_L} \left(\frac{V_L}{V_R} \right)^o \tag{48}$$

The reference concentration $C_{1,G}^o$ is computed from:

$$C_{1,G}^o = \frac{P}{RT^o} y_1^o / \sum_{i=1}^{5} y_i^o \tag{49}$$

Mass transfer coefficients for all species but water were taken as they were reported by Karandikar et al., (1987):

For H_2 and CO

$$(k_La)_i = 0.1607\left(\frac{N}{1000}\right)^{3.42} \exp(0.108\ P_i) - 0.046 \qquad (50)$$

For CO_2 and CH_4

$$(k_La)_i = 0.0171\left(\frac{N}{1000}\right)^{6.05} \exp(0.38\ P_i) + 0.00525 \qquad (51)$$

In case of water we followed Stern et al., (1985), who used this equation for relating CO mass transfer coefficient to the one for water

$$(k_La)_{H_2O} - (k_La)_{CO}\left[\frac{D_{H_2O}}{D_{CO}}\right]^{2/3} \qquad (52)$$

with $D_{H_2O}/D_{CO} = 1.60$ (Leib and Kuo, 1984).

Two remarks are pertinent here. The correlation presented by Karandikar et al. (1987) has a narrower temperature range of validity than the one we used (20% lower in its upper bound). Secondly, data available for calculation of the hydrocarbon product solubility and mass transfer is available for methane, which has a lower molecular weight than the species we assumed to be synthesizing ($C_3\ H_{6.6}$).

The data for computing the solubility of CO, H_2, CH_4 and CO_2 in the liquid medium was obtained from Karandikar et al., (1987). They measured them for pure FT liquid and for saturated FT liquid with water. The solubility coefficient for each species, m_i, was computed from Henry's law constants He_i through,

$$m_i = He_i\ RT \qquad (53)$$

The Henry's law constant is dependent upon the water content in the slurry phase. That is why we introduced the following equation to weigh the two kinds of constants that were reported by Karandikar et al., (1987):

$$He_i = He_i^N \left(1 = \frac{X_w}{X_w^s}\right) + He_i^s \frac{X_w}{X_w^s} \qquad (54)$$

where He_i^N and He_i^s are the Henry's law constants for component i in FT liquid media free of water and saturated with water, respectively. X_w^s stands for the water mole fraction in the liquid phase under saturation conditions and it is reported by Karandikar et al., (1987). The range of temperatures reported there is narrower than the one we had inside the reactor, so we assumed as an upper bound for water solubility at T = 723 K that $X_w^s = 0.8$. It can be clearly seen from the data reported in the quoted reference that a linear extrapolation for higher temperatures would give water mole fraction greater than one. That is the reason to provide an upper bound for X_w^s.

The Henry's law constant for water was obtained from the study of Nettelhoff et al., (1985). We expressed the Henry's law constant dependence on temperature through the well known relationship:

$$He_i = He_i^{\bullet} \exp(-\Delta H_{s_i}/RT) \qquad (55)$$

Table 2 lists the values for the parameters $He_i^{\bullet}$ and $-\Delta H_{s_i}$ for the species we considered and for both water saturated and non-saturated cases. The heats of solution for H_2, CO and CH_4 were computed using a similar procedure as for the Henry's law constants,

$$-\Delta H_{s_i} = (-\Delta H_{s_i}^N)\left[1 - \frac{X_w}{X_w^s}\right] + (-\Delta H_{s_i}^s) \frac{X_w}{X_w^s} \qquad (56)$$

where $(-\Delta H_{s_i}^N)$ and $(-\Delta H_{s_i}^s)$ are the heats of solution for the component i in Ft

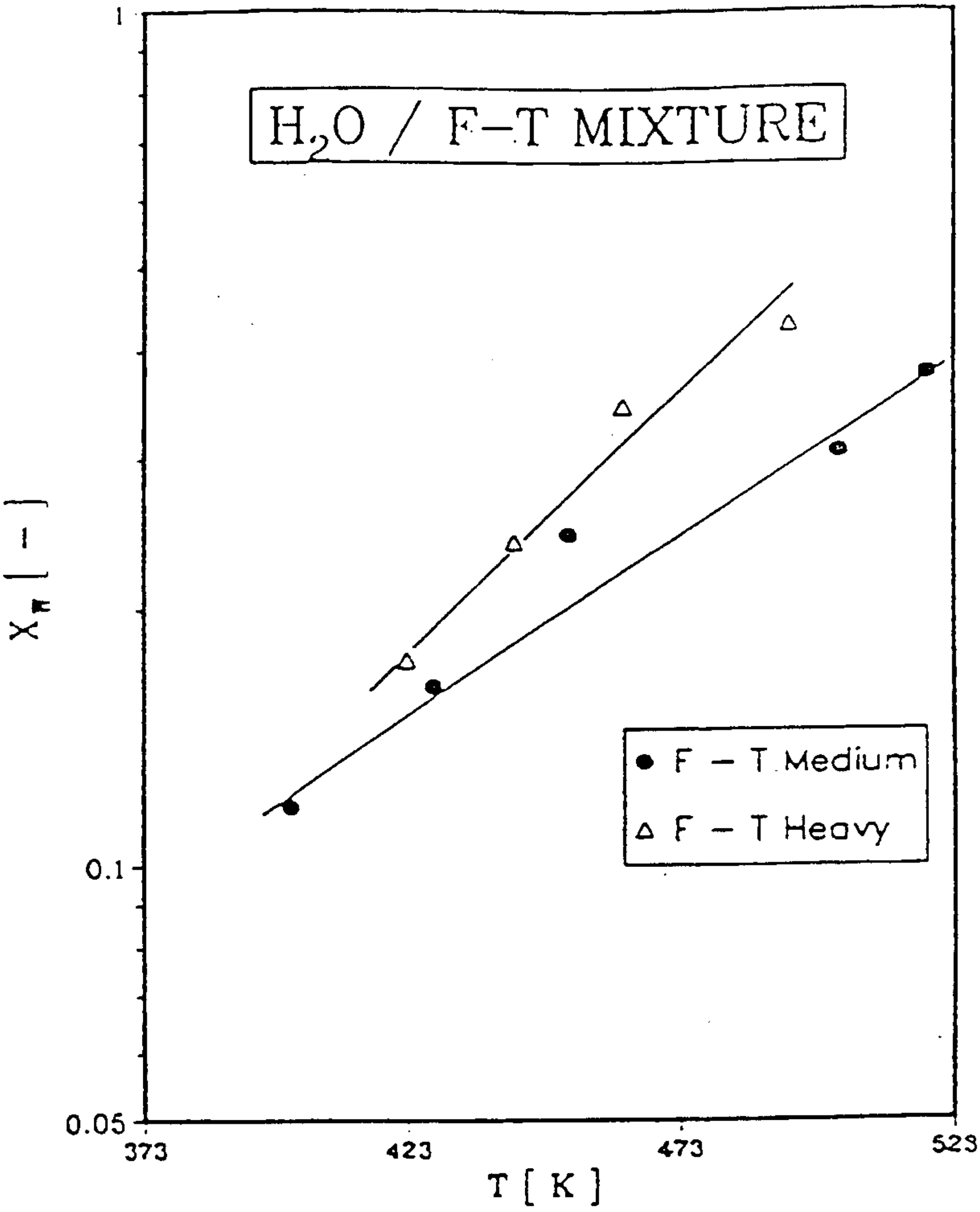

Figure 1: H_2O saturation curves on FT liquid.
Source: Karandikar et al., (1987).

liquid media free of water and saturated with water, respectively.

RESULTS AND DISCUSSIONS

The numerical solution of the system of nonlinear equations was carried out using an appropriate routine, NEQNF, available from the IMSL library. This routine is based on the MINPACK subroutine HYBRD1, which uses a modification of Powell's hybrid algorithm. This algorithm is a variation of Newton's method, which uses a finite-difference approximation to the Jacobian and avoids the use of large step sizes or increasing residuals (Moré et al. (1980)).

The listing of the computer code is given in the Appendix. It is worthwhile noting that it has to be compiled with the version 1.0 of the IMSL library. There are three major routines that have to be used. NEQNF is the one that solves the system of equations. CSINT and CSVAL do the interpolation for water solubility evaluation from a set of data points. PLOTP plots on the screen (NDECIS = 1) or on a file (NDECIS ≠ 1) the heat produced and removed from the system; namely RHS and LHS of eq. (40). This procedure allows to determine easily the occurrence of multiplicity.

Other options, not related to IMSL, can be used through: NORD, NNI. NORD ≠ 1 computes solubilities and mass transfer coefficients accounting for water effect, option NORD = 1 does not. NNI option computes V_L/V_R as function of temperature if it equals 1 or it fixes to its initial value otherwise.

The analysis of the above described equations shows the occurrence of multiple steady states. For all conditions examined, maximum of three steady states were observed. The results are illustrated in terms of pressure of operation and the liquid residence time, $\tau_L = V_R / F_L^o$. The liquid residence was changed, by varying the inlet volumetric flow rate, keeping the volume of the reactor, V_R, constant. The increase in liquid residence time implies the gradual transition from a continuous two-phase flow operation, with the slurry level assumed to be stagnant and constant.

In order to perform the analysis we selected some reference point for $(F_L^o / F_G^o)^*$ and τ_L^*, so that they were fixed. We computed the new τ_L as:

$$\left(\frac{F_L^o}{F_G^o}\right) = \left(\frac{F_L^o}{F_G^o}\right)^* \cdot \frac{\tau_L^*}{\tau_L} \qquad (57)$$

In this way, we kept the volume of the reactor and the inlet volumetric gas flow rate constant, while F_L^o was continously changed. We used the data reported in Tables 1 and 2 for the determination of other required parameters of the operation.

First we introduce the isothermal case to check its validity and compare it with some previous models for isothermal bubble column reactors. To do so, we have used the following set of variables.

$Da_L = 40.$

$Da_L^* = 2107.$

$K' = 60.$

$y_{10} = 1.$

$y_{20} = 0.5 - 2.0$

$x_{10} - x_{50} = 0.5, 0.8, 0.001, 0.2, 0.05$

$\upsilon_{11} - \upsilon_{51} = -0.671, -0.330, 0.330, 0.0, 0.066$

$\upsilon_{12} - \upsilon_{52} = 1., -1., 1, 0.$

$\beta_{1G} - \beta_{5G} = 2.30, 3.03, 18.5, 8.51, 5.53$

$\beta_{1L} - \beta_{5L} = 100.05, 100.00, 216.45, 150.63, 133.83$

$$m_1 - m_5 = 4.35, 3.30, 1.17, 1.77, 2.42$$

It has to be remarked that we have used for this particular case only, data for m_1 - m_5 and for $\beta_{i,G}$, $\beta_{i,L}$ according to Stern et al. (1985) and Bukur and Zimmerman (1987). These data are not function of water content and have been used just for comparison purposes.

Figure 2 shows for a fixed inlet H_2/CO ratio, F, the H_2 + CO conversion attained by the CSTR as a function of the Damkohler number for FTS. In the case of a bubble column slurry reactor, there also exists an optimum inlet H_2/CO ratio for which maximum conversion is obtained. In the case examined by Bukur and Zimmerman (1986) (see Figure 3) the best value for F was 0.67. But it is dependent upon the kinetic expression that they used, which is slightly different from the one we used. Even so, our optimum H_2/CO ratio lays in the range of F = 0.67 - 1.0. And for even higher Da_L numbers F = 0.67 becomes the best even that it is not so differentiated from F = 1 as in the case of the quoted paper.

This result is a good indication that CSTR behavior is very much comparable to BCSR behavior. It should be noted that in the Rheinpreussen demonstration plant (Kolbel and Ralek, 1980) the synthesis gas with H_2/CO molar ratio of 0.67 was used.

We used the reported kinetic expressions for the Fischer-Tropsch synthesis, and the kinetic parameters were fixed throughout the study. The variables of operation that were varied in the study were: inlet temperature, mass transfer coefficients, inlet H_2/CO ratio, total slurry volume and external heat removal. In addition, we also evaluated the effect of water production upon solubilities and mass transfer coefficients.

Figure 4 shows the effect of the inlet temperature, which is assumed to be the same for both phases, upon the transition from one to three steady states.

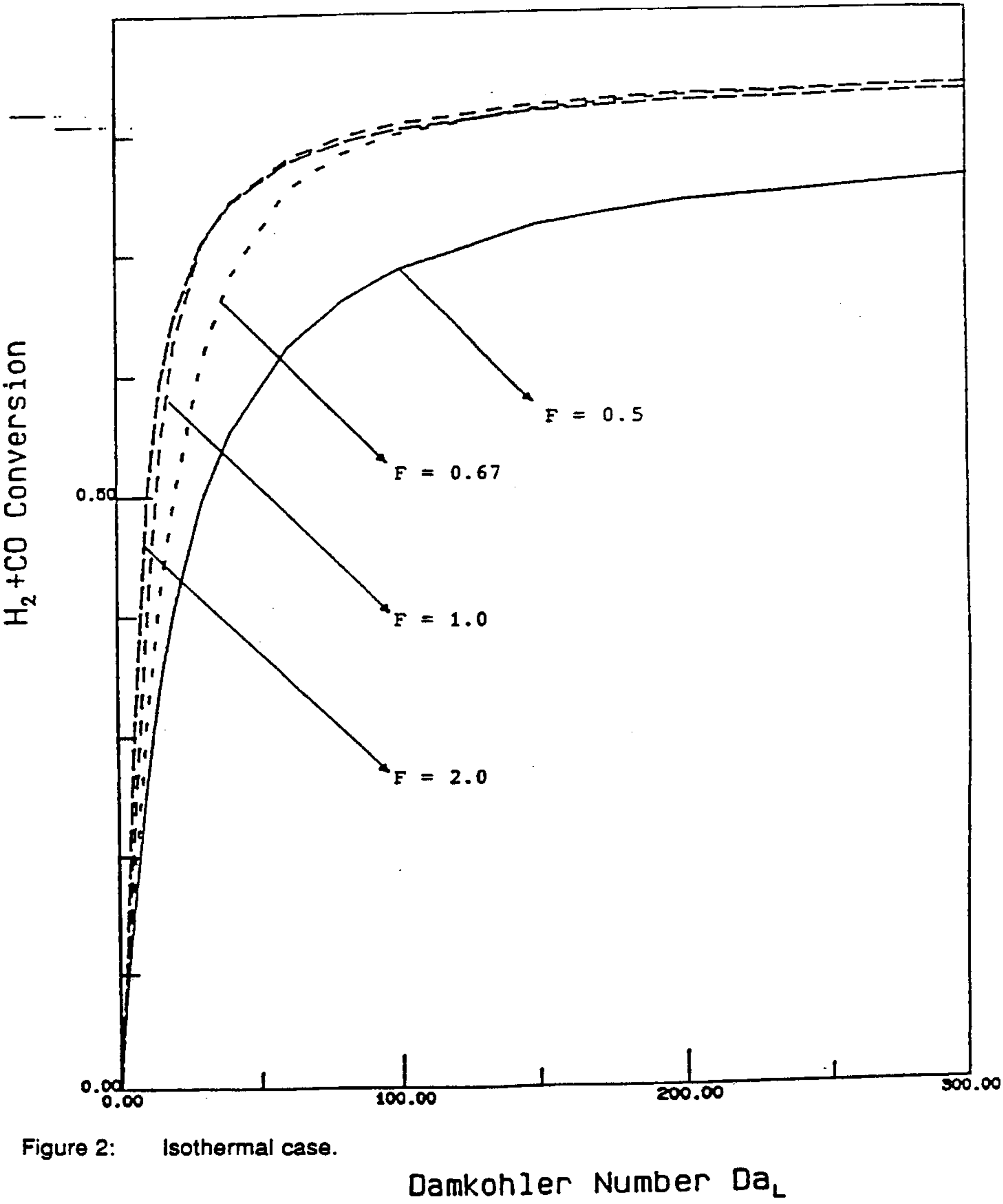

Figure 2: Isothermal case.

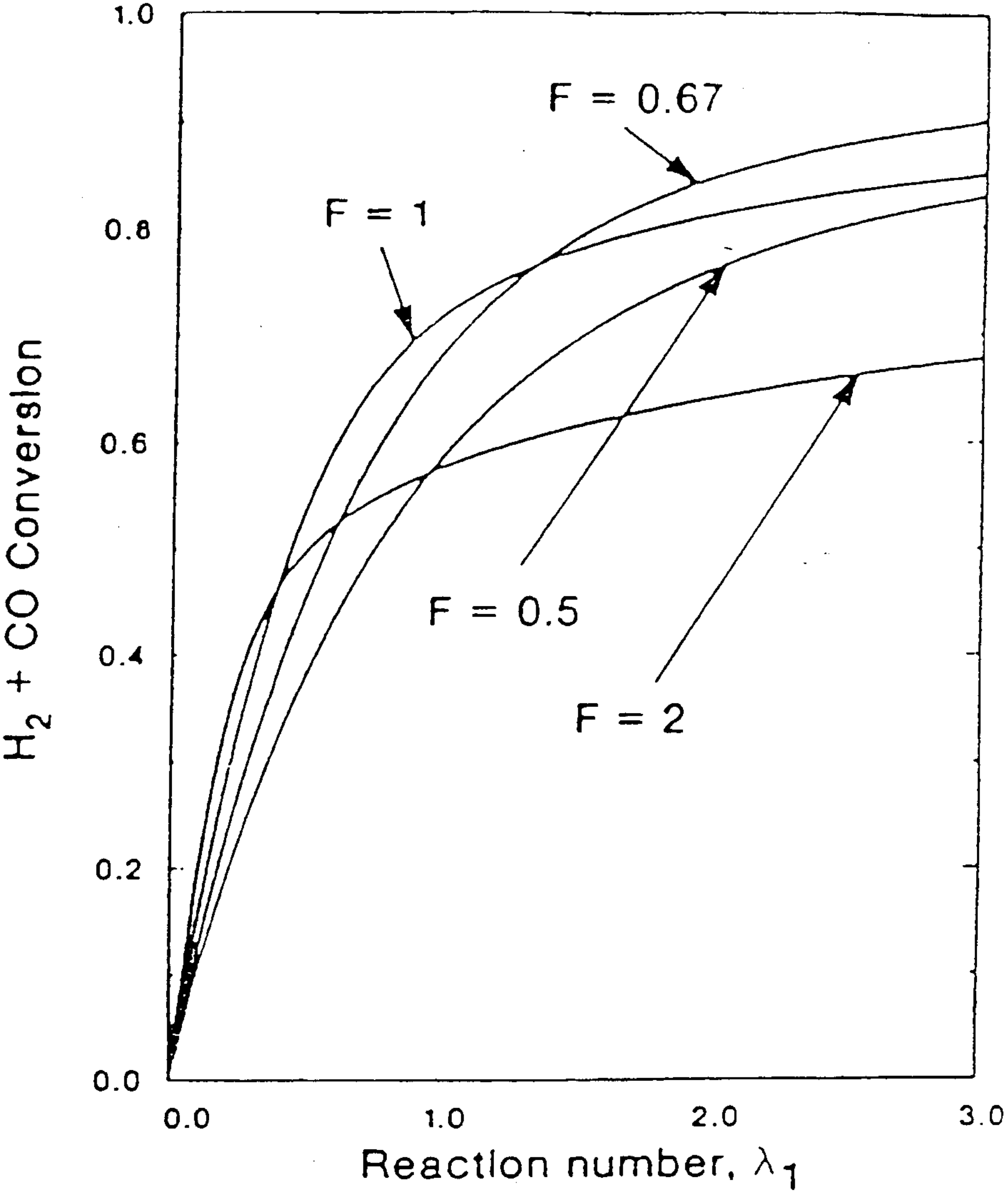

Figure 3: Isothermal BCSR. Results from Bukur and Zimmerman (1987). λ_1 is a parameter similar to Da_L in this work.

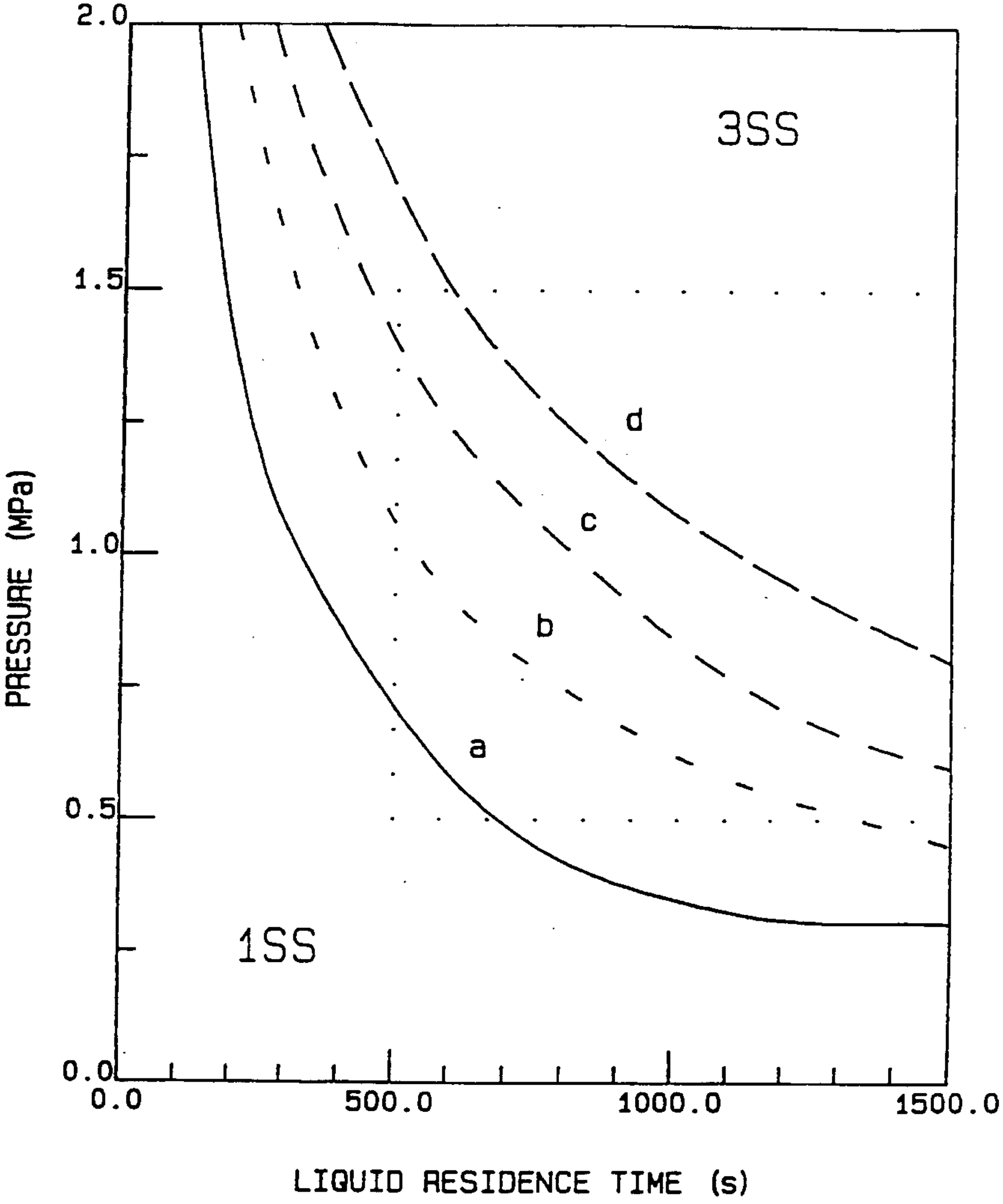

Figure 4: Effect of Inlet Temperature

a) $T^o = 500°K$; b) $T^o = 450°K$; c) $T^o = 400°K$; d) $T^o = 350°K$.
$(V_L/V_R)^o = 0.5$, $y_1^o = 1.0$; $y_2^o = 1.4$; $x_2^o = 0.56$; adiabatic.
Dotted lines enclose normal practical operation conditions.

As it could be expected, the increase of the inlet temperature moves the boundary line towards lower pressures and liquid residence times, while operating below the ignition temperature (around the mid 500°K for this case).

We increased the liquid residence time up to 1500 seconds. Beyond that point the temperature of the upper stable steady state becomes too high (>720°K) and the performance of the catalyst could be affected. Also, the range of validity of the correlations for the transport properties can become questionable at those temperatures.

The correlations proposed by Karandikar et al. (1987) were obtained for a liquid-gas system, in the absence of solids in suspension. Deimling et al. (1984) measured mass transfer coefficients in Fischer-Tropsch liquid fractions and their results indicate that the presence of solids decreases $(k_L a)_i$ significantly. Thus, in order to account for this effect we decreased the mass transfer coefficients for the five species by a factor of 0.7. This is in line with the findings of Deimling et al. (1984) who found that even at 7.5 wt.% of solids, the decrease in the mass transfer coefficient values for CO and H_2 was about 10% - 30%. As it can be seen in Figure 5, for $T^o = 400°$ and 500°K, this decrease in $(k_L a)_i$ has a substantial effect in shifting the boundary line between one and three steady states. This occurs due to a decrease in the supply of reactive species from the gas phase into the slurry phase resulting in a lower amount of heat generation by the reactions.

Figure 6 illustrates the effect of inlet H_2/CO ratio on the multiple steady states. It can be seen from the figure that the decrease of this inlet ratio enhances the region of multiplicity. This is largely due to the increased conversion and heat generation with a decrease in H_2/CO ratio. The effect of the H_2/CO ratio on the reaction rate can be related to its effect on the activity of the catalyst with respect to FTS and WGS reactions (Bukur and Zimmerman

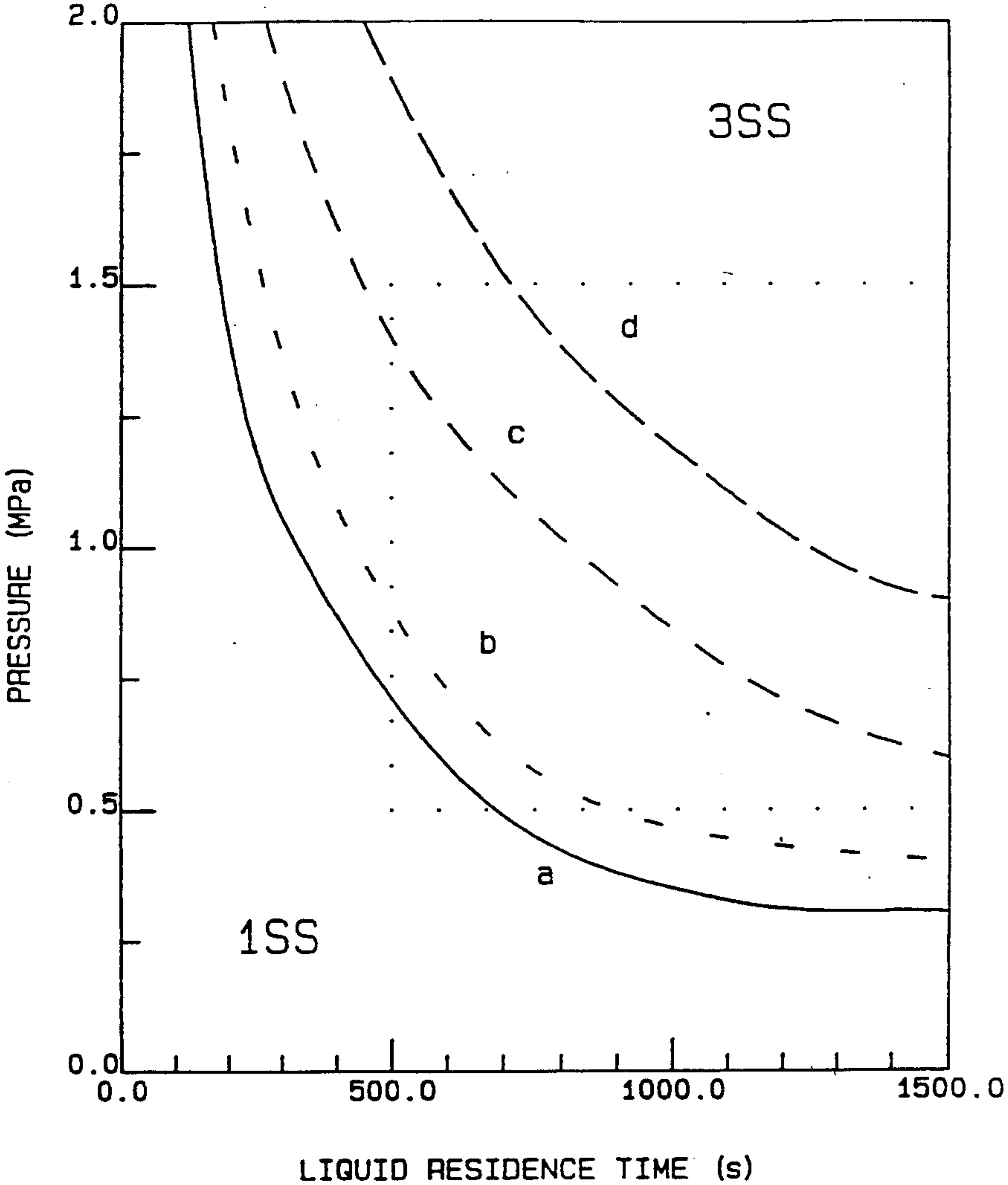

Figure 5: Effect of Suspended Solids.

a) $T^o = 500°K$, $(k_La)_i$ as from Karandikar et al. (1987).

b) $T^o = 500°K$, $(k_La)_i$ reduced by 30%.

c) $T^o = 400°K$, $(k_La)_i$ as from Karandikar et al. (1987).

d) $T^o = 400°K$, $(k_La)_i$ reduced by 30%.

Other conditions as in Figure 1. *Dotted lines enclose normal practical operation conditions.*

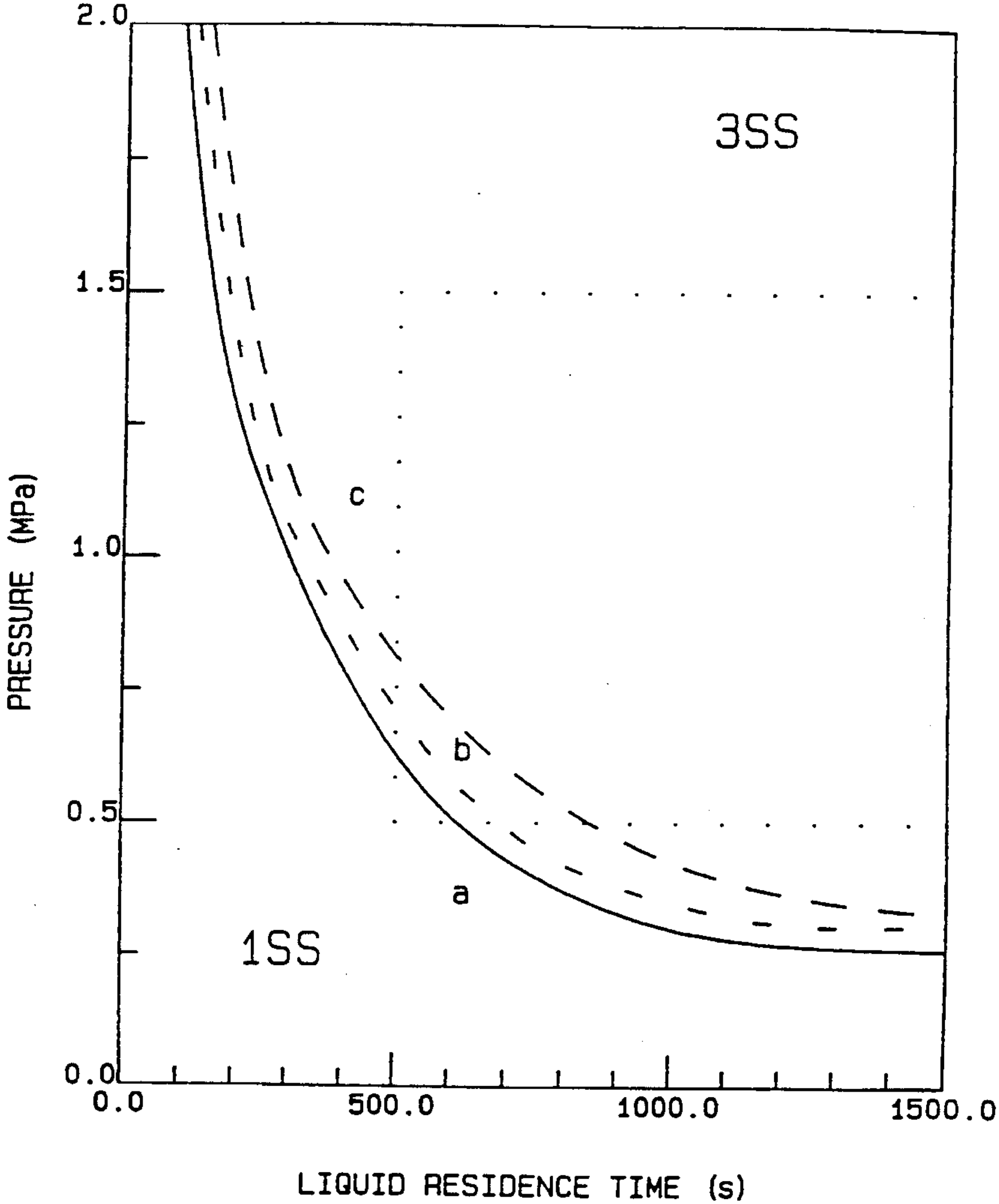

Figure 6: Effect of Inlet (H_2/CO) ratio.

a) H_2/CO = 0.5; b) H_2/CO = 0.71; c) H_2/CO = 1.0.
T° = 500°K. Other conditions as in Figure 1.
Dotted lines enclose normal practical operation conditions.

(1987)). The results shown in Figure 6 depend on the assumed values of the kinetic parameters in the FTS rate expression. Catalysts with different activities and constants may change the relation between H_2/CO ratio and the reaction rate, and ultimately, on the transition values from one to three steady states.

Figure 7 shows the effect of the initial V_L/V_R value on the region of multiple steady states. We considered the variation of specific liquid volume with temperature according to the correlation presented by Karandikar et al. (1987) and the ratio V_L/V_R is assumed to vary according to equation (48). An increase in the reference value (at inlet temperature conditions) increases the region of multiplicity. This is due to an increase in mass transfer coefficient with V_L/V_R which in turn results in greater heat generation and the region of multiplicity.

The effect of heat removal on the multiple steady states is illustrated in Figure 8. We used similar values to those reported by Deckwer et al. (1982) for the inlet and wall temperature (500°K). The observed shrinkage of the multiplicity region with an increase in heat removal is in agreement with the reported literature.

The results presented by Karandikar (1986) introduced the effect of the presence of water in the Fischer-Tropsch liquid on the mass transfer coefficients and solubilities for the species involved in FTS. As stated earlier, these effects were incorporated into our model. Since water production in F-T process depends on the nature of catalyst, it seemed pertinent to evaluate the sensitivity of the system to the effect of water production on the transport parameters. Figure 9 compares for two inlet temperatures (400° and 500°K) the regions multiplicity for the cases which includes and neglects the water effect on the mass transfer coefficients and solubilities for the reaction species. In general, the region of multiplicity increases with the inclusion of water effect on the

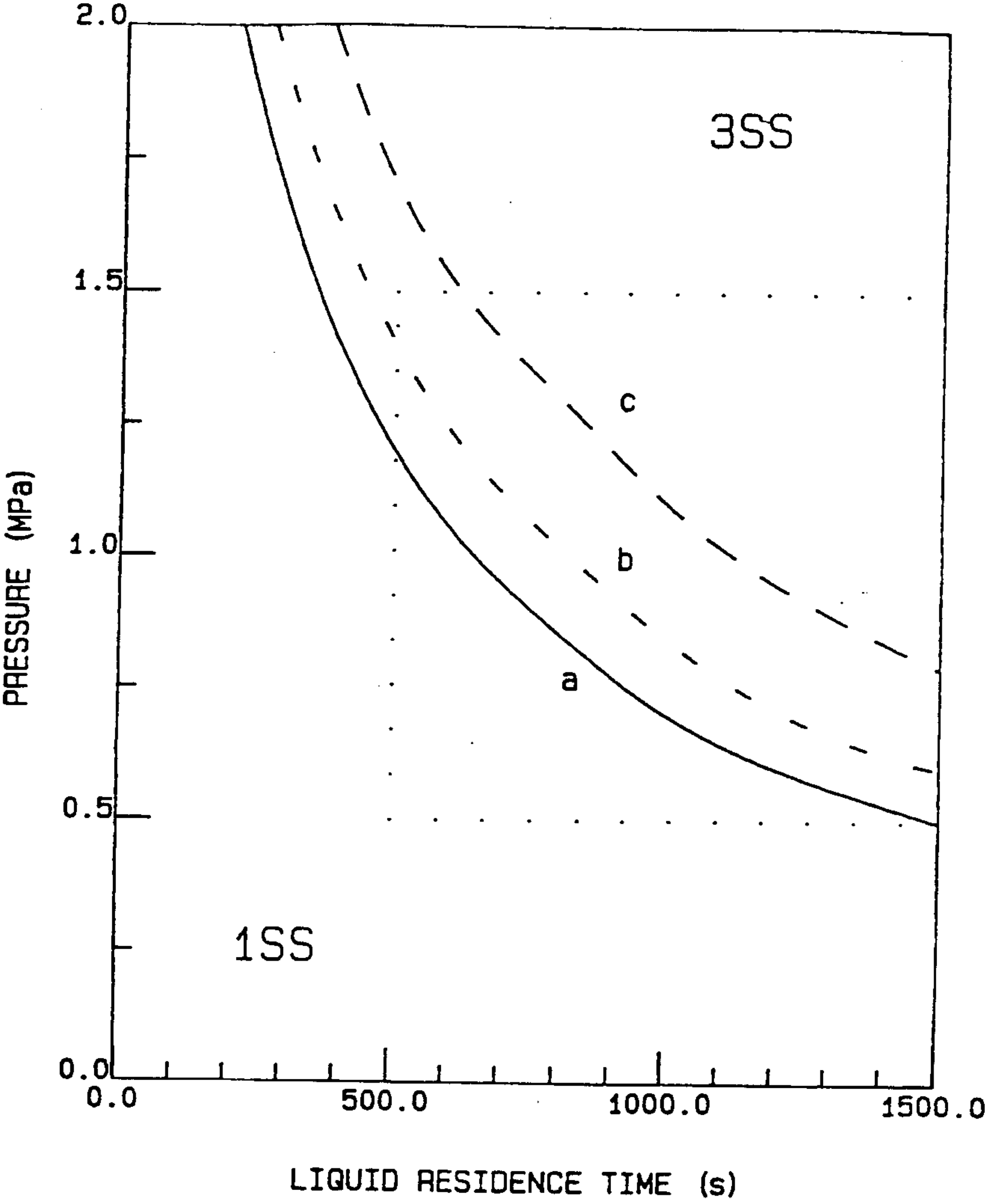

Figure 7: Effect of $(V_L/V_R)^o$.

a) $(V_L/V_R)^o = 0.6$; b) $(V_L/V_R)^o = 0.5$; c) $(V_L/V_R)^o = 0.4$
$T^o = 400$°K. Other conditions as in Figure 1.
Dotted lines enclose normal practical operation conditions.

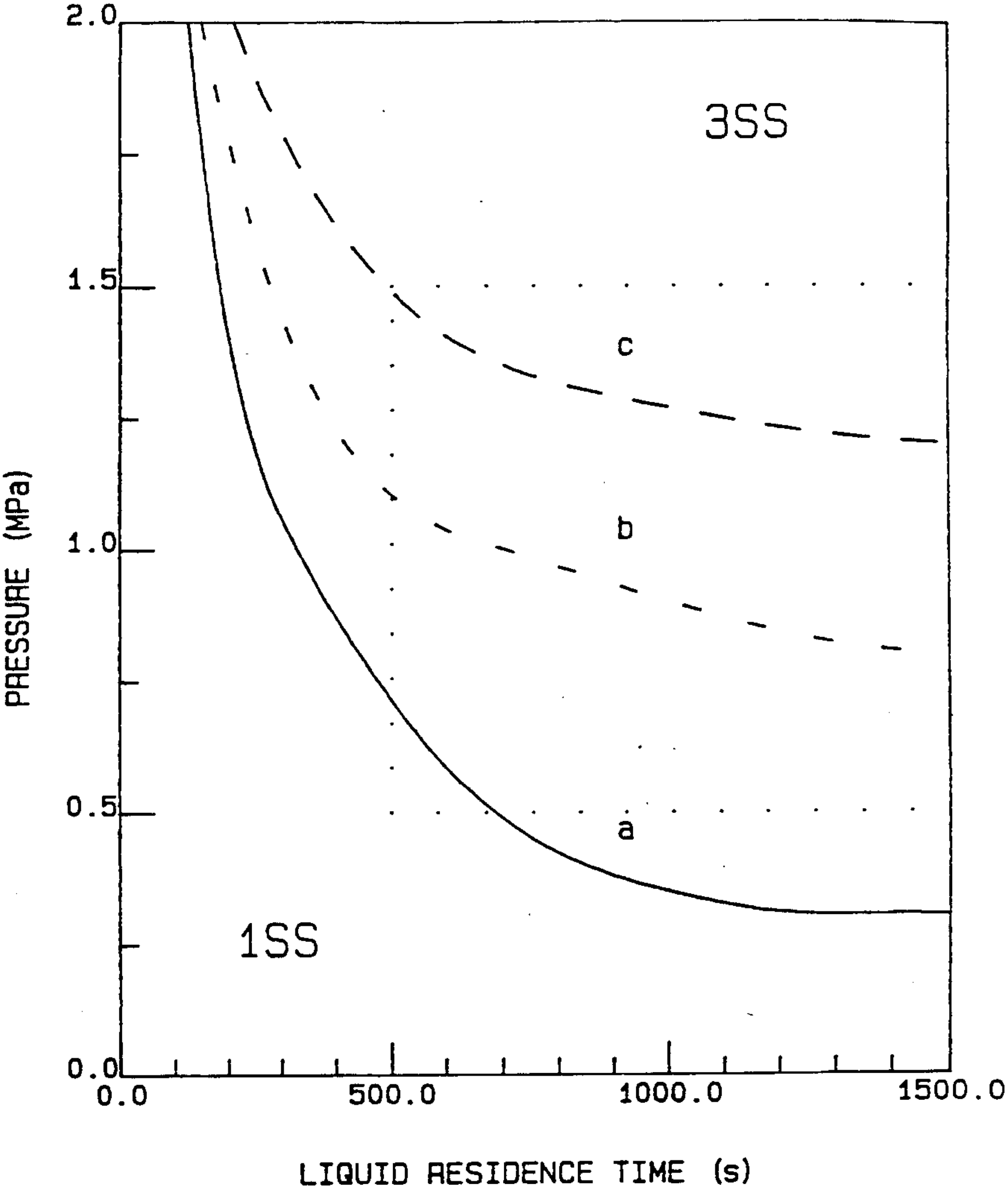

Figure 8: Effect of External Heat Removal.

a) adiabatic; b) UA = 0.05 kJ/K.s c) UA = 0.10 kJ/K.s
T^o = 500°K. $F_G^o = 2\ 10^{-3}\ m^3/s$. Other conditions as in Figure 1.
Dotted lines enclose normal practical operation conditions.

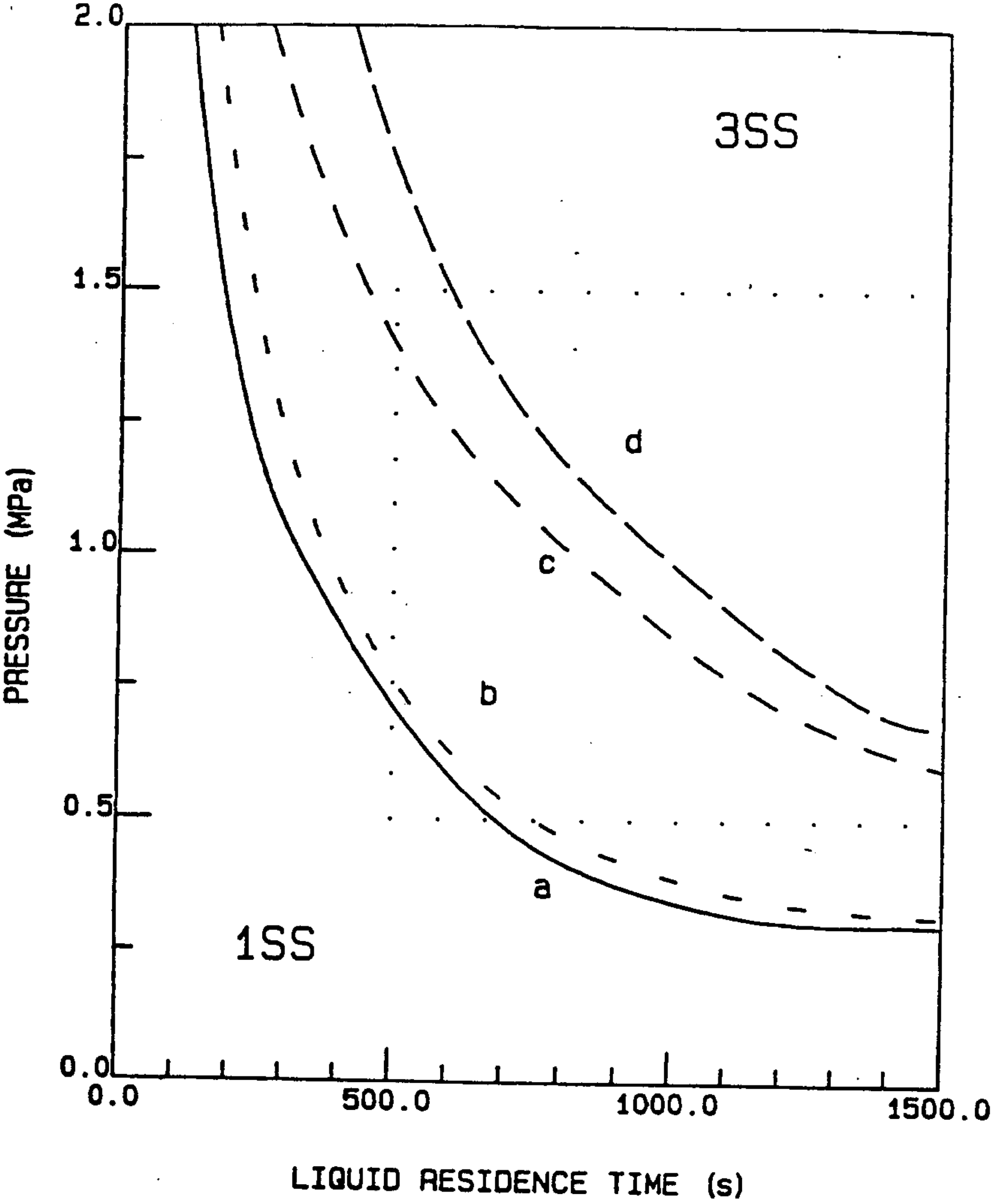

Figure 9: Water effect on Mass Transfer Coefficients and Solubilities.
water effect included: a) T° = 500°K, c) T° = 400°K.
water effect not included: b) T° = 500°K, d) T° = 400°K.
Other conditions as in Figure 1.
Dotted lines enclose normal practical operation conditions.

transport parameters. The effect is more dominant at the lower temperature, lower liquid residence times and high pressures. These results are due to the enhancement of mass transfer and the supply of reactive H_2 to the catalyst by the production of water.

In Figures 4 to 9, the ranges of operating conditions for normal FTS are outlined. These plots, thus indicate that if the slurry reactor is completely mixed and adiabatic, the likelihood of multiple steady states is high. In pilot or large scale operations, generally heat removal system is provided and the reactor is not likely to be completely backmixed. The effect of mass transfer resistances on the apparent reaction rate is also likely to be more important than the ones considered here. All of these factors reduce the possibility of multiple steady states. The study, however, does show that pilot or commercial scale slurry FTS should be carefully designed to avoid the multiple steady state.

CONCLUDING REMARKS

A model for a non-isothermal CSTR slurry reactor used for Fischer-Tropsch synthesis has been developed which includes mass transfer resistance in the slurry phase and the water content effect on the transport parameters. The temperature effects on the physical, transport and kinetic parameters for the system are obtained from the published literature. The governing equations are solved to evaluate the regions of multiple steady states in FTS reactor. The results show that both the presence of water in the Fischer-Tropsch liquid and solids in suspension have important influences on the area of multiplicity in pressure-liquid residence time plots. The inlet temperature and the removal of heat from the system also affect the region of multiple steady states. A decrease in the inlet H_2/CO ratio and an increase in the initial value of V_L/V_R-ratio increase the region of multiplicity.

The results indicate the importance of availability of accurate correlations for mass transport properties when modeling slurry phase Fischer-Tropsch synthesis. Poor heat removal, high catalyst activity, larger water production, high mass transfer and large catalyst concentration may result in possible multiple steady states in F-T slurry reactor. Commercial slurry reactor should be carefully designed to avoid possibility of multiple steady states.

Table 1

Physical and Kinetic Parameters for the System

$-\Delta H^{R}_{FTS} = 1.65\ 10^{5}$ kJ/kmol of CO

$-\Delta H^{R}_{WGS} = 4.09\ 10^{4}$ kJ/kmol of CO

$C_{P_H} = 2.19$ kJ/kg.K

$C_{P_S} = 0.8$ kJ/kg.K

$C_{P_G} = 0.95$ kJ/kg.K

$\rho_C = 5200$ kg/m^3

N = 1000 rpm

$MW_H = 366$ kg/kmol

$W_C = 0.1$

n = 2.2

$E_{FTS} = 77.9\ 10^{3}$ KJ/kmol

$E_{WGS} = 4.1\ 10^{4}$ KJ/kmol

$q_{ads} = 82.8\ 10^{3}$ KJ/kmol

$b_{10} = 0.277\ 10$ m^3/kg.s

$b_{20} = 9.17\ 10^{-11}$ kmol/m^3

$k^{\infty}_{WGS} = 1.25\ 10^{3}$ (m^3)^2/kmol.kg.s

$a_e = 0.0132$

$b_e = 4578$ K^{-1}

Average Carbon Chain Length = 3

$x_3^o = 0.05$

$x_4^o = 0.05$

$x_5^o = 0.05$

Table 2

Solubility Parameters of the System

	H_i^* [MPa.m^3/kmol]		$-\Delta H_{s_i}$ [kJ/kmol]	
	1	2	3	4
H_2	3.98	0.165	8319.6	15569.0
CO	6.59	0.125	4989.0	16793.0
CH_4	117.2	0.840	-8333.3	7727.9
CO_2	423.0	5.30	-14567.8	-----
H_2O	55.43	-----	-10790.7	-----

NOMENCLATURE

A	area for heat exchange, m^2.
a_e	preexponential factor in WGS equilibrium constant expression.
b_e	exponential factor in WGS equilibrium constant expression, K^{-1}.
$b_e^{'}$	dimensionless value of b_e.
b_{10}	preexponential factor in FTS kinetic parameter, $m^3/kg.s$
$b_1^{'}$	dimensionless value of b_{1_0}.
b_{20}	preexponential factor in FTS kinetic parameter, $kmol/m^3$.
$b_2^{'}$	dimensionless value of b_{2_0}.
b_1	parameter in FTS kinetic expression, $m^3/kg.s$.
b_2	parameter in FTS kinetic expression, $kmol/m^3$.
C	concentration, $kmol/m^3$.
$C_{i,G}$	concentration of i species in gas phase, $kmol/m^3$.
$C_{i,L}$	concentration of i species in liquid phase, $kmol/m^3$.
$C_{i,L}^{*}$	concentration of i species at the gas–liquid interface, in equilibrium with the gas phase, $kmol/m^3$.
$C_{1,G}^{o}$	inlet hydrogen concentration in the gas phase,$kmol/m^3$.
C_{pc}	catalyst heat capacity, kJ/kg.K
C_{PG}	gas phase heat capacity, kJ/kg.K
C_{PH}	FT liquid heat capacity, kJ/kg.K
C_{PL}	slurry heat capacity, kJ/kg.K
d_1	expression defined in eq. (20).
d_2	expression defined in eq. (21).
Da_L	Damkohler number defined in eq. (18).
$Da_L^{'}$	Damkohler number defined in eq. (19).
D_{CO}	CO diffusivity coefficient , m^2/s.
D_{H_2O}	H_2O diffusivity coefficient, m^2/s.

E_{FTS}	activation energy for the FT reaction, kJ/kmol.
E'_{FTS}	dimensionless activation energy for FTS, defined in eq. (22).
E_{WGS}	activation energy for WGS reaction, kJ/kmol.
E'_{WGS}	dimensionless activation energy for WGS, defined in eq. (23).
F_G	exit volumetric gas flowrate, m^3/s.
F_G^o	inlet volumetric gas flowrate, m^3/s.
F_L	exit volumetric liquid flowrate, m^3/s.
F_L^o	inlet volumetric liquid flowrate, m^3/s.
He_i	Henry's law constant for component i, $MPa.m^3/kmol$.
He_i^*	factor in Henry's law constantexpression for component i, $MPa.m^3/kmol$.
He_i^N	He_i^* factor for component i in FT liquid, $MPa.m^3/kmol$.
He_i^s	He_i^* factor for compoenent i in FT water saturated liquid, $MPa.m^3/kmol$.
$-\Delta H^R_{FTS}$	FTS heat of reaction, kJ/kmol of CO.
$-\Delta H^R_{WGS}$	WGS heat of reaction, kJ/kmol of CO.
$-\Delta H_{s_i}$	heat of solution for component i, kJ/kmol.
$-\Delta H^N_{s_i}$	heat of solution for component i in FT liquid, kJ/kmol.
$-\Delta H^s_{s_i}$	heat of solution for component i in FT water saturated liquid, kJ/kmol.
K	equilibrium coefficient for WGS reaction, based on liquid concentrations.
k_{WGS}	rate coefficient for WGS reaction, $(m^6/kmol)/kgs$.
k^{∞}_{WGS}	preexponential factor in WGS rate coefficient, $(m^6/kmol)/kg.s$.
$(k_La)_i$	mass transfer coefficient for component i from gas-liquid interface to the bulk of the liquid, s^{-1}.

m_i	solubility coefficient for component i, $(kmol/m^3)_G/(kmol/m^3)_L$
MW_i	molecular weight of i species, kg/kmol.
N	stirrer speed velocity, rpm.
n	stoichiometric parameter in FTS.
P	pressure of the system, MPa.
P_i	partial pressure of component i, MPa.
q_{ads}	apparent heat of adsorption, kJ/kmol.
q'	dimensionless heat of adsorption, defined in eq. (24).
R	universal gas constant.
r_{FTS}	rate of FTS reaction, kmol/kg.s.
r_{WGS}	rate of WGS reaction, kmol/kg.s.
T	temperature, K.
T^o	inlet temperature, K.
T_w	wall temperature, K.
U	heat transfer coefficient, $kJ/m^2.K.s$
V_L	volume of the slurry, m^3.
V_R	volume of the reactor, m^3.
υ_{cat}	volume fraction of catalyst in slurry.
W_c	catalyst weight fraction.
x_i	dimensionless liquid phase concentration of component i.
x_i^o	dimensionless inert liquid phase concentration of component i.
X_w	water mole fraction.
X_w^*	water mole fraction for saturation.
y_i	dimensionless gas phase concentration of component i.
y_i^o	dimensionless inlet gas phase concentration of component i.
y_G	dimensionless total gas phase concentration.
y_G^o	dimensionless inlet total gas phase concentration.

GREEK LETTERS

α	$= F_G/F_G^o$
$\beta_{i,G}$	parameter defined in eq. (5).
$\beta_{i,L}$	parameter defined in eq. (17).
γ	parameter defined in eq. (13).
η_1	dimensionless heat of reaction for FTS.
η_2	dimensionless heat of reaction for WGS reaction.
θ	dimensionless temperature.
θ_W	dimensionless wall temperature.
κ	parameter defined in eq. (38).
ν_{ij}	stoichiometric coefficient.
ζ_i	dimensionless heat of solution of component i.
ρ_c	catalyst density, kg/m^3.
ρ_G	gas phase density, kg/m^3.
ρ_G^o	inlet gas phase denisty, kg/m^3.
ρ_H	FT liquid density, kg/m^3.
ρ_L	slurry density, kg/m^3.
ρ_L^o	inlet slurry density, kg/m^3.
τ_L	$= V_R/F_L^o$, liquid-phase residence time, s.

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