HYDROGEN CONSUMPTION AND THERMAL BEHAVIOR OF ADIABATIC THREE PHASE REACTORS

Introduction:

Many industrial reactions are exothermic in nature. For any exothermic reaction (or reactions), operation of a partially or a completely backmixed reactor in a multiple steady state region is a distinct possibility. Typical examples of such operations are: coal liquefaction, hydrocracking of crude or furnace oil, and hydrodesulfurization. The temperature rise in these exothermic processes is normally proportional to the hydrogen consumption, and it is important that the temperature rise is not large enough to result in undesirable performance. Hence, in most industrial reactors, "quench fluids" (either in the form of pure gas, pure liquid or as a mixture of gas and liquid) are used to restrict the temperature rise within the desired limits.

This report discusses the hydrogen consumption kinetics in a SRC-II coal liquefaction reactor. This is important in determining the thermal behavior of the reactor. The report further elaborates on the thermal behavior of adiabatic reactors, and in particular, coal liquefaction reactors. The existence of multiple steady states and the ways to control them are discussed.

Hydrogen Consumption Kinetics:

The thermal response of the reactor as a result of perturbations in the process variables is critical, since safeguards must be taken to prevent temperature excursions which may lead to significant solid deposition and ultimately a shut down or a significant reduction in liquid yield. Therefore, it is important that the temperature effect on the kinetics of coal liquefaction be established. Many kinetic models explaining different aspects of coal liquefaction have been discussed in the previous section of this report. One of the most important parameters which affect the thermal behavior is the hydrogen consumption in the reactor.

It is reported in the literature that the hydrogen consumption depends on the temperature of the reactor, partial pressure of hydrogen, and total (recycle) ash content. Singh et al. (1982b) proposed a reaction model based on the assumption that the liquefaction process results from an instantaneous dissolution of coal followed by a relatively slow conversion of SRC into coal products. They proposed that the hydrogen consumption rate is directly proportional to the SRC conversion, where SRC conversion can be written as,

$$-r_{SRC} = 8.256 \text{ X } 10^4 \exp \left[\frac{-18,900}{RT}\right] (P_{H_2})^{0.28} X_{ash} \qquad (1)$$

where P_{H_2} is the partial pressure of hydrogen. X_{ash} is the mass fraction of the ash in the reactor and T is the reaction temperature. Han et al. (1978) proposed that for pressures greater than 50 atm., the reaction rate should be proportional to $(P_{H_2})^{0.5}$. Jones (1980) pointed out that in addition to temperature and recycle ash, the inlet coal concentration also significantly affects the hydrogen consumption.

To validate these predictions, Carr et al. (1981) carried out experimental measurements in a continuous stirred tank reactor. The reactor consisted of a tubular preheater having 0.312 in inside diameter and 108 in. length, and a 1-liter, continuous, stirred tank vessel with the slurry entering through the bottom. The constant temperature throughout the reactor space and reaction time was insured using a combination of an electric furnace and an internal temperature monitoring system. The products are separated into six separate categories, namely; (i) C_1-C_4; ii) by product gases; iii) water, iv) C_5 - 900°F, v) SRC (Solvent Refined Coal), and vi) IOM (Insoluble

Organic Matter). Sixteen runs were carried out using an Ireland coal. An Ireland-based process solvent and recycle slurry were used to prepare the feed slurry blends. Coal composition was fixed as 30 wt% for all runs. The major variables of interest were temperature (430-470°C), hydrogen partial pressure (1500-3000 psig), recycle ash content (2 - 10.4 wt%), and nominal slurry residence time (0.57 - 1.5 hr.). The experiments were divided into three categories; namely, maximum, minimum, and baseline set of reaction rates. Maximum rate of reaction in SRC-II liquefaction reactor corresponds to the maximum feasible (before the reaction reaches runaway conditions) conditions of temperature, hydrogen partial pressure, and recycle ash content. Analogously, the minimum reaction rate conditions correspond to minimum feasible (where the reaction rates are measurable) conditions of the same process variables.

The results of the hydrogen consumption kinetics measurements are summarized in Table I-5. The hydrogen consumption rate reported in Table I-5 is obtained by taking the quantity of hydrogen consumed during the on-stream period, dividing this by both the length of the on-stream period and the reactor volume. In addition to hydrogen consumption measurements, complete product yields on a normalized % MAF (Moisture and Ash Free) coal basis are reported in Table I-5.

As can be seen from Table I-5, the process conditions of 470°C and 3000 psig, and 10 wt% recycle ash for the maximum reaction rate can yield a significantly higher hydrogen consumption level compared with the process conditions of 455°C, 2000 psig and 10.4 wt% recycle ash for the baseline reaction rate case. Also, it can be seen that the amount of recycle ash significantly affects the hydrogen consumption rate. Since the recycle ash acts as a catalyst, this observation is consistent with Han et al. (1978), who observed that presence of catalyst affects the rate of hydrogen consumption. They reported that this additional consumption is due to further hydrogenation of coal liquid to lighter products and subsequent hydrodesulfurization and hydrodenitrogenation reactions taking place. If one observes the trend in Table I-5, it can be seen that the liquid yield (C_5-900°F), the C_1-C_4 yield, and the hydrogen consumption increase as the nominal slurry residence time increases, while the SRC yield decreases with increasing the residence time. This observation is consistent with the observation made by Jones (1980). Furthermore, as expected, the rate at which yields changed with respect to slurry residence time was greatest for the maximum reaction rate conditions.

This table indicates a significantly lower IOM yield obtained for the maximum reaction rate condition runs. These runs indicate an average IOM yield on the order of 2.0 wt% as compared to an average IOM yield of the order of 3.0 wt% for the base line reaction rate cases and an average IOM yield on the order of 7.0 wt% for the minimum reaction rate cases. A lower IOM yield has very important implications from the standpoint of optimal operating conditions and the maximization of total liquid yield. Specifically, a lower IOM content in the separator bottoms (recycle slurry) permits a relatively higher fraction of recycle ash (catalyst) while maintaining either a lower or constant level of total solids throughout the process. Furthermore, a lower IOM yield obviously reduces the level of an undesirable product of coal liquefaction.

It should be noted that all these experiments are carried out under highly turbulent conditions such that all the mass transfer resistances were eliminated, and the reaction was kinetically controlled. As pointed out by Han et al. (1978), the slurry Reynolds number plays an important role in determining the mass transfer resistance. The consumption rate shows an increase with an increase in turbulence until a certain point, beyond which the rate coefficients seem to level off. Also, the hydrogen consumption increases linearly with superficial gas velocity for low values of superficial gas velocity until the reactor is no longer starved for hydrogen. Singh et al. (1981) carried out a theoretical analysis to evaluate the relative magnitudes of mass transfer and kinetic resistances. They calculated the value of overall mass transfer coefficient in the SRC-II bubble column reactor using the data by Kara (1981) in a stirred tank vessel, with the help of the mixing energy concept. After calculating the relative magnitudes of the resistances, they observed that in the region of practical interest (superficial gas velocity > 1 cm/s), the fractional decrease in rate of hydrogen consumption due to mass transfer resistance is less than 3.72 percent. Therefore they concluded that the mass transfer effects can be considered to be insignificant in all operations of SRC-II reactors.

Thermal Behavior of Adiabatic Reactors:

Many industrially important gas-liquid and gas-liquid-solid reactions are exothermic in nature. The generation of heat can cause problems of undesired side reactions, rapid catalyst deactivation and an uncontrolled production of the desired reaction products. In gas-liquid reactions two types of heat are generated: (a) heat of solution, which is generated at the gas-liquid interface due to physical dissolution process, and (b) the heat of reaction which can either be generated in the film near the gas-liquid interface (fast reaction) or in the bulk liquid (slow reaction). In case of a gas-liquid-solid reaction wherein the reaction occurs at the catalyst surface, it is often difficult to distinguish between heats of reaction and solution and they are generally reported together as an apparent overall heat of reaction (Shah and Bhattarchargee, 1982).

In a gas-liquid reaction, a gaseous reactant diffuses through the gas-liquid interface and the subsequent reaction with the liquid component may occur in the diffusion film, in the bulk liquid or at a plane close to the gas-liquid interface. The three resistances which are important are: gas side and liquid side mass transfer coefficients and the kinetic rate of the reaction. For an exothermic reaction, the rise in temperature caused by the heat of dissolution or the heat of reaction may cause a substantial increase in the reaction rate and/or change in the solubility of gaseous component. This may lead to changes in the absorption rate and the reaction regimes. Generally, the heat effects are more pronounced for the systems with high solubility of gases in liquids. Since highly soluble gases have more probability of encountering the gas-side mass transfer resistance at the gas-liquid interface, this resistance is more pronounced in non-isothermal systems than in isothermal systems.

For a gas-liquid-solid system, the problem is more complex because of the presence of a series of heat and mass transfer resistances at the gas-liquid interface, liquid-solid interface and within the catalyst particle. The reaction generally takes place within the catalyst particle and the reaction products may again undergo through similar heat and mass transfer resistances. When fine catalyst particles are used in slurry reactors, liquid-solid slurry temperature is considered to be uniform because of high thermal diffusivity of the slurry phase and the intraparticle mass and heat resistances are small.

For highly exothermic systems, apparent absorption reaction rates are generally described by coupled heat and mass transfer equations. In an actual gas-liquid or gas-liquid-solid reactor, the prevailing hydrodynamics and mixing characteristics of the system may further complicate the reactor design problem and it becomes almost inevitable to make varying degrees of assumptions to evaluate the reactor performance.

Different models have been proposed in the literature to evaluate the reactor performance under exothermic reaction conditions. A typical energy balance on a reactor can be written as,

$$\begin{Bmatrix}\text{Rate of heat}\\ \text{accumulation}\end{Bmatrix} = \begin{Bmatrix}\text{Rate of}\\ \text{heat in}\end{Bmatrix} - \begin{Bmatrix}\text{Rate of}\\ \text{heat out}\end{Bmatrix} + \begin{Bmatrix}\text{Rate of heat}\\ \text{generation}\\ \text{by reaction}\end{Bmatrix} - \begin{Bmatrix}\text{Rate of heat loss}\\ \text{to the surroundings}\end{Bmatrix} \qquad \text{-(1)}$$

In the above equation, rate of heat accumulation represents the increase in heat content of the control volume with an increase in temperature. For decrease in temperature, the heat content of the control volume is reduced, and the heat accumulation term has a negative value. Rate of heat in (or out) represents the amount of sensible heat in the flowing streams entering (or leaving) the control volume. It should be noted that the control volume can be the whole reactor or a differential section of it. Further mathematical development of the model depends on the assumptions involved. Three types of reactor models are commonly considered in the literature: (i) continuous stirred tank reactor (CSTR) where liquid and gas are assumed to be completely backmixed; (ii) partially backmixed reactor (PBR) where liquid and gas are assumed to be partially backmixed (e.g. bubble column or packed column reactors), and (iii) tank in series reactor (TSR) where the backmixed reactor is assumed to be of N perfectly mixed stages with recirculation between adjacent stages. Additional assumptions are made before the actual equations are written. For two or three phase reactors the typical assumptions involved are as follows.

i) There is no gas side mass transfer resistance for the mass transfer of reactant from the gas phase into the liquid phase. There is, however, liquid-side mass transfer resistance.

ii) The gas phase behaves according to the ideal gas law.

iii) The reactor is operated under isobaric conditions.

iv) No significant evaporation of liquid phase takes place in the reactor.

v) The physical and thermal properties such as density and specific heat of each of the three phases, the liquid side mass transfer coefficient and specific area of gas-liquid mass transfer, the volumetric gas and liquid flow rates, and the heat of reaction and solution are independent of temperatures and conversion.

vi) The three phases are at the same temperature at any position in the reactor. The total pressure of the gas bubbles and the gas and liquid holdups are constant in different sections of the reactor.

vii) Solids are uniformly distributed in the liquids and for definition of properties such as density and specific heat, the slurry can be treated as a homogeneous fluid.

viii) The extent of reaction has an insignificant influence on the volumetric flow rates and heat capacities of gaseous and slurry phases.

In addition to these assumptions, certain assumptions are made regarding the state (fast, slow as instantaneous) and the order (first, second or nth) of the reaction, based on the available kinetic data. When all the considerations are ready, mass balance and energy balance equations are written along with the appropriate boundary conditions and solved either analytically or numerically.

In general, for the reactions with simple kinetics isothermal backmixed gas-liquid reactors are operated at stable steady states (Ho and Lee, 1980). Many industrially important gas-liquid reactions are highly exothermic and commercially they are often carried out in an adiabatic backmixed reactor, which can lead to multiple steady states. Early studies on the stability of two phase reactions in CSTR were published by Schmitz and Amundson (1963, a, b) and Luss and Amundson (1967). However, in their models it was implicitly assumed that the interfacial mass transfer and chemical reaction are two independent resistances acting in series, an assumption not valid for all reaction regimes encountered in gas-liquid systems. Furthermore, as pointed out by Hoffman et al. (1975) these models fail to describe the shift of reaction regime that may occur during the non-isothermal operation. Hoffman et al. (1975) conveniently utilized the concept of reaction factor by Van Krevelen and Hoftijzer (1948) and Teramoto et al. (1969) and treated the interfacial mass transfer and chemical reaction as interdependent processes. This concept allows the overall rate of gas-liquid reaction to be expressed over a wide range of temperature in which the controlling resistance may shift from kinetics to mass transfer.

Raghuram and Shah (1977) derived analytical conditions for uniqueness and multiplicity of steady states for three different cases, and concluded that the major reason for the multiple steady states in a CSTR reactor is the temperature dependence of the rate constant and the solubility of the gas in the liquid phase. They also observed that for a simple first order gas-liquid reaction, there can be a maximum of five steady states. Raghuram et al.

(1979) extended this analysis for a non-isothermal reactor and observed that in this case, the effect of increasing heat transfer coefficient to a very large value is to destroy the multiplicity of steady states. Huang and Varma (1981a) further extended this work and derived less conservative, explicit, necessary and sufficient criteria for the steady state multiplicity and stability and for the prediction of direction and stability of limit cycles for a pseudo first order fast reaction in a non-adiabatic CSTR. The study of multiplicity in gas-liquid-solid reaction systems in CSTR has not been carried out by many investigators. For a reaction of type

$$A(g) + B(slurry) \rightarrow Products\ (slurry + gas) \qquad \ldots (2)$$

being carried out in a CSTR, Shah and Singh (1981) derived the criteria for stability which can be applied to both low as well as high pressure systems wherein a substantial amount of heat is carried by the gas phase. They further showed that the predicted steady state reactor temperatures from a simple model agree reasonably well with the measured ones.

The other two models, namely, axial dispersion model and n-CSTR tank in series model are used for partially backmixed reactors; the most important are bubble column reactors. While the axial dispersion model results in a series of differential equations, the tank in series model results in algebraic equations.

Raghuram et al. (1979) developed an n-CSTR in series model for a pseudo-first order reaction which also included backflow to account for the different extent of mixing for the gas and liquid phases. They observed that the uniqueness of steady state is attained at higher degrees of backmixing than in the single phase reactor. Furthermore, with an analysis of 2-CSTR's with liquid backflow, it was concluded that the attainment of five steady states is possible only when the liquid and gas phases are backmixed to the same extent.

Huang and Varma (1981b) developed a steady state model and derived an analytical criterion for the prediction of uniqueness and multiplicity of the steady states for a fast pseudo-nth order reaction in a non-adiabatic bubble column reactor. They concluded that the possibility of occurence of multiple steady states in a bubble column reactor is more than in a gas-liquid CSTR under the same operating conditions.

Parulekar et al. (1980) applied the axial dispersion model to three phase adiabatic reactors where solids act as catalyst; and observed that for a small value of catalytic reaction constant, there is distinct and fairly large region of five steady states. They observed that the region becomes smaller and smaller and eventually disappears as the reaction constant is increased. The value of the rate constant at which this transition appears is much smaller than the observed values in the literature. Therefore, they concluded that the phenomenon of five steady states in an adiabatic CSTR is unique to gas-liquid reactions. Singh et al. (1982a) pointed out that in case of high pressure gas-liquid reactions, thermal behavior of cocurrent and countercurrent bubble column reactors may have some distinct differences. They derived analytical criteria for the uniqueness of steady state and examined the effects of operating variables on the regions of multiplicity for these two cases.

Thermal Behavior in SRC-II Coal Liquefaction Reactor:

Reactions in SRC-II reactor are exothermic. It is observed that its start-up procedure involves holding of the reactor temperature to the desired value and continuous quench gas feed back control is used to maintain the reactor temperature. This indicates that operation of SRC-II reactor may be under unstable steady-state conditions.

To check the validity of these hypothesis, many investigators (Shah and Parulekar, 1982; Singh and Carr, 1982a; Singh and Carr, 1982b; King et al., 1983) carried out theoretical as well as experimental analysis. In all these studies, it was assumed that SRC-II reactions are pseudo-first order in nature. CSTR as well as PBR models were used to evaluate the reactor performance. It should be noted that to solve the model equations, one requires a reliable estimate of all the physico-chemical parameters. Evaluations of hydrodynamic, backmixing and transport parameters are already discussed in the first part of this report. In addition to these parameters, a good estimate of values of the properties of the components of the system in the model equations is necessary for any meaningful analysis of the thermal behavior. Independent measurement of each of the properties is often not possible, and even where independent measurements are used to evaluate some of the properties, its applicability under the reaction conditions cannot be easily ascertained. The Gulf Research Center in Harmarville has collected data from various sources on small boiling range fractions of coal liquefaction products. However, most of these data are not published in the open literature. Singh and Carr (1982a) present some of the values of these physical properties. The most important among them is the heat of reaction.

Stephenson (1981) has reported the values of heat of reaction as a function of inlet hydrogen concentration. He analyzed the data from heat surveys and process operating conditions around the dissolver of SRC-II Process Development Unit P-99 in Gulf Research and Development Center at Pittsburgh. The dissolver was installed in a way to provide adiabatic operation of the vessel. A number of heat surveys were conducted to ensure the adiabatic operation of the unit. The net exothermic heat of reaction in the dissolver was calculated from the change of the process stream enthalpies in the form of sensible heat and heat of vaporization across the dissolver. The data showed a trend of decreasing heat of reaction with increasing hydrogen consumption, and could be linearly correlated by

$$\Delta H \text{ reaction} = 112.66 - 12.82 \text{ (wt\% } H_2\text{); Btu/scf } H_2 \qquad -(3)$$

with a standard deviation of 2.93 Btu/scf. This was explained on the basis that the most energetic hydrogenation reaction is the saturation of aromatic rings (77 Btu/scf), while other reactions such as hydrocracking are less exothermic (40 Btu/scf); and that additional hydrogen is consumed in the hydrocracking reactions.

Once all the physico-chemical properties are determined, the next step is to write an appropriate model to simulate the thermal behavior of a coal liquefaction reactor. A first attempt in this direction was made by Shah and Parulekar (1982) and Parulekar et al. (1980). They used an axial dispersion model to simulate the reactor. In addition to the assumptions already stated they assumed the reactor to be cocurrent upflow type; and the reaction to be pseudo first order with respect to dissolved gas and of the type,

$$A(g) + B\ (l) \xrightarrow{k} \text{products} \qquad -(4)$$

where A refers to hydrogen and B represents portion of liquefied coal-solvent mixture. Based on these assumptions, Shah and Parulekar (1982) wrote the material and energy balance equations with appropriate boundary conditions. These equations were solved using a Newton-Raphson method. Their study was restricted to steady state behavior of coal liquefaction reactor. They studied the effect of different variables on the hydrogen consumption and thermal behavior of a coal liquefaction reactor.

One of the most important considerations in any exothermic reactor is the temperature rise from bottom to top. If the temperature rise is excessive the reaction will reach run away conditions. Some experimental data on the temperature rise is available from the Ft. Lewis reactor, and is found to be in the vicinity of 25-35°C. Based on this temperature profile, Shah and Parulekar (1982) concluded that the axial dispersion coefficient in the SRC-II reactor is almost one third of the dispersion coefficient value based on the available literature correlations. They observed that increase in the slurry velocity reduces the residence times of slurry in the reactor and hence reduces the overall temperature rise in the reactor. On the other hand, an increase in the gas velocity results in an increase in the temperature rise. The diameter of the reactor was also found to have similar effect on the temperature rise. Jones (1980) carried out a similar analysis using the axial dispersion model, and observed that this model is adequate in explaining the temperature rise in the reactor.

The first preliminary analysis on the stability of coal liquefaction reactor was carried out by Parulekar et al. (1980). Using the axial dispersion model, they reported that multiplicity of steady states exists for a very small range of slurry residence time. They also observed that as the Peclet number of the liquid phase increases, the possibility of multiple steady state increases in a bubble column reactor. This analysis was further extended by Singh and Carr (1982a) using the experimental data collected in the Fort Lewis pilot plant reactor. They used the axial dispersion model, and made an additional assumption that the variation in hydrogen partial pressure inside the reactor is insignificant. Therefore, hydrogen partial pressure throughout the reactor is the same as that at the outlet. They also assumed the rate of heat loss to the surroundings per unit reactor surface to be independent of reactor temperature.

If multiple steady states exist, for any given feed temperature (T_f) there is more than one reactor outlet temperature (T_o), or temperature profile, which can satisfy the boundary conditions; whereas there is only one feed temperature corresponding to a reactor outlet temperature. Therefore, Singh and Carr (1982a) numerically integrated the model equation, starting at the reactor outlet. A fourth order Runge-Kutta integration scheme was used. The validity of axial dispersion model was checked using two experimental runs carried out in a Fort Lewis pilot plant reactor. The discrepancy between the measured and calculated values of feed temperature was explained based on the ideality of the boundary condition which assumes that mixing of feed and reactor contents is achieved instantaneously at the inlet of the reactor. However, it is observed that any real system would take a non-zero space or length for completion of mixing based on the available data. Singh and Carr (1982a) plotted the rate of heat generation and the rate of heat removal as a function of reactor outlet temperature. It was clearly shown that.

$$\frac{dh_g}{dT_o} > \frac{dh_r}{dT_o} \qquad -(5)$$

i.e. the sensitivity of rate of heat generation to reactor outlet temperature is greater than that of the rate of heat removal. This is a necessary and sufficient condition for the steady state to be stable.

Under an unstable steady-state operation, a small perturbation in any one of the process conditions is expected to grow. A similar situation was observed in one of the experimental runs where after eight hours of operation, the run conditions changed significantly so that quench gas control had to be used. In the other experimental run, the operation could be continued without quench control for only two hours. It should be noted, however, that in spite of the unstable nature of the steady-state and or large difference between the required and actual feed temperatures, the reactor could be operated for two hours. This is probably due to slow response of the reactor temperature to changes in feed temperature. To confirm this, the sensitivity of the reactor outlet temperature to feed temperature and mass fraction of ash in the slurry was carried out. It was observed that, with a decrease in the mass fraction of ash in reactor from 16 to 10 wt% of slurry, reactor ignition temperature increased from 439 to 470°C. Therefore, at an ash level of 10 wt% in slurry, the reactor operation would be stable at reactor outlet temperatures of less than 470°C. The results further showed that if stability of operation is to be guaranteed, liquid yields will have to be reduced by at least 4 wt% mf (moisture free) coal. However, as stated before, very slow response of the reactor temperature to changes in feed temperature, do indicate the possibility of an easy temperature control for SRC-II reactor of any size. However, this must be verified by a dynamic simulation of the process.

Two recent publications deal with this dynamicity of a coal liquefaction reactor. First, Singh and Carr (1982b) extended their analysis to the dynamic thermal behavior of the reactor. All the assumptions for a steady-state model where considered to be valid for the dynamic model also. In addition, the bubble column reactor was assumed to be fully backmixed. This assumption was supported by the observed small temperature variation (4 to 6°C) in the reactor used in the dynamic experiment. Another assumption made was that the hydrogen concentration inside the reactor attained its steady-state value, corresponding to the reactor temperature, instantaneously. This assumption was justified on the basis of a very small residence time for the gas compared to that of the slurry.

Based on these assumptions, an unsteady state energy balance was written for a CSTR. The criterion for unstable steady state is already given in equation (5). Based on the dynamic energy balance equations, Singh and Carr (1982b) showed that irrespective of the nature of the steady state, an increase in steady state feed temperature initiates an increase in reactor temperature and a decrease in feed temperature initiates a decrease in reactor temperature. However, it can be mathematically proved that the rate of change in reactor temperature and the variation in this rate with time depend on the nature of the steady state. Mathematically for $t_2 > t_1$ where t is time

$$o < \left(\frac{dT}{dt}\right)_{t_2} < \left(\frac{dT}{dt}\right)_{t_1} \quad \text{for a stable steady state} \qquad (6)$$

and

$$\left(\frac{dT}{dt}\right)_{t_2} > \left(\frac{dT}{dt}\right)_{t_1} > 0 \quad \text{for an unstable steady state} \qquad (7)$$

Equation (6) shows that for a stable steady state of t=0, any step increase in feed temperature would increase the reactor temperature. However, the rate of increase in reactor temperature would decelerate with time. Whereas for an unstable steady state operation at t=0, the rate of increase in reactor temperature initiated by the step increase in steady feed temperature would accelerate with time (Equation 7). Thus the nature of rate of change in the temperature of a reactor subject to change in its steady-state feed temperature can be used as a conclusive experimental identification of the nature of the steady state. Singh and Carr (1982b) further showed that if at any time during the transient, the feed temperature is restored to its original steady state value, the direction of change in reactor temperature would be reversed for the stable case, whereas that for the unstable case it would remain unaffected. For reversal in the direction of temperature of the unstable case, the opposing change will have to be much larger than the original step change.

To validate these mathematical interpretations, a batch reactor was operated under similar operating conditions to the actual SRC-II reactor. A step input of $10^{o}C$ was introduced in the feed temperature, and rate of heat generation and removal were carefully monitored. Singh and Carr (1982b) showed that the difference between the heat generation and removal rate increases with time and this causes the acceleration in the rate of change in reactor temperature. This clearly is a result of an unstable steady state. To show the difference between stable and unstable steady states, experiments were carried out under stable steady states by reducing the ash concentration to a lower value such that the rate of reaction and hence the rate of heat generation is reduced. It was clearly illustrated by Singh and Carr (1982b) that the reactor temperature decreases with a decelerating rate, in opposition to the accelerating rate for the unstable operation.

Further experimental evidence was provided by King et al. (1983), who carried out coal liquefaction experiments in CSTR under adiabatic reactor conditions. The objective of the work was to search for ignition points and possibility of stable steady states under various sets of operating and initial conditions for SRC-II operation. In one of the runs, the feed slurry corresponded to that of typical SRC-II slurry with a significant quantity of recycle ash (11 wt%). It was noted that the reactor temperature kept on increasing while the feed temperature remained constant. When a further step change was given to feed temperature, the reactor temperature increased dramatically signifying ignition. When the reactor temperature approached 470°C, the emergency operations were initiated to cool off the reactor. This further proved the instability of the operation. In another run, with 5 wt% recycle ash, the reactor temperature leveled off at 460°C for a period of about 7 hours. During this time, the feed temperature remained relatively constant at about 415°C. King et al. (1983) attributed this to the possibility of a stable steady state for the open loop reactor. However, it can be argued that this might be a result of the thermal inertia of the system which takes a long time to react to any changes or perturbations. Thus, even at unstable steady state conditions, the reactor can appear at steady state. This should be researched further, before any conclusions can be drawn. It should be noted further that ash content in the reactor plays a very important role in determining the stability of the reactor. For low recycle ash ($\sim$2 wt%) the reactor can be operated under stable steady state conditions, while for high recycle ash content ($\sim$11 wt%) the reactor is normally operated under unstable steady state conditions.

Recently, Ledakowicz et al. (1983) analyzed the coal liquefaction reactor using a simplified model. They assumed that three phase gas-coal slurry vertical flow may be approximated by two phase flow without any essential differences of the experimentally determined hydrodynamic parameters for these two systems. Further, for large diameter reactors, the value of Peclet number for the liquid phase was found to be less than 0.1. Therefore, the liquid phase can be assumed to be completely backmixed. It was shown that use of axial dispersion model and CSTR model for gas phase do not show any significant difference between two gas phase concentration profiles;

therefore, the gas phase can also be assumed to be completely backmixed. Ledakowicz et al. (1983) wrote a simple steady state energy balance, where the rate of heat generation was assumed to be proportional to the hydrogen consumption. Typical thermal properties were calculated from the available literature. When the calculated steady state behavior was plotted it was observed that the heat generation curve and heat removal line intersect each other at three points indicating three possible steady states. Surprisingly, in both the cases studied, the operating temperature of the liquefaction reactor is near the unstable steady state. This further validates the hypothesis by Singh and Carr (1982b).

Since it is clearly observed that the SRC-II reactor is operated under unstable steady state conditions, it cannot be operated without controls. The best way to control this reactor is by using hydrogen quench.

Shah and Parulekar (1982) reported that an increase in slurry velocity reduces the quench requirement to maintain constant outlet temperature. Increase in the gas velocity also reduces the quench requirement, while increase in the length increases this requirement. With an increase in quench temperature the effectiveness of quench in reducing the temperature rise is reduced and therefore the critical amount of quench increases with quench temperature. Also, the critical quench ratio (ratio of volumetric flow rate of quench to that of feed gas) decreases as the quench location is moved from inlet towards the outlet of the reactor.

Typically the difference between the rate of heat generation and removal, i.e., (hg-hr) for normal SRC-II process conditions, is less than 40 kJ/(L. hr) which is about 10% of the magnitude of hg or hr. Since the difference between the reactor feed (370 to 410°C) and quench gas (35 to 40°C) temperatures is very large, the heat removal capacity of the quench gas is very large. It is important to note that the heat capacity of the gas is also significant due to high pressure in the reactor (Singh et al., 1982). For example, for a change in quench gas flow rate from 20 to 50% of the total gas flow rate, the reactor would typically obtain an additional heat capacity of 90 kJ/L.hr. The latter is more than twice the maximum difference between hg and hr. Since the distribution of gas between the feed through the preheater and quench streams can be varied significantly, it can safely be assumed that the quench gas control can be effectively used to meet the changes in the requirement of heat removal rate with changes in process conditions. This quench gas control would be very important for the cases in which the properties of the feed or feed temperature are changed for a significant amount of time. This is a distinct property for the SRC-II process whose rate depends on coal properties which are variable and the variations cannot be known accurately beforehand or during the operation itself.

Concluding Remarks:

Most of the industrial large scale reactors are operated adiabatically. Many of them have been reported to be operating under unstable steady state conditions. However, control of these reactors is relatively easy. One of the most important reasons for this easy control is the thermal inertia of these reactors. Most of these reactors are operated under pressure. When the pressure inside these reactors is increased significantly, two things happen, one, due to high pressure, density and hence the heat capacity of the gas phase increases significantly; two, at high pressures, the reactor wall thickness increases significantly (for example, a 10 foot diameter reactor can have 14 inch walls) and hence the heat carying capacity of the reactor itself increases significantly. As a result of this increase in the overall heat capacity, the response of the reactor to any changes in the feed variables becomes sluggish, and hence the control of the operation becomes relatively easy. The SRC-II reactor is a special case of these high pressure reactors where quench gas is effectively used to control the outlet temperature of the reactor.

Experimental data on the thermal behavior of gas-liquid-solid reactors are scarce. It is very difficult to build a prototype bench scale reactor due to high surface area to volume ratio in the small scale reactors. Also, if the small reactor is operated under high pressures, the thermal capacity of the reactor walls, stirrer and the other internals increases significantly compared to the reactants and the products. This results in an increase in the thermal inertia of the reactor, and may cause experimental difficulties in the measurement of the reactor temperature. Even if the reactor is operating under unstable steady state conditions, the high thermal inertia may result in small temperature rise (Bhattacharjee, 1983). Also, the extent of adiabaticity in a bench scale reactor should be carefully monitored, before any reliable data can be generated which may be used for scale-up purposes.

Nomenclature:

hg	Heat generated, kJ/(L.h)
hr	Heat removed, kJ/(L.h)
$\Delta H_{reaction}$	Heat of reaction, kJ/kg of H_2 reacted
P_{H_2}	Partial pressure of hydrogen, MPa
r_{SRC}	Rate of reaction of SRC (Solvent Refined Coal), kg/(L.h)
R	Gas constant, kJ/(Kmole-K)
t	Time, h
T	Temperature in the reactor, K
T_f	Feed temperature, K
T_o	Outlet temperature, K
X_{ash}	Mass fraction of the ash in the reactor

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Table I-5
Experimental Conditions and Hydrogen Consumption Results (Carr et al., 1981)

Severity Level	Run No.	Reactor Temp. (°C)	Reactor Pressure (psig)	Recyle Ash in Feed (wt%)	Nominal Slurry Residence Time (hr)	Hydrogen Consumption (g/hr-l)	Product Yields (Normalized % MAF Coal)						
							C_1-C_4	By-Product Gases	Water	C_5-900°F	SRC	IOM	H_2 Consumption
	1	470	3000	10.4	1.09	22.2	30.5	4.4	3.6	46.0	20.1	3.0	7.6
	2	470	3000	10.4	1.67	23.2	36.5	4.2	2.1	62.0	6.3	0.4	11.7
Maximum	3	470	3000	10.4	1.06	23.7	35.4	5.3	5.6	35.5	25.0	3.7	10.5
	4	470	3000	10.4	1.54	23.8	35.2	4.4	6.0	52.4	10.2	3.4	11.6
	5	470	3000	10.4	0.58	25.8	17.2	3.8	4.7	32.6	42.7	3.7	4.7
	6	470	3000	10.4	1.11	21.5	24.7	3.7	3.0	53.8	21.4	0.1	6.7
	7	455	2000	10.4	1.54	14.0	25.2	3.6	4.1	60.6	12.1	1.3	6.9
	8	455	2000	10.4	0.58	18.9	12.9	4.1	4.9	24.9	55.1	2.1	4.0
Baseline	9	455	2000	10.4	1.51	15.5	27.5	5.1	5.6	57.0	9.6	3.6	7.8
	10	455	2000	10.4	0.91	15.9	19.5	3.8	4.1	40.5	34.6	5.0	7.6
	11	455	2000	10.4	1.02	18.5	15.7	4.2	3.7	36.9	42.4	2.8	5.7
	12	430	1500	2.0	0.97	9.4	7.6	3.6	3.4	11.2	70.5	6.6	2.9
	13	430	1500	2.0	1.44	8.9	9.1	3.6	3.3	21.8	57.7	8.4	3.9
Minimum	14	430	1500	2.0	1.00	9.6	7.2	3.6	2.9	17.3	66.0	6.0	3.0
	15	430	1500	2.0	1.55	7.9	10.2	3.3	2.8	18.6	72.6	6.5	4.0
	16	430	1500	2.0	0.59	11.2	4.5	3.5	1.9	12.0	73.2	7.0	2.1