MATHEMATICAL MODELING FOR OPTIMUM OPERATION OF HIGHLY EXOTHERMIC EQUILIBRIUM GAS PHASE CATALYTIC REACTIONS USING MULTI-TUBULAR COOLED REACTOR

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Abstract

In this paper rigorous modeling of an industrial multi-tubular reactor (MTR) was used to help identify potential pitfalls and avoid foreseeable problems during operations. The type of equilibrium reactions considered is initially fast and highly exothermic, therefore effective thermal conduction should be distinguished between the gas and solid catalysts because solid temperature profile is generally higher than that of gas, and temperatures predicted by the two-dimensional (2D) heterogeneous models are very different from the one-dimensional (1D) homogeneous models.

Radial heat removal is strongly influenced by the effective radial thermal conductivity which decreases significantly near the tube wall. Considering the possible presence of thermal runaway due to lack of efficient heat removal, a two-dimensional model serves a better purpose in design and control than a corresponding one-dimensional model. The development of the modern-day computer allows efficient computation in a two-dimensional model for most steady-state and some dynamic calculations.

Comparisons of some basic types of mathematical models for industrial operations are presented. Validation of the model requires experimental work to determine key process parameters. Because basic physical properties and reaction kinetics of the system are either collected from literature or from experiments, mathematical modeling of the process options could allow early visualization of certain aspects of the proposed design and help develop necessary control strategies for the effective operation of such reactors. For process intensification purposes design conditions are often close to those of operational runaway, sensitivity of the critical parameters related to stability are studied before sound control strategy can be developed. Lastly, a hybrid kinetic in situ equilibrium method was used to approximate true product allotropic distributions using the existing kinetics so that approximate product dew point can be predicted and potential product condensation could be avoided.

Keywords

Modeling for optimized operations, Simultaneous gas phase catalytic reactions and heat transfer, Transient behavior of exothermic reversible reactions in an industrial multi-tubular fixed bed reactor

Introduction

Many industrially important vapor phase reactions are chemical equilibrium limited and highly exothermic in nature. Very often a cascaded multi-staged adiabatic reaction system is adopted in the industry where equilibrium limitation is relieved by inter-stage cooling and sometimes by partial removal of product through condensation. The number of passes would sometimes have to be uneconomically large to limit temperature rise per pass which requires many heat exchangers and large surface area, in addition to higher overall pressure drop across the series of reactors and heat exchangers. Total installation and operating costs to carry out these conversions are generally high, especially if high conversion is expected under stringent economic and environmental constraints for concentrated inlet reactants. One possible improvement in configuration is to design and operate a thermally cooled multi-tubular reactor system where both heat of reaction and equilibrium limitation can be alleviated in a stand-alone reactor (Eigenberger and Ruppel, 2012), as shown in Figure 1.

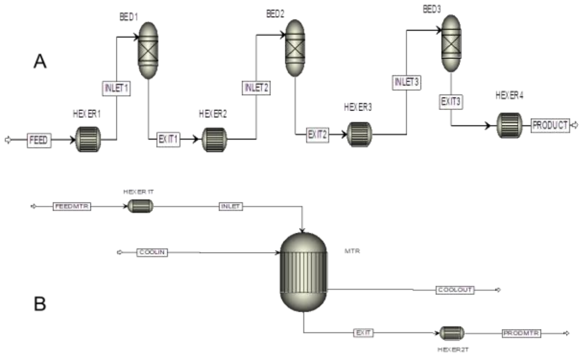

Figure 1. Typical industrial configurations of (A) Cascaded multi-bed adiabatic reactors with inter-stage coolers and (B) Standalone MTR with shell side cooling

Although previously regarded as a low capacity alternative to carry out these reactions, we believe that if controlled properly, option B in Figure 1 can offer milder temperature profile within the reactor which keeps the catalyst within its thermal stability limit and avoid hot spots. A schematic diagram of temperature pathway of these two options is depicted in Figure 2.

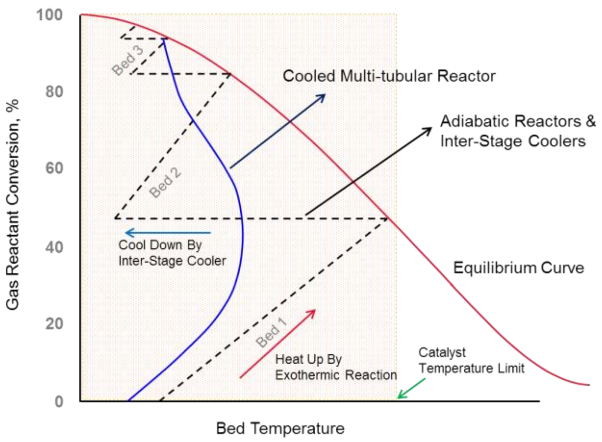

Figure 2. Typical temperature curves vs. conversions of the two reactor configurations for gas phase catalytic reactions

In order to evaluate the merits of the options in confidence and properly design and operate the preferred system many variables and parameters have to be considered and studied. Mathematical modeling along with experimental validation is essential before costly capital expenditure is made on pilot testing and commercial plants.

The selection of a model depends on the simplifying assumptions made to the enormous complexity residing in this simultaneous reaction and transport system. For the gas phase industrial MTR considered heat transfer is limiting across the catalyst gas interphase and mass transfer is limiting inside catalyst particles. On the bulk tube scale both mixing, mass, and heat transport is important in axial flow direction. Solid heat transfer is only important in the radial direction in which most of the reaction heat is relieved. Four degrees of sophistication for model building is attempted according to the well accepted classification in the field, namely one-dimensional (1D) and two-dimensional (2D) pseudo-homogeneous and heterogeneous models (Froment and Bischoff, 1990, Lordanidis, 2002, Koning, 2002).

$$\frac{\partial C_i}{\partial t} + u_s\frac{\partial C_i}{\partial z} - D_{ez}\frac{\partial^2 C_i}{\partial z^2} - \frac{D_{er}}{r}\frac{\partial}{\partial r}\left(r\frac{\partial C_i}{\partial r}\right) = k_f a_v\left(C_i^s - C_i\right) \quad (1)$$

$$\frac{\partial T}{\partial t} + u_s\rho_f C_p\frac{\partial T}{\partial z} - \lambda_{ez}^f\frac{\partial^2 T}{\partial z^2} - \frac{\lambda_{er}^f}{r}\frac{\partial}{\partial r}\left(r\frac{\partial T}{\partial r}\right) = h_f a_v\left(T^s - T\right) \quad (2)$$

$$k_f a_v\left(C_i^s - C_i\right) = -R_i\left(C^s, T^s\right) \quad (3)$$

$$\frac{\partial T_s}{\partial t} + h_f a_v\left(T^s - T\right) = R_T\left(C^s, T^s\right) + \frac{\lambda_{er}^s}{r}\frac{\partial}{\partial r}\left(r\frac{\partial T_S}{\partial r}\right) \quad (4)$$

Equations (1-4) depicts the general 2D heterogeneous mass and energy relationship of gas and catalyst phases used for subsequent studies. Where u_s is the superficial gas velocity, ρ_f and C_p are gas density and heat capacity respectively, D_{ez} and λ_{ez}^f are gas axial diffusivity and heat conductivity respectively, λ_{er}^f and λ_{er}^s are radial heat conductivity for gas and catalyst respectively, and k_f and h_f are gas catalyst film mass and heat transfer coefficients. R_i and R_T are rate and heat of reactions. C_i and a_v are gas concentration and catalyst interfacial area. Boundary conditions for the above 2D heterogeneous model are listed in the following equations:

$$z = 0: \quad u_s C_i = u_s C_{0i} - D_{ez}\frac{\partial C_i}{\partial z},$$

$$z = 0: \quad u_s\rho_f C_p T = u_s\rho_f C_p T_0 - \lambda_{ez}^f\frac{\partial T}{\partial z} \quad (5)$$

$$r = 0: \qquad \frac{\partial C_i}{\partial r} = 0, \quad \frac{\partial T}{\partial r} = \frac{\partial T_S}{\partial r} = 0 \quad (6)$$

$$r = R: \qquad \frac{\partial C_i}{\partial r} = 0, \quad \alpha_w^f\left(T_w - T\right) = \lambda_{er}^f\frac{\partial T}{\partial r}, \quad \alpha_w^s\left(T_w - T_s\right) = \lambda_{er}^s\frac{\partial T_s}{\partial r} \quad (7)$$

Equation (7) introduces the need to separately specify the fluid-wall and catalyst-wall heat transfer for energy conservation. In pseudo-homogeneous models it is assumed that the catalyst surface is totally exposed to bulk gas therefore the k_f and h_f terms in the equations are essentially zero. The gas and catalyst temperatures are equal in a homogeneous system. The 1D models should eliminate the radial dispersion terms and the radial boundary conditions and add an explicit heat transfer term $\frac{4U_w}{2R}(T-T_w)$ to the energy balance equations (for both catalyst and gas if heterogeneous 1D model is desired).

Shell side heat removal can be either steam generation or using concurrent flow of a fluid or molten salts. Shell side water nucleate boiling heat transfer coefficient can be described as function of heat flux:

$$h_{boil} = J_{2r}\,({}^{Q}/_{A})^{0.673}\,F_b\,F_p \qquad (8)$$

where F_b and F_p are correction factors of the tube bundle and shell side steam pressure respectively, J_{2r} is the dimension constant and ${}^{Q}/_{A}$ is the heat flux across the tube (HTRI, 2015). The shell side steam boiling heat transfer coefficient is normally a few orders of magnitude higher than that of tube side effective heat transfer coefficient. Heat transfer is also limited in the tube side for shell side coolant cooling and temperature in shell side bulk is often very close to wall temperature provided that the coolant has large heat capacity and flowrate. The single phase coolant energy balance equation is as the following:

$$\rho_c V_c C_{pc}\left(\frac{\partial T_c}{\partial t}\right) = F_c C_{pc}(T_{cin} - T_c) + Q \qquad (9)$$

where $\rho_c, V_c, F_c\ and\ C_{pc}$ are coolant density, volume in shell, flowrate and heat capacity respectively. $T_{cin}\ and\ T_c$ are coolant inlet and exit temperature respectively. Q is the rate of heat transferred across the tube wall from tube side to the shell side.

Case Study I – Model Comparisons

Gas physical properties were determined by the ideal gas law or equation of state and parameters were retrieved from DIPPR (2006). The catalytic system studied comprises a network of several gas phase equilibrium reactions such as the following:

$$\mathrm{A} + \mathrm{B} \leftrightarrow \mathrm{I} + \mathrm{P}\ \text{(exothermic)} \qquad (10)$$

$$\mathrm{C} + \mathrm{I} \leftrightarrow \mathrm{A} + \mathrm{E}\ \text{(exothermic)} \qquad (11)$$

$$\mathrm{D} + \mathrm{I} \leftrightarrow \mathrm{A} + \mathrm{E}\ \text{(exothermic)} \qquad (12)$$

where A and B are main gas phase reactants and P is the product. Intermediate I can react with minor reactants C and D to form reactant A and a byproduct E. Reaction kinetics can be of a reversible Langmuir-Hinshelwood type like the one for equation (13) described as the following:

$$r = k_0 \exp\left(-\frac{E_a}{RT}\right)\frac{\left(p_A^a p_B^b - \frac{1}{K_{eq}} p_I^i p_P^p\right)}{(1 + K_A p_A + K_B p_B + K_I p_I + K_P p_P)^2} \qquad (13)$$

In order to evaluate performance of various models discussed some common transport parameters and empirical correlations have been used for all models. Table 1 summarizes fixed values of major transport parameters used consistently to compare the heat transfer performance of different models.

Table 1. Simulation parameters and conditions of one typical MTR system in industrial setting

Parameter Description	Parameter Value	Parameter Unit
Catalyst activity	1	
Catalyst mass specific heat capacity	0.5	kJ/kg/K
Tube internal diameter	1	inch
Tube length	3.048	m
Catalyst particle diameter	3	mm
Number of tubes	4000	
Total gas pressure drop within the tubes	0.1	bar
Peclet number for axial heat transfer	10	
Peclet number for radial heat transfer	2	
Peclet number for axial mass transfer	10	
Peclet number for radial mass transfer	2	
Catalyst bulk density	721	kg/m^3
Catalyst/wall heat transfer coefficient	60	Btu/hr/ft^2/°F
Gas/catalyst heat transfer coefficient	100	Btu/hr/ft^2/°F
Gas/wall heat transfer coefficient	60	Btu/hr/ft^2/°F
Catalyst bed void fraction	0.65	
Catalyst thermal conductivity	5	W/m/K
Catalyst specific surface	1500	m^2/m^3
Coolant flow rate	2266	ton/hr
Shell side coolant exit temperature	340	℃
Shell side coolant inlet temperature	330	℃
Rate of energy transferred	94.889	GJ/hr
Feed gas total flow rate	7730	kmol/hr
Feed gas pressure	1.724	bar
Feed gas temperature	148.5	℃
Mole fraction of A in feed mixture	0.633	
Mole fraction of B in feed mixture	0.205	
Mole fraction of C in feed mixture	1e-6	
Mole fraction of D in feed mixture	1e-6	
Mole fraction of E in feed mixture	0.095	
Mole fraction of I in feed mixture	0.067	
Mole fraction of P in feed mixture	1e-6	

The above set of distributed differential and algebric equations with boundary and initial conditions were solved using Aspen® Custom Modeler, an equation based modeling environment. Mixed Newton method and Gear's method have been used for the non linear solver and the integrator respectively. Temperature profiles of four different models based on the same inlet and initial conditions were compared in the same chart which is listed in Figure 3. For 2D models the temperatures are averaged across the radius of the tubes. Obviously there are large differences between the 1D and 2D models and between the pseudo-homogeneous and heterogeneous models. There is a dramatic early departure of the catalyst from the gas temperature profiles near tube entrance and catalyst temperatures are significantly higher than gas temperatures predicted by the heterogeneous models indicating pronounced heat transfer resistance between the phases. Near the hot spot positon catalyst temperatures are much higher predicted by the 2D than those predicted by 1D heterogeous models because the 1D model predicts easier radial heat removal across the tube wall even though similar transport parameters were used.

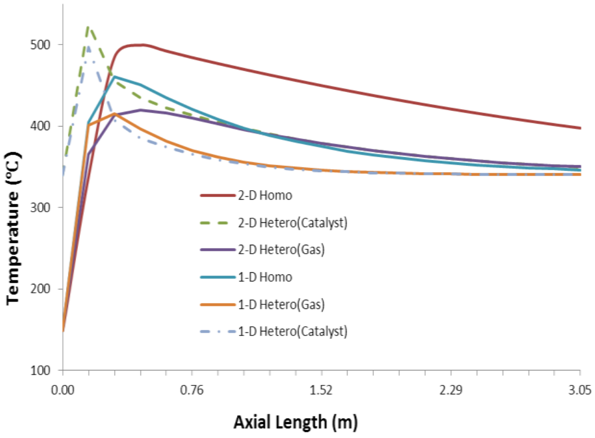

Figure 3. Temperature profiles (averaged over tube radius for 2D model) vs. tube length predicted by various models at consistent input conditions

This higher initial catalyst hot spot should be the main reason for thermal overheating and possible runaway conditions. This overheating situation gets worse when feed reactant A concentration increases and results in lower overall reactant conversions as shown in Figure 4.

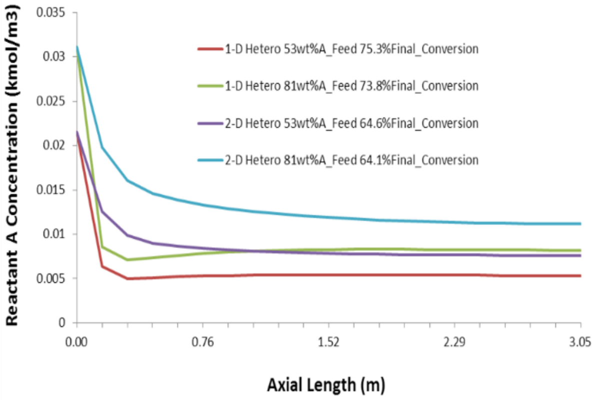

Figure 4. Reactant A concentration profiles (averaged over tube radius for 2D model) vs. tube length predicted by the heterogeneous models at two feed concentrations

One can see clearly that higher initial catalyst temperature profile predicted by the 2D heterogeneous model or brought about by the higher feed concentration leads to lower conversions. These lower conversion numbers happen to agree very well with those from other heterogeneous pseudo-1D models which use certain radial correction factor to approximate heterogeneous 2D models.

Because the 1D model underpredicts radial heat transfer resistance than the corresponding 2D model, one can image that the predicted temperature difference would have been smaller if tube diameter is smaller and heat transfer pass length is reduced. Figure 5 shows that the 1D model temperature profile is approaching that of a 2D model when tube diameter is smaller and gas superficial velocity is higher. As the tube diameter approaching zero, the 2D model reduces to the 1D model where boundary resistance is the only radial heat transfer resistance.

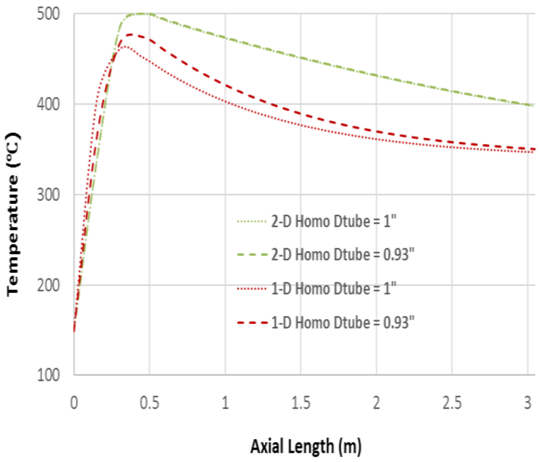

Figure 5. Comparison of predicted 1D temperature and 2D center temperature at two tube diameter sizes

Comparisons between the centerline (highest) catalyst temperature and radial averaged catalyst temperature can be made to visualize parameter sensibilities to temperature predictions, as shown in Figure 6 and Figure 7 indicating minimized cross temperature difference with increased gas catalyst heat transfer coefficient.

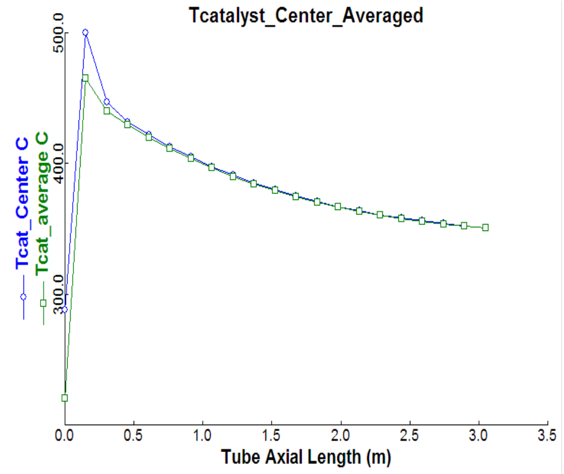

Figure 6. Tube centerline and averaged temperature profiles along the tubes when gas catalyst heat transfer coefficient is 100 btu/hr/ft2/°F

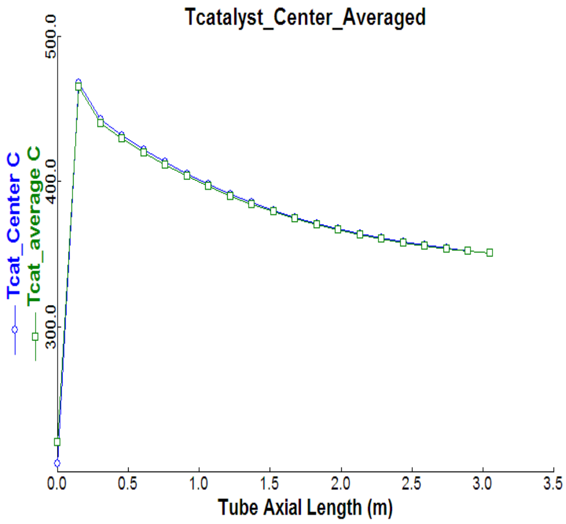

*Figure 7. Tube centerline and averaged temperature profiles along the tubes when gas catalyst heat transfer coefficient is 170 btu/hr/ft2/°*F

Tube radial heat transfer in a multi-tubular reactor has been studied extensively by Bauer and Schlunder (1978), Dixon and Cresswell (1979), Dixon (1985, 1988), Specchia et al. (1980), Yagi and Wakao (1959), Li and Finlayson (1977), De Wash and Froment (1972), Martin and Niles (1993), Borkink (1991), Winterberg et al. (2000) and Kunii and Smith (1960). Besides interactions between the different mechanisms of transport there are also strong interactions between reaction and transport. Averaged reaction rate across radius of tube is not equal to reaction rate calculated from averaged temperature across radius of the tubes, i.e.

$$Rate(\overline{T_k}) \neq \overline{Rate(T_k)} \qquad (14)$$

where there are k discretization points along the tube radius. Comparing to the 2D model, the 1D model calculating rates from radial averaged temperature would not predict reaction rate accurately. Improved 1D models such as the α model and the δ model use correction factors calculated from reduced 2D equation to correct the simple 1D model and their predictions have improved significantly. The improved 1D model predictions approach closer to those of the 2D models.

Case Study II – System Transient Behavior

Dynamic studies were carried out starting from a stable steady state such as the one with parameters listed in Table 1. It is interesting to learn the dynamic behavior of the catalyst temperature profiles inside the tubes when process conditions changes since catalyst pellets were found to be the possible hot spot near the entrance. Figure 8 shows catalyst temperature responses to a step increase in feed gas temperature from 110 to 150 ℃ and it is apparent that alterations of catalyst temperature are mainly in the front entrance region.

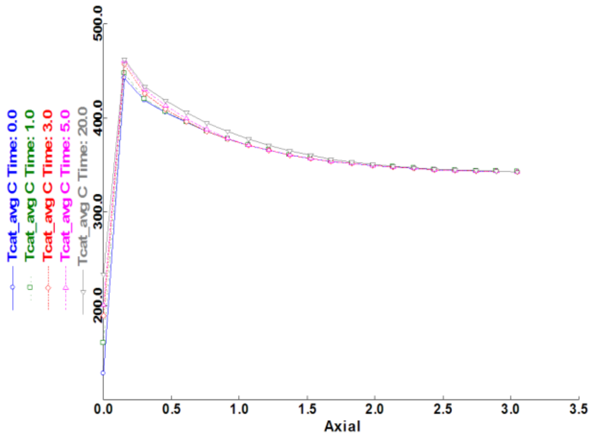

Figure 8. Transient catalyst temperature rises near the front tube entrance as feed temperature increases from 110 to 150 ℃ (At 20 seconds it is close to equilibrium)

Further disturbance in feed temperature could create dramatic changes where catalyst near the tube entrance gets overheated to extreme temperatures shown in Figure 9.

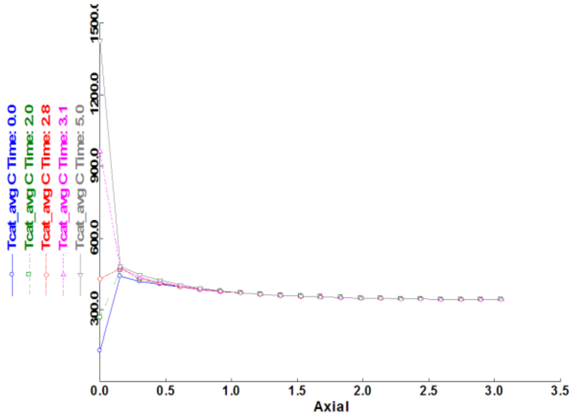

Figure 9. Potential run away condition: catalyst temperature near tube entrance rises sharply as feed temperature increases from 110 to 200 ℃

This transient phenomena is related to the nature of kinetic relationships for initial reaction and heat release. It also depends on reactor initial conditions and how different these initial values are from the feed conditions. The relatively fast and exothermic forward reactions maybe responsible for this behavior under these conditions. The reverse reaction, on the other hand, can not catch up fast enough at the entrance of the reactor if initial rates are too high caused by the high feed temperature.

Case Study III – Prediction of Product Precipitation

Radially cooled multi-tubular reactor system has intensified heat transfer and shifted some of the cooling from inter-stage coolers to the reactor. The inter-stage cooler has advantage in handling condensation and removal of the product and shifting the equilibrium forward by incorporating separation devices in the cooler. In a MTR the heating partially relieved the reaction moves forward and forms more product which increases its chance to precipitate out on the catalyst surface due to simultaneously increased concentration and reduced temperature within a single tube pass.

Another complication is that reaction kinetics was developed for short multi-bed adiabatic reactor systems where frequent inter-stage cooling narrows down product formation temperature range and frequent product removal keeps the product concentration low so identification of the form of dilute product can be more straightforward. Therefore, the kinetics developed uses single form of product in all its possible allotropic forms described in equation (15) because single form is predominating under certain reaction conditions:

$$P_{n1} \xrightleftharpoons[Exothermic]{Endothermic} P_{n2} \xrightleftharpoons[Exothermic]{Endothermic} \dots \xrightleftharpoons[Exothermic]{Endothermic} P_{ni} \dots P_{nn} \qquad (15)$$

where P_{n1} is a higher molecular weight allotropic form than P_{n2} and so on. At higher total concentration and lower tube side temperature the product could exist in several forms of P_{ni} which makes the existing kinetics equations more difficult to use. True product species distribution is determined by solving thermodynamic phase equilibrium among all species present and product chemical equilibrium (such as equation(15)) simultaneously. Constant process condition changes along the tube axial positions dictates that both total concentration and distribution of product forms are constantly changing, which requires simultaneous solution of chemical equilibrium, phase equilibrium and reaction kinetic equations. This would require much more information on system thermodynamic and chemical equilibrium parameters due to the increased number of allotropic species of the reaction product and kinetics needs to be revamped to use true product species. Very often speed of kinetics development lags behind process synthesis and design so a hybrid method was used here for a possible work around.

Total concentration of the all the allotropic species present at any axial location can be converted into a equivalent concentration of the representative allotropic compound which can then be used in the previously developed reaction kinetic equations. The kinetically calculated representative product concentration is then allowed to flash based on chemical and phase equilibrium so that realistic distribution of the species and approximate product dew point can be predicted at any point of the tube axial position. Verification of the allotropic product species concentrations are shown in Figure 10. TotalPnn represents equivalent concentration of species Pnn converted from the molar equivalent summation of all product concentrations. And it was used in the kinetic equations to represent equivalent total product concentration. From the calculated curves in Figure 10 it is clear that even though there are minor differences between the individual species values predicted by kinetics and chemical equilibrium due to the calculations were not entirely simultaneous, the approximation of total product formed in kinetic equations should still be a satisfactory one.

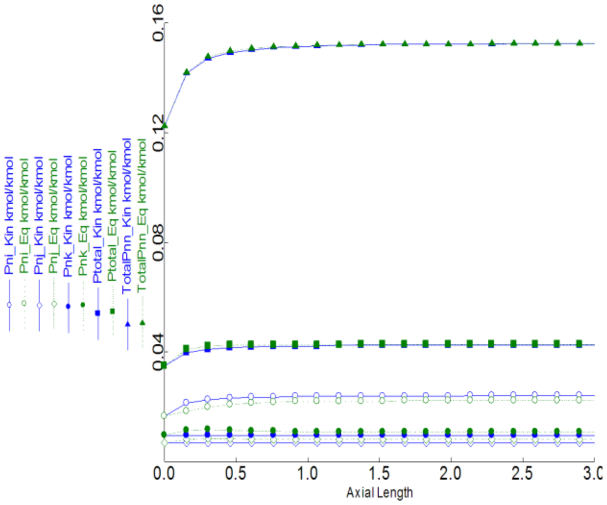

Figure 10. Individual and total molar fractions of main product allotropic species present in the kinetic reaction system and in the equilibrium flashes in situ

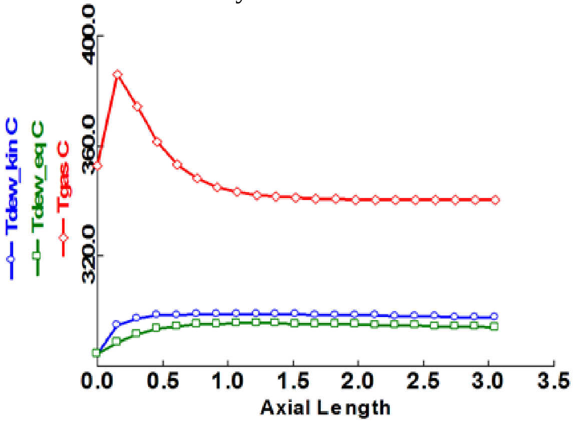

Figure 11. demonstration of the slight differences in terms of product dew point predictions compared to gas phase temperature in reactor tubes

Predictions on product dew point in gas mixture can be made once pressure and true species concentrations are known in tube axial locations. For the same reason this equilibrium based calculation will predict slight different results at each axial tube location due to the approximation of true species distribution by chemical equilibrium flash in situ. Figure 11 compares the predicted dew point values to gas phase temperature in reactor tubes. Dew point profiles predicted by this hybrid method are close enough to the ones predicted by the concentrations calculated by in situ flash and in this case both predicted dew points are within a safe distance below the reactor gas temperature.

Conclusions

Compared to the cascaded adiabatic beds with inter-stage coolers technology, the multi-tubular catalytic reactor system attempts to accomplish both reaction and heat transfer effectively within single piece of equipment, it could intensify exothermic reactions by simplifying the flowsheet and potentially reduce costs. Analysis of such system for control requires rigorous process modeling using two-dimensional heterogeneous models that brings in all important process mechanisms and parameters affecting reactor operations. The 1D models over-predict the radial heat transfer rate and pseudo-homogeneous models do not account the large temperature difference between the phases under most process conditions. For the reversible gas phase reaction studied, hot spots are located in catalyst pellets near the tube entrance and it could lead to run away conditions if feed gas temperature is increased suddenly. Due to increased product concentration and reduced temperature in gas phase proper predicting of dew point and controlling process conditions to avoid product precipitation and catalyst deactivation is critically important in operations of such systems. Reconciliation between chemical kinetics, chemical and phase equilibrium is essential in predicting condensation conditions.

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