REACTOR MODELING AND SIMULATION FOR INTENSIFYING THE PROPYLENE PRODUCTION IN A PETROCHEMICAL PLANT

S. Y. Chin[1], A. Hisyam[2], N. S. Che Din[3], H. Prasetiawan[4],
A. Azahari[5] and I. H. Maharon[6]

[1,2,3,4]Faculty of Chemical and Natural Resources Engineering,
Universiti Malaysia Pahang, LebuhrayaTunRazak, Gambang, 26300 Kuantan,
Pahang, Malaysia
[5,6]Petronas Chemicals MTBE SdnBhd
Lot 111 & 112, Gebeng Industrial Estate, PO Box 1, Balok, 26080 Kuantan,
Pahang, Malaysia.

chin@ump.edu.my, ahisyam@ump.edu.my, norulshahida@yahoo.com,
haniifprasetiawan@yahoo.com,abdullah.azahari@petronas.com.my,ikmalhisham_maharom@petronas.com.my

ABSTRACT: In a business environment where the future feedstock is gradually decreasing, a petrochemical plant needs to look into innovative ways of increasing their yields with minimal increase in the feed volume and capital investment. To date, most of the propane dehydrogenation plants have been operating the reactor as a black box and optimization was performed based on feedback from licensor as well as trial and error. Therefore, knowledge in reactor and kinetic modeling is needed to introduce a new level of understanding to the catalytic step in the plant for the optimization purposes. In the present work, the dehydrogenation of propane to propylene in adiabatic radial-flow moving bed reactor was studied. Several meetings and industrial lecture sessions were conductedto exchange information required for the reactor modeling and simulation. Rate expressions developed from lab scale reactor were considered for the main reaction, side reactions and deactivation kinetics, incorporating the reversibility of dehydrogenation reaction. The model was solved numerically by dividing the reactor into differential isothermal moving-bed reactors. The kinetic parameters were fine-tuned and the reactor model was validated using the plant data obtained at different operating parameters. The conversion of propane to propylene was found to be equilibrium limited in commercial-sized reactors. The model predicted the trends of the reactor performance in terms of conversion, yield, temperature, and catalyst activity. The graphical user interface was developed to simplify the future usage of the model by the plant personnel. The accuracy of the developed model requires further refinement before it is used for optimization purposes.

Keywords: dehydrogenation, propylene, reactor model, simulation, process intensification

INTRODUCTION

Propylene is one of the most important intermediate products in petrochemical industries. Plotkin (2005) stated that the propylene demand has grown rapidly in the last 10 years which is more than 60% is consumed by production of polypropylene. Since the propylene production changed from by-production into on-purpose production, propane become the main feedstock to produce propylene. This fact become a dilemmatic problem for industries, propylene demand is growing in one side but propane as the feed stocks will gradually decrease.

In view of this problem, industries have to find a way to optimize the process in order to increase the yield of the product with minimal increase in feed volume and capital investment. Mathematical modelling and simulation for the plant, especially for the reactor unit is essential to be carried out for the aforementioned purpose.

In the present work, modelling and simulation of the dehydrogenation of propane to propylene in an adiabatic moving bed reactor are carried out. An reactor model incorporated with kinetic model and thermodynamic model is developed. The model is validated with the plant data.

LITERATURE REVIEW

Propane dehydrogenation reaction although is simple in stoichiometric point of view (as shown in Equation 1), but it is very complex because of its' strongly endothermic nature and significant conversion limitations caused by thermodynamic equilibrium. Therefore higher temperatures are required to achieve acceptable conversion (Heinritz et al.,2008). Unfortunately, this condition also promotes several side reactions which reducing the yield. These reactions include oligomerization to heavier compounds, cracking to lighter hydrocarbons, skeletal isomerization, aromatization, alkylation of the formed aromatic rings, eventually leading to coke formation. (Sanfilipoo et al., 2006).

$$C_3H_8 \rightleftarrows C_3H_6 + H_2, \quad \Delta H_{298} = +129 \, kJ/mol \tag{1}$$
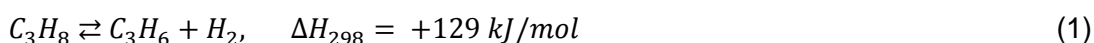
A number of propane dehydrogenation commercial processes have been developed. These processes differ in terms of the catalyst, reactor type and catalyst regeneration system.UOP Oleflex dehydrogenation process is catalysed by modified Pt alumina-supported catalyst in an adiabatic moving-bed reactorswith continuous catalyst regeneration (CCR) (Buonomo et al., 1997; Sahebdelfar et al., 2011; Sanfilippo et al., 2006). The gas flows from the bottom of reactor is then distributed equally by plug distributor to the horizontal direction. Meanwhile, the catalyst moves down towards catalyst collector and is then transferred to next reactor by lift engager. The catalyst leaves the last reactor is sent to the CCR unit, where the coked catalysts are regenerated(Chaiyavech, 2002). The schematic representation of moving bed reactor can be seen in Figure 1.
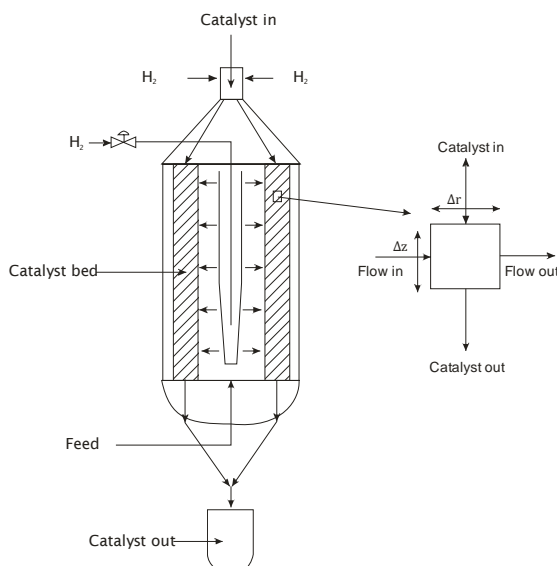

Figure 1. UOP Oleflex Moving Bed Reactor

Moving bed reactor is also used in production of isobutene. Sahebdelfar et al. (year) has developed mathematical modelling for moving bed reactor in isobutane dehydrogenation process. The model accuracy was validated by

comparing to industrial data with an error for conversion and activity catalyst are 0.2555% and 0.8567% correspondingly. The mathematical model of moving bed reactor for isobutene dehydrogenation can be adopted for propane dehydrogenation process since the same equipment is used. Simulation of propane dehydrogenation process using in-house software was reported by Chin et al. (2011). Several side reactions such as cracking, aromatization and hydrogenolisis were considered in the simulation (Chin et al., 2011). Catalyst activity in each reactor was assumed to be constant.Among the kinetic models studied, plug flow reactor model incorporated with the kinetic developed by Loc et al. (1996) wasrobust to predict the changes in composition when there were changes in the operating conditions. To date, an accurate moving bed reactor model for propane dehydrogenationis yet to be developed for process optimisation.

METHODOLOGY

Simulation of Moving Bed Reactor is carried out using MATLAB platform by translating the required equations into MATLAB code. These equations include the reactor model, thermodynamic model, kinetics for the main reaction, side reaction and deactivation. Equation 2shows the rate of reaction for main reaction of propane dehydrogenation:

$$r_1 = -k_1 * \frac{\left(P_{C3} - \left(\frac{P_{=C3}*P_{H2}}{K_1}\right)\right)}{(1 + K_e P_e)} ; mol/kg.h \tag{2}$$

whereK_e is the equilibrium constant for propane dehydrogenation:

$$K_e = 1.33e5 * exp\left(\frac{-86058}{RT}\right) ; bar^{-1} \tag{3}$$

andk_1 and K_1 is:

$$k_1 = 388 * exp\left(\frac{-68824}{RT}\right) ; mol/kg.min.bar \tag{4}$$

$$K_1 = 8.49e8 * exp\left(\frac{-118765}{RT}\right) ; bar^{-1} \tag{5}$$

In addition to propane dehydrogenation, the side reaction considered is the cracking propane to methane and ethylene.

$$C_3H_8 \rightarrow C_2H_4 + CH_4 \tag{6}$$

The cracking rate is assumed to be first order with respect to propane,

$$r_2 = -k_2 * P_{C3} \tag{7}$$

wherek_2 is :

$$k_2 = 688 * exp\left(\frac{-116531,81}{RT}\right) ; mol/kg.min.bar \tag{8}$$

Governing equation for discretization of bed catalyst, activity of catalyst, energy balance and propane conversion is shown in equation 9 – 12.

$$\Delta W_{i,j} = W \Delta r \Delta z \left(\frac{2R_1 + (2i-1)\Delta r}{h(R_2^2 - R_1^2)}\right) \tag{9}$$

$$a_{i,j+1} = a_{i,j} - \frac{k_d a_{i,j} W}{n U_s} \tag{10}$$

$$T_{i+1,j} = T_{i,j} + \Delta W_{i,j} \left[\frac{r'_A (\Delta H_{Rx})}{\sum F_i C p_i} \right]_{i,j} \qquad (11)$$

$$X_{i+1,j} = X_{i,j} + \Delta W_{i,j} \left[\frac{-r'_A}{F_{A_0}} \right]_{i,j} \qquad (12)$$

where, W is weight of catalyst in reactor, R_1 and R_2 are reactor bed inner radius and outer radius respectively, and h is the reactor bed height. The subscripts i and j refer to the element numbers in r and z direction respectively, and n is the number of axial steps.
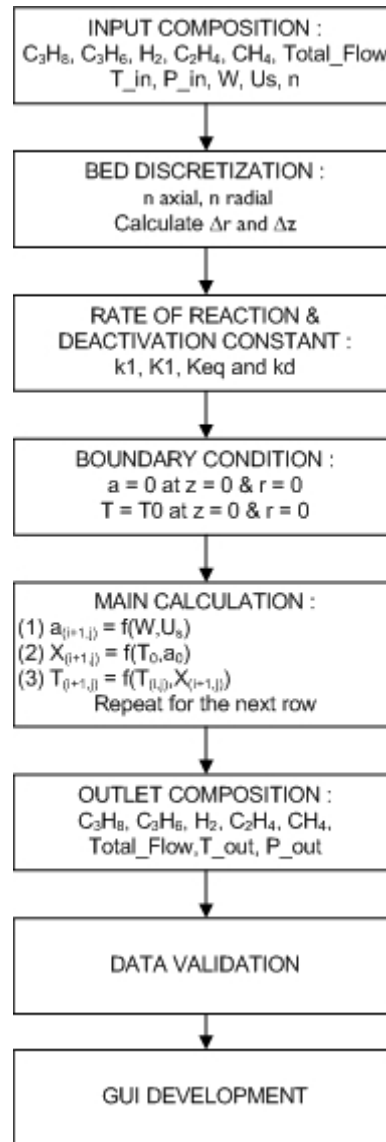

Figure 2. Steps involved during the Modelling and Simulation of the Moving Bed Reactor in MATLAB

The boundary conditions for propane conversion and temperature are those of the feed entering the bed at the inner wall. The boundary conditions for catalyst activity are $a = 1$ at $z = 0$ for the first reactor and the activity of the catalyst leaving the previous reactor at $z = 0$ for the next three reactors.

Equation (9) was calculated first to divide the reactor bed into small increment volume. The conversion in radial direction was calculated by considering

each ring as an isothermal reactor at input temperature. The next ring temperature calculated using incremental conversion and energy balance in equation (11). In the end of calculation of the first row, temperature profile in the first row and activity of catalyst in second row were obtained. The procedure then repeated until the lowest row. The conversion of propane and temperature profile along the radius of reactor can be plotted in a graph. Graphical User Interface (GUI) was developed in MATLAB to make the moving bed reactor calculation easier to modify the input information. The steps involved in modelling and simulation of moving bed reactor is shown in Figure 2.

RESULTS AND DISCUSSION

A. Catalyst Deactivation

Catalyst deactivation in moving bed reactor depends on the catalyst weight (W) and the catalyst flow rate (U_s) through the reactor. The U_s for each reactor is the same, its value between 400 – 500 kg/hr and the total catalyst transferred is around 10.000 to 20.000 kg. The predicted catalyst activity profile inside the reactor along the axial and radial direction of the first reactor is shown in Figure 3.

The catalyst activity declines in the radial direction. The dehydrogenation process and its side reactions mostly occur in inner diameter of the reactor as the gas flows horizontally across the catalyst bed from inner diameter to outer diameter. The coke is possibly produced in outer diameter of the reactor because product from side reaction such methane is cracked to carbon and hydrogen.
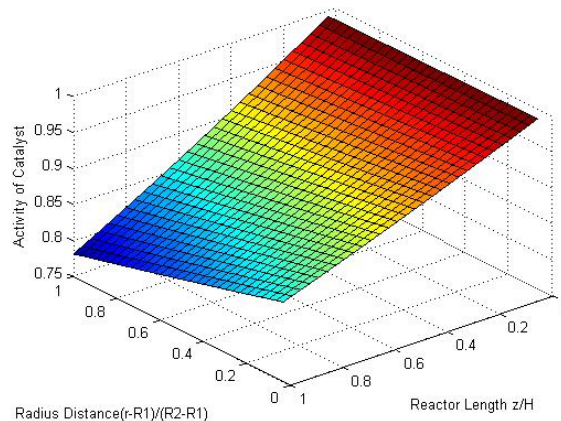

Figure 3. Catalyst Activity in the First Reactor as a Function of Axial and Radial Distances

Catalyst activity also decreases in the axial distance. This is attributed to the reactant downward flow direction. The catalyst from the top feeder will be used in propane dehydrogenation process continuously until reach the bottom of the reactor. The activities of the catalyst leaving reactors 1, 2, 3 and 4 are 0.82, 0.67, 0.56 and 0.47, respectively. The catalyst activity profiles for other reactors are shown in Figures 4.
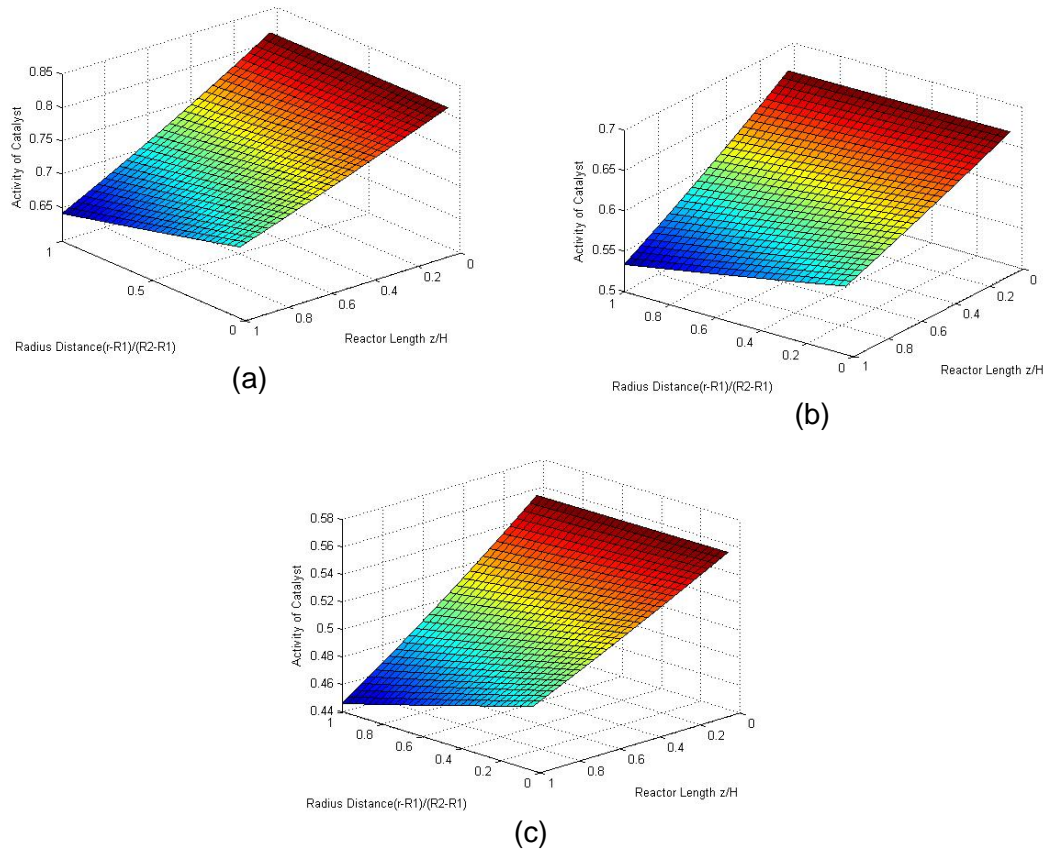
(a)

(b)

(c)

Figure 4. Catalyst Activity as The Function of Axial and Radial Distances In The (a) Second Reactor (b) Third Reactor and (c) Fourth Reactor

B. Conversion of Propane

Figure 5 shows the propane conversion profile in the axial and radial distances in the first reactor. Conversion increases significantly in radial directionbecause the reactants flow radially. On the other hand, propane conversion increases slightly along the axial direction. The conversion at the outer wall is constant in axial direction because it reached the equilibrium conversion. As stated in several literature, the propane total conversion presented in this paper is 34.18% (Heinritz et al, 2008). The propane conversion profiles for 2nd, 3rd, and 4th reactors are shown in Figure 6. Similar trends are found in these profiles.
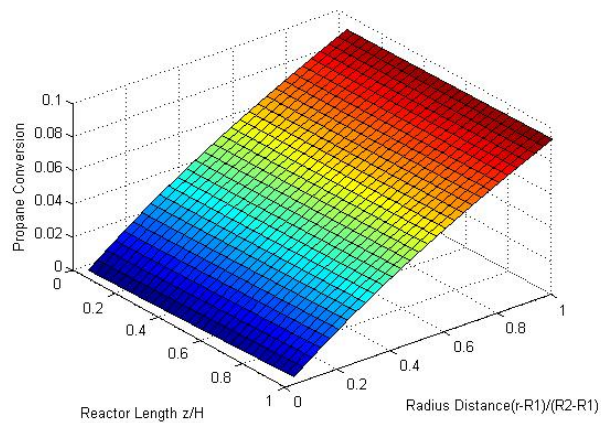

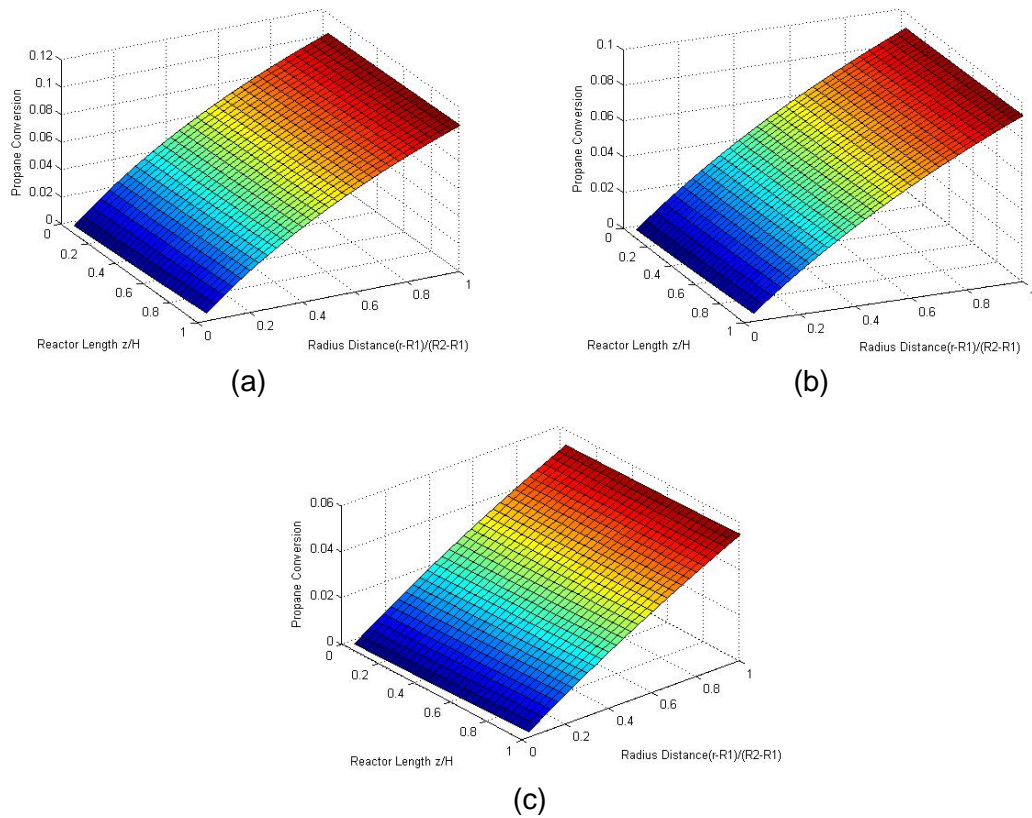Figure 5.Conversion of Propane in the First Reactor as a Function of Axial and Radial Direction.

Figure 6.Propane conversion profile as a function of axial and radial distances in the (a) second reactor (b) third reactor and (c) fourth reactor.

C. Temperature Profile

Figure 7 shows the temperature profile at different bed depth and radial distance. The temperature profile in radial direction declines along the direction of flow due to the endothermic reaction. Temperatures at the outer and inner wall decrease slightly along the axial direction as shown in Figure 8, the temperature difference between inner wall and outer wall drops along the axial direction due to the catalyst decay occurred as the catalyst flows along this direction.
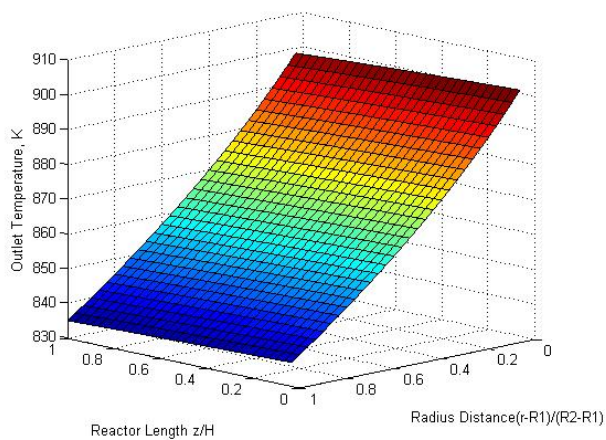

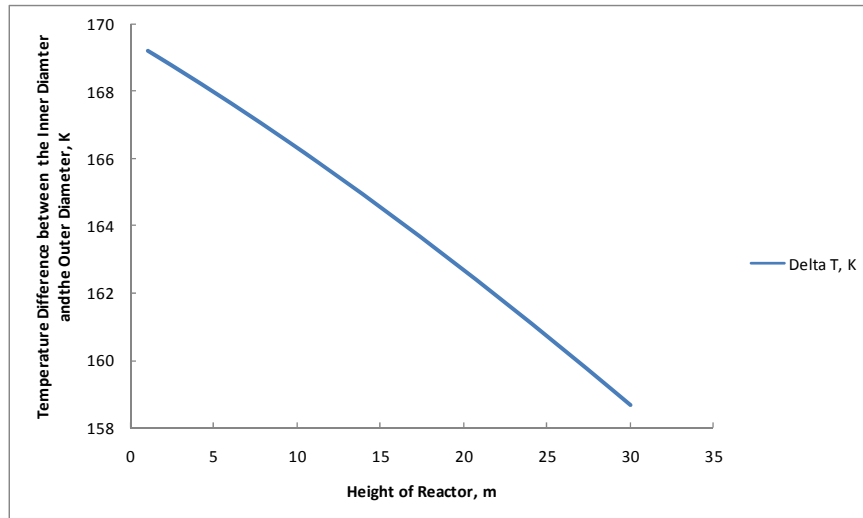Figure 7.Temperature in the First Reactor as the Function of Radial and Axial Distances.

Figure 8. Temperature Differences between the Inner Diameter and Outer Diameter as a Function of Axial Direction

D. Data Validation

In order to simplify the usage of the moving bed reactor model, a user interface is developed using MATLAB GUI. Input composition and another required information such temperature, pressure, catalyst flow rate can be easily changed. The graphical user interface is shown in Figure 9.
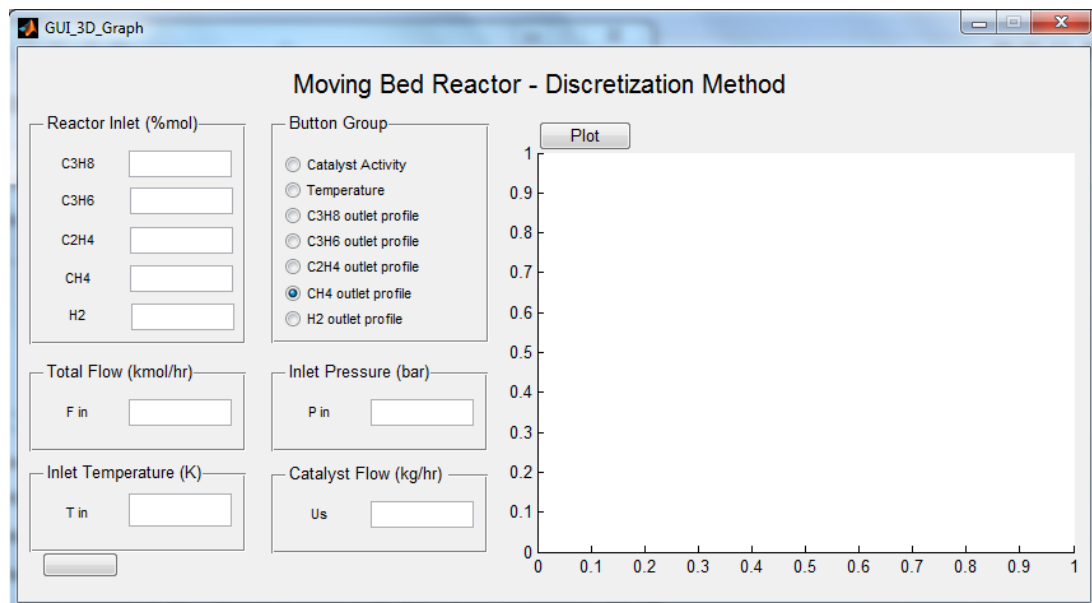

Figure 9. Graphical User Interface for Moving Bed Reactor Simulation

The simulation results are validated with the 4 different set of plant data. Figure 9 presents the parity plots for the outlet compositions of propane, propylene and hydrogen. The difference between experimental results and model estimation is within 20%. The average error for propane, propylene, and hydrogen outlet compositions are 6.14%, 5.95% and 6.93% respectively.
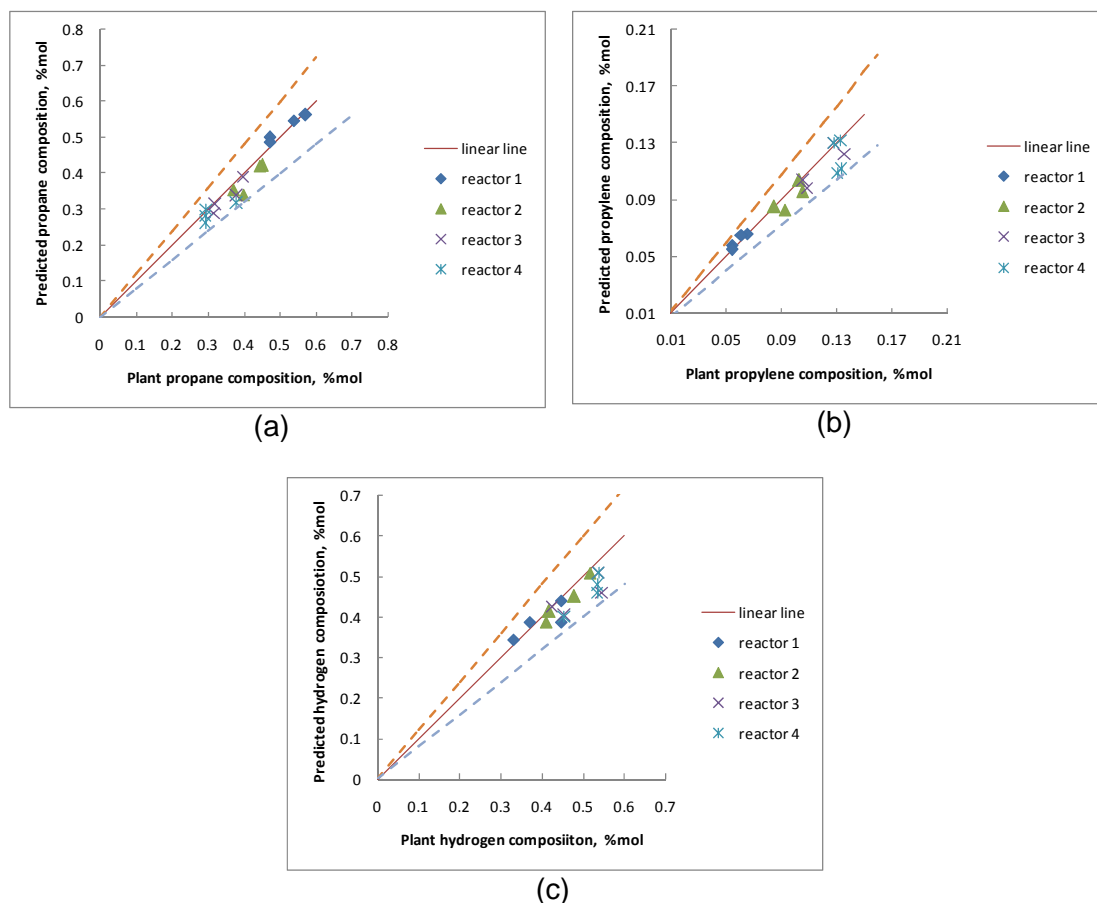
(a)

(b)

(c)

Figure 9. Correlation between Plant Data and Model Prediction for Propane, Propylene and Hydrogen Outlet Composition

SUMMARY

In this study, model of moving bed reactor has been validated with the plant data. A reaction kinetic model also included propane cracking as side reaction and catalyst deactivation are established. The discretization method is used to get more accurate calculation for the propane dehydrogenation process. This method resulted an average error 6.14%, 5.95% and 6.93% for propane, propylene, and hydrogen outlet composition respectively. A graphical user interface also have been developed to simplify the usage of moving bed reactor model.

ACKNOWLEDGEMENTS

REFERENCES

Buonomo, F.,Sanfilippo and D.,Trifiro, F. (1997)in :Ertl, G.,Knoezinger, H.,Weitkamp, J. (eds.).Handbook of Heterogeneous, 4, Wiley-VCH, Weinheim.

Chaiyavech, P. (2002). Commercialization of the world's first oleflex unit. The Journal of The Royal Institute of Thailand. Vol. 27 (3).

Chin S. Y., Radzi, S. N. R., Maharon, I. H. and Shafawi, M. A. (2011). Kinetic model and simulation analysis for propane dehydrogenation in an industrial moving bed reactor. World Academy of Science, Engineering and Technology. Vol. 52(2011). pp. 183 – 189.

Heinritz-Adrian, M., Wenzel, S. andYoussef, F. (2008).Advanced propanedehydrogenation.Petroleum Technology Quarterly.PTQ Q1 2008.p.84.

Li, Q., Sui, Z., Zhou, X. and Chen, D. (2011).Kinetics of propane dehydrogenation over Pt-Sn/Al_2O_3 catalyst.applied Catalysis A: General. Vol. 398 (2011), pp. 18 – 26.

Plotkin, J. S. (2005). The changing dynamics of olefin supply/demand. Catalysis Today. Vol. 106 (2005), pp. 10 – 14.

Proven on-purpose and by-product solutions.(2013). Retrieve June 19 2013. http://www.uop.com/processing-solutions/petrochemicals/olefins/#propylene.

Sahebdelfar, S., Bijani, P. M., Saeedizad, M., Zangeneh, F. T. and Ganji, K. (2011).Modeling of adiabatic moving-bed reactor for dehydrogenation of isobutene to isobutene. Applied Catalysis A: General. Vol. 395 (2011), pp. 107 – 113.

Sanfilippo, D. and Miracca, I. (2005). Dehydrogenation of paraffins : synergies between catalyst design and reactor engineering. Catalysis Today. Vol. 111 (2006), pp. 133 – 139.