

## Computer-Aided Design of Industrial Catalytic Reactor

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### ABSTRACT

This research attempt to develop computer program used to monitor the complex series-parallel reaction process for the upgrading of 100 percent naphtha-lump feed in reactor design processes. The design equation developed, calculates the length of the tubular reactor required to obtain a specified conversion. The resulting solution yields the conversion profile, temperature profile and reactor residence-time as a function of tube length. The following functional parameter obtained; space-time, Space-velocity, length of the reactors, volume of the reactors, pressure effect and heat generated per unit volume of the reactors. Finally, the results obtained were benchmarked with industrial plant data, and they lies within the industrial model-constraints. Hence the design work meets the industrial reactor operating conditions.

**Keywords:** *Computer-Aided Design, Complex Series-Parallel Reactions, Plug-flow Reactor, Naphtha-lump feed.*

### 1. INTRODUCTION

Reactor and reaction engineering plays a vital role in petroleum and chemical processing industries. The purpose of this work is to acquaint the reader with the interaction between reactor design/selection and the characteristics of the chemical reaction of interest. Reactor selection and design are the basis of economical and safe operation.

Chemical reactions in petroleum refining include a huge spectrum of unique properties. This includes how the reactants are contacted, whether a catalyst is used, how much heat is evolved or absorbed, and how fast the reaction takes place (Taylor and Francis, 2006).

Commercial refineries represent huge investments in capital. Small errors in equipment design and sizing translates to millions of dollars in unnecessary expense. Hence, it is extremely important to do the best job possible on design, sizing, modeling and specifying reaction conditions for petroleum refining reactors (Robinson, 2009).

Catalyst reactions and reactors have a wide spread applications in the production of chemicals in bulk,

petroleum and petrochemicals, pharmaceuticals, specialty chemicals etc.

The simultaneous developments in catalysis and reaction engineering in 1930s and 1940s acted as a driving force for the onset of rational design of catalytic reactors. These rigorous design efforts, which firmly based on sound mathematical principles, in turn triggered the development of several profitable catalytic processes. In the mid 1940s, chemical reaction engineering developed into a separate branch of chemical engineering. Rapid expansion of petroleum and petrochemical based industries in 1950s and the 1960s fueled the growth of catalytic reactors. Denbigh proposed the concept of ideal reactors and explained the importance of reaction kinetics on reactor performance (Denbigh, and Tuner, 1984). Scholarly contributions from several eminent researchers like Denbigh, Danckwarts, Levenspiel, Honghen and Watson laid the foundation of catalytic reactor modeling. Several alternative reactor configurations were examined for conducting industrially important catalytic reactions.

### 2. MATERIALS AND METHOD

The following functional data were mathematically determined using appropriate computational procedure and bench-marked with industrial plant data.

**Table 3.1: Kinetic Parameters of Naphtha lumps feed**

Reactions	Activation energy (Ei ) kj/kmol	Pre-exponential constant (Ao)	Heat of reaction $\Delta H_R$ kg/kmol of H <sub>2</sub> liberated
Conversion of Naphthenes to Aromatics	174500	$1.19 \times 10^8$	70928

Conversion of Paraffins to Naphthenes	125408.4	$7.727 \times 10^8$	-44185
Conversion of Naphthenes to Paraffins	88743.64	$6.733 \times 10^5$	41185

Table 3.2: Volume of Catalyst

Reactors	Volume of catalyst (M <sup>3</sup> )
Reactor 1	16.40
Reactor 2	27.33
Reactor 3	65.60

Table 3.3: Catalyst Distribution in the 3 reactor

	Weight Of Catalyst (kg)	No of drums
R1	8,030	73
R2	15,40	140
R3	40,040	364

Table 3.5: Feed Characterization

Feed to reactor 1	
Feed component	Feed composition mol%
Paraffins	34.78%
Naphthenes	51.78%
Aromatics	13.44%

Table 3.6 Reactor Operating Parameters

Parameters	Value
Temperature of the reactor	543°C
Pressure of the reactor	928kpa
H <sub>2</sub> /HC molar recycle ratio	0.747
Molecular mass of feed Naphtha	0.284307kg/mol
Feed flow rate	167970kg/hr
Feed flow rate	590.81 kmol/kg
Feed density	766.6kg/m <sup>3</sup>
Volumetric flow rate	220m <sup>3</sup> /hr
Catalyst distribution in the 3 reactors	1:2:5
Dynamic viscosity	1.19Centipose

The principles of energy and material balance of process plant design were adopted to the functional depleting pathway of the following kinetic sequence as follows: Dehydrogenation, Hydrogenation, Isomerisation, Decyclisation and eventual HC cracking into C<sub>1</sub>, C<sub>2</sub>, C<sub>3</sub>, and C<sub>4</sub>. In a plug flow reactor design, reactants are fed to the reactor at the inlet and the products are removed from the reactor outlet. The reacting mixture is assumed to move as a plug and its properties are assumed to be uniformly distributed across the cross-section of the reactor maintaining the fundamental mass balance equation 3.1 below:

$$\left( \begin{matrix} \text{mass of A} \\ \text{entering} \\ \text{the volume } dv \\ \text{per unit time} \end{matrix} \right) = \left( \begin{matrix} \text{mass of A} \\ \text{leaving} \\ \text{the volume } dv \\ \text{per unit time} \end{matrix} \right) + \left( \begin{matrix} \text{mass of A} \\ \text{accumulated} \\ \text{within the volume } dv \\ \text{per unit time} \end{matrix} \right) + \left( \begin{matrix} \text{mass of A} \\ \text{disappearing} \\ \text{by reaction} \\ \text{within the volume} \\ \text{per unit time} \end{matrix} \right) \quad (3.1)$$

Equation 3.1 is mathematically transformed into equation 3.2 as,

$$F_A = (F_A + dF_A) + (-r_A)dv \quad (3.2)$$

Simplifying

$$F_{AO}dX_A = (-r_A)dv \quad (3.3)$$

Considering, catalyst weight

$$\frac{dX_i}{dW_1} = \frac{r_i}{F_{AO}} \quad (3.4)$$

Equation 3.4 is the required design equation for the computer-aided design of industrial catalytic reactor studies. It is therefore subjected to catalytic reforming which is a continuous cracking catalytic process carried out in the presence of platinum based catalyst at a pressure of 928KPa and temperature of 543°C.

## 2.1 Rate Law

The rate law follow power law on the rate of depletion or disappearance of feed component to form the product reformat through the reactions 1 to 4 in the reactor, maintaining first-order kinetics, constant catalyst activity and operating at steady-states process.

$$-r_1 = K_1 C_N - K_2 C_A P_{H_2}^3 \quad (3.5)$$

$$-r_2 = K_3 C_P - K_4 C_N P_{H_2} \quad (3.6)$$

$$-r_3 = K_5 C_N \quad (3.7)$$

$$-r_4 = K_6 C_P \quad (3.8)$$

Where  $K_{1-6}$  are the various rate constants for the individual reactions.

Thus in general:

$$K_i = A_0 \text{Exp} \left( \frac{-Ea}{RT} \right) \quad (3.38a)$$

## 2.2 Rate Controlling Step

In chemical kinetics, the rate or velocity of a reaction with several steps is often determined by the slowest step, known as the rate determining step (Zumdali, 2005).

Therefore a rate determining step is the step in a multi-step chemical reaction with the slowest rate of reaction. This step's rate will set the overall rate of reaction for the multi-step reactions. This step is mainly determined experimentally and it's being employed extensively in the real design of the relevant equipment necessary for such reaction process.

In catalytic reforming, the most important reaction is the transformation of the cychoalkane (Naphthene) into aromatics. It is a rapid reaction which approaches equilibrium in a very short time. Cycloalkane formation (i.e. paraffin isomerization) is the slowest step. Once this compound have being formed dehydrogenation to benzene, methyl benzenes (toluene) and dimethyl benzenes (xylene) is very rapid (Smith, 1959).

In the course of this design work, the principle of rate, controlling step, which is the dehydrocyclization reaction (paraffin isomerization) step, will be adopted for the real design since it is the slowest step.

From the design equation we have:

$$\frac{dX_i}{dW} = \frac{r_i}{F_{AO}} \quad (3.9)$$

Rearranging equation (3.9)

$$\frac{dW}{F_{AO}} = \frac{dX_i}{-r_i} \quad (3.10)$$

Integrating equation (3.10)

$$\frac{1}{F_{AO}} \int_0^W dW = \int_0^{X_{AF}} \frac{dX_i}{-r_i} \quad (3.11)$$

$$\frac{W}{F_{AO}} = \int_0^{X_{AF}} \frac{dX_i}{-r_i} \quad (3.12)$$

$$W = F_{AO} \int_0^{X_{AF}} \frac{dX_i}{-r_i} \quad (3.13)$$

But reactor volume is mainly the catalyst weight divided by the bulk of the catalyst density  $\rho_b$  thus,

$$V_R = \frac{W}{\rho_b} \quad (3.14)$$

Combining equation (3.13) and (3.14)

$$V_R = \frac{F_{AO}}{\rho_b} \int_0^{X_{AF}} \frac{dX_i}{-r_i} \quad (3.15)$$

For the paraffin isomerization

$$-r_2 = K_3 C_p - K_4 C_N P_{H_2} \quad (3.16)$$

In term of conversion

$$-r_2 = K_3 C_{p_0} (1-x) - K_4 C_{N_0} (1-x) P_{H_2} \quad (3.17)$$

From ideal gas equation

$$\frac{P_i}{RT} = C_i \quad (3.18)$$

Combining equation (3.17) and (3.18)

$$-r_2 = K_3 \frac{P_{PO}}{RT} (1-x) - K_4 \frac{P_{NO}}{RT} (1-x) P_{H_2} \quad (3.19)$$

But

$$P_i = P_T y_i \quad (3.20)$$

Combining equation (3.19) & (3.20)

$$-r_2 = K_3 \frac{P_T y_P}{RT} (1-x) - K_4 \frac{P_T y_N}{RT} (1-x) P_{H_2} \quad (3.21)$$

Putting equation (3.21) in to (3.15)

$$\frac{\pi D_R^2 L_R}{4} = \frac{F_{A0}}{\rho_b \left( \frac{K_3 P_T y_P}{RT} - K_4 \frac{P_T y_N P_{H_2}}{RT} \right)} \int_0^{X_{AF}} \frac{1}{(1-x)} dx \quad (3.24)$$

$$L_R = \frac{4 F_{A0}}{\pi D_R^2 \rho_b \left[ \frac{K_3 P_T y_P}{RT} - K_4 \frac{P_T y_N P_{H_2}}{RT} \right]} \int_0^{X_{AF}} \frac{1}{(1-x)} dx \quad (3.25)$$

Just as the reaction time  $t$  is the natural performance measure for a batch reactor so are the space-time and space velocity the proper performance measures of flow reactors: (Levenspiel, 2007).

These terms are defines as follows:

$$\tau = \frac{\frac{F_{AO}}{\rho \left( \frac{K_3 P_T Y_P}{RT} - K_4 \frac{P_T Y_N P_{H_2}}{RT} \right)} \int_0^{X_{AF}} \frac{1}{(1-x)} dx}{V_o} \quad (3.27)$$

Space velocity ( $S$ ) =  $\left( \begin{array}{l} \text{Number of reactor volume of feed at specified} \\ \text{conditions which can be treated in unit time} \end{array} \right)$

$$S = \frac{1}{\tau} \quad (3.28)$$

$$S = \frac{\left( \int_b \frac{F_{AO}}{\left( \frac{K_3 P_T Y_P}{RT} - K_4 \frac{P_T Y_N P_{H_2}}{RT} \right)} \int_0^{X_{AF}} \frac{1}{(1-x)} dx \right)^{-1}}{V_o} \quad (3.29)$$

$$V_R = \frac{F_{A0} \int_0^{X_{AF}} \frac{dx_i}{K_3 \frac{P_T y_P}{RT} (1-x) - K_4 \frac{P_T y_N}{RT} (1-x) P_{H_2}}} \quad (3.22)$$

The shape of the reactor is cylindrical in nature therefore equating the volume of the reactor to that of cylinder we have

$$V_R = \frac{\pi D_R^2 L_R}{4} \quad (3.23)$$

Combining equation (3.23) and (3.27)

space time ( $\tau$ ) =  $\left( \begin{array}{l} \text{time required to process one reactor} \\ \text{volume of feed measured at specified conditions} \end{array} \right)$

$$\tau = \frac{V_R}{V_o} \quad (3.26)$$

Combining equation (3.22) and (3.26)

**Holding Time** ( $t$ ) mean residence time of flowing material in the reactor.

For constant density systems (all liquids and constant density gases)

$$\tau = t \quad (3.30)$$

**Heat Generated Per Unit Volume of the Reactor** is the involvement of heat in the design of the reactor, and from operational of point view, heat generated along the plug flow reactor is a function of, Heat of reaction of the species, feed flow rate, conversion term

Mathematically stated as,

$$q = \frac{\left( \frac{-\Delta H_r F_{AO} X_i}{\rho_b \left( \frac{F_{AO}}{K_3 P_T Y_P - K_4 P_T Y_N P_{H2}} \right)} \int_0^{x_{Af}} \frac{1}{(1-x)} dx \right)}{RT} \quad (3.34)$$

### 2.3 Pressure Effects

Pressure is a determinant factor in reactor design. It is very important in characterizing the flow of reacting fluid in a reactor, particularly plug flow reactors.

Pressure drop is a function of:

- i. Frictional factor
- ii. Fluid density
- iii. Flow velocity
- iv. Kinetic rate data or variable
- v. Length of the reactor

Reactor diameter and hence, mathematically

$$\Delta P_R = \frac{f 2 \rho V^2 L_R}{g D_R} \quad (3.39)$$

Where

- $\Delta P_R$  = Pressure drop along the reactor length
- $V^2$  = Fluid velocity
- $D_R$  = Diameter of the reactor
- $L_R$  = Length of reactor

$$\Delta P_R = \frac{2f\rho V^2}{gD_R} \left( \frac{4F_{AO}}{\pi D_R^2 \rho_b \left( \frac{K_3 P_T Y_P - K_4 P_T Y_N P_{H2}}{RT} \right)} \int_0^{x_{Af}} \frac{1}{(1-x)} dx \right) \quad (3.42)$$

$$Q = (-\Delta H_r) F_{AO} X_i \quad (3.31)$$

By induction principle

$$q = \frac{Q}{V_R} = \frac{\Delta H_r F_{AO} X_i}{V_R} \quad (3.32)$$

$$q = \frac{\Delta H_r F_{AO} X_i}{V_R} \quad (3.33)$$

Equation (3.33) is the required heat generated per unit volume of the reactor. Combining equation 3.33 and 3.22

$f$  = Frictional factor

Interestingly  $f$  depends on the flow regime and obtain in reference literature. where,

$$f = \frac{0.4}{(\text{Re})^{0.16}} \quad (3.40)$$

*For flow through pipes*

$$R_e = \frac{QD_H}{VA} \quad (3.41)$$

Where:

- $D_H$  = hydraulic diameter of the pipe;
- $Q$  = Volumetric flow-rate ( $\text{m}^3/\text{s}$ )
- $A$  = Pipe cross sectional area ( $\text{m}^2$ )
- $V$  = Kinematic viscosity of the fluid

Combining equation 3.49 and 3.28

### 3. RESULTS AND DISCUSSION

The following figures 4.1, 4.2, 4.3, 4.4, 4.5, and 4.6 of results are presented and discussed accordingly

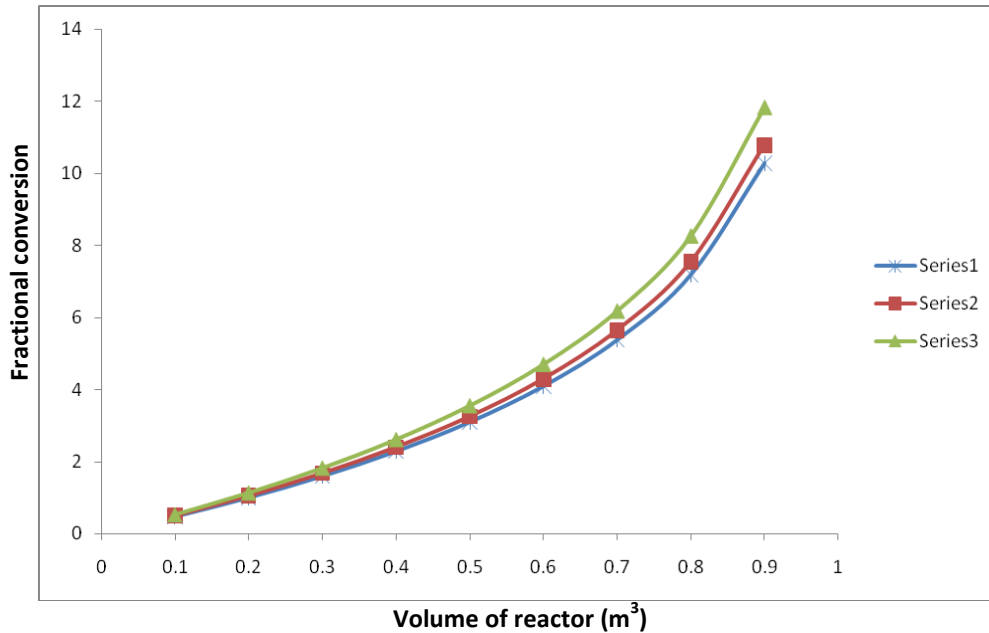


Figure 4.1: Plot of fractional conversion on volume of reactors

From the table of volume of reactors 1, 2, 3 against the fractional conversion, it shows that increase in the conversion of the naphtha feed brings about increase in the reactor volumes necessary for its reaction. The increasing volume in the different reactors depends on the catalyst loading in each of them, since the catalyst

distribution among the three different reactors incorporated to one are different. But in general observation, there is a general increase as the conversion increases, thus at 90% conversion which is the design conversion limit, we have the minimum size of the reactor that can give us realistic output.

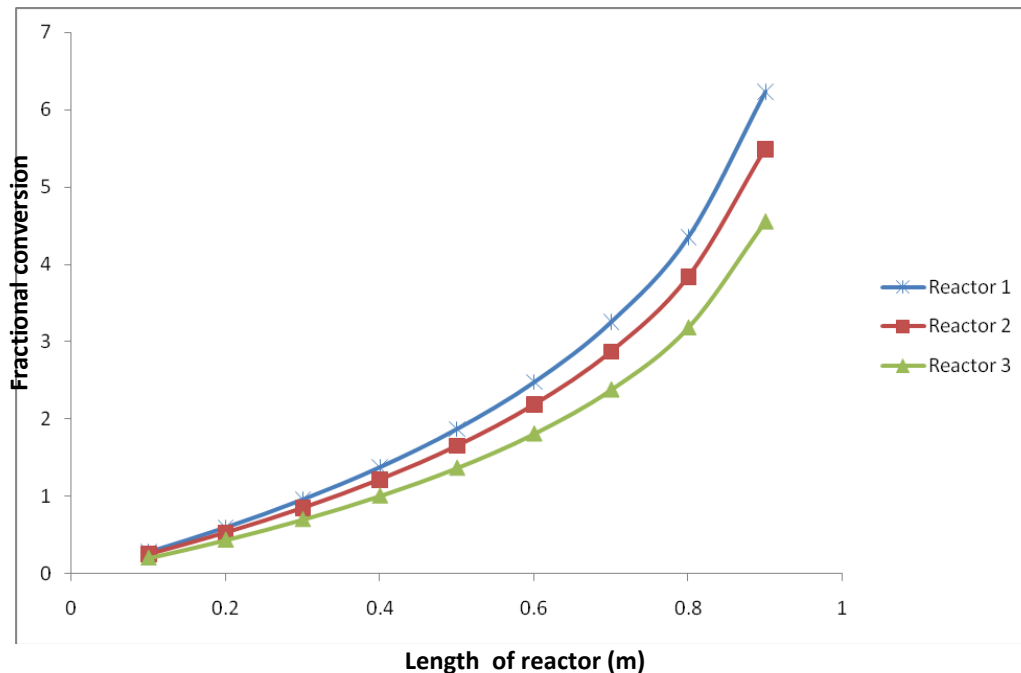


Fig 4.2: Plot of fractional conversion against length of reactors

From the table of length of reactors 1, 2, 3 against the fractional conversion, increase in the conversion of the reactant brings about increase in the length of the reactor required for its conversion. From observations the change in the length of the reactors in the three different reactors are different but very close, probably because of different

operating conditions such as catalyst loading and volume of the reactor. At about 90% conversion of the reactant we have 6.234m, 5.496m and 4.560m, respectively for the reactors 1, 2, 3, these design values represent the minimum size of reactor which at the give operating condition produces a realistic and expected product.

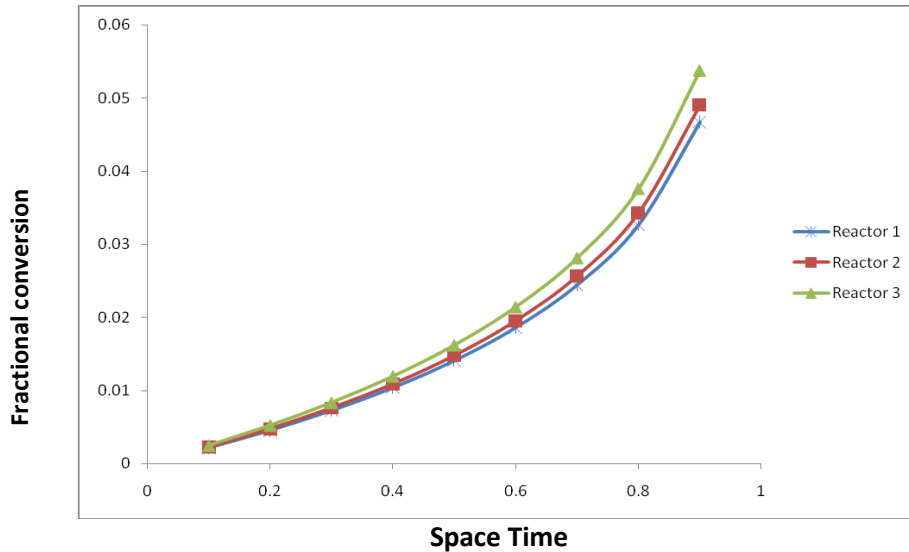


Fig 4.3: plot of fractional conversion against space time

Space time is the time necessary to process one reactor volume of feed given a particular set of entrance conditions. This parameter is obtained by dividing the reactor volume by the volumetric flow rate entering the reactor.

conversion of the naphtha feed brings about minimal increase in the space time of the three different reactors incorporated together as one unit, but the change in space time as a result of change in conversion are different because of the catalyst distribution within the three reactors, of course the reactor with the highest catalyst loading have the smallest space time.

From the table of space time against the fractional conversion of the feed component, increase in the

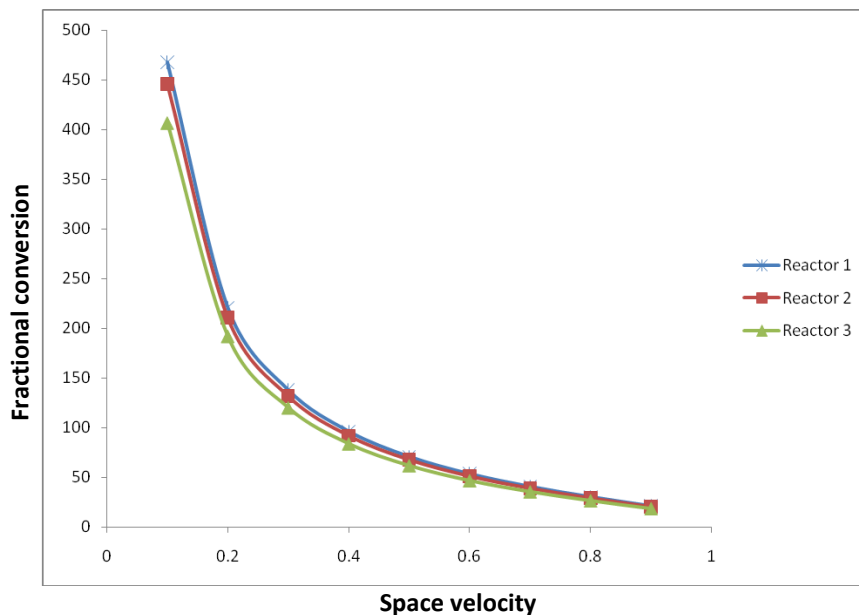


Fig 4.4: plot of fractional conversion against space time

Space velocity is the number of reactor volume of feed at specified conditions which can be treated in unit time. This parameter is a reciprocal of the space time. From the table of space velocity against the fractional conversion, increase in the conversion of the naphtha feed brings

about decrease in the space velocity in the three different reactors incorporated as one unit. This result complements the relationship between the space velocity and space time.

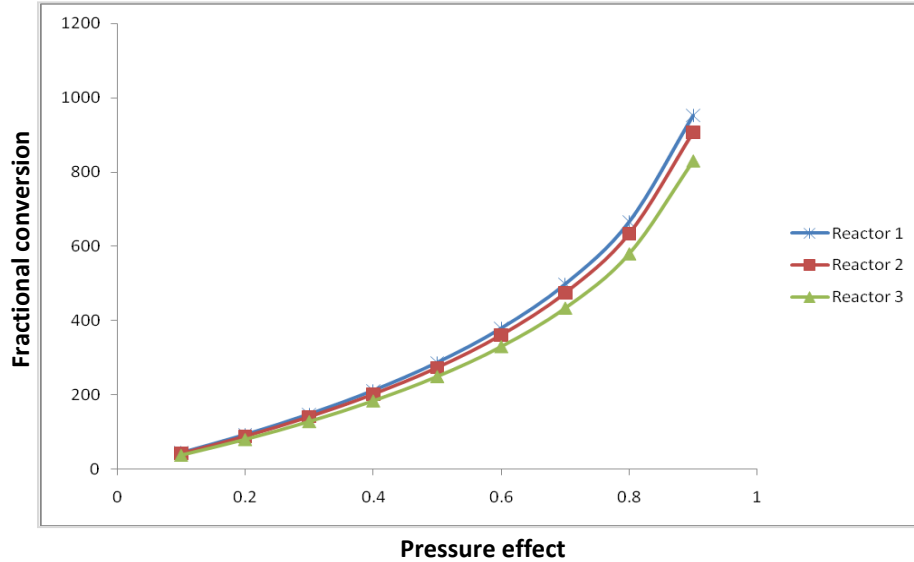


Fig 4.5: plot of fractional conversion against pressure effect on the system

From the table of result of pressure effect as a function of fractional conversion, it is seen clearly that generally the pressure generated within the three reactors increases as the fractional conversion is increasing, at about 90% conversion, the pressure effect within the reactors attains the design value. From the graph, it shows that the pressure effect depends on fractional conversion i.e the

amount of feed converted to product, it then means that at higher pressures, more of the reactant is being converted to product. Within the range of 10% to 40% conversions, the pressure effect was relatively infinitesimal, but a sharp response in pressure effect is being observed from 50% conversion and above.

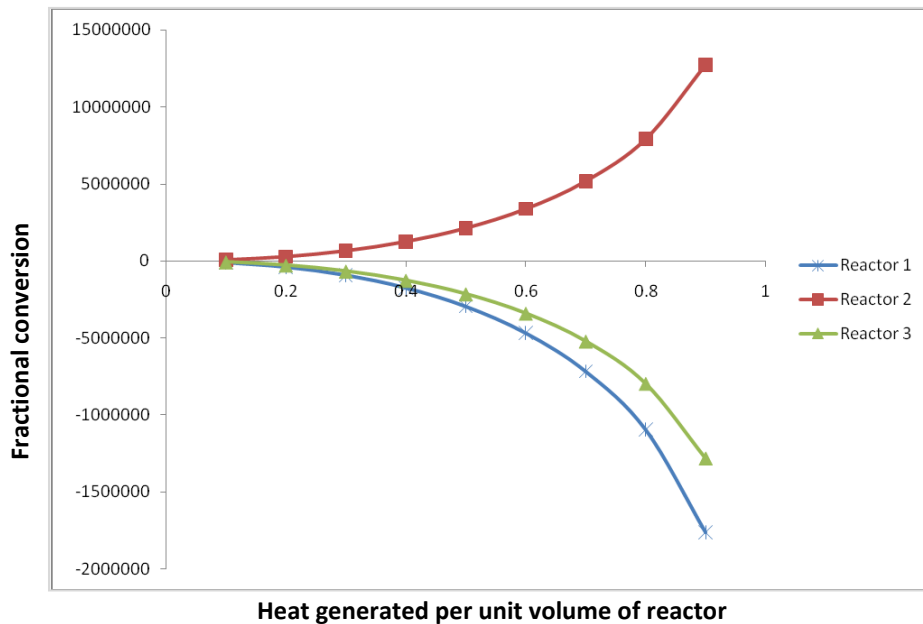


Fig 4.6: Plot of fractional conversion against heat generated per unit volume of reactors



From the table of results of heat generated by the reactors per unit volume of the reactor as a result of change in fractional conversion of the feed components, it will be clearly seen that reactor 1 and reactor 3 generated a negative heat effect and reactor 2 has a positive heat effect, these effects is a function of the chemical reactions taking place within the system. In the reactors 1 and 3, much heat is consumed resulting in a negative heat effect while in the reactor 2; heat is being generated resulting to a positive heat effect within the reactor. From the graph of heat effect as a result of fractional conversion, the graph show clearly that the level of heat generated or consumed depends so much on the level of feed conversions.

#### 4. CONCLUSION

Over the past two decades much progress has been made on the theory and practice of kinetic lumping, largely in response to increasingly stringent requirements for fuels/lubes quality, crude slate flexibility and reactor control and optimization. Several new approaches have been developed for constructing robust process designs used in petroleum refining. In certain areas, high

resolution designs have proved their worth by making molecular management reality.

The design of a typical catalytic has being carried out involving most of its key constituent units. Kinetic modeling of the reactions occurring in the bed of the reactors connected in series formed the most significant part of the overall simulation effort. A reactor for the reaction schemes involving about 2 pseudo-component connected together by a network of 4 reactions in the  $c_5$ - $c_{10}$  range has being designed considering the necessary operating conditions and parameters. The design method was parameterized by bench marking the kinetic model against plant data.

The research utilizes the fundamental principles of material component balance approach to formulate the required steady state design equations. The design parameters were analyzed and solved numerically with the help of mat-lab software.

The design result also showed that catalyst has a greater influence on the rate and speed of the reaction mechanism and equipment design in general.

#### NOMENCLATURES

$F_{AO}$	The molar flow rate of the feed at the inlet (moles/time)
$F_{AF}$	The molar flow rate of the feed at the exit (moles/time)
$V_0$	Volumetric flow rate at the inlet (volume per time)
$V_F$	Volumetric flow rate at the exit (volume per time)
$-r_A$	Rate of reaction of the feed
P	Paraffin hydrocarbon
N	Naphthene hydrocarbon
A	Aromatics hydrocarbon
$H_2$	Hydrogen
G	Hydrocarbon gases
$K_1$	Rate constant of forward reaction in the aromatization reaction
$K_2$	Rate constant of backward reaction in the formation of Naphthenes
$K_3$	Rate constant of forward reaction for the dehydrocyclization reaction
$K_4$	Rate constant of backward reaction in the formation of paraffins
$K_5$	Rate constant for Naphthene cracking
$K_6$	Rate constant for paraffin cracking
$-r_1$	Rate of Aromatization reaction
$-r_2$	Rate of dehydrocyclization reaction
$-r_3$	Rate of Naphthene cracking
$-r_4$	Rate of paraffin cracking
$C_N$	Molar concentration of Naphthene
$C_A$	Molar concentration of Aromatic
$A_0$	Pre-exponential constant
$E_a$	Activation energy
R	Gas constant
T	Temperature (K)
$X_i$	Conversion term for specie i
W	Weight of catalyst
$\rho_b$	Catalyst density

$D_R$	Diameter of the reactor
$L_R$	Length of the reactor
$\tau$	Space time
$S$	Space velocity
$t$	Holding time
$q$	Heat generated per unit volume of reactor
$\Delta H_R$	Heat of reaction
$\Delta P_R$	Pressure drop
$R$	Reynold number
$\rho$	Density of fluid
$V$	Fluid flow velocity
$F$	Frictional factor
$Q$	Volumetric flow-rate
$A$	Pipe cross sectional area
$\mu$	Kinematics viscosity

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