

**MODEL DISCRIMINATION FOR  
n- HEPTANE REFORMING ON DECAYING  
PLATINUM/ ALUMINA CATALYST IN A  
PULSE REACTOR**

**BY**

**IDRIS. M. K.  
MAT NUMBER 91/1782**

*Thesis in partial fulfillment of B. Eng  
Department of Chemical Engineering  
Federal University of Technology Minna.*

**February, 1998.**

# TABLE OF CONTENT

DECLARATION	ii
APPROVAL	iii
PREFACE	iv
DEDICATION	v
ACKNOWLEDGEMENT	vi
TABLE OF CONTENT	vii
ABSTRACT	ix
<b>CHAPTER ONE</b>	
<b>INTRODUCTION</b>	1
General Introduction	1
Pulse Reactor Technique	2
Justification of the Project	3
Objective / Scope	4
<b>CHAPTER TWO</b>	
<b>LITERATURE SURVEY</b>	5
Kinetics	5
Catalysts	6
Catalytic - Reactor Models	7
Deactivation - Reaction Models	8
Data Analysis in Term of various Models	10
Conclusion	12
<b>CHAPTER THREE</b>	
<b>AYO AND SUSU'S MODEL FOR A CATALYST OF</b>	
<b>VARIABLE ACTIVITY</b>	13
<b>CHAPTER FOUR</b>	
Experimental Data	18

## **CHAPTER FIVE**

**MATHEMATICAL METHOD FOR PARAMETER ESTIMATION** 20

**Linear Regression** 20

## **CHAPTER SIX**

**ANALYSIS OF RESULTS** 24

## **CHAPTER SEVEN**

**DISCUSSION OF RESULT** 29

## **CHAPTER EIGHT**

**Conclusion** 31

**Recommendation** 31

**Appendix 1** 32

**Appendix 2** 34

**Nomenclature** 47

**References** 48

# DECLARATION

I hereby certify that the content of the project Report reflect the studies actually carried out by me during my final year Research project at the Department.

Thank you for usual co-operation



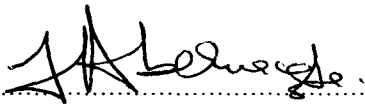
.....  
**IDRIS. MUHAMED KUTIGI**

25-FEB-1998

.....  
**DATE**

# APPROVAL

This is to certify that I have supervised, read and approved this research project which I found adequate both in scope and the quality for the fulfillment of the requirements for the award of Bachelor Degree in Chemical Engineering.



DR (Engr) F. Aberuagba  
PROJECT SUPERVISOR

25/02/98

.....  
Date

.....  
DR. K. R. ONIFADE  
HEAD OF DEPARTMENT

.....  
DATE

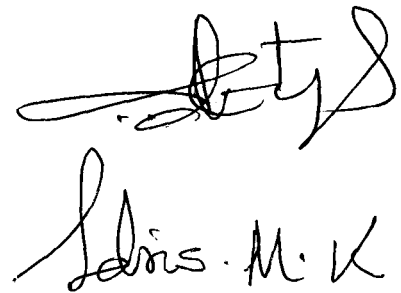
.....  
EXTERNAL SUPERVISOR

.....  
DATE

# PREFACE

The experience and exposure gained in the course of undertaking this project has given me an insight into this detrimental and protactic problem of catalyst deactivation which gave me inspiration to continue more project/research work in the subject in the bid to minimize or possible help to eliminate the problem.

I was motivated by the considerable interest with which petroleum and chemical industries have in this subject matter, consequently geared up by the thesis available, my able supervisor and the emence benefit of the project to a chemical engineer in training.



Louis M. K

# DEDICATION

MY LATE FATHER ALHAJI IDRIS KATU KUTIGI may SUBHANAHU WATA'ALA put  
RAHAMA in his life after death Amen.

# ACKNOWLEDGMENT

My special thanks and acknowledgement goes to SUBHANAHU WATA'ALA for given me the opportunity and strength to under take the project successfully may He in His infinite mercy shower more opportunity that will be of RAHAMA to me in life here and here after Amen.

I will like to gratefully acknowledge the good spirit of working relationship and willingness to get me through with the project content by my able supervisor Engr (Dr) Folorunsho Aberuagba.

My special thanks to my mother Mallama Aishatu Idris for her motherly role she played in the course of the project. Umar. Abdulkadir, Muhammed Muhammed, Jibrin Waziri Hassan Adamu and Muhammed Adamu, for their mutual cooperation by providing advises and background information in the writing of this report. This support is deeply appreciated.

The Assistance, fatherly and philosophical support given by my Uncles Alhaji Alhassan Hassan and Alhaji usman Gbongbo were of considerable help and are gratefully acknowledge.



# ABSTRACT

Catalytic reforming usually conducted on a dual - functional catalyst (Platinum - Alumina) in presence of Hydrogen is being critically examined with it's deactivation characteristics in focus, by using a model proposed for evaluating rate parameters as regards to catalyst deactivation on the pulse kinetic scheme. For catalyst decay the variable catalyst activity as a function of pulse is related to the deactivation rate constants.

The proposed deactivation model is tested on the deactivation of  $pt/Al_2O_3$  catalyst by reforming of n - heptane to cracked product, benzene and Toluene occurring in a pulse reactor (data acquired at temperatures of  $440^\circ C$ ,  $460^\circ C$ ,  $480^\circ C$  and  $500^\circ C$ ) and observing for first order the linearity of the deactivation plots on the stable catalyst. And second/third order by using parametric estimation to obtained the rate constants which are not in agreement with the proposed model. However the deactivation rate constants 0.0417, 0.0334; 0.01486; 0.0200 obtained at corresponding increasing temperatures investigated were reasonably in agreement with the first order.

# CHAPTER ONE

## 1.0 INTRODUCTION

### 1.1 GENERAL INTRODUCTION

In most petroleum industries, dehydrocyclization and hydrogenation reaction of alkane in a unit called catalytic reforming unit to improve the octane number of potential fuels and a commercial source of aromatic hydrocarbons. Like hydrocracking, catalytic reforming is conducted on a dual-functional catalyst such as platinum Alumina in the presence on both mono functional and dual-functional catalyst are still the subject of on going discussion. Side reaction accompanying the reforming reactions lead to the formation of coke on the surface of the catalyst; the result is the deactivation common to all catalytic hydrocarbon process. The reactions involve acids<sup>s</sup> site catalytic polymerization and cyclization of olefins to give higher molecular-weight polynuclear compounds which under go extensive dehydrogenation, aromatization and further polymerization. They occur rapidly under reforming conditions at low hydrogen partial pressures, but their effect is markedly reduced by increase hydrogen partial pressure.

In reforming with a paraffinic feed, poisoning begins on the metal with the formation of olefinic species and aromatics. These can slowly form coke on the metal, but they can also be transported by gas-phase diffusion and surface migration to the acid sites, they slowly form more where they form more resistant coke The long term deactivation in reforming probably due to this second term of coke formation. Most of the reactions are reversible because a significant fraction of the catalyst activity could be generated by purging with nitrogen for several days. This regeneration is probably the result of depolymerization and desorption. Regeneration with hydrogen was about twice as effective, but still about a week was required to regain most of the activity lost is a one week reforming run. More effective (still slow) regeneration could be achieved by increasing the hydrogen partial pressure to more them 400 atm. This slow coke removal particularly in the presence of hydrogen, represent removal from the surface of the acidic support. Hydrogen also removes coke reforming residue on the acidic support during the reforming processes. And regeneration also involves burning the coke off<sup>(13)</sup> of the catalyst under

carefully controlled conditions with a gas containing from 0.5 to 1 percent O<sub>2</sub>; the maximum bed temperature does not exceed 450°C. Such careful procedure are required to prevent damage to the catalyst, particularly sintering and loss of surface area of the Pt component.

## 1.2 PULSE REACTOR TECHNIQUE

The pulse microcatalytic technique has been widely used to kinetic studies of simple and complex catalytic reaction. The utility of the pulse scheme has depended largely on the availability of theoretical frame work for analysis of simple power law kinetics and Langmuir-Hinshelwood rate equations<sup>1,4,5,7</sup> prediction based on these analysis have yielded in several cases kinetic parameters in agreement with results from continuous flow experimentation<sup>8,9</sup>. However some of these analysis has addressed the issue of pulse reaction occurring on catalysts with variable activity which we intend to reasonably confirmed.

In this study, we are interested in the pulse operation of a reactor consisting of reforming of n-heptane over decaying platinum -Alumina catalyst. Despite the numerous publication some aspects of the kinetics and mechanism of these reactions remain obscure. The pulse technique allows quick exploration to the ease of experimentation and analysis of product (on-time catalyst). Thus, in this research Dr Aberuagba acquired a number of experiments on both. Hydrogen and inert carriers using different pulse sizes over the choice temperatures of 440°C, 460°C, 480°C and 500°C which are within the range that catalytic reforming unit operate. A comparison results from flow experiment for these reaction show, that the pulse techniques can be employed for gathering useful kinetic data for catalyst screening and mechanistic studies.

Nevertheless this technique involves the injection of micro samples of reactant into a carrier gas stream flowing through a reactor. The carrier stream may be an inert or may react with the injected pulse on the reactor which is usually packed with a small amount of catalyst. Often the catalyst bed acts as a chromatographic column resulting in the separation of product from unconverted reactants. This may give rise to conversions greater than the maximum predicted by the thermodynamics at equilibrium. Expressions describing chromatographic column are usually

based on the assumption of an isobaric system. When the catalyst volume is small the assumption does not pose any threat to the validity of parameters obtained by the pulse techniques to only one reactants in the injected pulse. This is because a pulse of mixed reactants may be separated into its components on the catalyst bed if the adsorption parameters of reactants are significantly different. Thus, very low conversion will be obtained. However, the carrier streams may contain as many reactants as desired.

The greatest limitation of the pulse reaction technique is probably its inability to yield parameters where rate equations are complex. This is due to the variation of the reactant partial pressure from point to point through the reactant pulse. Treatments of langmuir-Hinshelwood rate type equations and simple power laws have been reported. Butt and Weekmans <sup>(6)</sup> rating of pulse reaction is summarised in the table below.

**Table 1.1 Pulse reactor Rating**

Problem	Comment	Rating
Sampling and analysis of product composition	Can fire direct to chromatograph.	Good
Isothermality	small amount of catalyst in large heat sink	Fairly Good
Residence-contact time measurement	Transient surface coverage and chromatographic	poor
Selectivity time average Disguise	Short pulses can flow instartenous behaviour	Fairly -Good
Construction difficulty and cost	One of sample	Good

### 1.3 JUSTIFICATION OF THE PROJECT

Catalyst deactivation and regeneration are subjects of considerable interest to Refinery and chemical industries. And reactor engineers need to be able to accomplish.

- \* Developing algebraic rate law consistent with experimental observation.

- Linearizing the rate law in such a manner that the rate law parameter (eg  $K_1$ ,  $K_d$ ) can possible fit experimental data.
- \* Finding a mechanism and the order of reaction consistent with the experimental data
- \* Designing a catalytic reactor to achieved a specified conversion.

Despite the fact mathematical products have been use to represent and stimulate this deactivation problem. With some of these analysis addressing the issue of pulse reactors occurring on catalyst variable activity, therefore with particularly reference to n-heptane reforming we intend to confirmed it guinness.

### **OBJECTIVE/SCOPE**

Use various models arising from the modelling work of Ayo and Susul for a catalyst of changing activity in a pulse reactor to test the data obtained by Dr Aberuagba during n-heptane reforming on a decaying pt/Alumina catalyst under a carrier gas consisting of 60%  $H_2$  in  $N_2$ .

# CHAPTER TWO

## 2.0 LITERATURE SURVEY

### 2.1 KINETIC

To understand the behaviour of reforming reactors, we must understand the reaction kinetics and the influence of heat effects. A qualitative summary of the rate behaviour of the important reaction. are given in table 2.1

**Table 2.1** Rate behaviour and heat effects of important reforming reactions<sup>a</sup>

Reaction type	relative rate <sup>b</sup>	Effect of increase in total pressure	Heat effects
hydrocracking	Slowest	Increase rate	Quite exothermic
Dehydrocyclization	Slow	None to small decrease in rate	Endothermic
Isomarization of paraffins	Rapid	Decrease rate	Mildly exothermic
Paraffin dehydrogenation	Rapid	Decrease rate	Mildly exothermic
Paraffin dehydrogenation	Quite rapid	Decrease conversion	Endothermic
Naphthene dehydrogenation	Very rapid	Decrease conversion	Very endothermic

a - Partly from krane et al

b - Relative rate are for a modern bifunctional catalyst

Classes catalyzed by a modern bi-functional catalyst is given in the table above with statement of the heat effects. This information largely determines what is needed for the reactor design. Naphthene and paraffin dehydrogenation reactions are so rapid that they are essentially in equilibrium, and rate need not be considered explicitly. Similarly, the equilibrium between n-paraffins and isoparaffins is usually closely approached. In contrast, the rates of cyclization and

hydrocracking are typically low and in need of explicit consideration. Hydrogen partial pressure is an important variable since it strongly affects the conversion to aromatics and the rate of hydrocracking. Since reforming reactions which produce hydrogen, essentially aromatization, predominate over those which consume hydrogen, the process is a net hydrogen producer.

## 2.2 CATALYSTS

Reforming reactions typically proceed through a number of elementary steps. For example, a straight-chain paraffin is converted into an olefin, which is isomerized to an isoolefin and then converted into an isoparaffin. Correspondingly, the catalyst has two functions, a hydrogenation-dehydrogenation function for the paraffin-olefin conversions and an isomerization function, which is associated with the catalyst's acidity. The catalysts used until the early 1950s were chromium oxide or molybdenum oxide supported on alumina, which incorporated both the catalyst functions on the surface of the metal oxide. More recently developed reforming catalysts have crystallites of a metal such as Pt on an acidic support such as alumina, and the two functions are present in separate phases. The metal (Pt, Pd, and Rh) or a noble metal-containing trimetallic alloy provides the hydrogenation-dehydrogenation activity of the supported metal and the isomerization activity of the alumina is much greater than the respective activities of the early-generation metal oxides.

Catalyst deactivation by coke formation involves both the metal and support but primarily the support. Coking results from secondary reactions of the hydrocarbons, particularly olefins, at low conversions and when the temperature is high. Deactivated catalyst is regenerated in place by slowly burning off the coke. However, the operational strategies for a reactor subject to catalyst deactivation can be summarized as follows<sup>14</sup>:

- Vary reactor temperature with time to maintain a constant conversion with a constant reactor feed flow rate. A typical policy for large throughput and slow deactivation rates.
- \* Vary throughput of the reactor feed while holding the reactor temperature and conversion constant. A possible policy for medium deactivation rates and small to medium

throughout.

- Allow the conversion to fall while holding the reactor feed flow rate and reactor temperature constant. Similar application as in item:
- \* Maintain the fresh feed rate and reactor temperature constant and let the recycle flow increase. Similar application as in item 2
- Use a combination of reactors on parallel and the policies of items 1 or 3. Usually, with two reactors in parallel and the policies of item 1 or 3. Usually with two reactors in parallel, one will be off-line for catalyst regeneration while the other is operating. A typical policy for large throughput and medium to fast deactivation rates.
- Continuous catalyst regeneration while maintaining constant conversion, throughout and reactor temperature. A typical policy for large throughput, rapid deactivation system.

### **2.3 CATALYTIC - REACTION MODELS**

When we speak of surface - reaction kinetic models, it is to be understood that rate phenomena of an exclusively chemical nature are under consideration i.e chemisorption, desorption or surface chemical reaction. Excluded by definition are all limiting physical-transport steps, such as mass transfer of species from the bulk-fluid phase to the external surface of the catalyst particle (interphase transport) and those diffusive events which convey the species to within the pores of the catalyst where reaction occurs simultaneously with diffusions (intra particle transport). It is assumed at this junction that interphase and intra particle transport processes are very rapid relative to the chemical rate processes occurring on and within the catalyst particle. Also implicit is the additional assumption of a zero gradient (interphase or intraphase) with respect to the diffusion of heat. Thus isothermality exists about and within the catalyst. Extensive treatment of both heat and mass transport to and within porous catalyst. Usually provided where appropriate chemical kinetics will be combined (when possible) with those of heat and mass transfer to fashion overall rate.

Catalytic reaction - rate expressions can be derived for ideal surface in two ways:(1) by



expression the rate in terms of surface coverage  $Q$  and then employing the langmuir isotherm to relate  $Q$  to fluid concentrations. This is the approach employed by Hinshelwood and is commonly termed the langmuir - Hinshelwood formulation(2). A somewhere more explicit approach as established by Hougen and watson, who derived equations interms of surface concentration in terms of the langmuir isotherm.

While it may appear that little difference in form exists between langmuir - Hinshelwood rate expressions and those of Hougen-watson, it must be emphasized that the developments of watson and Hougen prove to be far more comprehensive. For in addition to surface reaction per se, the waston - Hougen formulations include explicit terms for catalyst activity (sites), catalyst effectiveness due to diffusion and provision for catalyst decay. Further, as well as adjacent - site models were anticipated. The Hougen - watson catalytic rate equations represent not merely a modification of the langmuir - Hinshelwood formulations but highly constructive extensions and refinements, the unique utility of which is demonstrated in the analysis and design of catalytic reactors.

In so far as ideal postulate yield useful results, the Hougen - watson formulations being more explicit in their derivation, are to be preferred so as long as it is clearly understood the models results, not mechanistic description to do justice to the signal contribution of both school, such ideal - surface models will be preferred toas langmuir Hinshewood - Watson (LHHW) formulations.

## **2.4 DEACTIVATION - REACTION MODELS**

Levenspiel and his students<sup>6</sup>, have fruitfully analyzed the deactivation problem in simple yet negotiable terms which emcompass a wide diversity of poisoning - fouling precursor networks as were as well as the important case of species - independent deactivation. Since their analysis assumes  $n^{\text{th}}$ - order catalytic reaction and  $d^{\text{th}}$ - order activity decline, It is a phenomenological treatment of a problem which, although of immense. Intrinsic sophistication, is best attacked from a point of view devoid of detailed mechanistic speculation. In sofar as many LHHW hyperbolic

rate models can be gainfully phrased items of a power law  $n^{\text{th}}$ - order model, the levenspiel - szejpe approach retain potency particularly with respect to the uncoupling of the deactivation - reaction events.

Following levenspiel, the catalyzed - reaction rate is given by:

$$r_A = -\frac{dA}{d\theta} = KA^na$$

Where

$$a = \frac{\text{rate at any } t}{\text{rate at } t = 0}$$

Then a is an activity which is initially equal to unity and declines with time. Now the kinetic model of activity decline is presumed to be

$$r_p = -\frac{da}{d\theta} = K(A, B, P)^m a^d$$

Catalyst	Reaction	Type of poisoning	Poisons
silica - alumina	Cracking	chemisorption Desorption stability selectivity	Organic bases carbon, hydrocarbon water
Nickel, platinum copper	Hydrogenation Dehydrogenation	Chemisorption	Heavy metals compounds s,se Te, P, AS, Zn, halide Hg, Pb, NH <sub>3</sub> , C <sub>2</sub> H <sub>2</sub> , H <sub>2</sub> S Fe <sub>2</sub> O <sub>3</sub> etc
Cobalt	Hydrocracking	chemisorption	NH <sub>3</sub> , S, Se, Te, P
Silver	C <sub>2</sub> H <sub>4</sub> +O -- C <sub>2</sub> H <sub>4</sub> O	Selectivity	CH <sub>4</sub> , H <sub>2</sub> , H <sub>6</sub>
Vanadium oxide	Oxidation	chemisorption	AS
Iron	Ammonia synthesis hydrogenation Oxidation	chemisorption chemisorption chemisorption	O <sub>2</sub> , H <sub>2</sub> O, CO, S <sub>2</sub> , H <sub>6</sub> Bi, Se, Te, P, H <sub>2</sub> D V <sub>6</sub> O <sub>4</sub> , Bi,

Where A = reaction concentration

B = Product or intermediate concentration

P = Poison or fouling concentration

m,d = Empirical orders of deactivation with respect to species concentration and activity, respectively.

The precise functionality which of eq will assume depends upon the reaction - deactivation network. Several networks suggest themselves depending on the mechanism ranging from simultaneous deactivation, consecutive deactivation, parallel deactivation independent deactivation to simultaneous - consecutive deactivation possible depending on feed composition.

These phenomenological reaction- deactivation functions have the merit of adequately describing a number of deactivation - time on stream observations such as exponential, hyperbolic, and power law decay, as Levenspiel notes. Use of these models to determine rate coefficients and orders from laboratory data has been precluded.

## 2.5 DATA ANALYSIS IN TERMS OF VARIOUS MODELS

From their development and presentation, LHHW method of catalytic rate data analysis and correlation gained wide adoption. Despite the caution urged by those responsible for the development of these models, numerous enthusiasts flooded the literature with mechanistic assertions derived from agreement between their rate data and particularly LHHW models. Well aware of the inherent limitation of any kinetic models, Weller initiated a fruitful dialogue by pointing out that insofar as LHHW rate equations cannot reflect a unique mechanistic physio-chemical reality, for simple methods of rate - data correlation demand attention. Specifically, Weller suggested that rates of heterogeneous catalytic reaction be expressed in terms of a simple power law.

$$r = KA^{\alpha} B^{\beta} P^{\gamma}$$

In addition to simplicity of form and in many cases, ease of integration clearly rest a non - ideal, real - surface process namely, one characterized by a logarithmic q - versus.

Q functionality a basis of the Freundlich isotherm

$$Q = KA_i^n$$

So if  $r = K_1 Q A Q P$ , then

$$r = K_1 K_A K_B K_P A^{1/n} B^{1/m} P^{1/p}$$

Weller supported his thesis by analysing data for a number of reaction systems previously corrected in terms of complex LHHW expression. Weller justly focussed attention upon the folly of inferring a mechanism from a model and the utility of a simpler model when data do not demand excessive elegance. However Boudart asserted in a companion paper, some telling advantages are to be found in the proper use of LHHW rate equations. Primarily, a judiciously selected LHHW form conveys very useful information about the effects of component partial pressure and temperature upon reaction rate, as we shall illustrate shortly. This sort of information can be conveyed by the organizing equation in spite of the well-known fact that the LHHW model and its equivalent the Freundlich - based power law model, the LHHW form is to be preferred, Boudart notes, because greater understanding and control of reaction conditions are provided by this, the more flexible model. Here then the merits of the LHHW form relative to the Freundlich functions are established. In the previous section, These merits relative to Brunauer - Love - Keenan - based rate equations were stated. The demonstrated equivalence of these apparently diverse relationships suggest that distinction between ideal and real surfaces, from an applied kinetic point of view, are meaningless.

Furthermore, adsorption coefficient extracted from LHHW rate equations bear little relationship to those found directly in chemisorption equilibrium studies. For example, in correlating the temperature dependency of adsorption coefficients in a rate equation of the form.

$$r = \frac{k K_1 A}{1 + K_1 A + K_2 B}$$

The derived heat of chemisorption is often found to be small about 2 to 10 kcal/mol, although independent calorimetric studies might suggest values in the range of 10 to 5 kcal/mol, depending upon coverage, it is tempting to assert that if steady state reaction occurs at high coverage, a low chemisorption heat would be expected on analysis of the rate equation K values.

Such an assumption is not necessary when one recalls that while surface occupancy is a function of pressure, It is more drastically effected by temperature with increasing temperature, coverage decreases, in consequence the chemisorption heat increases, as an approximation Boudart postulates.

$$q = q_0 + aT$$

Where  $q_0$  is the chemisorption heat at high coverage (con temperature). Assuming the usual adsorption equilibrium coefficient temperature relation and applying we have.

$$K = K_0 \exp \frac{q}{RT} = K_0 e^a \exp \frac{q_0}{RT}$$

With the result that for any coverage, a plot of  $\ln K$  versus  $1/T$  will reveal a slope equivalent to  $q_0$ , the lowest value of  $q_0$  corresponding to high coverage. The adsorption heats derived from kinetic models, as well as those inferred by pulse-flow techniques are not likely to be of great meaning so long as non - ideal surfaces are involved.

## CONCLUSION

The literature survey highlights the reaction kinetics and the influence of heat effect on the modern bi-functional catalyst and since catalyst deactivation of hydrocarbons are principally caused by preceding secondary reactions, the chemical natures under consideration in this study are desorption, surface chemical reaction and most importantly (referring to the type of poisoning on platinum during hydrogenation) chemisorption.

However, Deactivation - Reaction models have been fruitfully analysed in simple yet negotiable terms with the usage of either langmuir - Hinshelwood formation, among others in proposing models to determine rate coefficient and orders from laboratory data been procured. In spite of the well known fact that the actual mechanism of these reactions are obscure, data analysis in terms of various models is admonished by the like of weller, Boudart, love - keenan<sup>6</sup> with there thesis and freundlich - based power law model.

# CHAPTER THREE

## 3. AYO AND SUSU'S MODEL FOR A CATALYST OF VARIABLE ACTIVITY.

By considering the mass balance on a small section of catalyst bed, eq. (1) has been derived for first order reaction

$$\frac{dn}{dt} = \frac{kK_{An}RT}{(V_g + V_R)} \dots\dots\dots(1)$$

For a catalyst with variable activity this equation may be modified by adding an activity term thus:

$$\frac{dn}{dt} = \frac{kK_{An}RT}{(V_g + V_R)} \dots\dots\dots(2)$$

In the terminology of Butt et al <sup>10</sup> this corresponds to separable deactivation on integration, eq. (2) becomes

$$\ln \frac{1}{1-xi} = K_1 \int_0^1 a dt \dots\dots\dots(3)$$

Where

$$K_1 = \frac{K_1 k K_A RT}{(V_g + V_R)} \dots\dots\dots(4)$$

$K_1$  is a constant at a given temperature

In order to solve eq (3) the following assumption is made:

The deactivation rate is independent of gas phase concentration and may be described by:

$$-\frac{da}{dt} = k_d a^y \quad \dots\dots\dots(5)$$

Considering pulse number  $i$  eq. (3) becomes

$$\ln\left(\frac{1}{1-xi}\right) = k_1 \int_0^1 a_o dt \quad \dots\dots\dots(6)$$

Equ. (6) was then considered for catalyst decay.

**catalyst decay**

Deactivation is assumed to occur as result of reaction of injected pulse so that the activity of the catalysts remains constant in between injection. Integration of Eq (5) gives:

$$a = a_o \exp (-K_d t) \quad (y = 1) \quad \dots\dots\dots(7)$$

$$a = [a_o^{(1-y)} - (1 - y) k_d t]^{1/(1-y)} \quad Y \neq 1 \quad \dots\dots\dots(8)$$

cases of  $y = 1$ ,  $y = 2$  and  $y \neq 1,2$  shall be considered separately.

Case 1:  $y = 1$ . The activity after pulse number  $(i - 1)$  is obtained from eq: (7) as:

$$a_{i-1} = a_o \exp (-k_d (i - 1)t) \quad \dots\dots\dots(9)$$

Thus,

$$\begin{aligned} a_o &= a_{i-1} \exp (-k_d t) \\ &= [a_o \exp (-(i - 1) k_d t)] \exp (-k_d t) \quad \dots\dots\dots(10) \end{aligned}$$

Using eq. (10) in eqn. (6) gives:

$$\ln\left(\frac{1}{1-xi}\right) = k_2 \exp(-(i-1)k_d t) \quad \dots\dots\dots(11)$$

Where

$$K_2 = a_o (k_1/k_d [1 - \exp (-k_d t)]) \dots\dots\dots(12)$$

Taking logarithm of both side eq. (13) is obtained:

$$\ln \ln \left( \frac{1}{1-x_i} \right) = \ln k_2 - (i-1)k_d t \dots\dots\dots(13)$$

case 2:  $y \neq 1$  The activity after pulse number  $(i - 1)$  is given by:

$$a_{i-1} = (a_o^h - (i - 1) h k_d t)^{1/h} \dots\dots\dots(14)$$

where

$$h = 1 - y \dots\dots\dots(15)$$

Hence

$$\begin{aligned} a_o &= [(a_{i-1})^h - h k_d t]^{1/h} \\ &= [a_o^h - (i - 1) h k_d t - h k_d t]^{1/h} \dots\dots\dots(16) \end{aligned}$$

Equation (16) is used to evaluate the integral in eq. (6). The solution shall be considered for two cases:  $y = 2$  ( $h = -1$ ) and  $y \neq 1, 2$  ( $h = 0, 1$ )

case 2a:  $y = 2$  ( $h = - 1$ )

$$\int_0^1 a_o dt = \int_0^1 [a_o^{-1} + (i-1)k_d t + k_d t]^{-1} dt \dots\dots\dots(17)$$

$$= \frac{1}{k_d} \ln \left[ \frac{a_o^{-1} + ik_d t}{a_o^{-1}} + (i-1)k_d t \right] \dots\dots\dots(18)$$



Hence eq. (6) becomes

$$\ln\left(\frac{1}{1-xi}\right) = (k_1/k_d) \ln\left[\frac{a_o^{-1} + ik_d t}{a_o^{-1} + (i-1)k_d t}\right] \quad \dots(19)$$

case 2b :  $y \neq 1,2$  ( $h \neq 0,1$ )

$$\int_0^1 a_o dt = \frac{-1}{(k_d(1+h))} [(a_o^h - ihk_d t)^{(1+h)/h} - a_o^h - (i-1)hk_d t^{(1+h)/h}] \quad \dots(20)$$

and eq. (6) becomes

$$\ln\left[\frac{1}{1-xi}\right] = \frac{k_1}{k_d(1+h)} [J_{(i-1)} - J_{(i-1)}] \quad \dots\dots\dots(21)$$

Where

$$J_{(i)} = [1 - ihk_d t]^{(1+h)/h} \quad \dots\dots\dots(22)$$

**TABLE 3.0**

Pulse determination of deactivation rate constant

value of y	Deactivation by pulse $-\frac{da}{dt} = k_d a^y$
y = 1	$\ln \ln \left[ \frac{1}{1-x_i} \right] = \ln k_2 - (i-1) k_d t$ $K_2 = \frac{a_0 k_1}{k_d} [1 - e^{-h d^1}]$
y = 2	$\ln \left[ \frac{1}{1-x_i} \right] = \left\{ \frac{k_1}{k_2} \right\} \ln \left[ \frac{a_0^{-1} + i k_d t}{a_0^{-1} + (i-1) k_d t} \right]$
y ≠ 1,2	$\ln \left[ \frac{1}{1-x_i} \right] = \frac{k_1}{k_d(1+h)} J_{(i)} - J_{(i-1)}$ <p>Where</p> $J_{(i)} = 1 - i h k_d t$ $h = 1 - y$

# CHAPTER FOUR

## 4. EXPERIMENTAL DATA

The data for this study were obtained from the work of Aberuagba<sup>(2)</sup> on n – heptane reforming on a decaying pt/Al<sub>2</sub>O<sub>3</sub> catalyst and is tabulated in table below.

The data were obtained from a pulse microcatalytic reactor under a flow of a carrier gas consisting of 60% H<sub>2</sub> in N<sub>2</sub> at a total pressure of 4.0 kg/cm<sub>2</sub>. The product of n - heptane reaction were cracked products, benzene and toluene.

**TABLE 4.1** Conversion to cracked product, Benzene and Toluene

Number	T = 440° C	T = 460° C	T = 480° C	T = 500° C
1	0.4	1	1	1
2	0.32	1	1	1
3	0.28	0.9	-	1
4	0.2	0.88	-	1
5	0.17	0.83	1	1
6	0.15	0.85	-	0.99
7	0.13	0.72	1	0.98
8	0.12	0.65	0.94	0.97
9	0.09	0.6	0.84	0.97
10	0.08	0.57	0.72	0.72
11	0.08	0.51	0.76	0.68
12	0.07	0.48	0.72	0.62
13	0.08	0.45	-	0.58
14	0.07	0.44	0.66	0.56
15	0.06	0.39	0.58	0.49
16	0.07	0.38	0.57	0.47
17	0.04	0.35	-	0.42
18		0.33	-	0.39
19		0.32	0.52	0.35

20		0.3	-	0.26
21		0.28	0.46	0.23
22		0.27	0.43	0.21
23		0.25	0.41	0.12
24		0.24	0.37	0.03
25		-	-	
26		0.22	0.34	
27		0.22	0.36	
28		0.22	0.34	
29			-	
30			0.32	
31			0.3	
32			0.28	
33			0.33	
34			-	
35			0.27	
36			0.25	
37			0.19	
38			0.11	
39			0.16	
40			-	
41			0.13	

# CHAPTER FIVE

## 5: MATHEMATICAL METHOD FOR PARAMETER ESTIMATION

### LINEAR REGRESSION

Fitting the proposed models into a straight line<sup>(13)</sup> by linearizing tentatively assuming that the regression line of variable one denoted by Y has the form  $\beta_0 + \beta_1 x$ . Then writing the linear first order model  $Y = \beta_0 + \beta_1 x + \epsilon$ . However,  $\beta_0$  and  $\beta_1$  remain fixed and although we can find them exactly without examining all possible occurrences of Y and x, therefore using the information provided in table 3.1; 3.2; 3.3, 3.4 for second order kinetics and 4.1, 4.2, 4.3, & 4.4 for third order kinetics to give estimates  $b_0$  and  $b_1$  of  $\beta_0$  and  $\beta_1$ . Thus we can write

$$Y = b_0 + b_1 x$$

linearizing eqs (19) & (21) we have:

$$\ln\left(\frac{1}{1-xi}\right) = k_1/k_d \ln\left[\frac{a_o^{-1} + ik_d t}{a_o^{-1} + (i-1)k_d t}\right]$$

Taking ln of both of side

$$\ln\ln\left(\frac{1}{1-xi}\right) = \ln k_1/k_d \ln\ln\left[\frac{a_o^{-1} + ik_d t}{a_o^{-1} + (i-1)k_d t}\right]$$

$$\frac{1}{1-xi} = \ln k_1/k_d \frac{a_o^{-1} + ik_d t}{a_o^{-1} + (i-1)k_d t}$$

but  $\log(a.b) = \log a + \log b$

$$\therefore \frac{1}{1-xi} = \ln k_1/k_d + \frac{a_o^{-1} + ik_d t}{a_o^{-1} + (i-1)k_d t}$$

$$\Rightarrow \frac{1}{1-xi} = \ln \frac{k_1}{k_d} + \frac{a_o^{-1} + it}{a_o^{-1} + (i-1)t} \cdot k_d$$

$$\therefore Y = \frac{1}{1-xi}; x = \frac{a_o^{-1} + it}{a_o^{-1} + (i-1)t}$$

Similar applying to eqn. (21) for third order

$$n \ln \left[ \frac{1}{1-xi} \right] = \ln \frac{k_1}{k_d(1+h)} \ln \left( [1 - ihk_d t]^{(1+h)/h} - [1 - (i-1)hk_d t]^{(1+h)/h} \right)$$

$$\frac{1}{1-xi} = \ln \frac{k_1}{k_d(1+h)} \ln \left( [1 - ihk_d t]^{(1+h)/h} - [1 - (i-1)hk_d t]^{(1+h)/h} \right)$$

but  $\log(a.b) = \log a + \log b$  ; and  $\log \frac{a}{b} = - \log b$

$$\Rightarrow \frac{1}{1-xi} = \ln \frac{k_1}{k_d(1+h)} + \ln \frac{[1-hk_d f]^{(1+h)/h}}{1-(i-1)ht^{1+h}/h}$$

$$\frac{1}{1-xi} = \ln \frac{k_1}{k_d(1+h)} + \ln \frac{[1-hk_d f]^{(1+h)/h}}{1-(i-1)ht^{1+h}/h} \cdot \ln k_d^{(1+h)/h}$$

$$\therefore Y = \frac{1}{1-xi} ; x = \ln \frac{[1-hk_d f]^{(1+h)/h}}{1-(i-1)ht^{1+h}/h}$$

Correspondingly

$$y_i = \beta_0 + \beta_1 X_i$$

Where we substitute  $(b_0, b_1)$  for  $(\beta_0, \beta_1)$  to give normal equation

$$b_1 = \frac{\sum x_i y_i - [\sum(x_i) \sum(y_i)]/n}{\sum x_i^2 - (\sum x_i)^2/n} = \frac{\sum(x_i - \bar{x})(Y_i - \bar{Y})}{\sum(x_i - \bar{x})^2} \quad \dots\dots(1)$$

Where all summation are from  $i = 1$  to  $n$  and the two expression for  $b_1$  are slightly different forms of the same quantity since defining we find the following

$$X = (X_1 + X_2 + \dots\dots\dots X_n)/n = \sum x_i / n$$

$$Y = (Y_1 + Y_2 + \dots\dots\dots Y_n)/n = \sum Y_i / n$$

The first form in eqn. (\*) is normally used when actually computing the value of  $b_1$ . The value of

$b_0$  is given by:

$$b_0 = Y - b_1 x \dots\dots\dots(2)$$

Therefore using equations (1) and (2) to obtained the rate parameters by performing the calculations on the table 3.1, 3.2, 3.3. 3.4 and 4.1, 4.2, 4.3, 4.4 second and third order respectively.



# CHAPTER SIX

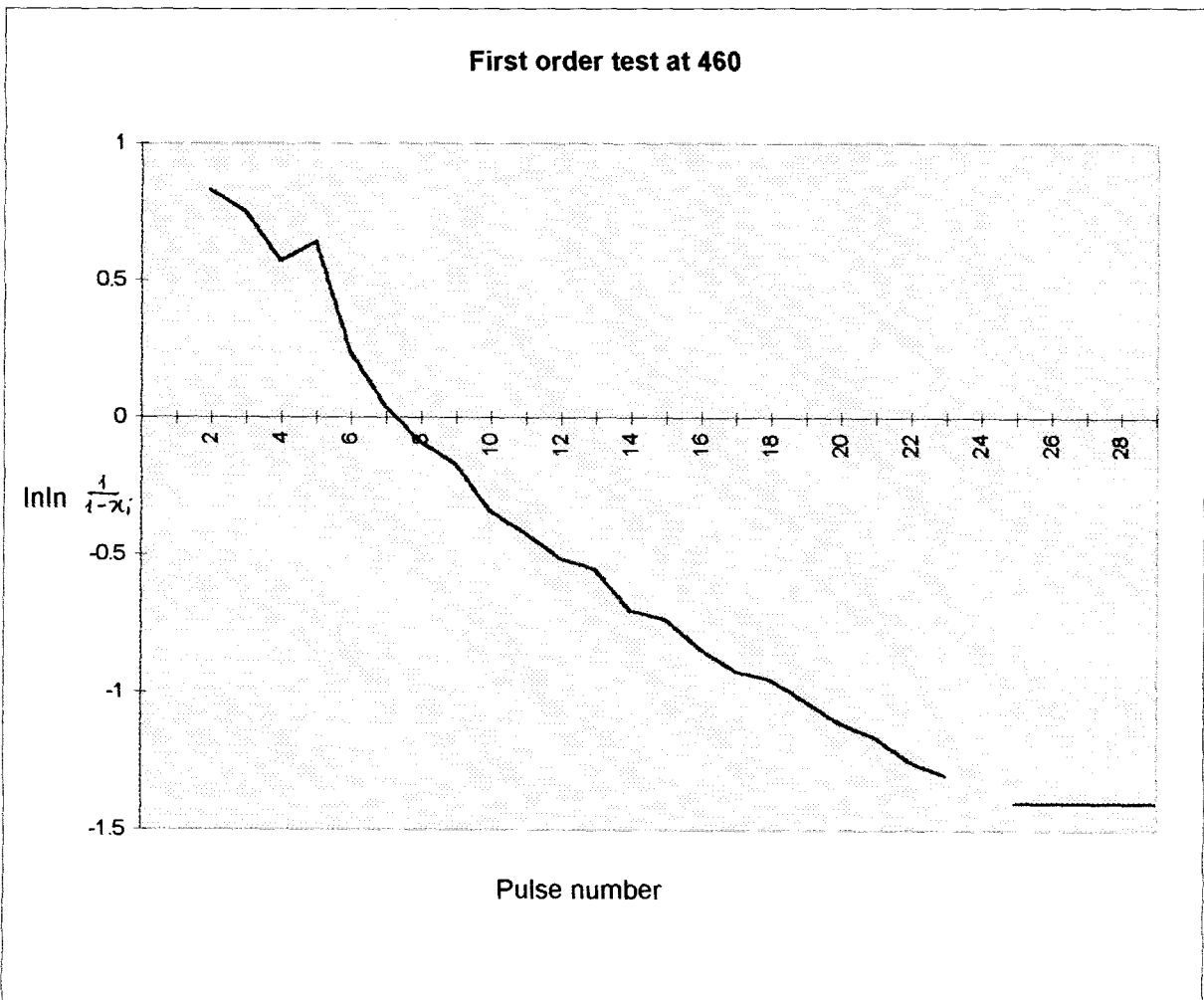
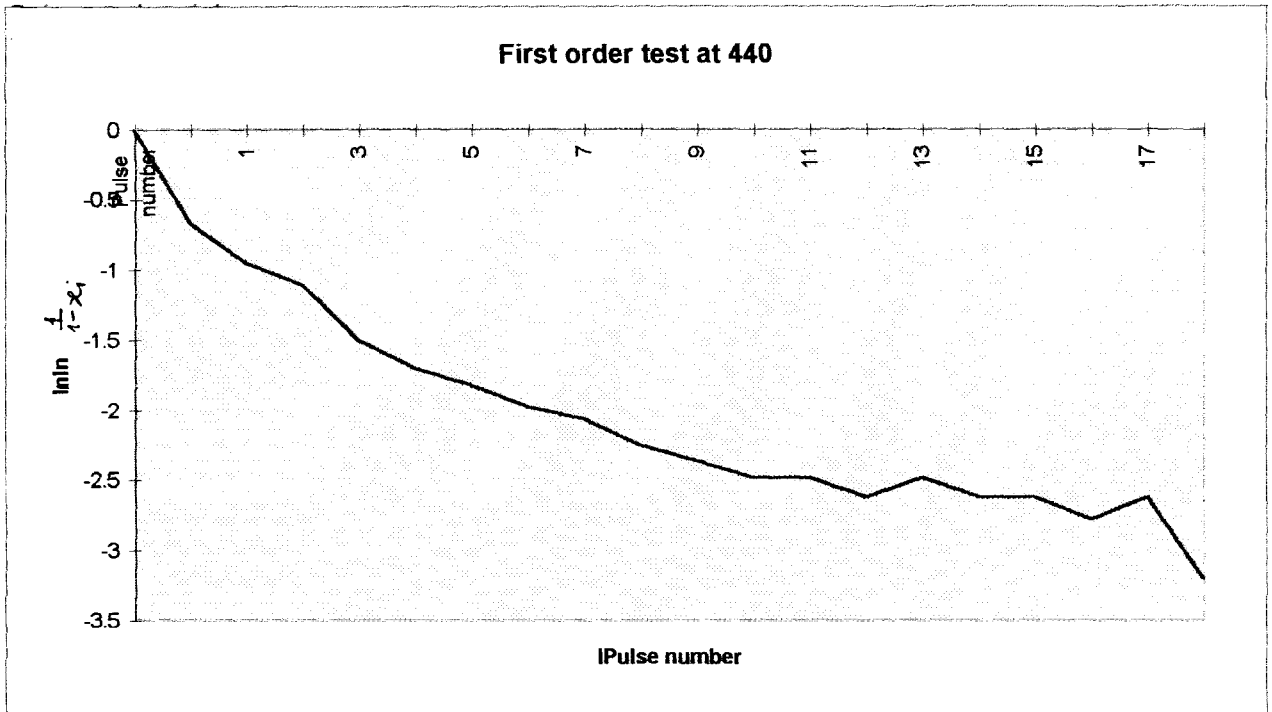
## ANALYSIS OF RESULT

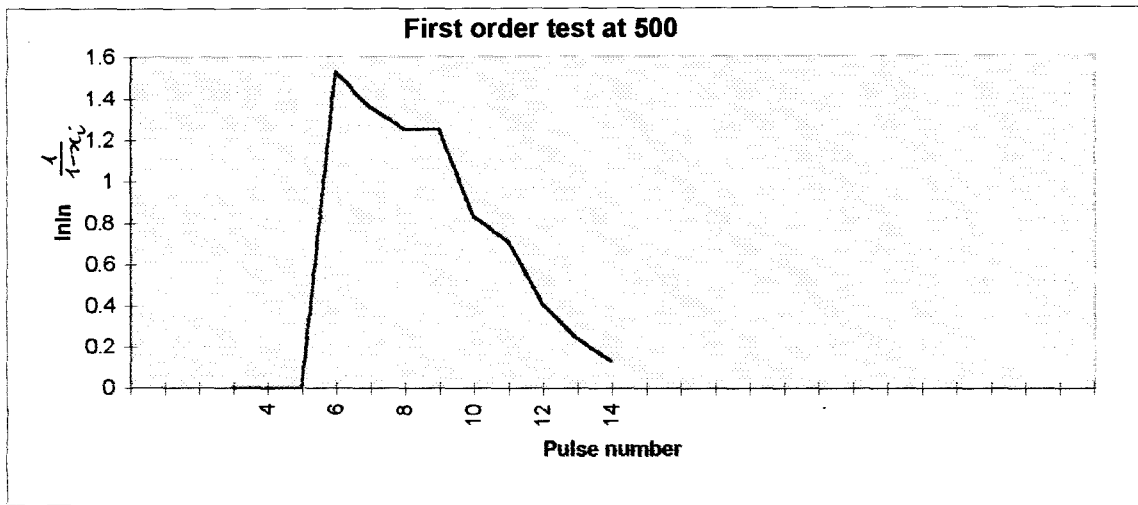
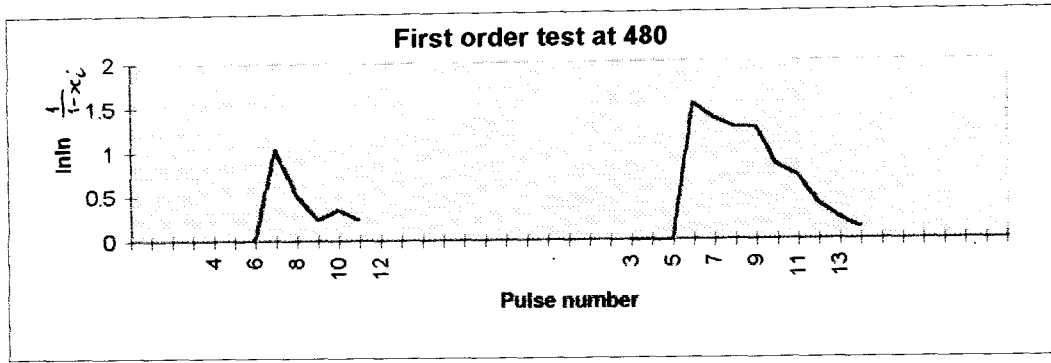
Pulse of reactant are injected repeatedly into the reactor system and conversion monitored as a function of pulse number. For catalyst decay with first order kinetics the quantity  $\ln(1/(1 - x_i))$  is plotted against  $(i - 1)$  as indicated in eq. (13) in model formulation which was done for the four group of datas at 440° C; 460° C; 480° C and 500° C. The slope of the plot gives  $k_d t$  from which  $k_d$  was extracted and  $t$  known to be 5 minute. When  $y \neq 1$  eqn. (19) and  $y \neq 1,2$  eqn. (20) was solved using parametric estimation (linear regression technique) to obtain  $k_1$  and  $k_d$  where  $h$  is given by eqn. (15) and  $a_0^{-1}$  an activity which is initially equal to unity and declines with time is assumed to be still unity (one), by fitting into a straight line by linearizing tentatively assuming that the regression line of variable  $Y$  has the form  $\beta_0 + \beta_1 x$ . Then writing the linear first order model  $Y = \beta_0 + \beta_1 x + \epsilon$ . However,  $\beta_0$  and  $\beta_1$  remain fixed and although we cannot find them exactly without examining all possible occurrence of  $Y$  and  $x$ , we can use the information provided in table 2.1, 2.2, 2.3, and 3.4 for second order kinetics test And table 3.1; 3.2; 3.3 and 3.4 for third order kinetics test as well to give us estimates  $b_0$  and  $b_1$  of  $\beta_0$  and  $\beta_1$ . Thus we can write  $Y = b_0 + b_1 x$  with

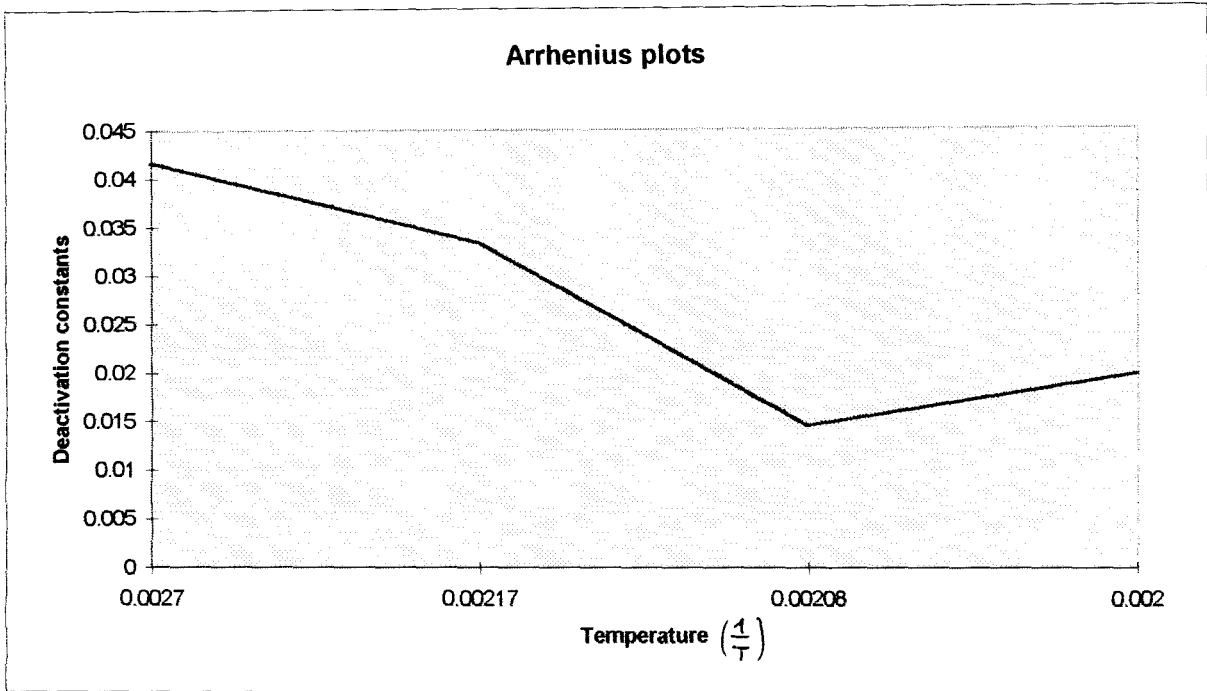
$$b_1 = \frac{\sum x_i y_i - [(\sum x_i)(\sum Y_i)]/n}{\sum x_i^2 - (\sum x_i)^2/n} = \frac{\sum (x_i - \bar{x})(Y_i - \bar{Y})}{\sum (x_i - \bar{x})^2}$$

obtaining the rate constants as follows:

TABLE 6.1: FOR SECOND ORDER					TABLE 6.2: FOR THIRD ORDER				
Temp	440° C	460° C	480° C	500° C	Temp	440° C	460° C	480° C	500° C
$k_d$	0.4665	0.037	-0.541	1.433	$k_d$	1.578	1.5908	-1.275	-3.781
$k_1$	-0.441	0.032	-0.578	3.5313	$k_1$	1.306	-2.384	1.7011	8.8002







# CHAPTER SEVEN

## 7.0 DISCUSSION OF RESULT

The development of models for catalyst decay been base on power law equation with an extension and inclusion of variable catalyst activity reflect the theoretical and experimental study for furthering the search for the mechanistic deactivation kinetic equation on pulse kinetic scheme. The reasonable assumption made with regards to the deactivation occurring as a result of injected pulses so that the activity of the catalyst remain constant in between injection, rein forced the model obtained to be sound. And the assumption during analysis (using parametric estimation) of the second/third order proposed, that  $a_0^{-1}$  (initial catalyst activity is unity (1) coupled together makes the model developed to be result oriented.

Equation (13) was used to analyse the deactivation data of n-heptane reforming and figure g:6.1, 6.2, 6.3, 6.4 shows the plots of  $\ln \ln (1/(1-x))$  against  $(i-1)$  as a test for first order. for the n-heptane reforming using Pt/Al<sub>2</sub>O<sub>3</sub> catalyst at the four temperature investigated. The plots yield straight line for the leading pulses, deviation from linearity where in the case of 440°C was observed after first 10-16 pulses; 460°C after first 26-29; at 480°C and 500°C there were no deviation from linearity with the intercepts ( $k_2$ ) increasing with increasing temperature. And the Arrhenius plots showing that the deactivation of n-Heptane was non activated (with activation energy of 37.062) in the temperature ranges investigated. However the second and third order investigation carried out using parametric estimation (linear regression) the two independent parameters  $K_1$  and  $K_d$  (rate constants) as indicated in table 6.1&6.2 both increment were not consistently defined (possibly increasing or decreasing with increasing temperature) contrary to the were known knowledge of the temperature effects (severity along the parked catalysed bed) contrary to this, we can say that it affirmed the deactivation rates is not second neither third order.

Therefore linearity of the deactivation plots on the stable catalyst suggest that n-heptane reforming was first order on reactant partial pressures, an observation made by a number of authority as regards to platinum on Alumina support catalyst. There is sufficient evidence that

platinum for metallic clusters on alumina support and these clusters are unstable in the presence of oxygen at elevated temperature. Therefore combining the reactor inlet temperature and kinetics of the catalyst (first order) and putting into consideration that the commercial system involved a partially deactivated catalyst, the reactor modelling could be well improved upon to take care of long life span of catalyst in reformers with temperature effects at a specified feedstock composition and assigned operating parameters.

Although higher hydrogen partial pressure decreases the catalyst deactivation rates (but still slow) and consequent regeneration frequency, in reforming unit at large for which we are using isomerization (n-heptane reforming) to represent or stimulate the operation occurrence, a trade off exists between deactivation and hydrocracking rate which among others makes the modelling of catalytic reforming complicated. Therefore industrial model development of reforming could find the clarification of the order of deactivation useful to predict models of better performance.

Finally a regeneration data being inclusive for analysis to elaborate more on the time of regeneration and consequent deactivation of the oxidised catalyst to see and suggest at what order it is being described would have been an information for proper reformer design to ascertain completely the operating cost at large.

# CHAPTER EIGHT

## CONCLUSION

The model developed or proposed for the determination of deactivation parameters of power - lower equation for catalyst decay kinetics during n-Heptane reforming was found not to be second neither third order but rather first order in reactant pressure. The deactivation reaction was found to be affected with the severity on the stable catalyst which is non activated.

## RECOMMENDATION

Taking into consideration the diffusional influences that exist in catalytic reforming, returning to the aforementioned studies with mechanical mixtures of the two separate catalyst components and combining the energy balance about each catalyst particle with that for the entire flow reactor and adding the kinetics equations including mass transfer influences with the reactor modelling can not be successfully enhance for optimum operating condition do to this obscure in catalyst kinetic trend.

This project among others is another step but not enough to confidently model an efficient reactor system due to inability to know the regeneration frequency on the reaction system which is strongly recommended to be look into as datas are available to project optimum operating reaction system.

# APPENDIX 1

Arrhenius plot Table for first order

**TABLE A**

$\frac{1}{T}$	$K_d$
$2.27 \times 10^{-3}$	$4.174 \times 10^{-2}$
$2.17 \times 10^{-3}$	$3.34 \times 10^{-2}$
$2.08 \times 10^{-3}$	$1.486 \times 10^{-2}$
$2.00 \times 10^{-3}$	$2.0 \times 10^{-2}$

Computed from the following: At  $t = 5$  min

at 440°C

$$K_d t = 0.2087$$

$$K_d * 5 = 0.2087$$

$$K_d = \frac{0.2087}{5} = 0.0417$$

at 480°C

$$K_d t = 0.0743$$

$$K_d * 5 = 0.0743$$

$$k_d 5 = 0.0743$$

$$k_d = \frac{0.0743}{5} = 0.01486$$

at 460°C

$$K_d t = 0.1667$$

$$K_d * 5 = 0.1667$$

$$k_d = \frac{0.1667}{5} = 0.334$$

at 500°C

$$k_d t = 0.1000$$

$$k_d 5 = 0.1000$$

$$k_d = \frac{0.1000}{5} = 0.02$$

Using Arrhenius equation:

$$K_d = K_0 e^{-E/RT}$$

Taking in of both side

$$\ln K_d = \ln K_0 - E/RT$$

$$\text{Slope} = 4.4545$$

Therefore:

$$-b = -E/R$$



$$E = R * b$$

$$= 8.31434 * 4.4545 = 37.0362$$

The intercept at each temperature

**TABLE B:**

$k_2$	Temperature
-130	440°C
0.75	460°C
1.10	480°C
1.35	500°C

## APPENDIX 2

**TABLE 2.1 AT T = 440°C**

Run	i	X <sub>1</sub>	X <sub>i</sub>	Y <sub>i</sub>	X <sub>i</sub> Y <sub>i</sub>	X <sub>i</sub> <sup>2</sup>
1	1	0.40	6	2.5	15	36
2	2	0.32	1.83	1.47	2.69	3.35
3	3	0.28	1.45	1.39	2.02	2.10
4	4	0.20	1.31	1.25	1.68	1.72
5	5	0.17	1.21	1.20	1.45	1.46
6	6	0.15	1.19	1.18	1.40	1.42
7	7	0.13	1.16	1.15	1.33	1.35
8	8	0.12	1.14	1.14	1.30	1.30
9	9	0.10	1.12	1.11	1.24	1.25
10	10	0.09	1.11	1.10	1.22	1.23
11	11	0.08	1.10	1.09	1.20	1.21
12	12	0.08	1.10	1.09	1.20	1.21
13	13	0.07	1.10	1.08	1.20	1.21
14	14	0.08	1.10	1.09	1.20	1.21
15	15	0.07	1.10	1.08	1.20	1.21
16	16	0.07	1.10	1.08	1.20	1.21
17	17	0.06	1.10	1.06	1.20	1.21
18	18	0.07	1.10	1.08	1.20	1.21
19	19	0.04	1.10	1.04	1.14	1.21
			= 27.42	= 20.17	= 40.07	= 62.07

**TABLE 2.2 AT T = 460°C**

Run	i	X <sub>1</sub>	X <sub>i</sub>	Y <sub>i</sub>	X <sub>i</sub> Y <sub>i</sub>	X <sub>i</sub> <sup>2</sup>
1	1	1.00	6	0	0	36
2	2	1.00	1.83	0	0.00	3.35
3	3	0.90	1.45	10	14.50	2.10
4	4	0.88	1.31	8.33	10.90	1.72
5	5	0.83	1.21	5.88	7.10	1.46
6	6	0.85	1.19	6.67	7.90	1.42
7	7	0.72	1.16	3.57	4.90	1.35
8	8	0.65	1.14	2.86	3.30	1.30
9	9	0.60	1.12	2.50	2.80	1.25
10	10	0.57	1.10	2.33	2.60	1.21
11	11	0.51	1.10	2.04	2.20	1.21
12	12	0.48	1.10	1.92	2.10	1.21
13	13	0.45	1.10	1.81	2.00	1.21
14	14	0.44	1.10	1.79	2.00	1.21
15	15	0.39	1.10	1.64	1.80	1.21
16	16	0.38	1.10	1.61	1.80	1.21
17	17	0.35	1.10	1.53	1.70	1.21
18	18	0.33	1.10	1.49	1.60	1.21
19	19	0.32	1.10	1.47	1.60	1.21
20	20	0.30	1.10	1.43	1.60	1.21
21	21	0.28	1.05	1.39	1.50	1.10
22	22	0.27	1.05	1.37	1.40	1.10
23	23	0.25	1.05	1.33	1.40	1.10
24	24	0.24	1.04	1.32	1.40	1.08
25	25	-	-	-	-	-
26	26	0.22	1.04	1.28	1.30	1.08
27	27	0.22	1.04	1.28	1.30	1.08
28	28	0.22	1.04	1.28	1.30	1.08
29	29	0.22	1.04	1.28	1.30	1.08
30	30	0.22	1.04	1.28	1.30	1.08

= 33.89

= 70.68

= 83.30

= 73.01

**TABLE 2.3 AT T = 480°C**

Run	i	X <sub>1</sub>	X <sub>i</sub>	Y <sub>i</sub>	X <sub>i</sub> Y <sub>i</sub>	X <sub>i</sub> <sup>2</sup>
1	1	1.00	6	0	0	36
2	2	1.00	1.83	0	0	3.35
3	3	-	-	-	-	-
4	4	-	-	-	-	-
5	5	0.00	1.24	0	0	1.46
6	6	-	-	-	-	-
7	7	1.00	1.16	0	0	1.35
8	8	0.94	1.14	16.70	19.04	1.30
9	9	0.82	1.12	5.56	6.23	1.25
10	10	0.72	1.10	3.57	3.93	1.21
11	11	0.76	1.10	4.17	4.59	1.21
12	12	0.72	1.10	3.57	3.93	1.21
13	13	-	-	-	-	1.21
14	14	0.66	1.10	2.94	3.23	1.21
15	15	0.58	1.10	2.38	2.62	1.21
16	16	0.57	1.10	2.33	2.56	1.21
17	17	-	1.10	-	-	-
18	18	-	1.10	-	-	-
19	19	0.52	1.10	2.08	2.29	1.21
20	20	-	1.10	-	-	-
21	21	0.46	1.05	1.85	1.94	1.10
22	22	0.43	1.05	1.75	1.84	1.10
23	23	0.41	1.05	1.69	1.77	1.10
24	24	0.37	1.04	1.59		1.08
25	25	-	-	-	-	-
26	26	0.34	1.04	1.52	1.58	1.08
27	27	0.36	1.04	1.56	1.62	1.08
28	28	0.34	1.04	1.52	1.58	1.08
29	29	-	-	-	-	-
30	30	0.32	1.03	1.47	1.51	1.06
31	31	0.30	1.03	1.43	1.47	1.06
32	32	0.28	1.03	1.39	1.43	1.06
33	33	0.33	1.03	1.49	1.49	1.06
34	34	-	-	-	-	-
35	35	0.27	1.03	1.37	1.41	1.06
36	36	0.25	1.03	1.33	1.37	1.06
37	37	0.26	1.03	1.35	1.39	1.06
38	38	0.19	1.03	1.23	1.27	1.06
39	39	0.11	1.03	1.12	1.15	1.06
40	40	0.16	1.03	1.19	1.23	1.06
41	41	-	1.03	-	-	-
42	42	0.13	1.02	1.15	1.17	1.04

= 38.79

= 69.30

= 73.47

= 72.65

**TABLE 2.4 AT T = 500°C**

Run	i	X <sub>1</sub>	X <sub>i</sub>	Y <sub>i</sub>	X <sub>i</sub> Y <sub>i</sub>	X <sub>i</sub> <sup>2</sup>
1	1	1.00	6	0	0	36
2	2	1.00	1.83	0	0	3.35
3	3	1.00	1.45	0	0	2.10
4	4	1.00	1.31	0	0	1.72
5	5	1.00	1.21	0	0	1.46
6	6	0.99	1.19	100.0	119.00	1.42
7	7	0.98	1.16	50.0	58.00	1.35
8	8	0.97	1.14	33.30	37.96	1.30
9	9	0.97	1.12	33.30	37.30	1.25
10	10	0.90	1.10	10.00	11.00	1.21
11	11	0.87	1.10	7.69	8.46	1.21
12	12	0.78	1.10	4.55	5.01	1.21
13	13	0.72	1.10	3.57	3.93	1.21
14	14	0.68	1.10	3.13	3.44	1.21
15	15	0.62	1.10	2.63	2.89	1.21
16	16	0.58	1.10	2.38	2.62	1.21
17	17	0.56	1.10	2.27	2.50	1.21
18	18	-	-	-	-	-
19	19	0.49	1.10	1.96	2.16	1.21
20	20	0.47	1.10	1.89	2.08	1.21
21	21	0.42	1.05	1.72	1.81	1.10
22	22	0.39	1.05	1.67	1.75	1.10
23	23	0.35	1.05	1.53	1.61	1.10
24	24	0.26	1.04	1.35	1.40	1.08
25	25	0.23	1.04	1.30	1.35	1.08
26	26	0.21	1.04	1.27	1.32	1.08
27	27	0.12	1.04	1.14	1.19	1.08
28	28	0.03	1.04	1.03	1.09	1.08

$\Sigma X_1 = 34.83 \quad \Sigma X_i = 267.48 \quad \Sigma Y_i = 307.85 \quad \Sigma X_i^2 = 70.9$

**TABLE 3.1 AT T = 440°C**

Run	i	X <sub>1</sub>	X <sub>i</sub>	Y <sub>i</sub>	X <sub>i</sub> Y <sub>i</sub>	X <sub>i</sub> <sup>2</sup>
1	1	0.40	1.20	2.5	3	1.44
2	2	0.32	0.32	1.47	0.47	0.10
3	3	0.28	0.19	1.39	0.26	0.04
4	4	0.20	0.13	1.25	0.16	0.02
5	5	0.17	0.11	1.20	0.13	0.01
6	6	0.15	0.09	1.18	0.11	0.008
7	7	0.13	0.08	1.15	0.09	0.006
8	8	0.12	0.07	1.14	0.08	0.005
9	9	0.10	0.06	1.11	0.07	0.004
10	10	0.09	0.05	1.10	0.06	0.003
11	11	0.08	0.04	1.09	0.05	0.003
12	12	0.08	0.04	1.09	0.04	0.002
13	13	0.07	0.04	1.08	0.04	0.002
14	14	0.08	0.04	1.09	0.04	0.002
15	15	0.07	0.03	1.08	0.04	0.002
16	16	0.07	0.03	1.08	0.03	0.009
17	17	0.06	0.03	1.06	0.03	0.009
18	18	0.07	0.03	1.08	0.03	0.009
19	19	0.04	0.03	1.04	0.03	0.009

= 2.58      = 13.98      = 4.76      = 1.6506

**TABLE 3.2 = 460°C**

Run	i	X <sub>1</sub>	X <sub>i</sub>	Y <sub>i</sub>	X <sub>i</sub> Y <sub>i</sub>	X <sub>i</sub> <sup>2</sup>
1	1	1.00	1.20	0.00	0	1.44
2	2	1.00	0.32	0.00	0	0.10
3	3	0.90	0.19	14.50	2.76	0.04
4	4	0.88	0.13	10.90	1.42	0.02
5	5	0.83	0.11	7.10	0.78	0.01
6	6	0.85	0.09	7.90	0.71	0.008
7	7	0.72	0.08	4.10	0.33	0.006
8	8	0.65	0.07	3.30	0.23	0.005
9	9	0.60	0.06	2.80	0.17	0.004
10	10	0.57	0.05	2.60	0.13	0.003
11	11	0.51	0.05	2.20	0.11	0.003
12	12	0.48	0.04	2.10	0.11	0.002
13	13	0.45	0.04	2.00	0.08	0.002
14	14	0.44	0.04	2.00	0.08	0.002
15	15	0.39	0.04	1.80	0.07	0.002
16	16	0.38	0.03	1.80	0.05	0.0009
17	17	0.35	0.03	1.70	0.05	0.0009
18	18	0.33	0.03	1.60	0.05	0.0009
19	19	0.32	0.03	1.60	0.05	0.0009
20	20	0.30	0.03	1.60	0.05	0.0009
21	21	0.28	0.02	1.50	0.03	0.0004
22	22	0.27	0.02	1.40	0.03	0.0004
23	23	0.25	0.02	1.40	0.03	0.0004
24	24	0.24	0.02	1.40	0.03	0.0004
25	25	-	-	-	-	-
26	26	0.22	0.02	1.30	0.03	0.0004
27	27	0.22	0.02	1.30	0.03	0.0004
28	28	0.22	0.02	1.30	0.03	0.0004
29	29	0.22	0.02	1.30	0.03	0.0004
30	30	0.22	0.02	1.30	0.03	0.0004

= 2.79      = 83.80      = 7.50      = 1.6551

**TABLE 3.3 = 480°C**

Run	i	X <sub>1</sub>	X <sub>i</sub>	Y <sub>i</sub>	X <sub>i</sub> Y <sub>i</sub>	X <sub>i</sub> <sup>2</sup>
1	1	1.00	1.20	0.00	0.00	1.44
2	2	1.00	0.32	0.00	0.00	0.10
3	3	-	-	-	-	-
4	4	-	-	-	-	-
5	5	1.00	0.11	0.00	0.00	0.01
6	6	-	-	-	-	-
7	7	1.00	0.08	0.00	0.00	0.006
8	8	0.94	0.07	16.70	1.17	0.005
9	9	0.82	0.06	5.56	0.33	0.004
10	10	0.72	0.05	3.57	0.19	0.003
11	11	0.76	0.05	4.17	0.21	0.003
12	12	0.72	0.04	3.57	0.14	0.002
13	13	-	-	-	-	-
14	14	0.66	0.04	2.94	0.12	0.002
15	15	0.58	0.04	2.38	0.10	0.002
16	16	0.57	0.03	2.33	0.07	0.0009
17	17	-	-	-	-	-
18	18	-	-	-	-	-
19	19	0.52	0.03	2.08	0.06	0.0009
20	20	-	-	-	-	-
21	21	0.46	0.03	1.85	0.06	0.0004
22	22	0.43	0.03	1.75	0.05	0.0004
23	23	0.41	0.03	1.69	0.05	0.0004
24	24	0.37	0.03	1.59	0.05	0.0004
25	25	-	-	-	-	-
26	26	0.34	0.02	1.52	0.03	0.0004
27	27	0.36	0.02	1.56	0.03	0.0004
28	28	0.34	0.02	1.52	0.03	0.0004
29	29	-	-	-	-	-
30	30	0.32	0.02	1.47	0.03	0.0004
31	31	0.30	0.02	1.43	0.03	0.0004
32	32	0.28	0.02	1.39	0.03	0.0004
33	33	0.33	0.02	1.49	0.03	0.0004
34	34	-	-	-	-	-
35	35	0.27	0.02	1.37	0.03	0.0004
36	36	0.25	0.01	1.33	0.01	0.0001
37	37	0.26	0.01	1.35	0.01	0.0001
38	38	0.19	0.01	1.23	0.01	0.0001
39	39	0.11	0.01	1.12	0.01	0.0001
40	40	0.16	0.01	1.19	0.01	0.0001
41	41	-	-	-	-	-
42	42	0.13	0.01	1.15	0.01	0.0001

= 2.46    = 69.30    = 2.87    = 1.5852



**TABLE 3.4 AT = 500°C**

Run	i	X <sub>1</sub>	X <sub>i</sub>	Y <sub>i</sub>	X <sub>i</sub> Y <sub>i</sub>	X <sub>i</sub> <sup>2</sup>
1	1	1.00	1.20	0	0	1.44
2	2	1.00	0.32	0	0	0.10
3	3	1.00	0.19	0	0	0.04
4	4	1.00	0.13	0	0	0.02
5	5	1.00	0.11	0	0	0.01
6	6	0.99	0.09	100.00	9.00	0.008
7	7	0.98	0.08	50.00	4.00	0.006
8	8	0.97	0.07	33.30	2.33	0.005
9	9	0.97	0.06	33.30	1.20	0.004
10	10	0.90	0.05	10.00	0.5	0.003
11	11	0.87	0.05	7.69	0.38	0.003
12	12	0.78	0.04	4.55	0.18	0.002
13	13	0.72	0.04	3.57	0.14	0.002
14	14	0.68	0.04	3.13	0.13	0.002
15	15	0.62	0.04	2.63	0.11	0.002
16	16	0.58	0.03	2.38	0.07	0.0009
17	17	0.56	0.03	2.50	0.07	0.0009
18	18	-	-	-	-	-
19	19	0.49	0.03	1.96	0.006	0.009
20	20	0.47	0.03	1.89	0.006	0.0004
21	21	0.42	0.02	1.72	0.003	0.0004
22	22	0.39	0.02	1.67	0.003	0.0004
23	23	0.35	0.02	1.53	0.003	0.0004
24	24	0.26	0.02	1.35	0.003	0.0004
25	25	0.23	0.02	1.30	0.003	0.0004
26	26	0.21	0.02	1.27	0.003	0.0004
27	27	0.12	0.02	1.14	0.002	0.0004
28	28	0.03	0.02	1.03	0.002	0.0004

= 2.75      = 267.91      = 18.45      = 1.6543

**TABLE 3.4 AT 460°C**

Run	i	$X_i$	$X_i$	$Y_i$	$X_i Y_i$	$X_i^2$
1	1	1.00	3.30	0.00	0.00	10.89
2	2	1.00	1.12	0.00	0.00	1.25
3	3	0.90	0.63	14.50	9.14	0.40
4	4	0.88	0.44	10.90	4.80	0.19
5	5	0.83	0.34	7.10	2.41	0.12
6	6	0.85	0.28	7.90	2.21	0.08
7	7	0.72	0.23	4.10	0.94	0.05
8	8	0.65	0.20	3.30	0.66	0.04
9	9	0.60	0.18	2.80	0.50	0.03
10	10	0.57	0.15	2.60	0.39	0.02
11	11	0.57	0.14	2.20	0.31	0.02
12	12	0.48	0.13	2.10	0.27	0.02
13	13	0.45	0.12	2.00	0.24	0.01
14	14	0.44	0.11	2.00	0.22	0.01
15	15	0.39	0.10	1.80	0.18	0.01
16	16	0.38	0.09	1.80	0.15	0.008
17	17	0.35	0.09	1.70	0.15	0.008
18	18	0.33	0.09	1.60	0.14	0.008
19	19	0.32	0.08	1.60	0.13	0.006
20	20	0.30	0.08	1.60	0.13	0.006
21	21	0.28	0.07	1.50	0.11	0.005
22	22	0.27	0.07	1.40	0.10	0.005
23	23	0.25	0.07	1.40	0.10	0.005
24	24	0.24	0.06	1.40	0.09	0.004
25	25	-	-	-	-	-
26	26	0.22	0.06	1.30	0.08	0.004
27	27	0.22	0.06	1.30	0.08	0.004
28	28	0.22	0.05	1.30	0.07	0.003
29	29	0.22	0.05	1.30	0.07	0.0009
30	30	0.22	0.05	1.30	0.04	13.2099
			= 8.38	= 83.8	= 23.71	= 13.2099

**TABLE 3.1 AT 440°C**

Run	i	$X_i$	$X_i$	$Y_i$	$X_i Y_i$	$X_i^2$
1	1	0.40	3.30	2.5	8.25	10.89
2	2	0.32	1.12	1.47	1.65	1.25
3	3	0.28	0.63	1.39	0.38	0.40
4	4	0.20	0.44	1.25	0.55	0.19
5	5	0.17	0.34	1.20	0.41	0.12
6	6	0.15	0.28	1.18	0.33	0.08
7	7	0.13	0.23	1.15	0.26	0.05
8	8	0.12	0.20	1.14	0.23	0.04
9	9	0.10	0.18	1.11	0.20	0.03
10	10	0.09	0.15	1.10	0.17	0.02
11	11	0.08	0.12	1.09	0.15	0.02
12	12	0.08	0.13	1.09	0.14	0.02
13	13	0.07	0.12	1.08	0.13	0.01
14	14	0.08	0.11	1.09	0.12	0.01
15	15	0.07	0.10	1.08	0.11	0.01
16	16	0.07	0.09	1.08	0.10	0.008
17	17	0.06	0.09	1.06	0.10	0.008
18	18	0.07	0.09	1.08	0.10	0.008
19	19	0.04	0.08	1.04	0.10	0.006

= 7.722

= 23.18

= 13.98

= 13.17

# NOMENCLATURE

$a_0^{-1}$	= Initial activity of catalyst
$a_i$	= activity of catalyst after pulse number $i$
$a_o$	= activity of catalyst during pulse number $i$ (function of time)
$h$	= constant
$i$	= pulse number
$k$	= surface reaction rate constant
$K_d$	= deactivation rate constant
$K_1$	= reactivation rate constant
$K_A$	= Void volume per unit weight of catalyst
$X_i$	= fractional conversion of reactant pulse number $i$
$y$	= constant
$t$	= pulse residence time
LHHW	= Langmuir, - Hinshelwood-Hougen-Watson.

## REFERENCES

1. Basset B.W and Habgood H.W.(1960): "A Gas chromatographic study of the catalytic Isomerization of Cyclopropane". J. Phy Chem; 64 769 - 773.
2. Aberuagba .F: Heptane Aromatization on a decaying pt/Al<sub>2</sub>O<sub>3</sub> catalyst sent for publication in Journal of pure and applied sciences.
3. Bruce C. Gates, James R.K, and G.C.A Schuit (1979): "chemistry of catalytic processes" chemical Engineering series 184 - 318
4. Sica. A.M Walles E.M and Gigola. C( 1974): "Analysis of pulsed microcatalytic Reactor microcatalytic Reactors".
5. Blanton W.A Byers C. and merrol.(1979): "Qualitative Rate coefficient from pulsed microcatalytic Reactors.
6. Carberry J.J (1979): "Chemical and catalytic reaction Engineering" chemical Engineering series.
7. Susu A.A Enoch. F.E (1980): "Cyclohexane Dehydrogenation kinetics on a platinum - Rhenium/Aluminium catalyst with Hydrogen and inert Diluents". J. Chem Technol Biochemical 30. 234 - 843.
8. Hattori T. marakami T (1968): " Study on the pulse Reaction Techniques on Theoretical study" L. catal, 30 114 -122.
9. Hishida, T. Uchijama T. and Yomeda Y (1970): "Linear Free Energy Relationship in Heterogeneous catalyst IX kinetic study of catalytic Dehydrogenation of cyclohexanes by the pulse technique "J. catal 17 87 - 286.
10. Delmon B and Froment O. (1980) "Catalyst Deactivation, proceedings of the International symposium" Antwerp EK scientific publishing company 13 - 150.
11. Figuerodo J. L. (Ed) (1981) Process in catalyst Deactivation, Advanced study institute series, E No 54 M. Nigh off Publishers London.
12. Daniel B. A. and Alfred A.S (1987) "Analysis of Pulse Microcatalytic Technique for

catalyst wi

13. "Variable activity" chem Eng comm vol. 70 1 - 44.
14. N.R DRAPER, H SMITH (1966): "Applied Regression Analysis "Wiley series in probability and mathematical statistics 1 - 35.
14. M Douglas, E.R ReiH, Jr, and J.R KiHrell "Journal of catalysis" Engineering science vol. 322 - 329.
15. Daniel B. Ayo and Alfred .A. Susu (1988): "Analysis of Pulse Microcatalytic Technique for Catalyst with Variable Activity" chem Eng comm. Vol. 70 1 - 44.