CHAPTER-V

STUDIES ON THE KINETICS OF DEHYDROGENATION OF n-DODECANE ON PLATINUM-TIN-LITHIUM ON ALUMINA CATALYST

V.I INTRODUCTION

The dehydrogenation of n-dodecane yields dodecene and hydrogen as the primary products of reaction. This reaction is complicated by accompanying reactions, viz. secondary dehydrogenation leading to the formation of dienes and trienes, dehydrocyclisation forming aromatic compounds from trienes, isomerisation of reactant and products which yield a large number of isomers and cracking and coking reactions which lead to the formation of lighter paraffins/olefins and coke. The latter leads to the deactivation of the catalyst and in order to decelerate coking, hydrogen is added to the reactant. This added hydrogen which is also one of the products complicate the kinetics of the reaction.

Sadykhova et al (237) have reported the kinetics of n-dodecane dehydrogenation over Pt-Sn/alumina catalysts, in the temperature range of 723 to 743 K at atmospheric pressure in a circulating flow system. Their data treatment consists of simultaneous solution of the rate equations for the monoolefins formation, dienes formation and aromatics formation. They report that the desorption of one of the products, viz. hydrogen, monoolefin or diene, from the surface of the catalyst is rate controlling. However, the resistance term as derived by them, does not conform to the classical Langmuir-Hinshelwood type of models. The classical L-H model for the reaction,

$$A \rightleftharpoons R + S$$

to which the n-dodecane dehydrogenation belongs, with desorption of "R" as the rate controlling step is written as:

$$r = k\ (P_A - P_R P_S / K_{eq}) \Big/ P_S (1 + K_A P_A + K_{RS} P_A / P_S + K_S P_S)$$

Here the partial pressure term for "R", viz. P_R does not appear in the denominator (resistance term) and the resistance term is multiplied by P_S, the partial pressure term of the product "S", desorption of which is not rate controlling. Sadykhova et al's equations show the resistance term to be,

$$(P_R^m + K_A P_A + K_S P_S + \ldots\ldots)^n$$

where $m=1.5$ & $n=1$.

Thus, they deviate from the Langmuir-Hinshelwood type of models and some amount of empiricism is observed. However, the study covers a wide range of operating parameters and is meticulous.

V.2 AIM AND SCOPE OF THE WORK

In the present work an attempt has been made at studying only one reaction, viz. dehydrogenation of n-dodecane to monoolefins, by suppressing the accompanying reactions. This was achieved by decreasing the reaction temperature to the range 658 to 703 K and working at low fractional conversions 0.005 to 0.125 mole. The study was carried out in a fixed bed tubular glass reactor of length 25 cm and inner diameter 4 mm operated under continuous flow, plug flow, isothermal conditions at atmospheric pressure with a hydrogen:hydrocarbon mole ratio 6. The reactor was heated by means of a resistance furnace.

Under these conditions only paraffin, monoolefins and their isomers were detected with a 9 m poly(phenyl ether) (25wt%) on Chromosorb-P, packed column, 1/8" O.D. in a Varian 6000 gas chromatograph using a thermal conductivity detector(TCD).

Therefore, in the present case it appears reasonable to neglect secondary dehydrogenation as well as dehydrocyclisation reactions leading to formation of dienes, trienes and aromatics. Catalyst deactivation too was slow with steady state conversions over a period of 2 to 3 h on stream. Thus, coking also was not taken into account. However, isomerisation could not be suppressed and all the isomers of the olefin were clubbed together. The data upto the first 2 h was used for studying the kinetics.

V.3 STUDIES ON MASS TRANSFER EFFECTS.

In order to obtain intrinsic rate data, the influence of interphase and intraphase mass transfer on the rate of the reaction must be rendered negligible. Influence of interphase mass transfer was assessed by studying the influence of reactant flow velocity on the reactant conversion under constant reaction conditions,viz. temperature 733 K, feed composition 14.28 % n-dodecane, 85.72 % hydrogen (molar basis), H_2:HC = 6 (mole/mole) reactant space time 1.24 g cat h/g mole dodecane and atmospheric pressure. Flow velocity of the reactant (n-dodecane) was varied in different experiments at constant space time, by changing reactant flow rate and the weight of the catalyst in equal proportions so that their ratio remained constant. Reactant flow velocity was varied from 0.3 cm/sec to 2.3 cm/sec. The reaction temperature was 733 K, much higher than that maintained while collecting the kinetic data (658 to 703 K) because the influence of interphase mass transfer on reaction rate is strongly affected by the reaction temperature and those flow velocity conditions that render interphase mass transfer influence negligible at any given temperature, can be used more confidently at lower temperatures. Catalyst particle size was in the range 0.5 to 0.6 mm. This was obtained by crushing followed by sieving.

The results of the interphase mass transfer study are presented in Fig V.1 and Table V.1. The results in Fig.V.1 show that the catalyst deactivates quite rapidly. Comparison of reactant conversions in the first 30 min of reaction indicates that a ten fold increase in the reactant flow velocity has negligible influence on conversion, hence the influence of external mass transfer on the reaction rate is negligible. However, a comparison of conversions with increasing time on stream, shows a divergence of the curves. For the same time on stream after the initial 30 min on stream, increase in reactant flow velocity lead to higher conversions, suggesting a decrease in the extent of deactivation. Since a H_2:HC mole ratio 6 was maintained for all the runs, increase in flow velocity of n-dodecane also led to an increase in the flow velocity of hydrogen. Hydrogen is added to most petrochemical reactors in a mole ratio, H_2:HC>1 because hydrogen rehydrogenates coke precursors, which are mostly poly unsaturated hydrocarbons and thereby decelerates coking and catalyst deactivation by fouling. From the current interphase mass transfer study it appears that this hydrogenation of coke precursors is interphase mass transfer limited. Visual examination of the catalyst suggested axial dispersion of coke in the bed. Therefore, to rule out the possibility of decreased deactivation due to availability of longer catalyst bed in experiments with increasing reactant flow velocity, the following experiments were carried out. Two experiments were carried out

TABLE V.1

Influence of Interphase Mass Transfer On Reactant Conversion

Temperature	: 733 K
Space time	: 1.24 g cat h/gmole
Pressure	: Atmospheric
Hydrogen:Hydrocarbon (mole)	: 6

No.	**Flow velocity (cm/sec)**	**Reactant conversion at 10th minute (%)**
1	2.36	21.0
2	1.18	20.8
3	0.59	21.2
4	0.29	20.8

TABLE V.2

Influence of Intraphase Mass Transfer On Reactant Conversion

Temperature	: 733 K
Space time	: 1.24 g cat h/gmole
Pressure	: Atmospheric
Hydrogen:Hydrocarbon (mole)	: 6

No.	**Particle size (mm)**	**Reactant conversion at 10th minute (%)**
1	0.1-0.3	22.5
2	0.5-0.6	22.3
3	1.0-1.2	21.4
4	1.7-2.0	15.0

wherein the reactant flow rates and weight of catalyst were doubled in one of the experiments. The inner diameter of the reactor was changed from 4 mm to 6 mm so that the length of the catalyst bed in the two reactors was almost equal. All other reaction conditions were kept constant as cited in earlier paragraphs of this section. The results of these experiments are shown in Fig. V.2. The curves in this figure too show a divergence with increasing time on stream and the extent of deactivation is larger (at any given time on stream) for the run with low flow velocity, although the catalyst bed lengths were comparable in both. Hence, the cause of slower deactivation with higher reactant flow velocity can safely be attributed to the interphase mass transfer limitation for the hydrogenation of coke precursors by hydrogen.

The influence of intraphase mass transfer on conversion was studied by varying the catalyst particle size in the range of 2.0 mm to 0.1 mm in different experiments. The results are shown in Fig. V.3 and in Table V.2. From the results it is clear that intraphase mass transfer has a negligible effect on the rate of the reaction provided the particle size of the catalyst is 0.6 mm or smaller. A particle size of 0.5 to 0.6 mm was maintained for all runs while collecting kinetic data.

V.4 KINETICS OF n-DODECANE DEHYDROGENATION ON Pt-Sn-Li/ALUMINA

Kinetic rate data were collected in the intrinsic region free from influence of inter and intraphase mass transfer effects Axial aspect ratio >50 and radial aspect ratio =8 were maintained for all the runs. Near isothermal conditions were maintained within the reactor. Various reaction parameters are given in

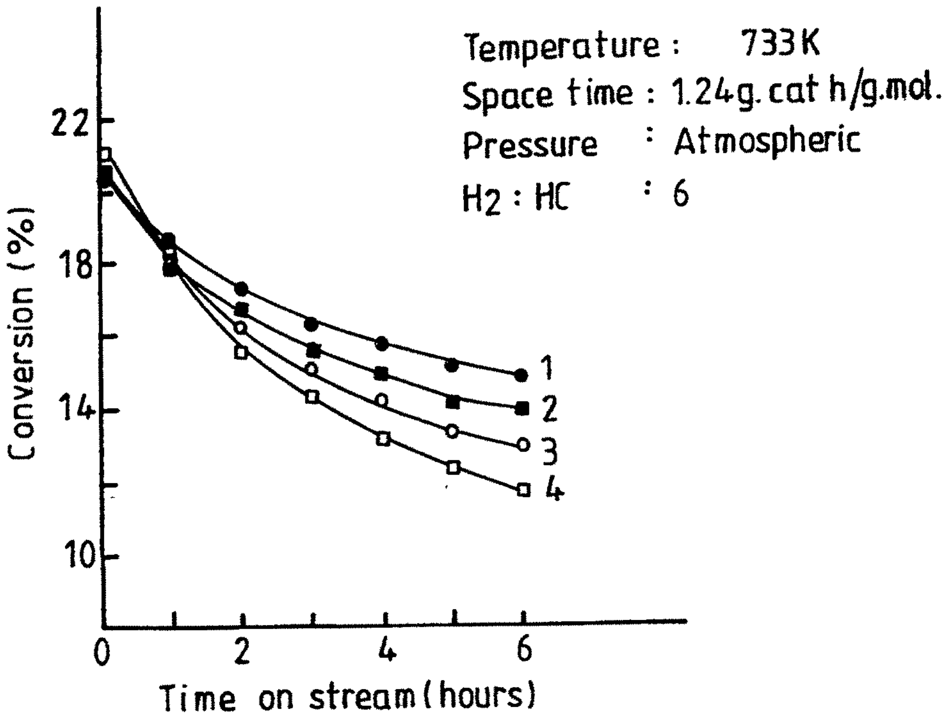


Fig. V.1. Effect of external mass transfer on conversion.

Flow velocities : 1. 2.36 cm/sec. 2. 1.18 cm/sec.
3. 0.59 cm/sec. 4. 0.29 cm/sec.

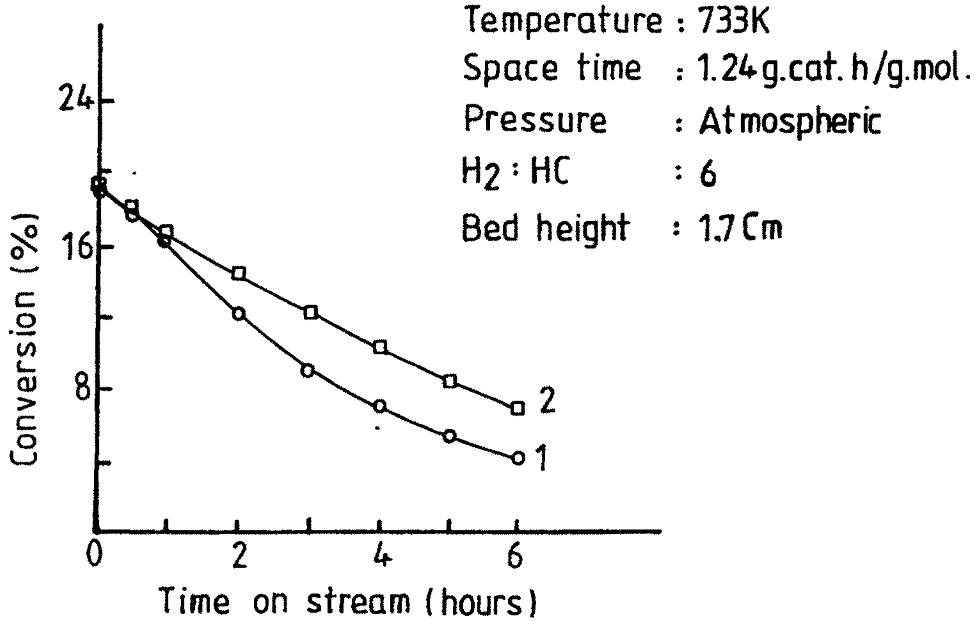
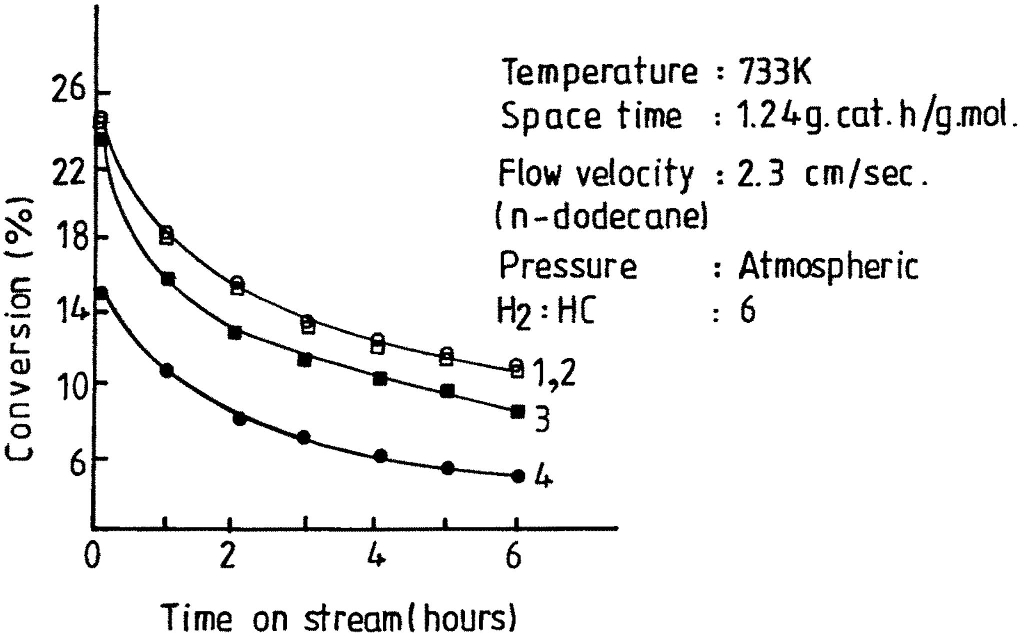


Fig. V.2. Effect of constant bed height and varying flow velocity on conversion.

Flow velocities : 1. 0.29 cm/sec. 2. 0.87 cm/sec.
(n-dodecane)



Temperature : 733K
Space time : 1.24g.cat.h/g.mol.
Flow velocity : 2.3 cm/sec.
(n-dodecane)
Pressure : Atmospheric
H_2 : HC : 6

Fig. V.3. Effect of internal mass transfer on conversion.

Particle size :	1.	0.10 - 0.30 mm	2.	0.5 - 0.6 mm
	3.	1.0 - 1.2 mm	4.	1.7 - 2.0 mm

Table V.3. Data were collected as paraffin converted vs. space time at different reaction temperatures.

TABLE V.3

Range of Reaction Parameters Studied

Reaction temperature	: 658 to 703 K
Space time, (g cat h/gmole)	: 0.17 to 0.90
Pressure	: Atmospheric
Fractional conversion (mole)	: 0.005 to 0.125
Paraffin partial pressure	: 0.13 to 0.03
Hydrogen partial pressure	: 0.97 to 0.19

Some runs were also carried out wherein the partial pressures of n-dodecane and hydrogen were varied (Table V.4).

V.4.1 Data Analysis

The data were smoothened by curve fitting using the following polynomial relationship,.

$$x = a(W/F) + b(W/F)^2 + c(W/F)^3 + \ldots..$$

Conversion was expressed as a polynomial function of space time. The values of the coefficients a, b, c.... were determined by polynomial regression. Point reaction rates were determined by differentiating this equation with respect to space time.

$$-r_p = \frac{dx}{d(W/F)} = a + 2b(W/F) + 3c(W/F)^2 + \ldots..$$

Reaction rates are tabulated in Table V.4 alongwith the coversion and space time data. The programme used for the polynomial regression is listed in appendix-2 (PRG:FTN, STAT:FTN). The stoichiometry of the reaction is given in appendix-4.

V.4.2 Model Development

Models were built based on the Langmuir-Hinshelwood type. The following assumptions were made;

(1) Only one step in the reaction is rate controlling.

(2) Homogeneous surface with respect to the type of active sites.

(3) Isomers of dodecene were all pooled up as olefins, therefore the isomerisation reaction was neglected.

(4) Secondary dehydrogenation reactions as well as dehydrocyclisation and coking reactions were neglected for reasons given in earlier paragraphs of this chapter.

Details of model derivation and equations for different models are given in appendix-1.

V.4.3 Criteria For Model Acceptance

1. Both global reaction rate constant and the adsorption coefficients should be valued greater than zero.
2. The reaction rate constant should exhibit Arrhenius dependency
3. The adsorption coefficients should show a well defined trend with reaction temperature.

V.4.4 Parameter Estimation

Parameter estimation was carried out using Simplex Search method of Nedler and Mead(241) as described in appendix-2. The method consists of optimisation based on a least squares approach wherein the sum of residual squares of an objective function, like reaction rate in the case of differential analysis and space time in the case of integral analysis, is minimised.

Seven models were tested in all, they were those with adsorption of reactant, surface reaction and desorption of the

TABLE V.4

Kinetic Rate Data

Effect of change in space velocity

No.	Reaction temp.(K)	Space time (W/F)	Fractional conversion (mole)	Reaction rate *
1	658	0.17	0.008	0.0354
2	"	0.31	0.013	0.0339
3	"	0.42	0.017	0.0325
4	"	0.60	0.023	0.0306
5	"	0.90	0.031	0.0275
6	673	0.17	0.015	0.0634
7	"	0.31	0.025	0.0613
8	"	0.42	0.032	0.0594
9	"	0.60	0.042	0.0568
10	"	0.90	0.058	0.0527
11	703	0.17	0.032	0.1490
12	"	0.31	0.052	0.1410
13	"	0.42	0.069	0.1330
14	"	0.60	0.094	0.1230
15	"	0.90	0.125	0.1060

Effect of change in partial pressure of paraffin
Weight of catalyst 0.0502 g

No.	Temp. (K)	Total space time	Partial pressure				Fract. conversion	React. rate **
			P	O	H	He		
16	673	0.0816	0.1347	0.00400	0.86	0.000	0.0081	0.0991
17	"	"	0.1007	0.00320	0.86	0.036	0.0063	0.0771
18	"	"	0.0672	0.00220	0.86	0.071	0.0044	0.0538
19	"	"	0.0331	0.00126	0.86	0.107	0.0025	0.0309

Effect of change in partial pressure of hydrogen
Weight of catalyst 0.05 g

20	673	0.0366	0.0310	0.00067	0.970	0.000	0.0420	0.035
21	"	"	0.0307	0.00073	0.770	0.190	0.0460	0.038
22	"	"	0.0305	0.00084	0.580	0.387	0.0530	0.046
23	"	"	0.0301	0.00100	0.390	0.580	0.0660	0.057
24	"	"	0.0300	0.00110	0.194	0.774	0.0700	0.063

* determined from 2nd order polynomial regression
** determined as (X.F)tot/W

products, viz. olefin and hydrogen as the rate controlling step. Forms of these equations are given in appendix-1.

Initial parameter estimation was done by linearising the rate equations as follows.

Considering the equation for the surface reaction as the rate controlling step,

$$r = k\,K_P(P_P - P_O P_H/K_{eq}) \big/ (1 + K_P P_P + K_O P_O + K_H P_H)^2$$

cross multiplication leads to,

$$r(1 + K_P P_P + K_O P_O + K_H P_H)^2 = k\,K_P(P_P - P_O P_H/K_{eq})$$

$$\frac{1}{\sqrt{kK_P}} + \frac{K_P}{\sqrt{kK_P}} P_P + \frac{K_O}{\sqrt{kK_P}} P_O + \frac{K_H}{\sqrt{kK_P}} P_H = \sqrt{\frac{(P_P - P_O P_H/K_{eq})}{r}}$$

which is of the form,

$$y = a + bx_1 + cx_2 + dx_3 + \dots + nx_n$$

Unknowns were obtained by simultaneous solution of 'n' equations and were used as initial guesses for the parameter estimation of the original nonlinear equations by the simplex search method.

V.4.5 Power Law Model

A power law model was also tested. The form of the power law model was as follows,

$$-r_P = k(P_P^{\alpha} - P_O^{\beta} P_H^{\gamma}/K_{eq})$$

where, $-r_P$ = rate of disappearance of the reactant,

k = reaction rate constant,

P_P = partial pressure of n-dodecane (paraffin),

P_O = partial pressure of dodecene (olefin),

P_H = partial pressure of hydrogen, and

α, β, γ are the reaction orders with respect to paraffin, olefin and hydrogen respectively.

In order to determine the order of the reaction with respect to the reactant and products, data was collected by varying the partial pressures of n-dodecane and hydrogen in different experiments by adding an inert gas He. The total space time was maintained constant for these runs and the conversions were calculated based on total space velocities. Since the reactant conversions were low (< 5 %) reaction rate was calculated directly as,

$$-r = x_{tot} \frac{F_{tot}}{W},$$ where x_{tot} is the conversion based on total flow rates and (F_{tot} /W) is the total space velocity.

Data for conversion as a function of space time at different reaction temperatures were also tested with the power law model. Results of both are presented in Table V.5. In the latter case the orders with respect to the reactant and with respect to the product n-dodecene are fractional. Since the influence of inter and intraphase mass transfer limitations were rendered negligible at a reaction temperature 773 K (whereas the range of temperature for the kinetic study was 658 to 703 K) the fractional orders are not likely to be due to mass transfer influences.

The estimated activation energy, 29.14 Kcal/mole, (Table V.5) is of the same order of magnitude as that calculated from the L-H adsorption type models, viz. 16.52 Kcal/mole (Table V.8).

V.4.6 Adsorption Type Models (Langmuir-Hinshelwood Type)

Data presented in Table V.4 were used in this case. Both differential and integral analysis of data were carried out. In

TABLE V.5

Results of Power Law Analysis of Data

(a) Data of conversion and rate on total basis; wherein partial pressures of reactant and hydrogen where varied at constant total space time (Table V.4)

Rate constant	**Order w.r.to**			**Residual sum of squares**	**Standard deviation**
	Paraffin (α)	**Olefin (β)**	**Hydrogen (γ)**		
0.95	1.02	0.99	1.06	0.35×10^{-2}	0.55×10^{-4}

(b) Data of conversion as a function of space time at constant reaction temperature and feed composition.

Temp. (K)	**Rate const-ant(k)**	**Order w.r.to**			**Residual sum of squares**	**Standard deviation**
		Paraffin (α)	**Olefin (β)**	**Hydrogen (γ)**		
658	0.66	1.49	1.10	0.95	0.14×10^{-3}	0.39×10^{-5}
673	1.62	1.45	0.73	0.97	0.10×10^{-3}	0.37×10^{-6}
703	2.96	1.37	0.88	1.10	0.40×10^{-4}	0.57×10^{-6}

Activation energy ($-E_a$) = 29.14 Kcal/mole

Pre-exponential factor (A) = 3.7×10^{9}

differential analysis rates were calculated by polynomial regression and the rate equations were linearised as explained in earlier sections of this chapter. In the case of integral analsis, raw data of conversion as a function of space time were used directly in the plug flow equation,

$$dW.dr = dx.dF$$

$$\frac{dW}{F} = dx.\frac{1}{r}$$

$$\frac{W}{F} = \int_{0}^{x} dx.\frac{1}{r}$$

For testing various models the term "r" was substituted with the relevant rate equation. This yielded equations of the form,

$$\frac{W}{F} = \alpha\int_{0}^{x}\frac{1}{dx} + 2\alpha\beta\int_{0}^{x}\frac{x}{dx} + \beta\int_{0}^{x}\frac{x^{2}}{dx}$$

analytical solutions to which are available. These analytical solutions were substituted and resulted in an equation with known space time (observable) on the left hand side and a nonlinear term consisting of conversion (observable) and parameters (unknowns) on the right hand side. The simplex search program of Nedler and Mead was used to obtain these unknown parameters. Terms representing the unknown parameters for various models are listed in appendix-3. Final result of differential and integral analysis are given in Table V.6 and V.7 respectively. All the other models excepting the dual site L-H model with surface reaction as the rate controlling step were rejected because of the occurence of one or more parameters with negative value or for reasons of the residual sum of squares being higher by atleast

TABLE V.6

Result of Differential Analysis of Data-Linearised Model

Models tested : 7, dual and single site models with adsorption of reactant, surface reaction and desorption of products as rate controlling steps. Models rejected : 6.

Model accepted : 1, Dual site with surface reaction controlling.

Temp. (K)	Values of parameters				Residual sum of squares	Standard deviation
	a	b	c	d		
658	0.6	0.85	9.0	1.5	3.3×10^{-2}	0.72×10^{-4}
673	0.96	0.43	8.0	0.53	2.8×10^{-3}	0.79×10^{-4}
703	0.82	0.29	1.88	0.11	2.5×10^{-3}	0.81×10^{-4}

where $a = \frac{1}{\sqrt{kK_P}}$, $b = \frac{K_P}{\sqrt{kK_P}}$, $c = \frac{K_O}{\sqrt{kK_P}}$ and $d = \frac{K_H}{\sqrt{kK_P}}$.

TABLE V.7

Results of Integral Analysis of Data

Temp. (K)	Model tested	Values of Parameters				Residual sum of squares	Standard deviation
		k	K_P	K_O	K_H		
658	DSSRC	1.97	1.42	16.02	2.48	0.72×10^{-2}	0.90×10^{-5}
673	DSSRC	2.57	0.46	8.63	0.50	0.54×10^{-2}	0.80×10^{-4}
703	DSSRC	4.42	0.36	2.34	0.12	0.29×10^{-2}	0.31×10^{-4}

Values of Parameters Obtained From Differential Analysis

Temp. (K)	Values of parameters			
	k	K_P	K_O	K_H
658	1.95	1.41	14.94	2.49
673	2.42	0.44	8.32	0.55
703	4.42	0.36	2.34	0.12

TABLE V.8

Activation Energy And Enthalpy of Adsorption : Calculated From Integral Analysis of Data

Parameter estimated	**Calculated value**	**Correlation Factor**
Activation Energy $(-E_a)$	16.56 Kcal/gmole	0.999
Pre-exponential Factor (A)	6.2×10^5	-----
Enthalpy of Adsorption of Paraffin	25.42 Kcal/gmole	0.860
Enthalpy of Adsorption of Olefin	39.49 Kcal/gmole	0.999
Enthalpy of Adsorption of Hydrogen	59.39 Kcal/gmole	0.978

one order of magnitude than in the case of surface reaction model. A comparison of the values of parameters obtained from differential and integral analysis is made in Table V.7 and it can be seen that they are comparable.

The activation energy of the reaction and the enthalpies of adsorption of the reactant and products are presented in Table V.8. The activation energy 16.5 Kcal/mole is comparable with that reported by Sadykhova et al (237), which is also approximately 16 Kcal/gmole. The enthalpies of adsorption, however, are much higher than what they have reported.