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RESEARCH ARTICLE

MODELING AND SIMULATION OF ISO-OCTANE PRODUCTION KINETIC BY USING NONLINEAR LEAST SQUARES METHOD.

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Abstract

Experimental reaction data must be fitted into a useful reaction rate equation in order to use in the simulation of reactor design and sizing. The optimization techniques of experimental data of homogenous reaction are well established, many challenges are encountered when experimental data are of catalytic reactions. A computer simulation tool has been developed to accept experimental reaction data and fit the data into a nonlinear reaction rate equation.

Five mathematical models have been developed of heterogeneous chemical reaction of iso-octene with hydrogen. Then nonlinear regression for these models done depending on the experimental data produced by Hougen and Watson (1959). Regression done by using Polymath V6.1 to evaluate the kinetic constants of the models. Results reveal the adsorption of hydrogen and iso-octene occur firstly on different active sites of a catalyst surface followed by a surface chemical reaction, and the hydrogenation chemical reaction is limiting by a surface reaction step according to dual sites mechanism. So it can be concluded that a Polymath program is a powerful tool to solve the optimization problem in heterogeneous catalysis.

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Introduction:-

In the industrial applications of kinetics, knowledge of chemical rate equation is essential in establishing the optimum conditions of pressure, temperature, feed composition, space velocity, extent of conversion and recycling [1]. The algorithm for collecting information for catalytic reactor design is shown in Figure (1).

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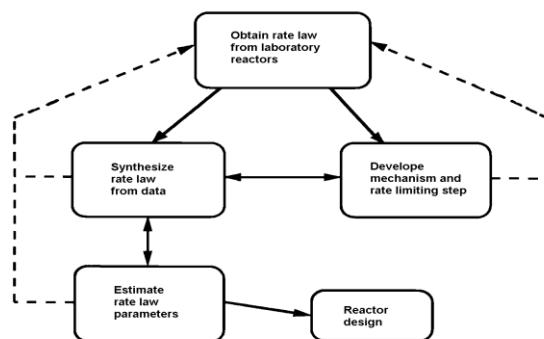


Figure 1:- Collecting Information for Catalytic Reactor Design [2].

Experimental data of a heterogeneous chemical reaction is fitted with a theoretical, semi-theoretical, or empirical rate equation. Kinetic model equation is employed to predict the reaction rate among the ranges of the variables studied in some cases to permit cautious extrapolation. This can be most often through with a group of Langmuir-Hinshelwood (L-H) rate equations. The L-H rate equation of heterogeneous catalysis is widely used by chemical engineers in the correlation of experimental catalytic reaction rate data [3]. L-H rate equations are used to represent heterogeneous reactions where adsorption effects are important. With the knowledge of kinetic constants these rate equations are screened to reject those that are inadequate in the light of the data [4].

The optimization problem can be quite difficult for L-H rate equations because of many factors. First, these rate equations are frequently nonlinear with respect to the rate constants within these rate equations. Second, the number of rate constants contained in each rate equation can be too many for the range of the experimental data [5]. Rate constants in L-H rate equation are optimized using the principle of minimization of sum of squares of residuals.

The present work can be used to find out possible rate equations for heterogeneous reactions. After testing corresponding rate equations versus available experimental data, the most suitable mechanism representing the reaction and the corresponding rate equation and constants can be selected on the basis of sum squares of residuals and sign of kinetic constant. Polymath V6.1 is used to optimize the rate constants in Langmuir-Hinshelwood equations. Nonlinear programming (NLP) solver is used to minimize the sum of square of residuals.

So, the objective of the manuscript is modeling and use a computer optimization tool to determine the best catalytic reaction rate equation, and reaction rate constants of obtained models based on available experimental data of a hydrogenation reaction of iso-octene as a case study.

Steps of Catalytic Chemical Reactions:-

Figure (2) shows a mechanism of catalytic reactions inside a tubular reactor packed with catalytic pellets. The overall process by which heterogeneous catalytic reactions proceed can be broken down into the sequence of individual steps shown in Table (1).

The overall rate of reaction is equal to the rate of the slowest step in the mechanism, when the diffusion steps (1, 2, 6, and 7 as shown in Table (1)) are very fast compared with the reaction steps (3, 4, and 5), the concentrations in the immediate vicinity of the active sites are indistinguishable from those in the bulk fluid. In this situation, the transport or diffusion steps do not affect the overall rate of the reaction. In other situations, if the reaction steps are very fast compared with the diffusion steps, mass transport does affect the reaction rate. In systems where diffusion from the bulk gas or liquid to the catalyst surface or to the mouths of catalyst pores affects the rate, changing the (low conditions) past the catalyst should change the overall reaction rate. In porous catalysts, on the other hand, diffusion within the catalyst pores may limit the rate of reaction. Under these circumstances, the overall rate will be unaffected by external flow conditions even though diffusion affects the overall reaction rate [2].

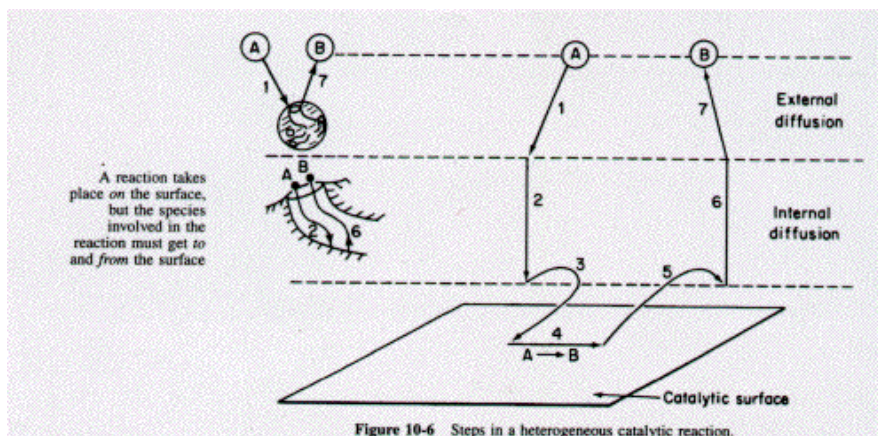


Figure 2:- Steps in a heterogeneous catalytic chemical reaction [2].

Table 1:-Steps in a catalytic chemical reaction [2]

| Steps |
|--|
| 1. Mass transfer (diffusion) of the reactant(s) (e.g., species A) from the bulk fluid to the external surface of the catalyst pellet. |
| 2. Diffusion of the reactant from the pore mouth through the catalyst pores to the immediate vicinity of the internal catalytic surface. |
| 3. Adsorption of reactant A onto the catalyst surface |
| 4. Reaction on the surface of the catalyst (e.g., $A \longrightarrow B$) |
| 5. Desorption of the products (e.g., B) from the surface |
| 6. Diffusion of the products from the interior of the pellet to the pore mouth at the external surface |
| 7. Mass transfer of the products from the external pellet surface to the bulk fluid |

There are many variations of the situation described in Table (1). Sometimes two reactants are necessary for a reaction to occur, and of these may undergo the steps listed above. Other reactions between two substances have only one of them adsorbed, also it may be treat individually the step involved in catalytic reactions.

Langmuir-Hinshelwood Approach:-

The approach in determining catalytic and heterogeneous mechanisms is usually termed as the Langmuir-Hinshelwood approach. It was derived from ideas proposed by Hinshelwood based on Langmuir's principles for adsorption. It is based on the following hypotheses [6]:

1. Uniformly energetic adsorption sites.
2. Monolayer coverage.
3. No interaction between adsorbed molecules.

Once the reactant has been adsorbed onto the surface, it is capable of reacting in number of ways to form the reaction product. Three of these ways are:

1. Single site mechanism
2. Similar or dissimilar dual site mechanism
3. Eley-Rideal Mechanism

Nonlinear Least Squares Method:-

The method of nonlinear least squares may be used to determine the best constants in a given form of equation and also for establishing the best form of equation for a given set of data. In a broad-gauged description of this method, one attempts to minimize Sum of Squares of Residuals (SSR), in an iterative fashion rather than in a single step. It is called Variance or (probability distribution) is a measurement of the spread between numbers in a data set. The variance measures how far each number in the set is from the mean.

Difficulties faced on linear least square method are eliminated in nonlinear least square method. The algebraic rate equation is used in the original form without imposing arbitrary transformations. Thus the minimization of the sum of squares of the errors is appropriate in terms of untransformed variables.

The nonlinear least square method has been extensively used to solve the problem of rate constant optimization in heterogeneous catalytic reaction rate equation.

Simulation of Kinetics by Using Polymath V6.1:-

Application of Polymath for Rate Constant Optimization Langmuir-Hinshelwood catalytic rate equations are essentially nonlinear. Polymath software V6.1 (The program was developed with the cooperation of The CACHE Corporation, The University of Connecticut, and The University of Michigan) is used for formulating, solving, and analyzing optimization problems. Polymath provides a solver called NLP to solve nonlinear programming problems. NLP solver based on minimize the sum of squares of residuals.

Lower bounds of rate constants to be estimated are needed to initialize the program. NLP solver in Polymath returns the optimized rate constants if the lower bounds are lower than optimum value. Polymath also returns the sum of squares of residuals along with the optimized rate constants.

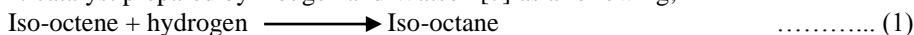
Criterion for Rate equation Selection:-

It is the requirement of the theory upon which L-H equations are based that all rate constants must have positive or zero values [7]. Rate constants actually are adsorption equilibrium constants. Adsorption equilibrium constant can either be positive or zero that is no adsorption is taking place. But it cannot be negative. All the rate equations are rejected which give negative rate constants. The rate equation with all positive rate constants and with lowest sum of squares of residuals is considered as the suitable rate equation.

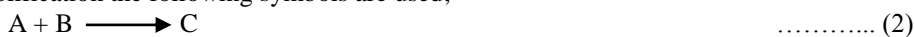
Polymath has facility to enter lower bounds for rate constants. So the rate constant will never take the negative value even if the rate equation is not suitable. To solve this problem one can try different lower bounds. For the best fitting rate equation all lower bounds will converge to the same values of rate constants, while for unsuitable rate equations the final values of rate constants will be different. After selecting the rate equations with positive rate constants one can compare the sum of squares of residuals to select the best rate equation.

Problem Statement:-

A heterogeneous chemical reaction of iso-octene with hydrogen occurs at temperature 200 °C and pressure 3 atm over Co/Pt catalyst prepared by Hougen and Watson [7] as a following;



For simplification the following symbols are used;



The mechanism of this heterogeneous chemical reaction may be represented by many models, but only one will be valid to express on the experimental results of this reaction.

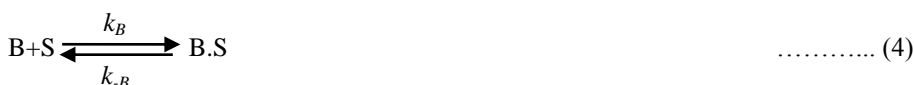
Mechanisms of Reaction Kinetic:-

In the following analysis, surface chemical reaction, adsorption, and desorption will be derivative according to the following mechanisms;

Dual Site Mechanism (Mechanism 1):-

The suggested mechanism are,

Adsorption;



Surface reaction;



Desorption;



The rate of these steps of mechanism are;
Rate of isothermal adsorption of iso-octene;



$$-r_{AD} = k_A P_A C_v - k_{-A} C_{A.S} \dots\dots\dots (7)$$

$$\therefore K_A = \frac{k_A}{k_{-A}}$$

$$\therefore -r_{AD} = k_A \left[P_A C_v - \frac{C_{A.S}}{K_A} \right] \dots\dots\dots (8)$$

Rate of isothermal adsorption of hydrogen;



$$-r_{AD} = k_B P_B C_v - k_{-B} C_{B.S} \dots\dots\dots (9)$$

$$\therefore K_B = \frac{k_B}{k_{-B}}$$

$$\therefore -r_{AD} = k_B \left[P_B C_v - \frac{C_{B.S}}{K_B} \right] \dots\dots\dots (10)$$

Rate of surface reaction;



$$-r_S = k_S C_{A.S} C_{B.S} - k_{-S} C_{C.S} C_v$$

$$K_S = \frac{k_S}{k_{-S}}$$

$$-r_S = k_S \left[C_{A.S} C_{B.S} - \frac{C_{C.S} C_v}{K_S} \right] \dots\dots\dots (11)$$

Rate of desorption;



$$-r_D = k_D \left[C_{C.S} - \frac{P_C C_v}{K_{DT}} \right]$$

$$K_D = \frac{1}{K_{DT}} = \frac{k_{-D}}{k_D}$$

$$-r_D = k_D [C_{C.S} - K_D P_C C_v] \dots\dots\dots (12)$$

Surface chemical reaction is the limiting rate (Model 1):-

$$\frac{-r_{AD}}{k_A} \cong \frac{-r_{AD}}{k_B} \cong \frac{-r_D}{k_D} \cong 0 \dots\dots\dots (13)$$

Now, going to evaluate of C_{A.S}, C_{B.S}, and C_{C.S} in terms of the partial pressures as following;

By applying Eqn. (13) in Eqn. (8) to gives;

$$\frac{-r_{AD}}{k_A} = 0 = P_A C_v - \frac{1}{K_A} C_{A.S}$$

$$C_{A.S} = K_A P_A C_v \dots\dots\dots (14)$$

By applying Eqn. (13) in Eqn. (10) to gives:

$$\begin{aligned} \frac{-r_{AD2}}{k_B} = 0 &= P_B C_V - \frac{1}{K_B} C_{B.S} \\ C_{B.S} &= K_B P_B C_V \end{aligned} \quad \dots\dots\dots (15)$$

By applying Eqn. (13) at Eqn. (12) to gives:

$$\begin{aligned} \frac{-r_D}{k_D} = 0 &= C_{C.S} - K_D P_C C_V \\ C_{C.S} &= K_D P_C C_V \end{aligned} \quad \dots\dots\dots (16)$$

Now by applying Eqns. (14-16) in Eqn. (11) to gives:

$$-r'_A = r_S = k_S \left[K_B P_B C_V * K_A P_A C_V - \frac{K_D P_C C_V^2}{K_S} \right] \quad \dots\dots\dots (17)$$

By rearrangement;

$$-r'_A = r_S = k_S \left[K_A K_B P_B P_A - \frac{K_D P_C}{K_S} \right] * C_V^2 \quad \dots\dots\dots (18)$$

Since Iso-octene, Hydrogen and Iso-octane; (A, B, and C) respectively attached on surface of the catalyst, so the total concentration of sites are:

$$C_t = C_v + C_{A.S} + C_{B.S} + C_{C.S} \quad \dots\dots\dots (19)$$

By substitution of Eqns. (14-16) in Eqn. (19);

$$\begin{aligned} C_t &= C_v + K_A P_A C_v + K_B P_B C_v + K_D P_C C_v \\ C_t &= C_v [K_A P_A + K_B P_B + K_D P_C] \\ C_v &= \frac{C_t}{[1 + K_A P_A + K_B P_B + K_D P_C]} \end{aligned} \quad \dots\dots\dots (20)$$

By substitution Eqn. (20) in Eqn. (18):

$$\begin{aligned} -r'_A = r_S &= k_S \left[K_A K_B P_A P_B - \frac{K_D P_C}{K_S} \right] * \left[\frac{C_t}{[1 + K_A P_A + K_B P_B + K_D P_C]} \right]^2 \\ -r'_A &= \frac{k_S K_A K_B C_t^2 \left(P_A P_B - \frac{P_C}{K_P} \right)}{[1 + K_A P_A + K_B P_B + K_D P_C]^2} \end{aligned}$$

Where:

$$K = k_S K_A K_B C_t^2 \quad \dots\dots\dots (21)$$

$$K_P = \frac{K_S K_A K_B}{K_D} \quad \dots\dots\dots (22)$$

So, final form is;

$$-r'_A = \frac{K \left(P_A P_B - \frac{P_C}{K_P} \right)}{[1 + K_A P_A + K_B P_B + K_D P_C]^2} \quad \dots\dots\dots (23)$$

Adsorption rate of Iso-Octene is the limiting rate (Model 2):-

$$\frac{-r_{AD}}{k_B} \cong \frac{-r_S}{k_S} \cong \frac{-r_D}{k_D} \cong 0 \quad \dots\dots\dots (24)$$

To find C_{A.S}, C_{B.S}, and C_{C.S} in terms of the partial pressure as follow:

By applying Eqn. (24) in Eqn. (10) to gives;

$$\begin{aligned} \frac{-r_{AD}}{k_B} = 0 &= P_B C_V - \frac{1}{K_B} C_{B.S} \\ C_{B.S} &= K_B P_B C_V \end{aligned} \quad \dots\dots\dots (25)$$

By applying Eqn. (24) in Eqn. (11) to gives;

$$\begin{aligned} \frac{-r_S}{k_S} = 0 &= C_{B.S} C_{A.S} - \frac{C_{C.S} C_V}{K_S} \\ C_{A.S} &= \frac{C_{C.S} C_V}{K_S C_{B.S}} \end{aligned} \quad \dots\dots\dots (26)$$

By applying Eqn. (24) in Eqn. (12)

$$C_{C.S} = K_D P_C C_v \dots\dots\dots (27)$$

So, by substitution of Eqns. (25 and 27) in Eqn. (26) to gives;

$$C_{A.S} = \frac{K_D P_C C_v^2}{K_B P_B C_v K_S}$$

$$C_{A.S} = \frac{P_C C_v}{K_{P_1} P_B} \dots\dots\dots (28)$$

Where, $\frac{K_B K_S}{K_D} = K_{P_1}$

By substitution of Eqns. (25, 27, and 28) into Eqn. (19) to yields;

$$C_t = C_v + \frac{P_C C_v}{P_B K_{P_1}} + K_B P_B C_v + K_D P_C C_v$$

$$C_v = \frac{C_t}{\left[1 + \left(\frac{P_C}{P_B K_{P_1}}\right) + K_B P_B + K_D P_C\right]} \dots\dots\dots (29)$$

By substitution of Eqn. (28) into Eqn. (8)

$$-r'_A = r_{AD} = k_A \left[P_A C_v - \frac{P_C C_v}{K_A K_{P_1} P_B} \right]$$

$$-r'_A = k_A \left[P_A - \frac{P_C}{K_A K_{P_1} P_B} \right] * C_v \dots\dots\dots (30)$$

By substitution of Eqn. (29) into Eqn. (30) to yields;

$$-r'_A = r_{AD} = k_A \left[P_A - \frac{P_C}{K_A K_{P_1} P_B} \right] \frac{C_t}{\left[1 + \left(\frac{P_C}{P_B K_{P_1}}\right) + K_B P_B + K_D P_C\right]}$$

$$-r'_A = r_{AD} = \frac{K \left(P_A - \frac{P_C}{K_P P_B} \right)}{\left[1 + \left(\frac{P_C}{P_B K_{P_1}}\right) + K_B P_B + K_D P_C\right]} \dots\dots\dots (31)$$

Where, $K = k_A C_t$, and $K_P = K_A K_{P_1} = \frac{K_A K_B K_S}{K_D}$

Adsorption rate of Hydrogen is the limiting rate (Model 3):-

$$\therefore -r_{AD} = k_B \left[P_B C_v - \frac{C_{B.S}}{K_B} \right] \dots\dots\dots (10)$$

$$\therefore \frac{-r_{AD}}{k_A} = \frac{-r_D}{k_D} = \frac{-r_S}{k_S} \cong 0$$

$$-\frac{r_{AD}}{k_A} = 0 = \left[P_A C_v - \frac{C_{A.S}}{K_A} \right]$$

$$K_A P_A C_v = C_{A.S} \dots\dots\dots (32)$$

$\therefore \frac{-r_S}{k_S} = 0$; so from Eqn. (11) gets on;

$$\therefore C_{A.S} C_{B.S} = \frac{C_v C_{C.S}}{K_S}$$

$$\frac{K_S C_{A.S} C_{B.S}}{C_v} = C_{C.S} \dots\dots\dots (33)$$

$$\therefore C_{B.S} = \frac{C_v C_{C.S}}{K_S C_{A.S}} \dots\dots\dots (34)$$

$\therefore \frac{-r_D}{k_D} = 0$ so, from Eqn. (12) gets on;

$$\therefore C_{C.S} = K_D P_C C_v \dots\dots\dots (35)$$

$$\therefore C_{B.S} = \frac{C_v K_D P_C C_v}{K_S K_A P_A C_v} = \frac{C_v K_D P_C}{K_S K_A P_A} = \frac{C_v P_C}{K_P P_A} \dots\dots\dots (36)$$

$$K_P = \frac{K_S K_A}{K_D} \dots\dots\dots (37)$$

$$C_t = C_v + C_{A.S} + C_{B.S} + C_{C.S} \dots\dots\dots (19)$$

$$C_t = C_v + K_A P_A C_v + \frac{C_v P_C}{K_P P_A} + K_D P_C C_v$$

$$C_t = C_v \left(1 + K_A P_A + \frac{P_C}{K_P P_A} + K_D P_C \right)$$

$$C_v = \frac{C_t}{(1+K_A P_A + \frac{P_C}{K_P P_A} + K_D P_C)} \dots\dots\dots (38)$$

So, Eqn. (10) becomes;

$$-r_{AD} = k_B \left[P_B - \frac{P_C}{K_B K_P P_A} \right] C_v$$

$$-r'_A = -r_{AD} = \frac{K \left[P_B - \frac{P_C}{K_P P_A} \right]}{(1+K_A P_A + \frac{P_C}{K_P P_A} + K_D P_C)} \dots\dots\dots (39)$$

Where, $K=k_B C_t$, and $K_{P1}=K_B K_P$.

Desorption rate of Iso-Octane is the limiting rate (Model 4):-



$$-r_D = k_D [C_{C.S} - K_D P_C C_v] \dots\dots\dots (12)$$

$$\because \frac{-r_{AD}}{k_A} \cong \frac{-r_{AD}}{k_B} \cong \frac{-r_S}{k_S} \cong 0 \dots\dots\dots (40)$$

From Eqn. (7) gets on;

$$\frac{-r_{AD}}{k_A} = 0 = P_A C_v - \frac{1}{K_A} C_{A.S}$$

$$C_{A.S} = K_A P_A C_v \dots\dots\dots (41)$$

From Eqn. (10) gets on;

$$\frac{-r_{AD}}{k_B} = 0 = P_B C_v - \frac{1}{K_B} C_{B.S}$$

$$C_{B.S} = K_B P_B C_v \dots\dots\dots (42)$$

From Eqn. (11) gets on;

$$\frac{-r_S}{k_S} = 0 = C_{A.S} C_{B.S} - \frac{C_{C.S} C_v}{K_S}$$

$$C_{C.S} C_v = C_{A.S} C_{B.S} K_S$$

$$C_{C.S} = \frac{C_{A.S} C_{B.S}}{C_v} K_S$$

$$C_{C.S} = \frac{K_B P_B C_v K_A P_A C_v}{C_v} K_S$$

$$C_{C.S} = K_S K_B K_A P_B P_A C_v$$

$$C_{C.S} = K_P P_B P_A C_v \dots\dots\dots (43)$$

Where, $K_P = K_S K_B K_A$

So, Eqn. (12) becomes;

$$-r_D = k_D [K_P P_B P_A - K_D P_C] C_v \dots\dots\dots (44)$$

From Eqn. (19) gets on;

$$C_t = C_v + K_A P_A C_v + K_B P_B C_v + K_P P_B P_A C_v$$

$$C_v = \frac{C_t}{(1+K_A P_A + K_B P_B + K_P P_B P_A)} \dots\dots\dots (45)$$

So, Eqn. (44) becomes,

$$-r_D = k_D C_t [K_P P_B P_A - K_D P_C] \frac{1}{(1 + K_A P_A + K_B P_B + K_P P_B P_A)}$$

$$\therefore -r'_A = -r_D = \frac{K[K_P P_B P_A - K_D P_C]}{(1 + K_A P_A + K_B P_B + K_P P_B P_A)} \dots\dots\dots (46)$$

Where, $K = k_D C_t$

Eley-Rideal Mechanism (Mechanism 2):-

If the reaction kinetic follows an Eley-Rideal mechanism, so the process became,

Adsorption of Iso-octene;



Surface reaction;



Desorption of Iso-octane;



The rate of these steps of mechanism are;

Rate of isothermal adsorption of Iso-Octene;



$$-r_{AD} = k_A P_A C_v - k_{-A} C_{A.S} \dots\dots\dots (7)$$

$$\therefore K_A = \frac{k_A}{k_{-A}}$$

$$\therefore -r_{AD} = k_A \left[P_A C_v - \frac{C_{A.S}}{K_A} \right] \dots\dots\dots (8)$$

Surface reaction of Eley-Rideal is;



$$-r_S = k_S C_{A.S} P_B \dots\dots\dots (50)$$

Rate of desorption;



$$-r_D = k_D \left[C_{C.S} - \frac{P_C C_v}{K_{DT}} \right]$$

$$K_D = \frac{1}{K_{DT}} = \frac{k_{-D}}{k_D}$$

$$-r_D = k_D [C_{C.S} - K_D P_C C_v] \dots\dots\dots (12)$$

Surface reaction is the limiting rate (Model 5):-

So, by using the same procedure described in previous section as following;

By substitution of Eqn. (14) into Eqn. (50) to gives;

$$-r_S = k_S * K_A P_A C_v P_B \dots\dots\dots (51)$$

$$-r_S = k_S K_A P_A P_B C_v \dots\dots\dots (52)$$

$$\therefore C_t = C_v + C_{A.S} + C_{C.S}$$

By substitution of Eqns. (14 and 16) in Eqn. (52) to gives;

$$C_t = C_v + K_A P_A C_v + K_D P_C C_v$$

$$C_v = \frac{C_t}{[1 + K_A P_A + K_D P_C]} \dots\dots\dots (53)$$

By substitution of Eqn. (53) into Eqn. (51) to gives;

$$-r'_A = r_S = \frac{K P_A P_B}{[1 + K_A P_A + K_D P_C]} \dots\dots\dots (54)$$

Where, $K = k_5 K_A C_t$

Now, by applying the experimental data that estimated by Hougen and Watson [7] on these five models to determination the best model fitting with experimental data. This simulation done using Polymath software V6.1. The obtained results are illustrated in results and discussion section.

Results and Discussion:-

The five mathematical models have been fitted with an experimental data that obtained by Hougen and Watson [7], to fitting and testing (simulation) to obtaining a best model that represent a mechanism of the Iso-octene hydrogenation. The simulation done by using a polymath software V6.1 to estimation constants that found in each model.

A simulation of the experimental data with kinetics models obtained are applied as follow;

Dual Sites Mechanism (Mechanism 1)

Model 1: The limiting rate by Surface Chemical Reaction

The kinetic model given as follow;

$$-r'_A = \frac{K(P_A P_B - \frac{P_C}{K_p})}{[1 + K_A P_A + K_B P_B + K_D P_C]^2} \dots\dots\dots (23)$$

Simulation results of this model with experimental data are given in Table (2); in which the calculated value of chemical reaction rates ($r_{calc.}$) are good satisfied with experimental data of chemical reaction rate ($r_{exp.}$).

Table 2:-Experimental data and results of Model No.1

| Point | P _A | P _B | P _C | r _{exp.} | r _{calc} | Delta r |
|-------|----------------|----------------|----------------|-------------------|-------------------|------------|
| 1 | 1 | 1 | 0 | 0.0345 | 0.0344478 | 5.216E-05 |
| 2 | 1 | 1 | 1 | 0.0239 | 0.0222203 | 0.0016797 |
| 3 | 1 | 3 | 1 | 0.039 | 0.0410791 | -0.0020791 |
| 4 | 3 | 1 | 1 | 0.0351 | 0.0337125 | 0.0013875 |
| 5 | 1 | 1 | 3 | 0.0114 | 0.0113416 | 5.837E-05 |
| 6 | 1 | 10 | 0 | 0.0534 | 0.052962 | 0.000438 |
| 7 | 10 | 1 | 0 | 0.031 | 0.0318164 | -0.0008164 |
| 8 | 1 | 1 | 10 | 0.0033 | 0.0027038 | 0.0005962 |
| 9 | 2 | 2 | 2 | 0.038 | 0.0377938 | 0.0002062 |
| 10 | 0.2 | 0.2 | 0.2 | 0.0032 | 0.002626 | 0.000574 |
| 11 | 0.1 | 0.1 | 0.1 | 0.0008 | 0.000759 | 4.101E-05 |
| 12 | 5 | 5 | 5 | 0.0566 | 0.0564527 | 0.0001473 |

The results obtained from a polymath V6.1 are shown below. A correlation coefficient (r^2) was 0.997 is a satisfactory, that reveals to the calculated data which are an excellent fit with experimental data because r^2 ranged between ($0 < r^2 < 1$) if its nearest to 1 that's meaning a good fit. Also a variance between experimental and theoretical data was 1.526×10^{-6} , it's a very small (less than 0.0001). That also indicates to this mechanism which is a good model to represent the experimental data.

Polymath Results

08-October-2018

Model No.1:

$$r = K \cdot (P_A \cdot P_B - P_C / K_p) / (1 + K_A \cdot P_A + K_B \cdot P_B + K_D \cdot P_C)^2$$

| Variable | Initial guess | Value | 95% confidence |
|----------------|---------------|-----------|----------------|
| K | 1. | 0.104829 | 8.469E-06 |
| K _p | 1. | 101.9999 | 1.580848 |
| K _a | 0.01 | 0.4439543 | 5.413E-05 |
| K _b | 0.01 | 0.3005004 | 3.346E-05 |
| K _d | 0.01 | 0.4169027 | 8.675E-05 |

Nonlinear regression settings

Max # iterations = 64

Precision

| | |
|--------------------|-----------|
| R ² | 0.9973555 |
| R ² adj | 0.9958444 |
| Rmsd | 0.0002724 |
| Variance | 1.526E-06 |

General

| | |
|-------------|----|
| Sample size | 12 |
| Model vars | 5 |
| Indepvars | 3 |
| Iterations | 32 |

These parameters are reflected in Figure (3), it shows that, the calculated data matching with experimental data as mentioned above. The final formula of Eqn. (23) is;

$$-r'_A = \frac{0.104829(P_A P_B - \frac{P_C}{101.999})}{[1 + 0.4439543P_A + 0.3005P_B + 0.4169P_C]^2}$$

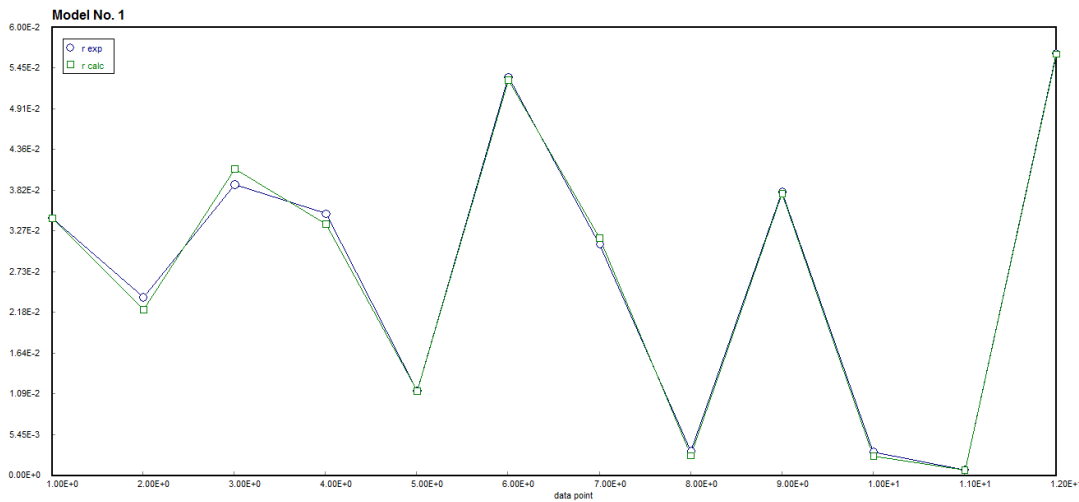


Figure 3:- Comparison between experimental data and calculated data of model No.1

Model 2: The limiting rate by adsorption rate of Iso-octene

The kinetic model given as follow;

$$-r'_A = r_{AD} = \frac{K(P_A - \frac{P_C}{K_P P_B})}{1 + (\frac{P_C}{P_B K_{P_1}}) + K_B P_B + K_D P_C} \dots\dots\dots (31)$$

Simulation results of this model with experimental data are given in Table (3); in which the calculated of chemical reaction rates (*r_{calc.}*) are not satisfied with experimental data of chemical reaction rate (*r_{exp.}*).

The results obtained from a polymath software are shown below. A correlation coefficient (*r²*) was -1.32×10^4 which is not satisfactory. It reveals to the calculated data are which is not fitting with experimental data because *r²* ranged between (0 < *r²* < 1). If its nearest to 1, it means a good fit. Also, a fitting variance between experimental and theoretical data was 7.64, it's a very high value (greater than 0.0001). It also indicates to this mechanism which it does not signify the experimental data or the process occurred in this chemical reaction.

Table 3:- Experimental data and results of Model No. 2

| Point | P _A | P _C | P _B | r _{exp.} | r _{calc} | Delta r |
|-------|----------------|----------------|----------------|-------------------|-------------------|------------|
| 1 | 1 | 0 | 1 | 0.0345 | 0.7305052 | -0.6960052 |
| 2 | 1 | 1 | 1 | 0.0239 | 0.0024855 | 0.0214145 |
| 3 | 1 | 1 | 3 | 0.039 | 0.0210657 | 0.0179343 |
| 4 | 3 | 1 | 1 | 0.0351 | 0.0208717 | 0.0142283 |
| 5 | 1 | 3 | 1 | 0.0114 | -0.0036741 | 0.0150741 |
| 6 | 1 | 0 | 10 | 0.0534 | 0.3436456 | -0.2902456 |
| 7 | 10 | 0 | 1 | 0.031 | 7.305052 | -7.274052 |
| 8 | 1 | 10 | 1 | 0.0033 | -0.0058546 | 0.0091546 |
| 9 | 2 | 2 | 2 | 0.038 | 0.011921 | 0.026079 |
| 10 | 0.2 | 0.2 | 0.2 | 0.0032 | -0.004791 | 0.007991 |
| 11 | 0.1 | 0.1 | 0.1 | 0.0008 | -0.0056842 | 0.0064842 |
| 12 | 5 | 5 | 5 | 0.0566 | 0.0427341 | 0.0138659 |

POLYMATH Results

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Model No. 2:

$$r = (K*(P_A - (P_C/(K_P*P_B)))) / (1 + (P_C/(P_B*K_{P1})) + K_B*P_B + K_D*P_C)$$

| Variable | Initial guess | Value | 95% confidence |
|-----------------|---------------|-----------|----------------|
| K | 1. | 0.8349428 | 0.0023484 |
| K _P | 1. | 1.370551 | 1.391069 |
| K _{P1} | 0.01 | 0.0109087 | 0.0038846 |
| K _B | 0.01 | 0.1429663 | 0.0031431 |
| K _D | 0.01 | -1.989967 | 7.713176 |

Nonlinear regression settings

Max # iterations = 64

Precision

| | |
|--------------------|------------|
| R ² | -1.324E+04 |
| R ² adj | -2.08E+04 |
| Rmsd | 0.6094327 |
| Variance | 7.640396 |

General

| | |
|-------------|----|
| Sample size | 12 |
| Model vars | 5 |
| Indepvars | 3 |
| Iterations | 12 |

These parameters are reflected in Figure (4), whereas the Figure shows that, the calculated data matching with experimental data as mentioned above. The final formula of Eqn. (31) is;

$$-r_A = r_{AD} = \frac{0.8345(P_A - \frac{P_C}{1.37P_B})}{1 + (\frac{P_C}{0.0109P_B}) + 0.1429P_B - 1.9899P_C}$$

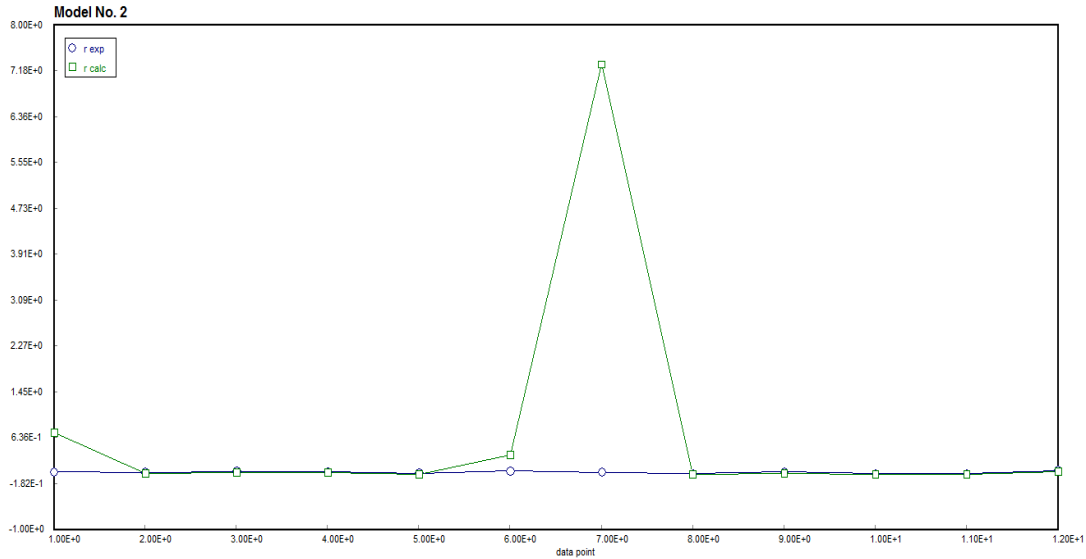


Figure 4:- Comparison between experimental data and calculated data of model No.2

Model 3: The limiting rate by Adsorption of Hydrogen

The kinetic model given as follow;

$$-r'_A = -r_{AD} = \frac{K \left[P_B - \frac{P_C}{K_{P1} P_A} \right]}{\left(1 + K_A P_A + \frac{P_C}{K_P P_A} + K_D P_C \right)} \dots\dots\dots (39)$$

Simulation results of this model with experimental data are given in Table (4); in which the calculated of chemical reaction rates ($r_{calc.}$) are not satisfied with experimental data of chemical reaction rate ($r_{exp.}$).

Table 4:- Experimental data and results of Model No. 3

| Point | P _B | P _C | P _A | r _{exp.} | r _{calc} | Delta r |
|-------|----------------|----------------|----------------|-------------------|-------------------|------------|
| 1 | 1 | 0 | 1 | 0.0362 | 0.0589177 | -0.0227177 |
| 2 | 1 | 1 | 1 | 0.0239 | 0.004923 | 0.018977 |
| 3 | 3 | 1 | 1 | 0.039 | 0.0148666 | 0.0241334 |
| 4 | 1 | 1 | 3 | 0.0351 | 0.0125859 | 0.0225141 |
| 5 | 1 | 3 | 1 | 0.0114 | 0.0017044 | 0.0096956 |
| 6 | 10 | 0 | 1 | 0.0534 | 0.5891768 | -0.5357768 |
| 7 | 1 | 0 | 10 | 0.031 | 0.0138657 | 0.0171343 |
| 8 | 1 | 10 | 1 | 0.0033 | 0.0004853 | 0.0028147 |
| 9 | 2 | 2 | 2 | 0.038 | 0.0104675 | 0.0275325 |
| 10 | 0.2 | 0.2 | 0.2 | 0.0032 | 0.000906 | 0.002294 |
| 11 | 0.1 | 0.1 | 0.1 | 0.0008 | 0.0004274 | 0.0003726 |
| 12 | 5 | 5 | 5 | 0.0566 | 0.0317608 | 0.0248392 |

The results obtained from a polymath software are shown below. A correlation coefficient (r^2) was -70.507 which is not satisfactory. It reveals to the calculated data are which is not fitting with experimental data because r^2 ranged between ($0 < r^2 < 1$). If its nearest to 1, it means a good fit. Also, a fitting variance between experimental and theoretical data was 0.0415, it's a very high value (greater than 0.0001). It also indicates to this mechanism which it does not signify the experimental data or the process occurred in this chemical reaction.

Polymath Results:-

08-October-2018

Model No. 3:

$$r = (K*(Pb-(Pc/(kP1*Pa))))/(1+KA*Pa+(Pc/(kP*Pa))+Kd*Pc)$$

| Variable | Initial guess | Value | 95% confidence |
|----------|---------------|-----------|----------------|
| K | 1. | 0.0922058 | 2.368E-05 |
| kP1 | 1. | 101.9851 | 102.9384 |
| KA | 0.01 | 0.5649943 | 0.0004021 |
| kP | 0.01 | 0.0538781 | 0.0001774 |
| Kd | 0.01 | -1.579636 | 0.0136184 |

Nonlinear regression settings

Max # iterations = 64

Precision

| | |
|----------|-----------|
| R^2 | -70.50702 |
| R^2adj | -111.3682 |
| Rmsd | 0.0449381 |
| Variance | 0.0415426 |

General

| | |
|-------------|----|
| Sample size | 12 |
| Model vars | 5 |
| Indepvars | 3 |
| Iterations | 24 |

These parameters are reflected in Figure of (5), whereas the Figure shows that, the calculated data matching with experimental data as mentioned above. The final formula of Eqn. (39) is;

$$-r'_A = \frac{0.0922 \left[P_B - \frac{P_C}{101.985 P_A} \right]}{\left(1 + 0.5649 P_A + \frac{P_C}{0.0538 P_A} - 1.5796 P_C \right)}$$

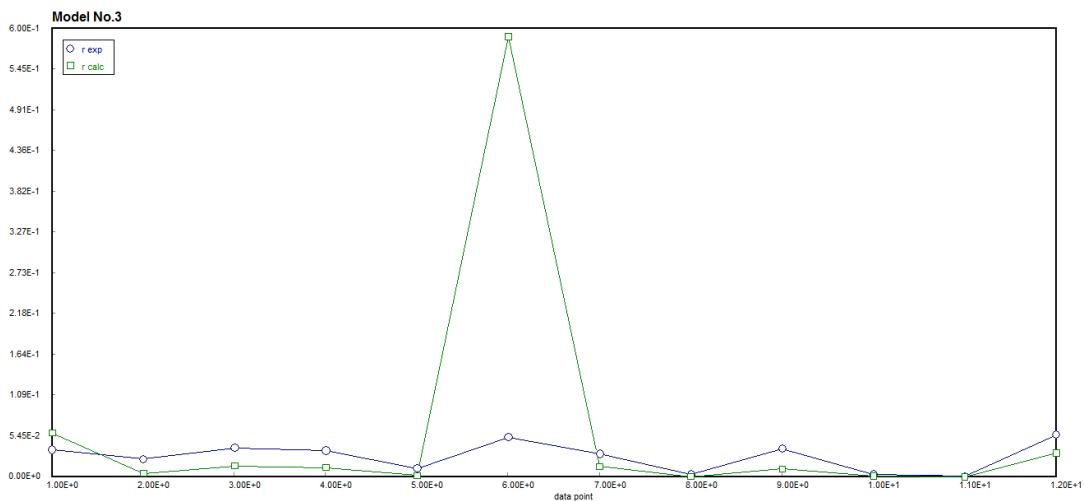


Figure 5:- Comparison between experimental data and calculated data of model No.3

Model 4:-The limiting rate by Desorption rate of Iso-Octane

The kinetic model given as follow;

$$\therefore -r'_A = \frac{K[K_P P_B P_A - K_D P_C]}{(1 + K_A P_A + K_B P_B + K_P P_B P_A)} \dots\dots\dots (46)$$

Simulation results of this model with experimental data are given in Table (5); in which the calculated of chemical reaction rates ($r_{\text{calc.}}$) are not satisfied with experimental data of chemical reaction rate ($r_{\text{exp.}}$).

Table 5:- Experimental data and results of Model No. 4

| Point | P _B | P _A | P _C | r _{exp.} | r _{calc.} | Delta r |
|-------|----------------|----------------|----------------|-------------------|--------------------|------------|
| 1 | 1 | 1 | 0 | 0.0362 | 0.0315526 | 0.0046474 |
| 2 | 1 | 1 | 1 | 0.0239 | 0.0294018 | -0.0055018 |
| 3 | 3 | 1 | 1 | 0.039 | 0.0443513 | -0.0053513 |
| 4 | 1 | 3 | 1 | 0.0351 | 0.0380363 | -0.0029363 |
| 5 | 1 | 1 | 3 | 0.0114 | 0.0251002 | -0.0137002 |
| 6 | 10 | 1 | 0 | 0.0534 | 0.0536061 | -0.0002061 |
| 7 | 1 | 10 | 0 | 0.031 | 0.0423847 | -0.0113847 |
| 8 | 1 | 1 | 10 | 0.0033 | 0.0100448 | -0.0067448 |
| 9 | 2 | 2 | 2 | 0.038 | 0.0456635 | -0.0076635 |
| 10 | 0.2 | 0.2 | 0.2 | 0.032 | 0.0032528 | 0.0287472 |
| 11 | 0.1 | 0.1 | 0.1 | 0.0008 | 0.000503 | 0.000297 |
| 12 | 5 | 5 | 5 | 0.0566 | 0.0617099 | -0.0051099 |

The results obtained from a polymath software are shown below. A correlation coefficient (r^2) was 0.601 which is not satisfactory. It reveals to the calculated data are which is not fitting with experimental data because r^2 ranged between ($0 < r^2 < 1$). If its nearest to 1, it means a good fit. Also, a fitting variance between experimental and theoretical data was 1.948×10^{-4} , it's a very high value (greater than 0.0001). It also indicates to this mechanism which it does not signify the experimental data or the process occurred in this chemical reaction.

Polymath Results:-

08-October-2018

Model No. 4:

$$r = (K \cdot (KP \cdot Pb \cdot Pa - Kd \cdot Pc)) / (1 + Ka \cdot Pa + Kb \cdot Pb + KP \cdot Pb \cdot Pa)$$

| Variable | Initial guess | Value | 95% confidence |
|----------|---------------|-----------|----------------|
| K | 1. | 0.0768094 | 6.226E-06 |
| KP | 1. | 2.704993 | 0.0004551 |
| Kd | 0.01 | 0.1843859 | 8.456E-05 |
| Ka | 0.01 | 2.01 | 0.0006757 |
| Kb | 0.01 | 0.8698554 | 0.000527 |

Nonlinear regression settings

Max # iterations = 64

Precision

| | |
|--------------------|-----------|
| R ² | 0.6011678 |
| R ² adj | 0.3732636 |
| Rmsd | 0.0030769 |
| Variance | 0.0001948 |

General

| | |
|-------------|----|
| Sample size | 12 |
| Model vars | 5 |
| Indepvars | 3 |
| Iterations | 25 |

These parameters are reflected in Figure (6), whereas the Figure show that, the calculated data matching with experimental data as mentioned above. The final formula of Eqn. (46) is;

$$-r'_A = \frac{0.0768[2.705P_B P_A - 0.1843P_C]}{(1 + 2.0099P_A + 0.8698P_B + 2.7P_B P_A)}$$

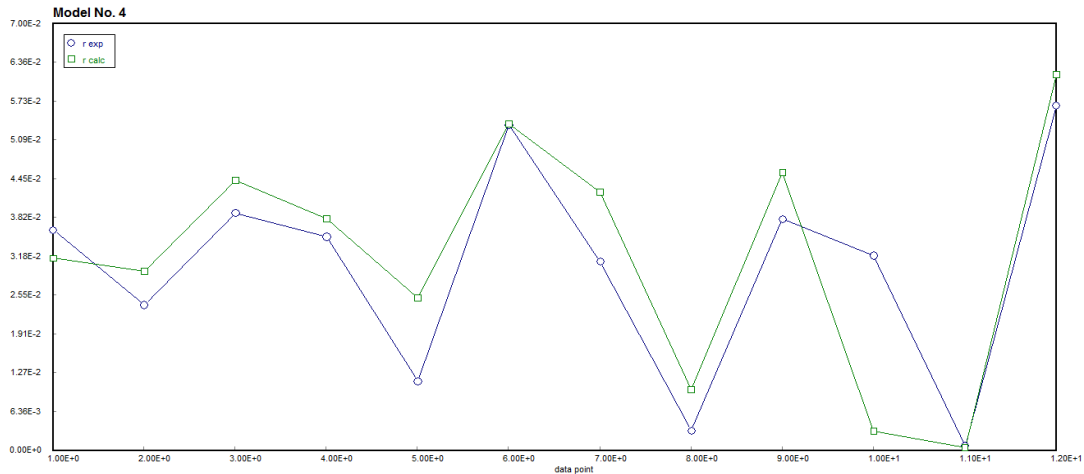


Figure 6:- Comparison between experimental data and calculated data of model No. 4

Model 5:-Eley-Rideal Mechanism (Mechanism 2)

If the surface reaction is the limiting rate;

$$-r'_A = r_S = \frac{K P_A P_B}{[1 + K_A P_A + K_D P_C]} \dots\dots\dots (54)$$

Simulation results of this model with experimental data are given in Table (6); in which the calculated of chemical reaction rates ($r_{calc.}$) are not satisfied with experimental data of chemical reaction rate ($r_{exp.}$).

Table 6:-Experimental data and results of Model No.5

| Point | P _b | P _a | P _c | r _{exp.} | r _{calc} | Delta r |
|-------|----------------|----------------|----------------|-------------------|-------------------|------------|
| 1 | 1 | 1 | 0 | 0.0362 | 0.0315526 | 0.0046474 |
| 2 | 1 | 1 | 1 | 0.0239 | 0.0294018 | -0.0055018 |
| 3 | 3 | 1 | 1 | 0.039 | 0.0443513 | -0.0053513 |
| 4 | 1 | 3 | 1 | 0.0351 | 0.0380363 | -0.0029363 |
| 5 | 1 | 1 | 3 | 0.0114 | 0.0251002 | -0.0137002 |
| 6 | 10 | 1 | 0 | 0.0534 | 0.0536061 | -0.0002061 |
| 7 | 1 | 10 | 0 | 0.031 | 0.0423847 | -0.0113847 |
| 8 | 1 | 1 | 10 | 0.0033 | 0.0100448 | -0.0067448 |
| 9 | 2 | 2 | 2 | 0.038 | 0.0456635 | -0.0076635 |
| 10 | 0.2 | 0.2 | 0.2 | 0.032 | 0.0032528 | 0.0287472 |
| 11 | 0.1 | 0.1 | 0.1 | 0.0008 | 0.000503 | 0.000297 |
| 12 | 5 | 5 | 5 | 0.0566 | 0.0617099 | -0.0051099 |

The results obtained from a polymath software are shown below. A correlation coefficient (r^2) was 0.303 which is not satisfactory. It reveals to the calculated data are which is not fitting with experimental data because r^2 ranged between ($0 < r^2 < 1$). If its nearest to 1, it means a good fit. Also, a fitting variance between experimental and theoretical data was 3.13×10^{-4} , it's a very high value (greater than 0.0001). It also indicates to this mechanism which it does not signify the experimental data or the process occurred in this chemical reaction.

Polymath Results

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Model No. 5:

$$r = (K * P_a * P_b) / (1 + K_A * P_a + K_D * P_c)$$

| Variable | Initial guess | Value | 95% confidence |
|----------|---------------|-----------|----------------|
| K | 1. | 0.00775 | 9.652E-05 |
| KA | 1. | 0.1722044 | 0.0076415 |
| KD | 0.01 | 0.220668 | 0.0111577 |

Nonlinear regression settings

Max # iterations = 64

Precision

| | |
|--------------------|-----------|
| R ² | 0.3031335 |
| R ² adj | 0.1482743 |
| Rmsd | 0.0044218 |
| Variance | 0.0003128 |

General

| | |
|-------------|----|
| Sample size | 12 |
| Model vars | 3 |
| Indepvars | 3 |
| Iterations | 16 |

These parameters are reflected in Figure (7), whereas the Figure show that, the calculated data matching with experimental data as mentioned above. The final formula of Eqn. (54) is;

$$-r'_A = \frac{0.00775P_A P_B}{[1 + 0.1722044P_A + 0.22066P_C]}$$

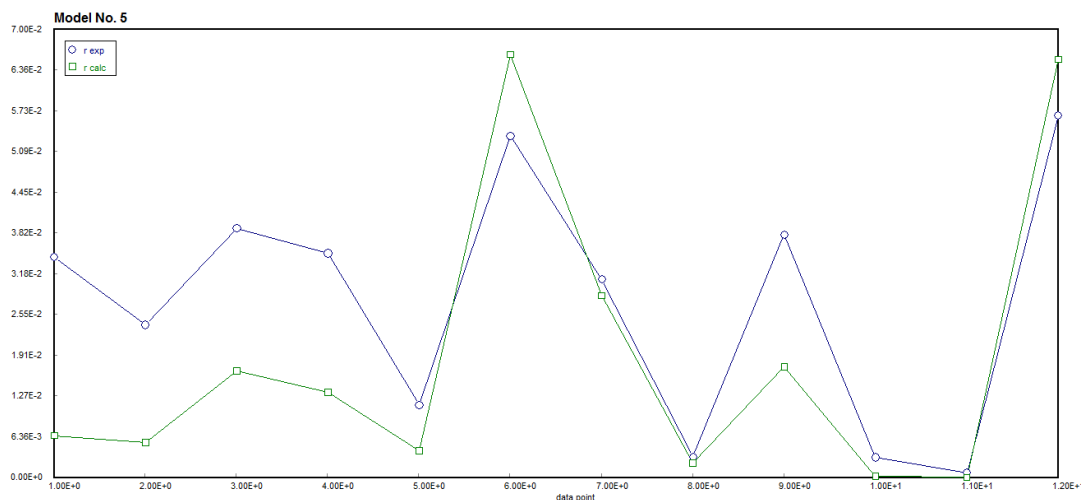


Figure 7:- Comparison between experimental data and calculated data of model No. 5

From the a simulation process done by using a five kinetic models attained; note that a model no. 1 of Dual site Mechanism (Mechanism 1) for Surface chemical reaction is the limiting rate and the dominant model of experimental data whereas fitted the experimental data with low variance and high correlation coefficient. This behavior is not strange because more than 75% of a heterogeneous chemical reactions are surface chemical reaction is limit step [2]. According this mechanism a adsorption process occurs for each molecules alone of both hydrogen and iso-octene then a surface chemical reaction occurs between these adsorbed molecules on a catalyst to producing iso-octane.

Conclusion:-

Five mathematical models have been developed of heterogeneous chemical reaction of isooctane with hydrogen. Then nonlinear regression for these models done depending on the experimental data produced by Hougen and Watson. Regression done by using Polymath V6.1 to evaluate the kinetic constants of the models. Results reveal the adsorption of hydrogen and iso-octene occur firstly on different active sites of a catalyst surface followed by a surface chemical reaction, and the hydrogenation chemical reaction is limiting by a surface reaction step according to dual sites mechanism.

The results generated by the program include the sum of squares of residuals (Variance) and the values of kinetic constants. These results can be stored in data files and further used for reactor design. It is possible to change the guess values of kinetic constants and see the effect on sum of squares of residuals. Also it is possible to check the fit of experimental data into various mechanisms and rate controlling steps.

Polymath proved to be a powerful tool to solve the optimization problem in heterogeneous catalysis. NLP solver in polymath converges the program even if initial guesses are far away from global optimum.

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