

## Reaction Kinetic of $\alpha$ -methylstyrene (AMS) Hydrogenation

Zaidoon M. Shakoor\*, Mumtaz A. Zablouk\* & Adel A. Shuhaib\*

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### Abstract

In this research hydrogenation kinetic of alpha-methylstyrene (AMS) on Pd/Al<sub>2</sub>O<sub>3</sub> catalyst was studied. The reaction is mildly exothermic ( $\Delta H = -109$  kJ/mol). Intrinsic kinetic law was investigated under wide range of operating conditions 0.1 and 0.2 gm catalyst loading, 0.5-100 wt% AMS, 10, 15 and 20 bar pressure and 343-373 K temperature.

The experiment data are fitted to estimate the kinetic parameters for different reaction mechanisms by using ACM (Aspen Custom Modeler) software. Finally the results of produced reaction mechanisms are compared with experimental results to obtain the optimum reaction mechanism.

**Keywords:**  $\alpha$ -methylstyrene, hydrogenation, mechanism, catalytic reaction.

### دراسة ميكانيكية تفاعل هدرجة الالفاميثيل ستايرين

#### الخلاصة

في هذا البحث تمت دراسة ميكانيكية تفاعل الهدرجة لمادة الفاميثيل ستايرين ( $\alpha$ -methylstyrene) على سطح عامل مساعد من نوع Pd/Al<sub>2</sub>O<sub>3</sub> في مدى واسع من الظروف التشغيلية. حيث كانت كمية العامل المساعد 0.1 , 0.2 غم والنسبة الوزنية لمادة الفاميثيل ستايرين 0.5-100% وزن والضغط المستخدمة كانت 10, 15, 20 بار و درجة الحرارة 343-373 كلفن. علما أن تفاعل الهدرجة هو تفاعل باعث بشكل معتدل حيث تبلغ طاقة التفاعل ( $\Delta H = 109$  كيلوجول/مول).

تم حساب الثوابت الخاصة للميكانيكيات المقترحة بالاعتماد على النتائج العملية باستخدام برنامج (Aspen Custom Modeler). في النهاية تمت مقارنة النتائج العملية مع نتائج الميكانيكيات وبعدها تم اختيار أحسن ميكانيكية والتي تعطي اقل نسبة من الخطأ.

### 1.Introduction

Many reactions proceed much faster in the presence of a substance that is not a product or reactant in the usual since. This substance is called a catalyst, and the process is called catalytic reaction ( Shuhaib 2008). Catalysts increase the reaction rate by lowering the energy requirements for the reaction. Thus, from the ability of the catalyst to form bonds for reaction intermediates to offset the energy required to break reaction bonds.

The presence of the catalyst does not affect the Gibbs energy of reactants or product therefore it does not affect the equilibrium constant for the reaction (Missen et al., (1999)).

The hydrogenation of  $\alpha$ -methyl styrene (AMS) to cumene over a palladium on  $\gamma$ -alumina catalyst is well known system used to understand three-phase reactor performance under mass transfer limited condition (e.g. Cini and Harold (1991), Khadilkar et al. (1996), Frank et al. (1999)

\* Chemical Engineering Department, University of Technology / Baghdad



The general equation of Thiele modulus for the hydrogenation AMS reaction, first order states (Meille et al., (2002)):

$$M_T = L_T \cdot \sqrt{\frac{-r_{H_2, \text{intr}}}{C_{H_2} \cdot D_{\text{eff}}}} \quad \dots (8)$$

The characteristic particle size  $L_T$  for spherical is 1/6 of the ball diameter.

For the definition Thiele module is the intrinsic, that is not directly measurable on the catalyst particle volume related reaction rate  $r_{H_2, \text{intr}}$ .

According to Herskowitz et al.(1978) the equilibrium concentration of hydrogen in pure AMS is given in equation (9) in the range of temperatures 288-347 K.

$$C_{H_2} = \frac{r}{\text{bar}} \cdot \frac{0.0145}{\text{g}} \cdot \frac{T}{K} - 1.6985 \cdot \frac{\text{mol}}{\text{g}} \cdot \frac{1}{\text{m}^3} \quad \dots (9)$$

Meille et al., (2002) observed that hydrogen solubility in cumene is the same as that in AMS. Also they used equation (9) in calculation of hydrogen concentration  $C_{H_2}$  in the liquid phase containing AMS and cumene.

Since  $r_{H_2}$  on the solid volume terms is not directly measured, therefore the conversion is required.

$$r_{H_2, \text{exp}} = \frac{1}{V} \cdot \frac{d_{n_{H_2}}}{dt} \quad \dots (10)$$

Using the equation (10) follows an expression for the diffusion inhibited through pores of the solid volume related reaction rate.

$$r_{H_2, \text{exp}} = \frac{(1 - e) p_{\text{cat}}}{m_{\text{cat}}} \frac{dCH_2}{dt} \cdot V_R \quad \dots (11)$$

The following description for the thiele module is formed from equations (9), (10), and (11):

$$M_T^2 = \frac{d^2}{36} \cdot \frac{(1 - e) p_{\text{cat}}}{m_{\text{cat}}} \frac{dC_{H_2, \text{intr}}}{dt} \cdot V_R \cdot \frac{1}{C_{H_2} D_{\text{eff}}} \quad \dots (12)$$

A direct calculation of the measured parameters is not possible, so the pores efficiency ( $\eta$ ) which represent the ratio of experimental and intrinsic reaction rate, calculated using the following equation:

$$h = \frac{r_{H_2, \text{exp}}}{r_{H_2, \text{intr}}} \quad \dots (13)$$

For spherical particles Levenspiel (1999) developed an equation for the pore efficiency in which only depend on Thiele module occurs:

$$h = \frac{1}{M_T} \cdot \frac{e}{\tanh(3 \cdot M_T)} - \frac{1}{3 \cdot M_T} \cdot \frac{\dot{u}}{\ddot{u}} \quad \dots (14)$$

### 3. Experimental Set-Up

The experimental work taken place in the department of chemical engineering and plant design-university of Dresden in Germany. Figure (1) shows a schematic diagram of the experimental set-up. The stirred tank reactor (STR) is operating in semi-batch mode in which the gas phase ( $H_2$ ) is feed continuously to the reactor which contains liquid phase (AMS). The experiments were carried out in 5100 fixed head bench top reactor with stainless steel cylinder. It was supplied by Parr Instrument Company. Pressure and temperature limits are 100 psi and 225 °C respectively. The different sections of the experimental setup discussed as below.

#### 3.1 Reactor Section

The reactor was offered in size of 300 ml with metal cylinder and heated using an electrical heating tape wound externally to the central portion of the reactor where the catalyst was placed in the reactor for each run. The reactor temperature was controlled by temperature controller.

#### 3.2 Measuring devices

##### 1. Pressure gage

2. A 150 psi gage pressure with a T 316 stainless steel Bourdon tubes is mounted on the reactor head using attachment fittings.

##### 3. Thermocouple

A J type thermocouple in a (1/8) inch diameter

stainless steel sheath is furnished with the reactor. This thermocouple is inserted into the head of thermo well and connected to the thermocouple socket on the rear panel of the temperature controller.

### 3. Refractometer

For analysis of the liquid samples, the refractometer RE 40D Company Mettler Toledo, was used. The measuring principles based on the determination of the refractive indexes. The refractive index of the medium depends on its composition.

To calculate the weight percent of AMS in the solution the following equation was used (Shuhaib 2008):-

$$wt_{AMS} = \frac{(n_0 + 0.0005[T/^{\circ}C - 20] - 1.4917)}{0.0474} \quad (15)$$

Further the following equation was used to calculate the concentration of AMS (Shuhaib 2008):-

$$C_{AMS} = \frac{1}{Mwt} \cdot \frac{1}{\frac{1}{r} + \frac{1 - wt\%AMS}{wt\%AMS} \frac{1}{r}} \quad (16)$$

And the conversion of AMS calculated by using the following equation:-

$$X_{AMS} = \frac{C_{AMS_0} - C_{AMS}}{C_{AMS_0}} \quad (17)$$

### 3.3 Chemical

**1. Liquid:-** The liquid used in this work is  $\alpha$ -methylstyrene. The properties of AMS and cumene can be seen in Tables (1 and 2).

**2. Gas:-** Two gases was used in the present work which are hydrogen and nitrogen, the hydrogen properties can be seen in table (3). Nitrogen was used only to discharge the Oxygen in the reactor at start of each experiment (Reactor flashing).

### 3. Solid catalyst

The catalyst which used in the present work is palladium with  $\gamma$ - $Al_2O_3$ , The used catalyst consists of two-fabric system (carrier material and active component). The carrier material is nearly spherical  $\gamma$ -

$Al_2O_3$  particles. The advantage of the carrier material is its high porosity and in comparison with the active component, low cost. The active layer consists of a washcoat with palladium. The mass proportion of active component is 0.3 wt% in the used catalyst. Table (4) contains the Characteristic of the used catalyst.

The catalyst porosity calculated using the following equation:

$$e = \frac{V_L / m_{cat}}{\frac{\rho V_L}{\rho_{cat}} + \frac{1 - \rho}{\rho_s}} \quad (18)$$

And the catalyst density calculated by following equation:-

$$r_{cat} = \frac{1}{\frac{1}{r_s} + \frac{V_L}{m_{cat}}} \quad (19)$$

## 4. Intrinsic Kinetics of Hydrogenation of AMS

Surface catalysis is involved in a large majority of industrial catalytic reactions. The rate laws developed in this section are based on the following assumptions:

1. The surface of the catalyst contains a fixed number of sites.
2. All the catalytic sites are identical.
3. The reactivity's of these sites depend only on temperature.

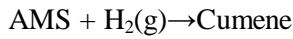
These assumptions are based on the simplest rational explanation of surface catalytic kinetics and models are formulated by Langmuir and Hinshelwood (Missen et al., (1999)). Figure (2) represent Langmuir-Hinshelwood mechanism.

### 4.1 Languimer – Hinshelwood (LH) Kinetics

By combining surface – reaction rate laws with Langmuir expression for surface coverage, the Languimer-Hinshelwood (LH) rate laws for surface-catalyzed reactions can be obtained.

Although by focus on the intrinsic kinetics of the surface-catalyzed reaction, the LH model should be set the context of a broader kinetics scheme to appreciate the significance of this.

A kinetics scheme for an overall reaction expressed as below:



A=AMS

C=Cumene

As follows:-

$\text{A} \rightarrow \text{A}$  (surface vicinity), mass transfer (fast)

$\text{H}_2(\text{g}) \rightarrow \text{H}_2$  (surface vicinity), mass transfer (fast)

$\text{A} + \text{S}_1 \xrightleftharpoons{K_A} \text{A.S}_1$   
adsorption-desorption (fast)

$\text{H}_2 + \text{S}_2 \xrightleftharpoons{K_{H_2}} \text{H}_2.\text{S}_2$   
adsorption-desorption

$\text{A.S}_1 + \text{H}_2.\text{S}_2 \rightarrow \text{C} + \text{S}_1 + \text{S}_2$  surface reactions (slow)

The reaction mechanism is derived depending on the following assumptions:

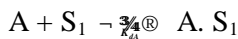
1. Reactant AMS and  $\text{H}_2$  is adsorped on different vacancy and  $\text{H}_2$  adsorped as a molecule.

2. Surface reaction is limiting step (determining step).

3. Reaction products is not desorbed.

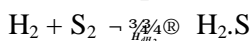
Therefore

**AMS – adsorption**



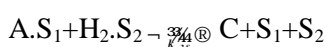
$$-r_1 = K_A \hat{e} C_A C_V - \frac{C_{AS_1}}{K_A} \hat{u} \quad (20)$$

**$\text{H}_2$  – adsorption**



$$-r_2 = K_{H_2} \hat{e} C_{H_2} C_{V_2} - \frac{C_{H_2.S_2}}{K_{H_2}} \hat{u} \quad (21)$$

**Surface reaction**



$$r_r = K_3 \hat{e} C_{A.S_1} C_{H_2.S_2} - \frac{C_C C_{V_1} C_{V_2}}{K_3} \hat{u} \quad (22)$$

Where

$$K_A = \frac{K_{aA}}{K_{dA}}, \quad K_{H_2} = \frac{K_{aH_2}}{K_{dH_2}}$$

$-r_1, -r_2$  are fast reaction then at equilibrium  $-r_1 = -r_2 = 0$

Therefore from equation (20)

$$C_{AS_1} = K_A C_A C_{V_1} \quad (23)$$

From equation (21)

$$C_{H_2.S_2} = K_{H_2} C_{H_2} C_{V_2} \quad (24)$$

Total concentration of sites vacance

$$\text{Type 1 } C_{T_1} = C_{V_1} + C_{AS_1} \quad (25)$$

Substitution equation (23) into equation (25) will give

$$C_{T_1} = C_{V_1} + K_A C_A C_{V_1}$$

$$C_{T_1} = C_{V_1} [1 + K_A C_A]$$

$$\therefore C_{V_1} = \frac{C_{T_1}}{[1 + K_A C_A]} \quad (26)$$

$$\text{Type 2 } C_{T_2} = C_{V_2} + C_{H_2.S_2} \quad (27)$$

Substitution equation (24) into equation (27) will give:

$$C_{T_2} = C_{V_2} + C_{H_2.S_2}$$

$$C_{T_2} = C_{V_2} [1 + K_{H_2} C_{H_2}]$$

$$C_{V_2} = \frac{C_{T_2}}{[1 + K_{H_2} C_{H_2}]} \quad (28)$$

Sub. equations (23, 24) into equation (22) will give

$$-r_3 = \frac{K_3 C_{T_1} C_{T_2} K_{H_2} K_A C_{H_2} C_A}{[1 + K_A C_A][1 + K_{H_2} C_{H_2}]}$$

$$K = K_3 C_{T_1} C_{T_2}$$

$$-r_3 = \frac{KK_A K_{H_2} C_A C_{H_2}}{[1 + K_A C_A][1 + K_{H_2} C_{H_2}]} \quad (29)$$

Also the other mechanisms for hydrogenation of AMS are derived in same way by using different assumption, this mechanisms can be seen in table (5).

#### 4.2 Catalyst activation

Activation means treating the catalyst to its full capacity before any experiment. There are three options to activation (without activation, wet activation, and dry

activation). A wet activation means that the catalyst in a cumene liquid in the reactor and the hydrogen was feed to it. The disadvantage of this procedure is that the concentration of hydrogen in the liquid is limited. For this reason, a dry activation was used always, in dry activation the catalyst in the reactor and hydrogen was feed. The advantage of the dry activation is that the catalyst can be enabled for several tests.

Therefore, in this work a dry activation is used. In figure (3) its clear the difference of the color between treated catalyst and untreated.

## 5. Results and discussion

Table (6) contains all of the experimental sets.

### 5.1 Effect of temperature

Experiments have been performed at different temperatures (343-373 K<sup>0</sup>). From these experiments an Arrhenius plots has been constructed to determine the apparent activation energy of the reaction.

The rate in this figure is corrected using a first-order assumption for decreasing hydrogen pressure as a result of increasing vapor pressure with temperature. For uses range, the reaction rate reaction increased with increasing temperature because the mass transfer coefficients ( $K_{GL}$ ,  $K_{LS}$ ,  $K_{GS}$ ) are proportional directly to the diffusivity and hence direct proportional to the temperature.

When temperature increases the reaction rate constant further increased, therefore the reaction rate increase (see Figure 4).

### 5.2 Effect of pressure

Experiments were performed at different hydrogen partial pressure to determine the reaction order for the reaction in hydrogen

(Figure (5)). It can be seen that at pressure up to 20 bar the reaction shows a first order behavior in hydrogen. This type of behavior was anticipated and is common for hydrogenation reaction. At higher hydrogen pressure the reaction rate levels off. This behavior of hydrogen on the catalyst surface (in that case the reaction rate no longer increases once the catalyst surface is fully occupied with hydrogen). Fitting such Langmuir-Hinshelwood expressions to the observed pressure dependency did not produce acceptable results. (Nijhuis et al., (2003)).

All the mass transfer coefficients are proportional to the hydrogen pressure, and increasing hydrogen pressure will enhance the mass transfer rates and then the reaction rate.

### 5.3 Effect of catalyst loading and size

The measured reaction rate at temperature (363 °K) is proportional to the catalyst weight (0.1 and 0.2 gm) of catalyst (see experiment 7 and 13) and it can be seen that the difference between them from figure (6).

The reaction rate was increased with increasing the amount of catalyst, because the increasing in surface area for the reaction and increasing vacancy concentration. The two experiments (5 and 15) at the same operating condition accept the particle size of the catalyst was different (4.28 and 37.36  $\mu_m$ ). The rate of reaction decreasing with increasing particle size because of decreasing in surface area  $\frac{a}{\xi} \propto \frac{1}{dp}$

where (a) is the surface area. The activity obtained with smaller particles was approximately 40% higher than that of the larger catalyst particles (see Fig. 7).

### 5.4 Effect of stirring speed

Experiments (7 and 14) at the same operating condition but at different of stirrer speed (1400 and 1000 rpm) respectively.

Figure (8) show different reaction rates at different stirrer speed. It can be seen that at a stirrer speed 1400 rpm the reaction rate is faster than that at 1000 rpm, indicating that hydrogen dissolution were limiting the reaction. Increasing the stirrer speed give high performance of mixing and there is no concentration gradient and increasing solubility of hydrogenation AMS.

### 6. Mechanism and kinetic mode

Based on the Langmuir-Hanshelwood theory and depending on the literature, various models were proposed to describe the reaction mechanism. The mechanisms vary in assumptions, such as number of different activated catalyst sites, the status of hydrogen and the rate-controlling step. The kinetic parameter estimation was performed with the ACM (Aspen Custom Modeler) software.

The Arrhenius equation represent the dependence of the reaction rate constant K on the temperature. With this equation from two measuring points in different temperatures the activation energy ( $E_A$ ) of the reaction was calculated.

$$K = K_0 \cdot \exp\left(-\frac{E_A}{RT}\right) \quad (30)$$

And to describe the adsorption the van't Hoff equation used. With this equation a correlation between temperature and adsorption equilibrium constants  $K_i$  and change in enthalpy of adsorption  $\Delta H_{ads}$  for component i.

$$K_i = K_{i0} \cdot \exp\left(-\frac{\Delta H_{ads}}{RT}\right) \quad (31)$$

Figure (9) represent a plot of sum of square error for each mechanism. The experimental data with the greatest correspondence was attained by two different expressions for the reaction mechanism (mechanism 3 and 4, table 7).

### 7. Conclusion

Hydrogenation of AMS on Pd is very fast reaction, and this leads to mass-transfer limitations, most often internal, or external. Therefore the stirrer speed is not sufficiently affected on the reaction rate such as the other conditions (temperature, pressure and catalyst weight).

In the present study, there are two most represented kinetic expressions for AMS hydrogenation as following.

$$-r_{AMS} = \frac{kK_A K_{H_2} C_A C_{A_2}}{(1 + K_A C_A + \sqrt{K_{H_2} C_{H_2}})^3}$$

$$-r_{AMS} = \frac{kK_A K_{H_2} C_A C_{A_2}}{(1 + K_A C_A)(1 + \sqrt{K_{H_2} C_{H_2}})^2}$$

These two mechanisms and there estimated parameters can be used in future to study the behavior of AMS hydrogenation in the monolith reactors or trickle bed reactors.

### Notation

- C: Concentration (mol/m<sup>3</sup>)
- D: Diffusivity (m<sup>2</sup>/s)
- dp: Particle mean diameter (m)
- Ea: Activation energy (J/mol)
- Kr: Rate constant (m/s)
- K<sub>0</sub>: Preexponential factor (m/s)
- K<sub>i</sub>: adsorption equilibrium constant of component (-)
- K<sub>GL</sub>: gas-Liquid volumetric mass-transfer coefficient (1/s)
- K<sub>LS</sub>: Liquid-Solid volumetric mass-transfer coefficient (1/s)
- K<sub>GS</sub>: Gas-Solid volumetric mass-transfer coefficient (1/s)
- M<sub>T</sub>: Thiele modulus (-)

$L_T$ : Particle size (m)  
 Mwt: Molecular weight (gm/mol)  
 P: Pressure (bar)  
 r: rate of reaction (mol/s.kg.catalyst)  
 R: Gas law constant (J/mol·K)  
 T: Temperature (K)  
 V: Volume (m<sup>3</sup>)  
 wt%: Weight fraction (-)  
 X: Conversion (-)

**Greek Letters**

$\epsilon$ : Holdup  
 $\eta$ : Catalyst effectiveness factor  
 $\rho$ : Density (kg·m<sup>-3</sup>)

**Subscripts**

AMS:  $\alpha$ -methylstyrene  
 cat: catalyst  
 C: Cumene  
 eff: effective diffusivity.  
 exp: experimental  
 G: gas  
 H: Hydrogen  
 Int: intrinsic  
 L: Liquid  
 P: Particle  
 Pd: Palladium  
 R: Reactor  
 S: Solid

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Table (1) properties of AMS and cumene (Shuhaib(2008))

Property	Symbol	Unit	AMS	C
Molecular weight	$M_{wt}$	g/mol	118.18	120.2
Boiling point	$T_B$	$^{\circ}K$	438.5	425.6
Critical temperature	$T_c$	$^{\circ}K$	654	631.1
Critical pressure	$P_c$	bar	34	32.1

Table (2) AMS and C density as a function temperature (Shuhaib(2008)).

Property	Component	Unit	Correlation
Density	AMS	g/l	$920.89348 - 0.86311 T$
Density	C	g/l	$878.49298 - 0.83719 T$

Table (3) hydrogen properties (Shuhaib(2008)).

Properties	Sample	Unit	Quantity
Molecular weight	$M_{wt}$	g/mol	2
Acentric Factor	$\omega$	-	- 0.218
Critical temperature	$T_C$	$K^{\circ}$	33.2
Critical pressure	$P_C$	Bar	13
Boiling point	$T_B$	$K^{\circ}$	20.3
Critical molar volume	$v_C$	$Cm^3/mol$	60
Molar volume at normal pressure	$v$	$Cm^3/mol$	25.77
Relative temperature	$T_{rel}$	K	0.61144

Table (4) Characteristic of catalyst

Active component	Palladium (Pd)
Associated material	$\gamma - Al_2O_3$
Palladium weight percent wt%	0.3
Specific area m <sup>2</sup> /g	210
Micro pore volume (r<10nm)[cm <sup>3</sup> /g]	0.71
Micro pore volume (10nm ≤ r ≤50nm)[cm <sup>3</sup> /g]	0.02
Micro pore volume (r>50nm)[cm <sup>3</sup> /g]	0.01
Catalyst density	0.58
Porosity (-)	0.74

Table (5) Variety of rate expressions for different assumptions

Entry	Assumption	Rate expression
1.	A is adsorbed H <sub>2</sub> is adsorbed (molecular) in different	$-r_{AMS} = \frac{kK_A K_{H_2} C_A C_{H_2}}{(1 + K_A C_A)(1 + K_{H_2} C_{H_2})}$
2.	A is adsorbed H <sub>2</sub> is adsorbed (molecular)	$-r_{AMS} = \frac{kK_A K_{H_2} C_A C_{A_2}}{(1 + K_A C_A + K_{H_2} C_{H_2})^2}$
3.	A is adsorbed H <sub>2</sub> is atomic desorbed	$-r_{AMS} = \frac{kK_A K_{H_2} C_A C_{A_2}}{(1 + K_A C_A + \sqrt{K_{H_2} C_{H_2}})^3}$
4.	A is adsorbed H <sub>2</sub> is atomic desorbed in different	$-r_{AMS} = \frac{kK_A K_{H_2} C_A C_{A_2}}{(1 + K_A C_A)(1 + \sqrt{K_{H_2} C_{H_2}})^2}$
5.	A is not adsorbed H <sub>2</sub> is atomic desorbed	$-r_{AMS} = \frac{kK_{H_2} C_A C_{H_2}}{(1 + \sqrt{K_{H_2} C_{H_2}})^2}$
6.	A is not adsorbed H <sub>2</sub> is adsorbed (molecular)	$-r_{AMS} = \frac{kK_{H_2} C_A C_{H_2}}{(1 + K_{H_2} C_{H_2})}$
7.	A is adsorbed H <sub>2</sub> is not adsorbed	$-r_{AMS} = \frac{kK_A K_{H_2} C_A C_{H_2}}{(1 + K_A C_A)}$
8.	-	$-r_{AMS} = \frac{kK_A C_A \sqrt{K_{H_2} C_{H_2}}}{(1 + K_A C_A)(1 + \sqrt{K_{H_2} C_{H_2}})}$
9.	-	$-r_{AMS} = \frac{kK_A C_A \sqrt{K_{H_2} C_{H_2}}}{(1 + K_A C_A + \sqrt{K_{H_2} C_{H_2}})^2}$

Table (6) Set of experiments

T(C°)	P(bar)	m <sub>cast</sub> (gm)	n(rpm)	V <sub>R</sub> (ml)
70	10	0.1	1400	200
70	15	0.1	1400	200
70	20	0.1	1400	200
80	10	0.1	1400	200
80	15	0.1(4.28 μ <sub>m</sub> )	1400	200
80	20	0.1	1400	200
90	10	0.1	1400	200
90	15	0.1	1400	200
90	20	0.1	1400	200
100	10	0.1	1400	200
100	15	0.1	1400	200
100	20	0.1	1400	200
90	10	0.2	1400	200
90	10	0.1	1000	200
80	15	0.1(37.36 μ <sub>m</sub> )	1400	200

Table (7) Kinetic parameters using (ACM) program

Entry	Mechanism	Kinetic parameter	Unit	Quantity
1	$-r_{AMS} = \frac{kK_A K_{H_2} C_A C_{H_2}}{(1 + K_A C_A)(1 + K_{H_2} C_{H_2})}$	$E_A$	KJ/mol	34.059
		$K_o$	mol/gm.min	$2.96764 \times 10^7$
		$DH_{ads.A}$	KJ/mol	-14.6361
		$K_{oA}$	L/mol	$1.94061 \times 10^{-3}$
		$DH_{ads.H_2}$	KJ/mol	$-1.9837 \times 10^{-4}$
		$K_{oH_2}$	L/mol	0.0914643
2	$-r_{AMS} = \frac{kK_A K_{H_2} C_A C_{A_2}}{(1 + K_A C_A + K_{H_2} C_{H_2})^2}$	$E_A$	KJ/mol	32.1518
		$K_o$	mol/gm.min	$2.1015 \times 10^7$
		$DH_{ads.A}$	KJ/mol	-16.1253
		$K_{oA}$	L/mol	$1.30063 \times 10^{-3}$
		$DH_{ads.H_2}$	KJ/mol	-0.0405814
		$K_{oH_2}$	L/mol	0.0659305
3	$-r_{AMS} = \frac{kK_A K_{H_2} C_A C_{A_2}}{(1 + K_A C_A + \sqrt{K_{H_2} C_{H_2}})^3}$	$E_A$	KJ/mol	34.427
		$K_o$	mol/gm.min	$2.30198 \times 10^7$
		$DH_{ads.A}$	KJ/mol	-17.4871
		$K_{oA}$	L/mol	$1.35032 \times 10^{-3}$
		$DH_{ads.H_2}$	KJ/mol	-0.0414532
		$K_{oH_2}$	L/mol	0.067506
		$E_A$	KJ/mol	39.2601

4	$-r_{AMS} = \frac{kK_A K_{H_2} C_A C_{H_2}}{(1 + K_A C_A)(1 + \sqrt{K_{H_2} C_{H_2}})^2}$	$K_o$	mol/gm.min	$3.24741 \times 10^7$
		$DH_{ads.A}$	KJ/mol	-19.0777
		$K_{oA}$	L/mol	$3.40568 \times 10^{-3}$
		$DH_{ads.H_2}$	KJ/mol	$-2.19613 \times 10^{-4}$
5	$-r_{AMS} = \frac{kK_{H_2} C_A C_{H_2}}{(1 + \sqrt{K_{H_2} C_{H_2}})^2}$	$E_A$	KJ/mol	38.0635
		$K_o$	mol/gm.min	$1.54852 \times 10^7$
		$DH_{ads.H_2}$	KJ/mol	$-2.48624 \times 10^{-4}$
		$K_{oH_2}$	L/mol	0.0746463
6	$-r_{AMS} = \frac{kK_{H_2} C_A C_{H_2}}{(1 + K_{H_2} C_{H_2})}$	$E_A$	KJ/mol	40.8385
		$K_o$	mol/gm.min	$2.74084 \times 10^7$
		$DH_{ads.H_2}$	KJ/mol	$-1.6939 \times 10^{-4}$
		$K_{oH_2}$	L/mol	0.082637
7	$-r_{AMS} = \frac{kK_A C_A C_{H_2}}{(1 + K_A C_A)}$	$E_A$	KJ/mol	45.103
		$K_o$	mol/gm.min	$2.1026 \times 10^7$
		$DH_{ads.A}$	KJ/mol	-10.6116
		$K_{oA}$	L/mol	0.0309901
8	$-r_{AMS} = \frac{kK_A C_A \sqrt{K_{H_2} C_{H_2}}}{(1 + K_A C_A)(1 + \sqrt{K_{H_2} C_{H_2}})}$	$E_A$	KJ/mol	49.4625
		$K_o$	mol/gm.min	$3.00966 \times 10^7$
		$DH_{ads.A}$	KJ/mol	-13.012
		$K_{oA}$	L/mol	0.017507
		$DH_{ads.H_2}$	KJ/mol	-0.00847844
9	$-r_{AMS} = \frac{kK_A C_A \sqrt{K_{H_2} C_{H_2}}}{(1 + K_A C_A + \sqrt{K_{H_2} C_{H_2}})}$	$E_A$	KJ/mol	46.0789
		$K_o$	mol/gm.min	$4.98754 \times 10^7$
		$DH_{ads.A}$	KJ/mol	-8.09857
		$K_{oA}$	L/mol	0.0248671
		$DH_{ads.H_2}$	KJ/mol	-4.76242
		$K_{oH_2}$	L/mol	0.0355481



Figure (1) Experimental set-up.

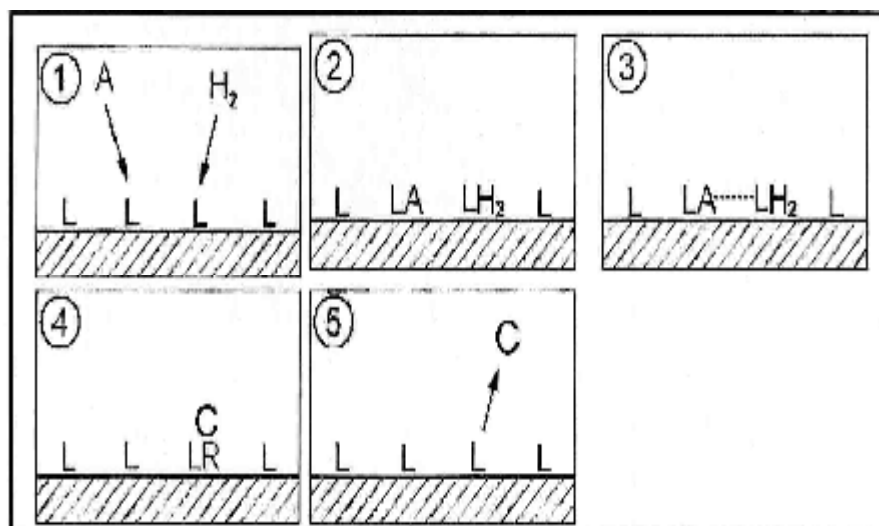


Figure (2) Langmuir-Hinshelwood- mechanism. (Missen et al. 1999)

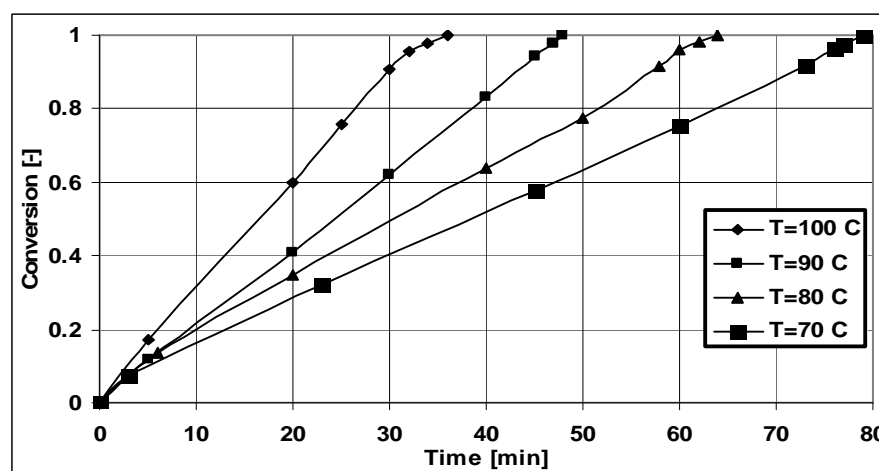


Figure (3) catalyst, right hand (treated) –Left (untreated)

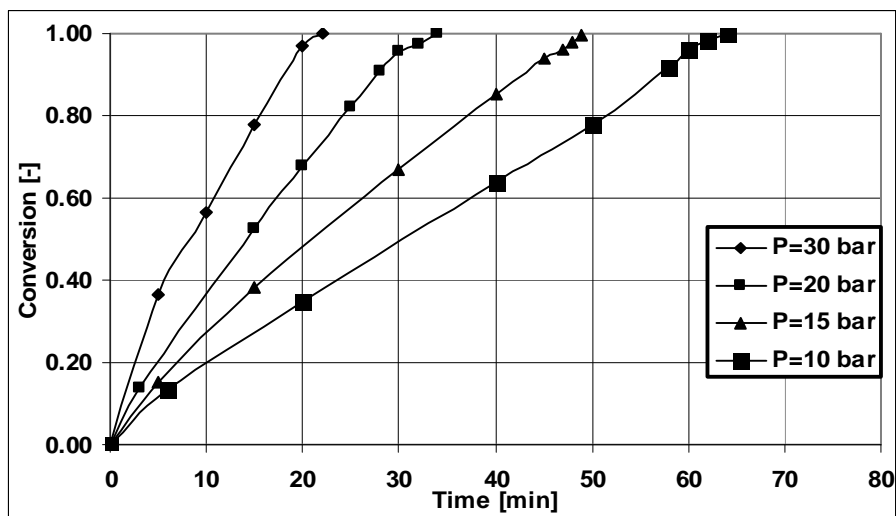


Figure (4) Effect of temperature on conversion (P=10 bar, RS=1400, Mcat=0.1 gm)

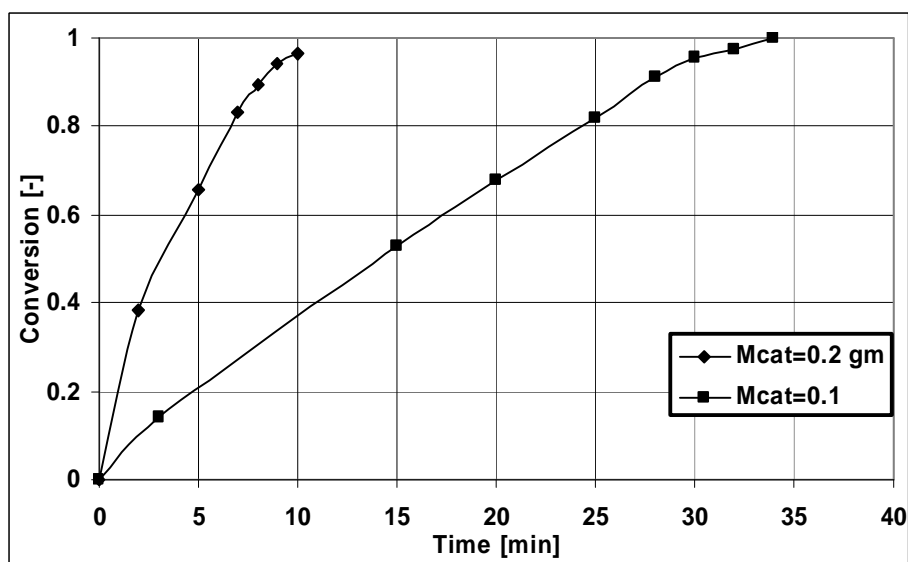


Figure (5) Effect of pressure on conversion for STR  
(T=80 C , S.S=1400 rpm , Mcat=0.1 gm)

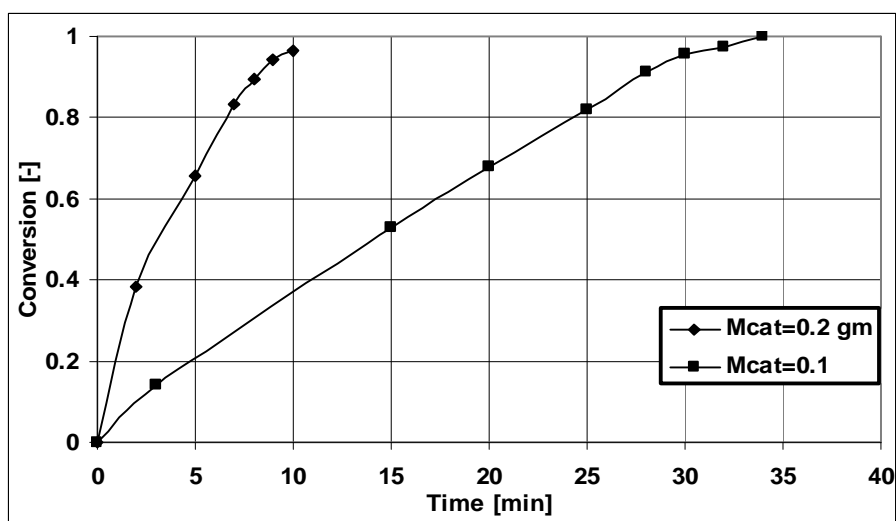


Figure (6) Effect of mass of catalyst on conversion for STR  
(P=20 bar, T=80 C, S.S=1400 rpm)

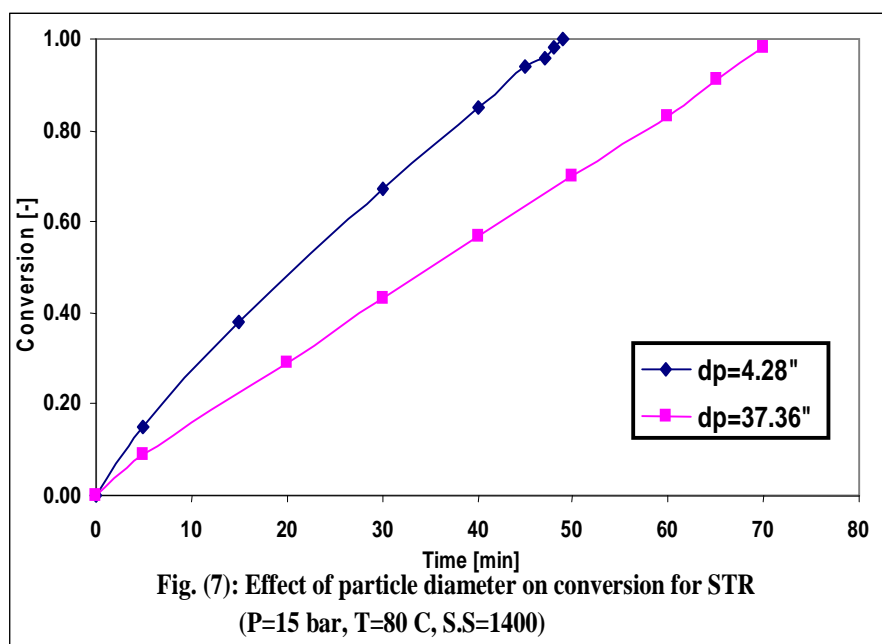


Fig. (7): Effect of particle diameter on conversion for STR  
(P=15 bar, T=80 C, S.S=1400)

Figure (7) Effect of particle diameter on conversion for STR  
(P=15 bar, T=80 C, S. S=1400)

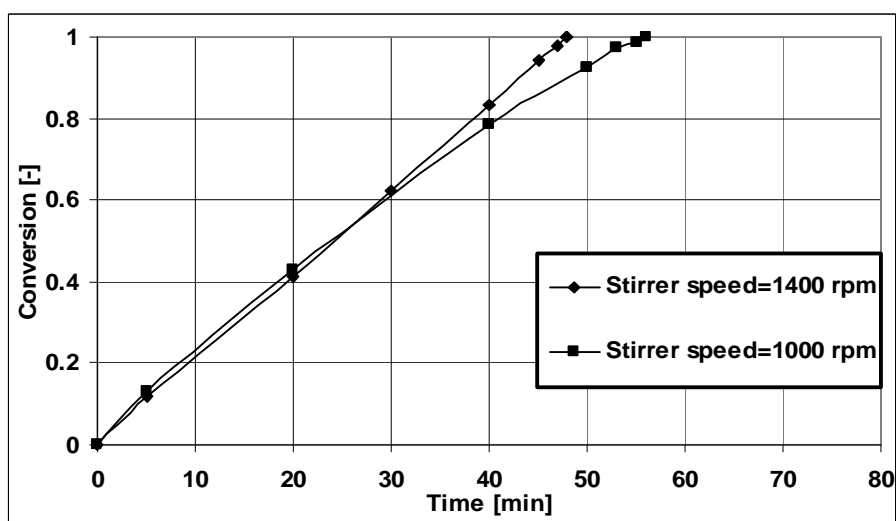


Figure (8) Effect of stirrer speed on conversion for STR  
(P=10 bar, T=90 C, Mcat=0.1 gm)

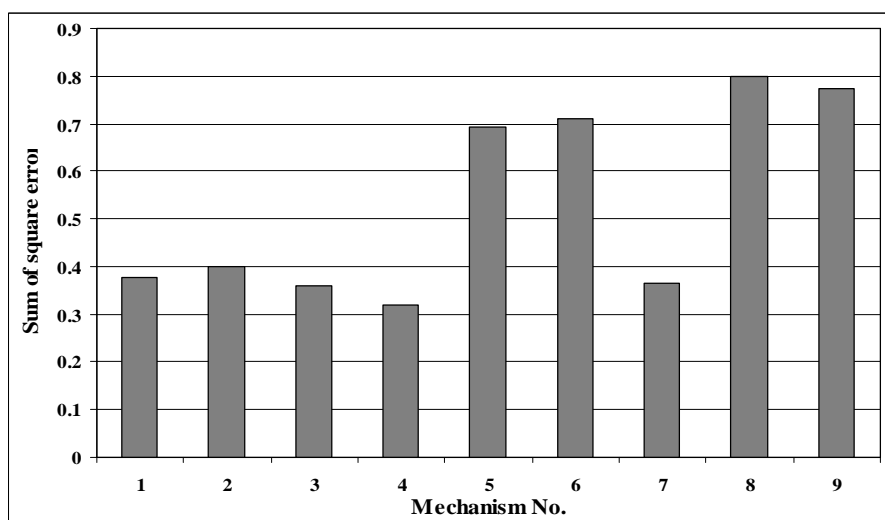


Figure (9) Sum of the square error vs mechanism