

CHAPTER 5  
KINETIC ANALYSIS

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For many reactions , the rate expression can be written as a product of a temperature dependent term and a composition dependent term , or

$$\begin{aligned} r_1 &= f_1 (\text{temperature}) \cdot f_2 (\text{composition}) \\ &= k \cdot f_2 (\text{composition}) \end{aligned} \quad (1)$$

For such reactions the temperature dependent term , the reaction rate constant , has been found in practically all cases to be well represented by the Arrhenius' law ;

$$k = k_0 e^{-E/RT} \quad (2)$$

Where  $k_0$  is the frequency or pre – exponential factor and  $E$  is called the activation energy of the reaction .

The temperature dependency of reaction is determined by the activation energy and temperature level of the reaction . as illustrated in Fig . (5.1).

These findings are summarized as follows :-

- 1- From Arrhenius' law a plot of  $\ln k$  vs  $1/T$  gives a straight line , with large slope for large  $E$  and small slope for small  $E$  .
- 2- Reactions with high activation energies are very temperature – sensitive ; reactions with low activation energies are relatively temperature – insensitive .
- 3- Any given reaction is much more temperature – sensitive at a low temperature than at high temperatures .
- 4- The value of the frequency factor  $k_0$  does not affect the temperature sensitivity

The reaction rate constant itself can be found by studying the kinetics of a given reaction under different operating conditions to determine the form of the concentration dependent term in Eq .1. as will be given in the following section .

**Testing for First Order Kinetics :-**

At a given temperature the reaction rate is usually expressed as a function of reactant concentration in the form :-

$$-r = k C^n \quad (3)$$

Where n is referred to as the order of reaction .

If the reaction volume changes during reaction like for example in case of gas reactions then the final volume of the reactant + products for a reactant A is given by :-

$$V = V_0 (1 + \epsilon_A X_A) \quad \text{or} \quad X_A = \frac{V - V_0}{V_0 \epsilon_A} \quad (4)$$

Where  $V_0$  = initial volume of reactants .

$X_A$  = conversion .

$\epsilon_A$  = change in the system volume between no conversion and complete conversion thus and called expansion factor .

$$\epsilon_A = \frac{V_{X=1} - V_{X=0}}{V_{X=0}} \quad (5)$$

Noting that moles of A left unreacted .

$$N_A = N_{A0} (1 - X_A) \quad (6)$$

$$\text{and concentration of A} = C_A = \frac{N_A}{V} = \frac{N_{A0}(1 - X_A)}{V_0(1 + \epsilon_A X_A)} \quad (7)$$

$$= C_{A0} \frac{(1 - X_A)}{(1 + \epsilon_A X_A)} \quad (8)$$

$$\text{Thus} \quad \frac{C_A}{C_{A0}} = \frac{(1 - X_A)}{(1 + \epsilon_A X_A)} \quad (9)$$

$$\text{or} \quad X_A = \frac{1 - C_A / C_{A0}}{1 + \epsilon_A C_A / C_{A0}} \quad (10)$$

The performance equation can be deduced as follows ( Levenspiel ; 1999), for a plug flow reactor containing porous catalyst particle , take a thin slice of the PFR see Fig. (5.2 ).

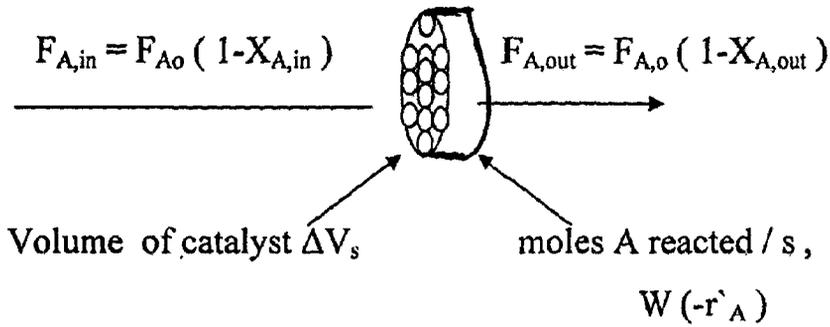


Fig. (5.1) . A thin slice of solid catalysed plug flow reactor .

At steady state a material balance for a reactant A gives :-

$$\text{Input} = \text{output} + \text{accumulation [ mol A ] / s .} \quad (11)$$

In symbols ;

$$F_{A0} - F_{A0} X_{in} = F_{A0} - F_{A0} X_{out} + (-r'_A) \Delta W \quad (12)$$

in differential form :-

$$F_{A0} dX_A = (-r'_A) \Delta W \quad (13)$$

Integrating over the whole reactor gives :-

$$\frac{W}{F_{A0}} = \int_0^{X_{Aout}} \frac{dX_A}{-r'_A} \quad (14)$$

$$\text{Let } \frac{WC_{A0}}{F_{A0}} = \tau \frac{\text{kg.s}}{\text{m}^3} \quad (\text{weight - time term}) \quad (15)$$

For a first order reaction :-

$$-r' = k' C_A \quad (16)$$

Substituting from (7) for  $C_A$  in (16) and integrating (14) taking into account the definition given in (15) .

The performance equation for a first order reaction in a plug flow reactor would be as given by Levenspiel ; (1999) as follows :-

$$k' \tau = (1 + \epsilon_A) \ln \frac{1}{1 - X_{out}} - \epsilon_A X_{out} \quad (17)$$

A plot of  $\tau'$  versus the r.h.s of Eq (17) should yield a straight line passing through the origin if the reaction obeys first order kinetics . The slope of the straight line is equal to  $k'$  , the reaction rate constant .

Reforming of methane using  $\text{CO}_2$  can be expressed as follows :-



To calculate the expansion factor  $\epsilon$  , one must consider the inert gas introduced with the reactants ( Levenspiel ; 1999 ) . The reactant feed gas was  $\text{CH}_4$  ,  $\text{CO}_2$  and  $\text{N}_2$  in the ratio 1:1:4 respectively . The six volumes of entering gases will produce eight volumes of leaving product gases then expansion factor would be calculated as ;

$$\epsilon = (8 - 6) / 6 = 1 / 3$$

Equation (17) was investigated for each of the reacting species , namely  $\text{CH}_4$  and  $\text{CO}_2$  for the three types of catalysts prepared  $\text{Rh} / \gamma\text{-Al}_2\text{O}_3$  ,  $\text{Ru} / \gamma\text{-Al}_2\text{O}_3$  and  $\text{Ir} / \gamma\text{-Al}_2\text{O}_3$  .

The conversion  $X$  is calculated from the mole % and partial pressure of the reacting species . The calculation procedure and the calculated results are given in appendix A.

The assumption of first order kinetics with the reactants  $\text{CH}_4$  and  $\text{CO}_2$  was found to be obeyed in all cases studied . Least squares regression analysis was used to fit the data according to Eq.(17) ,  $k'$  is calculated as the slope of the fitted straight lines as shown in Fig . ( 5 . 3 - 5 ) . These values together with the correlation coefficients are given in Table ( 5 .1).

Table (5.1) . Reaction rate constant as determined by least squares regression analysis.

Catalyst Type	Temperature	CO <sub>2</sub>		CH <sub>4</sub>	
		k'	c.c	k'	c.c
Rh / $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	600	5.74E4	0.96	3.80E4	0.981
	700	13.10E4	0.957	5.74E4	0.979
	800	19.1E4	0.99	8.13E4	0.911
Ru / $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	600	2.28E4	0.945	2.1E4	0.964
	700	3.66E4	0.952	3.48E4	0.848
	800	7.22E4	0.881	5.44E4	0.761
Ir / $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	600	1.66E4	0.897	1.64E4	0.936
	700	2.57E4	0.933	2.18E4	0.938
	800	5.20E4	0.918	3.49E4	0.968

For each catalyst type , the k' values thus calculated at different temperatures are fitted to Arrhinius' equation to calculate the activation energy by plotting  $\ln k'$  versus  $1 / T$  , the data are given in Table (5 .2 ) and shown in Fig. ( 5 . 2 A-C ) .

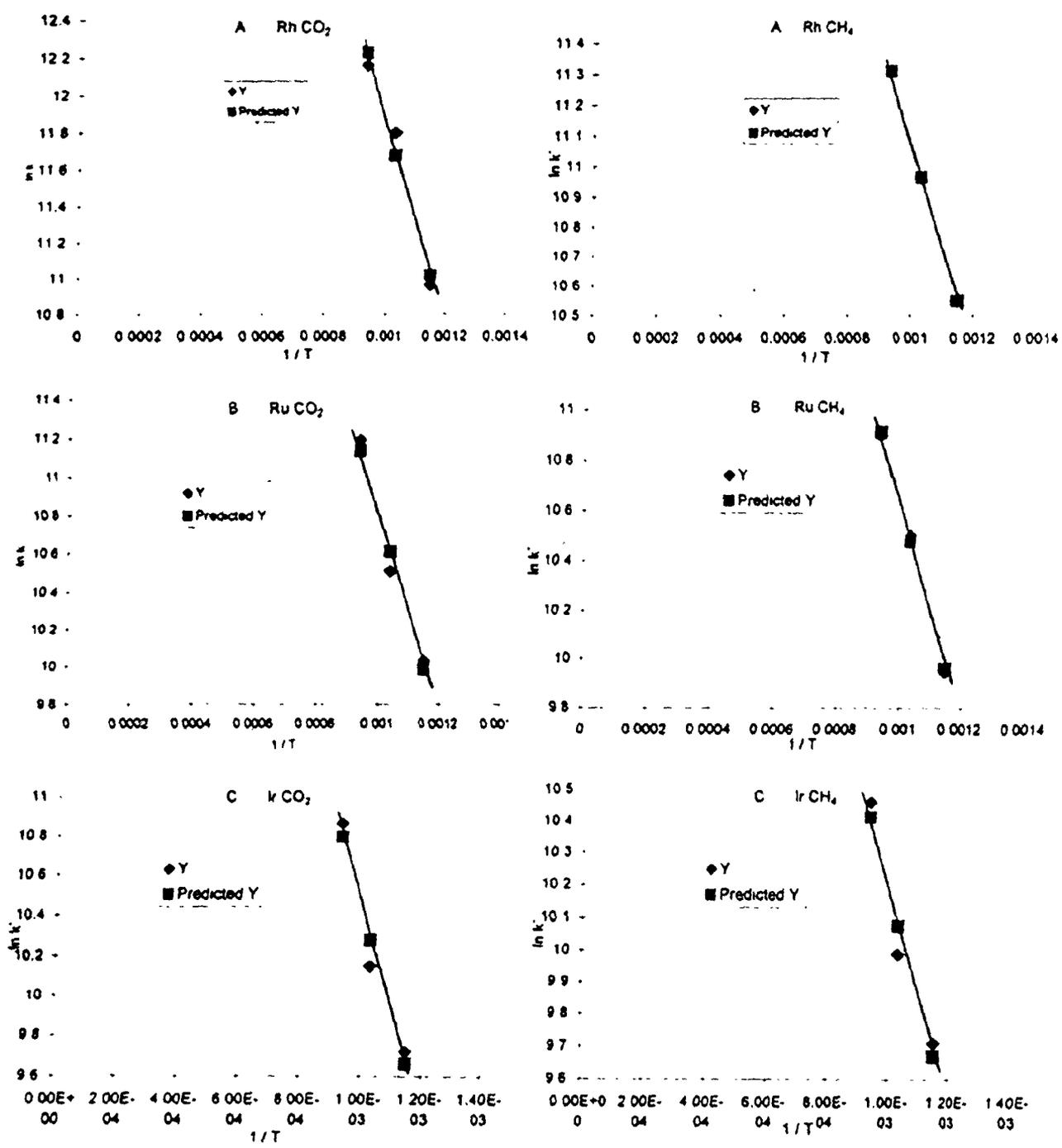


Fig ( 5.2 A - C ) . Arrhenius' plot ( A ) Rh /  $\text{Al}_2\text{O}_3$  , ( B ) Ru /  $\text{Al}_2\text{O}_3$  ,  
 ( C ) Ir /  $\text{Al}_2\text{O}_3$

Table (5.2).  $\ln k$  and  $1/T$  for 3- tested catalyst .

Catalyst Type	Temperature $1/T$	$\ln k'$	
		$\text{CO}_2$	$\text{CH}_4$
Rh / $\gamma\text{-Al}_2\text{O}_3$	0.00093	12.16	11.31
	0.001028	11.8	10.96
	0.001145	10.96	10.55
Ru / $\gamma\text{-Al}_2\text{O}_3$	0.00093	11.19	10.9
	0.001028	10.51	10.5
	0.001145	10.03	9.95
Ir / $\gamma\text{-Al}_2\text{O}_3$	0.00093	10.86	10.46
	0.001028	10.15	9.99
	0.001145	9.72	9.71

The results of the least squares regression analysis for  $k_0$  ( pre - exponential factor ) , the intercept and  $-E / R T$  , the slope are given in Table (5.3) .

Table (5.3). Activation energy and pre-exponential factor from Arrhenius' equation

Catalyst	CO <sub>2</sub>					CH <sub>4</sub>				
	ln k <sub>o</sub>	k <sub>o</sub>	-E / R	E J / mol	c.c	ln k <sub>o</sub>	k <sub>o</sub>	-E / R	E J / mol	c.c
Rh / γ-Al <sub>2</sub> O <sub>3</sub>	17.50	39.8E6	-5.66E3	47.06E3	-0.98	14.61	2.21E6	-3.55E3	29.51E3	-0.999
Ru / γ-Al <sub>2</sub> O <sub>3</sub>	16.14	10.2E6	-5.38E3	44.65E3	-0.988	15.01	3.30E6	-4.42E3	36.24E3	-0.999
Ir / γ-Al <sub>2</sub> O <sub>3</sub>	15.70	0.658E6	-5.27E3	43.81E3	-0.981	13.64	0.838E6	-3.47E3	28.85E3	-0.980

Discussion for each catalyst type is as follows:-

*5.1. Rh /  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>:-*

Testing for the first order assumption for methane and CO<sub>2</sub> reaction over Rh /  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst is shown in Fig. ( 5 . 3 ). It is shown that the first order reaction kinetics assumption is valid for both reactants under almost all operating conditions investigated .

However, higher deviation is observed at the highest temperature investigated for the longest reaction time. This point was therefore excluded from the correlation .

A correlation coefficient ( > 0.9 ) shown in Table ( 5 .1 ) reflects the validity of the 1<sup>st</sup> order kinetics .

The deviation from first order equation observed for both reactants at the highest temperature and the longest reaction time may indicate a change in the reforming reaction mechanism or the onset of other reactions .

As shown in Table ( 5 .1 ) the reaction rate constant for CO<sub>2</sub> is found to be approximately double that calculated for CH<sub>4</sub> at the same temperature , thus strongly suggesting a route other than reforming for the reaction of CO<sub>2</sub> for example the RWGS reaction .

This result is in confirmation with yields of CO which is higher than H<sub>2</sub> despite the equimolar volumes of the reacting gases as discussed in chapter 4 . Arrhenius' plot for this catalyst is shown in Fig.( 5 .2 .A) . The plot and Table (5 .3) reveal that the activation energy for CO<sub>2</sub> reaction is ( 47.06E3 J / mol ) which is more than that for CH<sub>4</sub> ( 29.51E3 J / mol ) i .e. CO<sub>2</sub> is more temperature – sensitive than CH<sub>4</sub> .

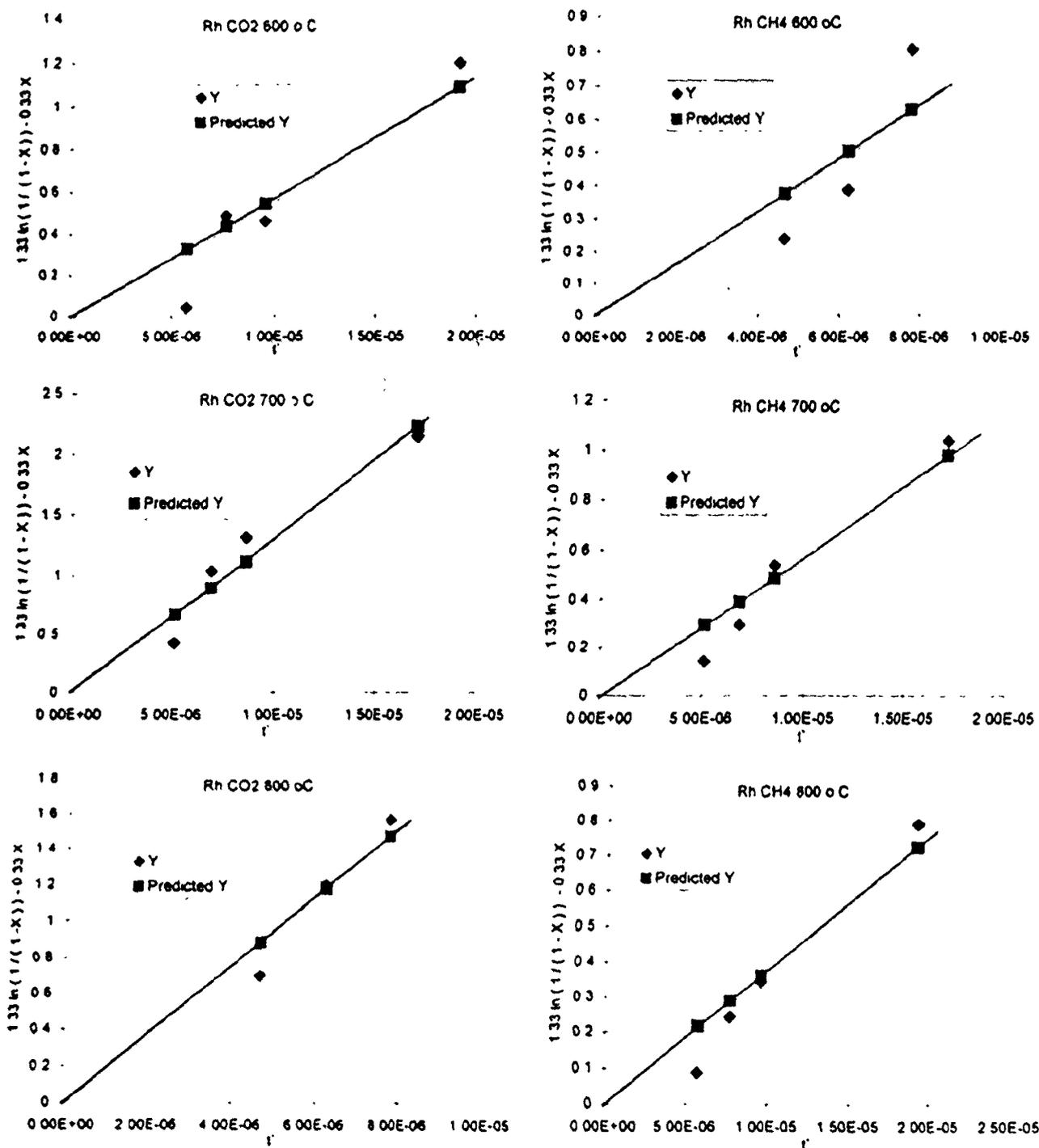


Fig ( 5. 3 ) . Test for First Order Reaction Kinetics w.r.t CO<sub>2</sub> and CH<sub>4</sub> Over Rh / Al<sub>2</sub>O<sub>3</sub> Catalyst .

## 5.2. Ru / $\gamma$ - Al<sub>2</sub>O<sub>3</sub> and Ir / $\gamma$ - Al<sub>2</sub>O<sub>3</sub> catalysts :-

Testing for the first order assumption for methane and CO<sub>2</sub> reaction over Ru /  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and Ir /  $\gamma$ - Al<sub>2</sub>O<sub>3</sub> catalysts is shown in Fig . ( 5 . 4 ) & ( 5 . 5). It is shown that the first order reaction kinetics assumption is valid for both reactants on the two catalysts under almost all operating conditions investigated .

However, higher deviation is observed at the longest reaction time. These points were therefore excluded from the correlation . The correlation coefficient ( $\geq 0.9$ ) in most of the cases as shown in Table ( 5 . 1 ) reflects the validity of the 1<sup>st</sup> order kinetics.

However ; Ir /  $\gamma$ - Al<sub>2</sub>O<sub>3</sub> gave better correlation coefficient which are close to those of Rh /  $\gamma$  Al<sub>2</sub>O<sub>3</sub> .

The deviation from first order equation observed for both reactants at the longest reaction time may indicate a change in the reforming reaction mechanism or deactivation of both catalysts Ir and Ru /  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> with time , contrary to Rh /  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> which showed increased activation at the highest temperature with time .

As shown in Table ( 5 . 1 ) the reaction rate constant for CO<sub>2</sub> is found to be approximately equal to or slightly higher than those calculated for CH<sub>4</sub> at the same temperature , thus suggesting a route other than reforming for the reaction of CO<sub>2</sub> for example the RWGS reaction at the higher temperature, this result is in confirmation with those on yields of CO which are higher than H<sub>2</sub> despite the equimolar volumes of the reacting gases as discussed in chapter 4 .

Arrhenius' plots for these catalysts are shown in Fig.( 5.2.B,C ) . The plot reveals that the activation energy for CO<sub>2</sub> reaction is more than that for CH<sub>4</sub> i.e. CO<sub>2</sub> is more temperature – sensitive than CH<sub>4</sub> .The activation energy for CH<sub>4</sub> dissociation is 28.85E3 J / mol while that for CO<sub>2</sub> is 43.81E3 J / mol for Ir/  $\gamma$ - Al<sub>2</sub>O<sub>3</sub> catalyst and 36.24E3 J / mol for CH<sub>4</sub> dissociation and 44.65E3 J / mol for CO<sub>2</sub> for Ru /  $\gamma$ - Al<sub>2</sub>O<sub>3</sub> catalysts .

# CONCLUSIONS

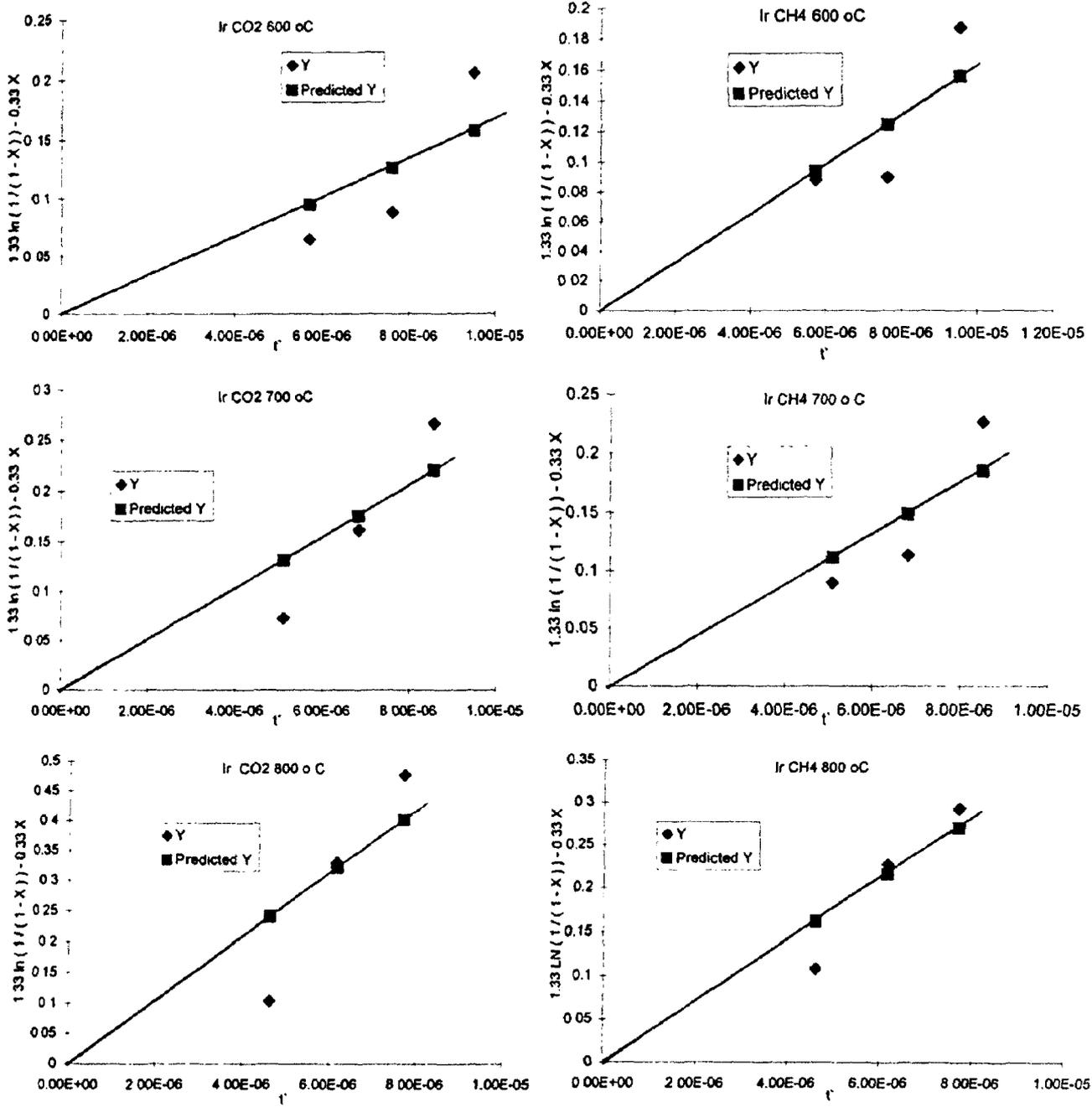


Fig ( 5 . 4 ) . Test for First Order Reaction Kineticses w . r . t CO<sub>2</sub> and CH<sub>4</sub> Over Ir / Al<sub>2</sub>O<sub>3</sub> Catalyst .

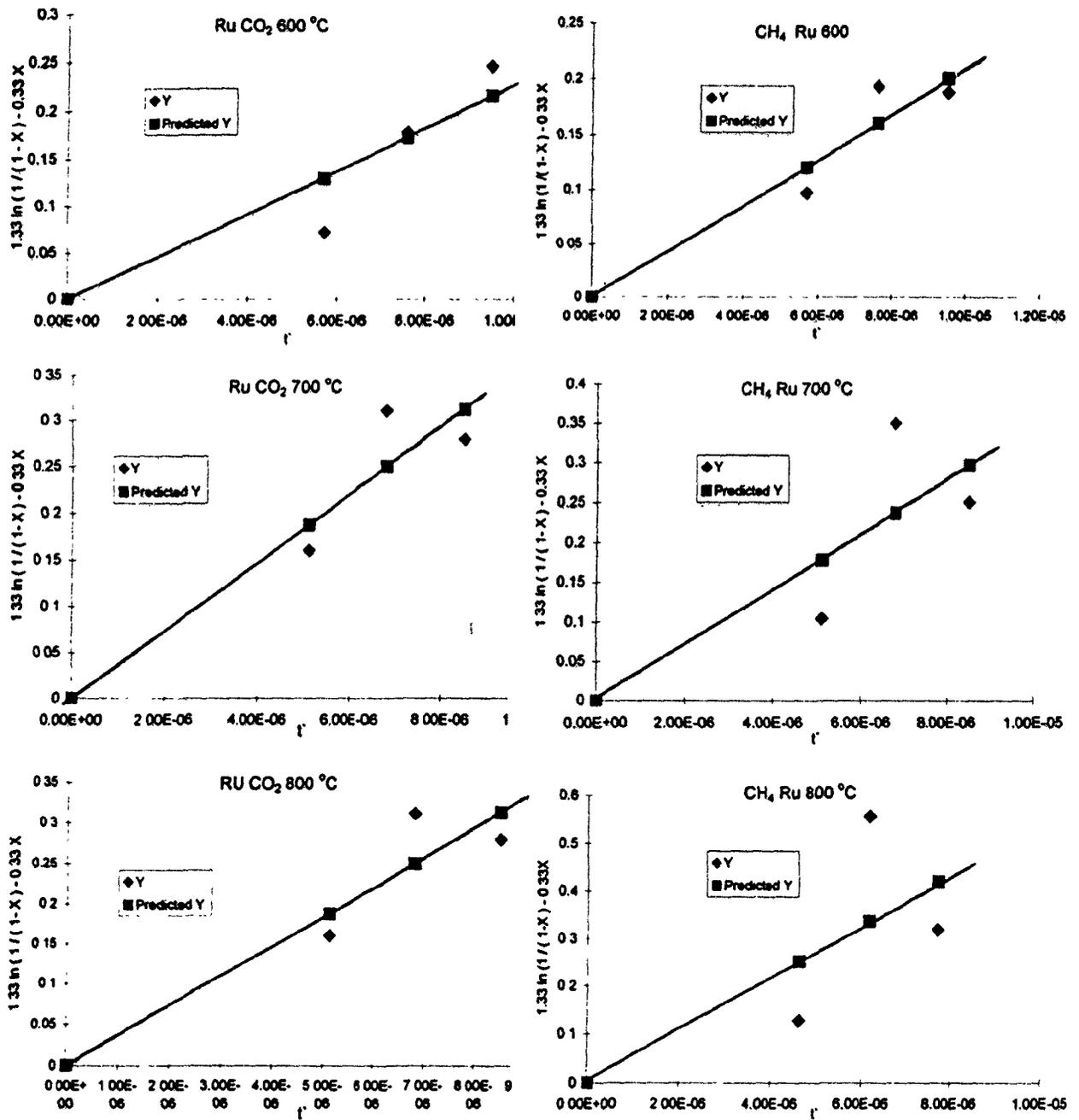


Fig ( 5 . 5 ) . Test for First Order Reaction Kinetics w . r . t CO<sub>2</sub> and CH<sub>4</sub> Over Ru / Al<sub>2</sub>O<sub>3</sub> Catalyst .

## CONCLUSIONS

The following conclusions can be drawn from the results of the present investigation:-

Generally ; for all the investigated catalysts the catalyst reactivity increased with increasing temperature and decreasing weight hourly space velocity .

a. For 0.5%Rh/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst:-

1. Rh/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst exhibits good reactivity within the whole temperature range and all the studied space velocities but with different degrees.
2. The space velocity 18000ccg<sup>-1</sup>h<sup>-1</sup> and the temperature 800°C are the optimum condition resulting in the highest conversion of not only methane but also the other heavy hydrocarbons in the natural gas ( ethane, propane, butanes, pentanes, hexanes, and heptanes).
3. The Rh / $\gamma$ -Al<sub>2</sub>O<sub>3</sub> selectivity with respect to H<sub>2</sub> and CO was achieved maximally at temperature of 800°C and space velocity 18000ccg<sup>-1</sup>h<sup>-1</sup> .
4. (H<sub>2</sub> / CO) ratio was always less than one , however the highest ratio (0.65) was obtained at the optimum conditions, space velocity 36000 cc g<sup>-1</sup>h<sup>-1</sup> and the temperature 700°C.
5. The first order kinetics assumption is valid for both CH<sub>4</sub> and CO<sub>2</sub> reactants under the operating conditions investigated . The reaction rate constant for CO<sub>2</sub> was higher than that of CH<sub>4</sub> (for example at 800°C reaction rate constants equal 19.1E4 and 8.13E4 J / mol ) respectively .
6. The activation energy was calculated from Arrhinius' equation as 47.06E3 J / mol. and 29.51E3 J / mol. for CO<sub>2</sub> and CH<sub>4</sub> respectively .

### b. For 0.5% Ru/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst:-

1. The space velocity 36000ccg<sup>-1</sup>h<sup>-1</sup> and the temperature 800°C are the optimum condition resulting in the highest conversion of methane but , the space velocity 18000ccg<sup>-1</sup>h<sup>-1</sup> and the temperature 800°C are the optimum condition resulting in the highest conversion of the other heavy hydrocarbons in the natural gas ( ethane , propane, butanes, pentanes, hexanes, and heptanes).
2. The Ru / $\gamma$ -Al<sub>2</sub>O<sub>3</sub> selectivity with respect to H<sub>2</sub> and CO was achieved maximally at temperature of 800°C and space velocity 18000ccg<sup>-1</sup>h<sup>-1</sup>
3. Maximum (H<sub>2</sub> / CO) ratio was achieved at the optimum conditions, space velocity 18000ccg<sup>-1</sup>h<sup>-1</sup> and the temperature 800°C.
4. The first order kinetics assumption is valid for both CH<sub>4</sub> and CO<sub>2</sub> reactants under the operating conditions investigated . The reaction rate constant for CO<sub>2</sub> was higher than that of CH<sub>4</sub> (for example at 800°C reaction rate constants equal 7.22E4 and 3.49E4 J / mol ) respectively .
5. The activation energy was calculated from Arrhinus' equation as 44.65E3 and 36.24E3 J / mol for CO<sub>2</sub> and CH<sub>4</sub> respectively .

### c. For 0.5% Ir/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst:-

1. The space velocity 45000ccg<sup>-1</sup>h<sup>-1</sup> and the temperature 800°C are the optimum condition resulting in the highest conversion of methane but, the space velocity 18000ccg<sup>-1</sup>h<sup>-1</sup> and the temperature 800°C are the optimum condition resulting in the highest conversion of not only methane but also the other heavy hydrocarbons in the natural gas ( ethane, propane, butanes, pentanes, hexanes, and heptanes).

2. The Ir/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> selectivity with respect to H<sub>2</sub> and CO was achieved maximally at temperature of 800°C and space velocity 18000ccg<sup>-1</sup>h<sup>-1</sup>
3. Maximum (H<sub>2</sub> / CO) ratio was achieved at the optimum conditions, space velocity 36000ccg<sup>-1</sup>h<sup>-1</sup> and the temperature 700°C.
4. The first order kinetics assumption is valid for both CH<sub>4</sub> and CO<sub>2</sub> reactants under the operating conditions investigated . The reaction rate constant for CO<sub>2</sub> was higher than that of CH<sub>4</sub> ( for example at 800°C reaction rate constants equal 5.20E4 and 3.49E4 J / mol ) respectively .
5. The activation energy was calculated from Arrhinius' equation as 43.81E3 and 28.85E3 J / mol for CO<sub>2</sub> and CH<sub>4</sub> respectively .

Finally 0.5% Rh/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst was the best as compared to the two other catalysts investigated . The optimum operating conditions were 18000 ccg<sup>-1</sup> h<sup>-1</sup> for the space velocity and 800°C for the reforming temperature . Maximum (H<sub>2</sub> /CO) ratio was obtained at 36000ccg<sup>-1</sup>h<sup>-1</sup> space velocity and the temperature 700°C.

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# APPENDIX A

## APPENDIX . A .

## First Order Reaction Kinetic's Calculations :-

Given the volumetric analysis ( percentage remained ) of the reacting species in Table ( A 1-3 ).

Table ( A.1 ) . Remaining Concentrations of  $\text{CO}_2$  and  $\text{CH}_4$  for Rh /  $\gamma\text{-Al}_2\text{O}_3$  at the studied conditions .

Temperature Space Velocity $\text{ccg}^{-1} \cdot \text{h}^{-1}$	600 °C		700°C		800°C	
	$\text{CH}_4$	$\text{CO}_2$	$\text{CH}_4$	$\text{CO}_2$	$\text{CH}_4$	$\text{CO}_2$
18000	41.53	28.38	32.97	22.37	5.17	6.56
36000	66.04	58.03	53.38	40.51	41.06	33.99
45000	73.99	56.59	69.59	48.95	63.02	43.2
60000	89.21	94.85	83.29	74.94	74.44	62.26

Table ( A.2 ) . Remaining Concentrations of  $\text{CO}_2$  and  $\text{CH}_4$  for Ru /  $\gamma\text{-Al}_2\text{O}_3$  at the studied conditions .

Temperature Space Velocity $\text{ccg}^{-1} \cdot \text{h}^{-1}$	600 °C		700°C		800°C	
	$\text{CH}_4$	$\text{CO}_2$	$\text{CH}_4$	$\text{CO}_2$	$\text{CH}_4$	$\text{CO}_2$
18000	88.26	91.04	87.44	81.62	85	69.91
36000	78.5	79.7	65.54	68.46	52.58	49.05
45000	78.95	73.69	73.38	70.95	67.83	59.35
60000	91.17	90.83	88.72	76.01	82.9	66.92

Table ( A.3 ) . Remaining Concentrations of CO<sub>2</sub> and CH<sub>4</sub> for Ir /  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> at the studied conditions .

Temperature Space Velocity ccg <sup>-1</sup> .h <sup>-1</sup>	600 °C		700°C		800°C	
	CH <sub>4</sub>	CO <sub>2</sub>	CH <sub>4</sub>	CO <sub>2</sub>	CH <sub>4</sub>	CO <sub>2</sub>
18000	89.26	91.43	89.04	90.99	87.02	87.48
36000	89.05	89.22	86.44	81.51	75.37	67.01
45000	79.03	77.25	75.44	72.02	69.89	57.12
60000	98.63	97.43	99.46	94.22	95.03	92.89

The following procedure was used to calculate the conversion and hence the r.h.s of Eq. (17 ) as well as the weight – time term of the l.h.s of the same equation

Take as an example Rh /  $\gamma$ - Al<sub>2</sub>O<sub>3</sub> catalyst for the reaction of CO<sub>2</sub> .

The partial pressure of CO<sub>2</sub> in the entering gases = 1 / 6 atm.

The entering CO<sub>2</sub> concentration =

$$C_{CO_2, in} = \frac{N_{CO_2}}{V} = \frac{P_{CO_2}}{RT} = \frac{0.167 atm.}{(0.082 lit.atm./ mol.^{\circ}K \times 873^{\circ}K)}$$

$$= 0.0023 mol./l.$$

For a feed rate of 600 cc / min at 25°C :-

The volumetric flow rate flow rate =

$$600 \text{ cc / min} \times (\text{lit. / } 10^3 \text{ cc}) \times (60 \text{ min / h}) = 36 \text{ lit. / h .}$$

This flow rate is corrected for reaction temperature by :-

$$V_2 = V_1 \times T_2 / T_1 = 36 \times 873 / 298 = 105 \text{ lit. / hr .}$$

Then the entering molar flow rate :-

$$F_{CO_2} = C_{CO_2, in} \times V_2$$

$$= (0.0023 \text{ mol CO}_2 / \text{lit.}) (105 \text{ lit. / hr}) = 0.2415 \text{ mol. / hr .}$$

given the weight of catalyst utilized = 2 g , then the weight – time term in equation is calculated as :-

$$\frac{C_{CO_2, \infty} W}{F_{CO_2, 0}} = \frac{0.0023 \times 0.002}{0.2415} = 1.9 \times 10^{-5} \text{ (kg .h / lit. )}$$

The conversion  $X_{CO_2}$  is calculated from equation :-

$$X_{CO_2} = \frac{C_{CO_2, in} - C_{CO_2, out}}{C_{CO_2, in} + 0.33C_{CO_2, out}}$$

Where  $\epsilon$  = expansion factor = 1 / 3 in our case as shown in chapter 5.

$C_{CO_2, out}$  is calculated as  $C_{CO_2, in} \times \% \text{ remained}$  .

The same calculation procedure is repeated at each flow rate for a given temperature .

The calculations results are given in Tables ( A .4-6 ) for the Rh /  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, Ru /  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and Ir /  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> respectively .

The value of  $\{1.3 \ln 1 / (1- X) - 0.3 X\}$  is plotted vs  $\frac{C_{CO_2, axW}}{F_{CO_2, o}}$  as shown in Fig ( 5.4-6 ) for each catalyst type .

The slope of the line =  $k'$  lit./hr. kg cat. the reaction rate constant .

For a first order reaction :-

$$- r'_{CO_2} = k' (\text{lit. / hr kg cat}) \times (C_{CO_2} \text{ mol / lit})$$

Table (A .4a) . The calculation needed to test the fit of Eq . ( 17 ) of CO<sub>2</sub> component for Rh /  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> .

Temperature	$X = \frac{C_i - C_o}{(C_i + 0.33C_o)}$	$A = 1.33 \ln (1 / 1 - X)$	$B = 0.33 X$	A - B	$F_i$	$C_i W / F_i$
$C_i = 0.0023 \text{ mol / lit.}$						
600 °C	0.0397	0.0539	0.0131	0.0408	0.805	5.7E-6
	0.3660	0.607	0.1210	0.486	0.605	7.6E-6
	0.3540	0.580	0.1168	0.463	0.483	9.5E-6
	0.6548	1.415	0.2161	1.199	0.242	19E-6
$C_i = 0.00209 \text{ mol / lit.}$						
700 °C	0.330	0.5326	0.1089	0.4237	0.8180	5.11E-6
	0.605	1.2354	0.1997	1.0357	0.6140	6.81E-6
	0.686	1.5406	0.2262	1.3142	0.4910	8.513E-6
	0.838	2.4208	0.2765	2.1443	0.2460	16.99E-6
$C_i = 0.0019 \text{ mol / lit}$						
800 °C	0.475	0.8569	0.1567	0.700	0.821	4.628E-6
	0.663	1.4466	0.2188	1.198	0.616	6.169E-6
	0.744	1.8122	0.2455	1.567	0.493	7.708E-6
	0.955	4.1245	0.3152	3.809	0.246	15.45E-6

Table (A .4b) . The calculation needed to test the fit of Eq ( 17 ) of CH<sub>4</sub> component for Rh /  $\gamma$  - Al<sub>2</sub>O<sub>3</sub> catalyst .

Temperature	$X = \frac{C_i - C_o}{(C_i + 0.33 C_o)}$	$A = 1.33 \ln (1 / 1 - X)$	$B = 0.33 X$	A - B	F <sub>i</sub>	$\frac{C_i W}{F_i}$
$C_{i_0} = 0.002139 \text{ mol / lit.}$						
600 °C	0.08269	0.114795	0.027288	0.087507	0.74866	5.714E-6
	0.2056	0.31192	0.06899	0.24293	0.5615	7.619E-6
	0.278833	0.43476	0.09215	0.34274	0.44919	9.524E-6
	0.514226	0.96028	0.16969	0.79058	0.2245	19.056E-6
$C_{i_0} = 0.00194 \text{ mol / lit.}$						
700 °C	0.13107	0.18686	0.04325	0.1436	0.7601	5.1046E-6
	0.2473	0.37785	0.081611	0.29623	0.570	6.8062E-6
	0.3964	0.67139	0.13080	0.54086	0.456	8.5087E-6
	0.60453	1.2336	0.19949	1.03431	0.228	17.017E-6
$C_{i_0} = 0.00177 \text{ mol / lit.}$						
800 °C	0.20519	0.30544	0.067714	0.2377	0.765	4.628E-6
	0.30613	0.48608	0.101024	0.38586	0.574	6.1716E-6
	0.51907	0.97359	0.17129	0.8023	0.459	7.715E-6
	0.93239	3.58307	0.300769	3.27538	0.229	15.432E-6

Table (A .5a) . The calculation needed to test the fit of Eq ( 17 ) CO<sub>2</sub> component for Ru /  $\gamma$  - Al<sub>2</sub>O<sub>3</sub> catalyst .

Temperature	$X = \frac{C_i - C_o}{(C_i + 0.33C_o)}$	$A = 1.33 \ln \frac{1}{1-X}$	$B = 0.33 X$	A - B	F <sub>i</sub>	$\frac{C_i W}{F_i}$
$C_i = 0.0023 \text{ mol / lit.}$						
600 °C	0.06890	0.094947	0.022737	0.07221	0.805	5.7E-6
	0.15931	0.230798	0.05257	0.178226	0.605	7.6E-6
	0.211635	0.316266	0.06984	0.24643	0.483	9.5E-6
	0.07055	0.097309	0.02328	0.074027	0.242	19.0E-6
$C_i = 0.00209 \text{ mol / lit.}$						
700 °C	0.144799	0.20803	0.0477836	0.16025	0.818	5.11E-6
	0.25728	0.39558	0.084903	0.310682	0.614	6.81E-6
	0.23538	0.35695	0.077678	0.27927	0.491	8.513E-6
	0.19179	0.28320	0.06329	0.21991	0.246	16.99E-6
$C_i = 0.0019 \text{ mol / lit.}$						
800 °C	0.24449	0.37289	0.03068	0.2922	0.821	4.628E-6
	0.43852	0.767646	0.14471	0.62293	0.616	6.169E-6
	0.33992	0.55248	0.112175	0.440308	0.493	7.708E-6
	0.27096	0.42032	0.08941	0.330901	0.246	15.45E-6

Table (A .5b) . The calculation needed to test the fit of Eq. ( 17 )CH<sub>4</sub> component for Ru /  $\gamma$  - Al<sub>2</sub>O<sub>3</sub> catalyst.

Temperature	$X = \frac{C_i - C_0}{(C_i + 0.33C_0)}$	$A = 1.33 \ln \frac{1}{1-X}$	$B = 0.33 X$	A - B	F <sub>i</sub>	$\frac{C_i W}{F_i}$
$C_i = 0.002139 \text{ mol / lit}$						
600 °C	0.0901	0.12678	0.030003	0.096774	0.74866	5.714E-6
	0.17076	0.24904	0.056352	0.192691	0.5615	7.619E-6
	0.16699	0.2430	0.055108	0.1879	0.44919	9.524E-6
	0.06787	0.09348	0.022399	0.07109	0.2245	19.05E-6
$C_i = 0.00194 \text{ mol / lit}$						
700 °C	0.09747	0.13640	0.03217	0.10424	0.7601	5.1046E-6
	0.2833	0.44306	0.09349	0.34956	0.570	6.8062E-6
	0.21431	0.32078	0.07072	0.25006	0.456	8.5087E-6
	0.08725	0.12142	0.02879	0.09263	0.228	17.017E-6
$C_i = 0.00177 \text{ mol / lit}$						
800 °C	0.11714	0.1657	0.038657	0.12705	0.765	4.628E-6
	0.40489	0.68848	0.133348	0.555137	0.574	6.171E-6
	0.26286	0.405622	0.08674	0.31888	0.459	7.715E-6
	0.13468	0.191759	0.044308	0.14745	0.229	15.432E-6

Table (A .6a) . The calculation of needed to test the fit of Eq ( 17 )CO<sub>2</sub> component for Ir /  $\gamma$  - Al<sub>2</sub>O<sub>3</sub> catalyst .

Temperature	$X = \frac{C_i - C_o}{(C_i + 0.33C_o)}$	$A = 1.33 \ln \frac{1}{1-X}$	$B = 0.33 X$	$A - B$	$F_i$	$\frac{C_i W}{F_i}$
$C_i = 0.0023 \text{ mol / lit.}$						
600 °C	0.061916	0.085008	0.020432	0.06457	0.805	5.7E-6
	0.08328	0.115647	0.02778	0.08817	0.605	7.6E-6
	0.18128	0.266026	0.05982	0.20620	0.483	9.5E-6
	0.01944	0.021197	0.006417	0.01970	0.242	19.0E-6
$C_i = 0.00209 \text{ mol / lit.}$						
700 °C	0.06929	0.095508	0.022867	0.07264	0.818	5.11E-6
	0.1457	0.20945	0.04808	0.161367	0.614	6.818E-6
	0.22607	0.34084	0.07460	0.26624	0.491	8.563E-6
	0.04409	0.05997	0.01455	0.04542	0.246	16.99E-6
$C_i = 0.0019 \text{ mol / lit.}$						
800 °C	0.09715	0.13593	0.03206	0.10387	0.821	4.628E-6
	0.27015	0.41885	0.08915	0.3297	0.616	6.169E-6
	0.36079	0.59521	0.11906	0.47615	0.493	7.708E-6
	0.05442	0.07442	0.01796	0.05645	0.246	15.45E-6

Table (A .6b) . The calculation of needed to test the fit of Eq ( 17 ) CH<sub>4</sub> component for Ir /  $\gamma$  - Al<sub>2</sub>O<sub>3</sub> catalyst .

Temperature	$X = \frac{C_i - C_o}{(C_i + 0.33C_o)}$	$A = 1.33 \ln \frac{1}{1-X}$	$B = 0.33 X$	A - B	F <sub>i</sub>	$\frac{C_i W}{F_i}$
$C_i = 0.002139 \text{ mol / lit.}$						
600 °C	0.08296	0.11519	0.02738	0.08781	0.74866	5.714E-6
	0.08463	0.11760	0.02793	0.08968	0.5615	7.619E-6
	0.1663	0.2419	0.05488	0.18705	0.44919	9.524E-6
	0.01033	0.01382	0.00341	0.0104	0.2245	19.05E-6
$C_i = 0.00194 \text{ mol / lit.}$						
700 °C	0.08471	0.11772	0.027954	0.089769	0.7601	5.105E-6
	0.10550	0.14829	0.034817	0.113473	0.570	6.806E-6
	0.19664	0.291214	0.064892	0.22632	0.456	8.509E-6
	0.00414	0.05519	0.001366	0.00415	0.228	17.017E-6
$C_i = 0.00177 \text{ mol / lit.}$						
800 °C	0.10084	0.14137	0.033278	0.108096	0.165	4.628E-6
	0.1972	0.2922	0.06509	0.22711	0.574	6.171E-6
	0.2446	0.37319	0.080741	0.29245	0.459	7.715E-6
	0.0378	0.05129	0.01248	0.03881	0.229	15.432E-6

# ARABIC SUMMARY

# تحويل الغاز الطبيعي بواسطة ثاني أكسيد الكربون لإنتاج غاز التخليق

رساله مقدمه للحصول على  
درجة ماجستير الفلسفة في العلوم

من

رضوى عباس مصطفى السيد السلاموني  
بكالوريوس علوم - جامعة عين شمس

تحت إشراف

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أ. د. عقيله كامل المرسي  
أستاذ الهندسة الكيمائية - معهد بحوث البترول .

إلى

قسم الكيمياء  
كلية العلوم - جامعة عين شمس

القاهرة - ٢٠٠٥ م

تحويل الغاز الطبيعي بواسطة ثاني أكسيد الكربون لإنتاج غاز التخليق

مقدمه من :-

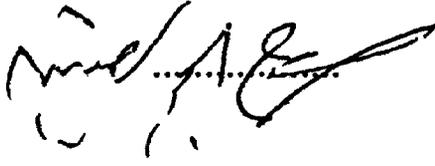
رضوى عباس السلاموني  
كيميائي بمعهد بحوث البترول

التوقيع

المشرفون :-

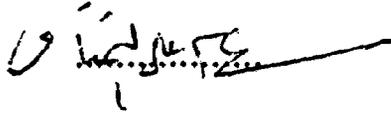
ا. د. صلاح عبد الغني أبو العينين

أستاذ الكيمياء الفيزيائية و مواد البناء  
بكلية العلوم - جامعة عين شمس .



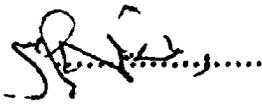
ا. د. سهام علي التمتامي

أستاذ الهندسه الكيمائيه  
قسم تطوير العمليات - معهد بحوث البترول .



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أستاذ الهندسه الكيمائيه - ورئيس قسم تطوير العمليات  
معهد بحوث البترول .



رئيس قسم الكيمياء بكلية العلوم  
جامعة عين شمس  
ا. د. محمد أحمد القصبى

القاهره - ٢٠٠٥ م

شكر

اشكر الساده الأساتذه الذين أشرفوا على رساله وهم :

١ - ا . د . صلاح عبد الغني أبو العينين .

٢ - ا . د . سهام علي التمتامي .

٣ - ا . د . عقيله كامل المرسي .

و أشكر كل من تعاون معي في هذا البحث وهما : -

د . أشرف يحي النجار .

د . سلوى عبد الواحد غنيم .

و كذلك الهيئات الآتيه : -

١ - جامعة عين شمس .

٢ - معهد بحوث البترول .

جامعة عين شمس  
كلية العلوم

اسم الطالب :- رضوي عباس مصطفى السيد السلاموني

الدرجة العلمية :- ماجستير الفلسفة في العلوم " كيمياء "

القسم :- الكيمياء .

الكلية :- العلوم .

الجامعة :- عين شمس .

سنة التخرج :- ١٩٩٨ م .

سنة المنح :- ٢٠٠٥ م .

رسالة ماجستير

اسم الطالبه :- رضوى عباس مصطفى السيد السلاموني .

عنوان الرسالة :- تحويل الغاز الطبيعي بواسطة ثاني أكسيد الكربون  
لإنتاج غاز التخليق .

اسم الدرجة :- ماجستير الفلسفه في العلوم " كيمياء " .

لجنة الإشراف :-

١- د. ا. صلاح عبد الغني أبو العينين  
أستاذ الكيمياء الفيزيائية و مواد البناء  
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٣- د. ا. عقيله كامل المرسي  
أستاذ الهندسه الكيمياءيه - ورئيس قسم تطوير العمليات  
معهد بحوث البترول .

لجنة التحكيم

الدراسات العليا

موافقة مجلس الكلية  
/ / ٢٠٠٥ م

أجيزت رساله بتاريخ  
/ / ٢٠٠٥ م

ختم الإجازة

موافقة مجلس الجامعة  
/ / ٢٠٠٥ م

### الملخص العربي

يلعب الغاز الطبيعي دورا مهما و حيويا في حياة الانسان ، اذ أنه من أهم المصادر الطبيعية النظيفة للحصول على الوقود و هناك العديد من الأبحاث التي تتم لتحويل الغاز الطبيعي الى غاز التخليق ( هيدروجين + أول أكسيد الكربون ) و الذي بدوره يشكل المصدر الرئيسي لصناعة العديد من المركبات الكيمائية مثل الميثانول و ثنائي ميثيل الايثر الذي يعتبر وقود القرن الحادي و العشرين باستخدام الحفازات ، كما أنه مصدر مهم لتفاعل Fisher – Tropsch الذي يحول الغاز الطبيعي الى وقود سائل و المعروف ب ( GTL ) أيضا يعتبر غاز التخليق المصدر الأساسي لكثير من العمليات الكيمائية كالهدرجة و الأختزال و غيرها .

اتجهت الأنظار في نهاية القرن الماضي لتحضير غاز التخليق من الغاز الطبيعي باستخدام غاز ثاني أكسيد الكربون كعامل مؤكسد و ذلك لما له من أضرار على البيئه فهو أحد العناصر الضاره المساهمه بشده في حدوث ظاهرة الاحتباس الحراري .

كذلك يعتبر ارتفاع المحتوى الحراري المرتبط بهذا التفاعل و تفاعله العكسي مصدرا مهما لتخزين الطاقه ( للطاقه المتجدده ) .

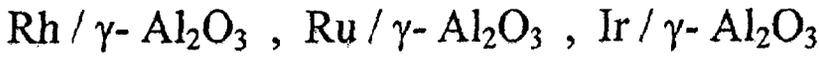
و كما هو معروف فقد تم اكتشاف كميات كبيره من الغاز الطبيعي في مصر خلال السنوات الأخيره مما يجدر بنا محاولة الاستفاده من هذا الكنز الذي أنعم الله به على هذه البلاد .

و لقد اعتمدنا في هذا البحث على دراسة الغاز الطبيعي المصري لانتاج غاز التخليق و ليس فقط الميثان و الذي يمثل المكون الرئيسي للغاز الطبيعي .

و قد استخدم المفاعل ذو المهد الثابت ( Fixed Bed ) والمكون من أنبوب زجاجي قطره ١٣ مم و طوله ١٢ سم حيث تدفع الغازات المغذيه ( ثاني أكسيد الكربون ، الغاز الطبيعي ، النيتروجين ) بنسبة ١ : ١ : ٤ في وجود ٢ جم من الحفاز تحت الاختبار.

## الملخص العربي

و قد تم تحضير ثلاثة أنواع من الحفازات المحتوية على نسبة ٥،٠ % من معادن الروديوم ، الروثينيوم ، و الايريديوم المحملة على الجاما ألومينا



و قد تم دراسة تأثير درجة الحرارة عند ثلاث مستويات هي ٦٠٠، ٧٠٠، ٨٠٠ °م لسرعه الفراغية عند أربع قيم هي ١٨٠٠٠، ٣٦٠٠٠، ٤٥٠٠٠، ٦٠٠٠٠ سم<sup>٣</sup> جم<sup>-١</sup> س<sup>-١</sup> لتحديد الظروف المثلى للتشغيل .

و أخيرا ، تمت دراسة كيناتيكية التفاعل و تحديد الطاقه المنشطه باستخدام معادلة Arrhenius .

بصفه عامه فان نشاط هذا التفاعل يزيد مع زيادة درجة الحرارة حيث أنه تفاعل ماص للحراره ، و كذلك يزيد نشاطه مع نقصان السرعه الفراغية (يعني زيادة وقت بقاء المتفاعلات على الحافز أو وقت التقاء المتفاعلات) .

كذلك وجد أن درجة الانتقائيه ( selectivity ) تجاه مكونات غاز التخليق CO/ H<sub>2</sub> تزيد مع زيادة درجة الحرارة و نقصان السرعه الفراغية ، و كانت دائما نسبة الهيدروجين / أول أكسيد الكربون أقل من ١ و ذلك يفسر حدوث العديد من التفاعلات الجانبية أهمها تفاعل ثاني أكسيد الكربون مع الماء و الذي ينتج عنه مزيد من أول أكسيد الكربون ( RWGS )



و قد تم تحديد الظروف المثلى للحصول على أعلى نسبة للهيدروجين/ أول أكسيد الكربون ووجد أنه بالنسبه للحافز Rh /  $\gamma\text{-Al}_2\text{O}_3$  فان أحسن ظروف هي درجة حراره ٧٠٠ °م و ٣٦٠٠٠ سم<sup>٣</sup> جم<sup>-١</sup> س<sup>-١</sup> و بالنسبه للحافز Ru /  $\gamma\text{-Al}_2\text{O}_3$  فان أحسن ظروف هي درجة حراره ٨٠٠ °م و ١٨٠٠٠ سم<sup>٣</sup> جم<sup>-١</sup> س<sup>-١</sup> أما بالنسبه

## الملخص العربي

للحافز  $\text{Ir} / \gamma\text{-Al}_2\text{O}_3$  فان أحسن ظروف هي درجة حراره  $700^\circ\text{C}$  و  $36000 \text{ سم}^2$   $\text{جم}^{-1} \text{س}^{-1}$ .

كذلك وجد أن جميع الحافزات تتبع سلوك تفاعل الدرجة الأولى  $1^{\text{st}} \text{ order}$  reaction بالنسبه لكل من الميثان و ثاني أكسيد الكربون عند كل درجات الحراره المختبره ، و تم ايجاد العلاقه بين ثابت التفاعل  $k'$  و درجة الحراره باستخدام علاقه Arrhenius و كان متوسط الطاقه المنشطه للتفاعل بالنسبه الى ثاني أكسيد الكربون  $46250 \text{ جول} / \text{مول}$  و بالنسبه للميثان كانت  $31530 \text{ جول} / \text{مول}$ .

في النهايه لوحظ أن الحافز  $\text{Rh} / \gamma\text{-Al}_2\text{O}_3$  أظهر أفضل النتائج بالمقارنه بالحافزين الآخرين المستخدمين .

و كانت الظروف المثلى لاستخدامه هي  $18000 \text{ سم}^2$   $\text{جم}^{-1} \text{س}^{-1}$  بالنسبه للسرعه الفراغيه و  $800^\circ\text{C}$  م بالنسبه لدرجة الحراره و أعلى نسبه للهيدروجين/ أول أكسيد الكربون كانت عند  $36000 \text{ سم}^2$   $\text{جم}^{-1} \text{س}^{-1}$  و  $700^\circ\text{C}$ .