Eng. &Tech. Journal, Vol.31, Part (A), No.18, 2013

Second Scientific Conference on Modern Technologies in Oil Refining In 14-16/5/2013

Experimental Study and Simulation of Iraqi Heavy Naphtha Catalytic Reforming Reactions Using Pt-Ir-Sn/AL_2O_3 and Pt-Ir/AL_2O_3 Catalysts

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ABSTRACT

In present study experimental and mathematical model have been carried out to describe the reaction kinetics of catalytic reforming process using Iraqi heavy naphtha as a feedstock for the process. Two types of catalysts were prepared (Pt-Ir-Sn/AL_2O_3 and Pt-Ir/AL_2O_3) supported on γ-AL_2O_3. The main three described reforming reactions were investigated (dehydrogenation, hydrocracking, and dehydrocyclization) to characterize catalysts performance in term of activity and selectivity. The performance of catalysts were investigated under the following operating condition: reaction temperature range of 480-510 ˚C, weight hour space velocity range of 1-2hr^{-1}, pressure at 6 atm, and hydrogen to hydrocarbon ratio of 4:1.

The results show higher conversion of Iraqi heavy naphtha components (i.e., Paraffins and Naphthenes) with higher temperatures whereas; weight hourly space velocity has shown negative impact on conversion (i.e., higher WHSV shows lower conversion). In general, it was noted that the yields of aromatics and light components are increased for both types of catalysts (Pt-Ir-Sn/AL_2O_3 and Pt-Ir/AL_2O_3) under the same operating conditions. Results of tri-metal catalyst better than bi-metal catalyst.

A comprehensive mathematical model and simulation was developed in the present work to describe the reaction kinetics of reforming reactions. The model predicts the concentration, conversion, and temperature profile with time and axial direction of the reactor. The comparison between experimental and simulation results of the concentrations of (Paraffin's, Naphthenes, and Aromatics), and temperature showed a good agreement with a deviation confined 19.50%.

https://doi.org/10.30684/etj.31.18A.2
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Keywords: Simulation, Mathematical Model, Catalytic Reforming, Heavy Naphtha, Reforming, Pt-Ir-Sn/Al_2O_3 and Pt-Ir/Al_2O_3.

دراسة عملية ومحاكاة تفاعلات التهذيب لمادة النفثا العراقية الثقيلة باستخدام عوامل مساعدة ثنائية وثلاثية المعدن Pt-Ir-Sn/Al_2O_3 and Pt-Ir/Al_2O_3

الخلاصـــــــة

تـضمن البحـث اعداد دراســة شـاملة عمليــة ونظريــة للعوامـل المسـاعدة ثنائيـة وثلاثيـة المعـدن المحملة على الالومينا(Pt-Ir-Sn/Al_2O_3 Pt-Ir/Al_2O_3) المستخدمة في عمليـة التهذيب باستخدام مــادة النفثـا الثقيـلة (العراقيـة) كمادة اولية للعملية. من اجل دراسة امكانية زيادة كفاءة العملية وتحسين أنتقائية العوامل المساعدة. تم خلال البحث دراســة التفاعـلات الرئيسية التي تحدث فـي عمليـة التهـذيب وهـي (تفاعـلات ازالـة الهيـدروجين، تفاعلات تكوين المركبـات الحلقيـة وكذلك تفاعـلات التكسـير الحـراري) بوجـود الهيـدروجين. تـم دراسـة اداء نـوعين مـن العوامـل المسـاعدة الثنائيـة والثلاثيـة المعـدن حسـب الضروف التشغيلية التالية : السرعة الفراغية للغاز(1-2ساعة$^{-1}$) ، درجـة حـرارة التفاعل تتـراوح بـين (510-480 م°) والضـغط الكلـي 6 بـار ونسـبة الهيـدروجين الـى المـواد الهيدروكاربونيـة 1:4. أثبتـت النتائج العمليـة ان نسبة التحول لمـادة النفثـا الثقيـلة (المـواد البرافينيـة والمـواد النفثينيـة) تـزداد مـع زيـادة درجـة حـرارة التفاعـل وتقـل مـع زيـادة السـرعة الفراغيـة. كـذلك لـوحظ ان الانتاجيـة (yield) للمـواد العطرية والمركبات الخفيفة تزداد لجميع انواع العوامل المساعدة المحضرة.

تم اعداد دراسة نظرية شاملة تضمنت بناء وتطوير موديل رياضي يصف ديناميكية التفاعل لعملية التهذيب بالعامل المساعد لمـادة النفثـا الثقيـلة. الموديـل الرياضـي يصـف توزيـع تراكيـز المـواد المتفاعلـة والناتجة، نسبة التحول، وتوزيع درجة الحرارة مع طول المفاعل. أثبتت النتائج وجود تطابق بين النتائج العملية والنظرية بنسبة انحراف تصل لحدود % (0 19,5).

Nomenclature

Symbol	Definition	Units	Symbol	Definition	Units
A	Aromatics	(-)	K_{eq}	Reaction equil. constant	(-)
$A_{\circ}$	Pre-exponential factor	(-)	LHSV	Liquid hour space velocity	hr^{-1}
A_i	Aromatics(6,7,8,9) carbon atom	(-)	Mwt	Molecular weight	g/gmole
C_N	Naphthenes concentration	$mole/cm^3$	N_i	Naphthene (5,6,7,8,9) C-atom	(-)
$C_{n\circ}$	Initial concentration of species n	$mole/cm^3$	n-P_i	Paraffine(5,6,7,8,9,10)C- atom	(-)
C_n	Concentration of species n	$mole/cm^3$	P	Paraffin	(-)
Cp	Specific heat	J/mole.°C	P_a	Total pressure	atm
Ea	Activation energy	kJ/mole	R	Gas constant	J/mole.K
$F_{n\circ}$	Initial molar flow rate of species n	mole/hr	r_i	Reaction rate of species i	mole/gcat. hr
F_n	Molar flow rate of species n	mole/hr	T	Reaction temperature	°C
f	Weight flow rate	g / hr	T°	Initial temperature	°C
G	Gases	(-)	V	Volume	cm^3

GC	**Gas chromatography**	**(-)**	**$V_\circ$**	**Volume of gas adsorbed**	**cm^3**
H_2	**Hydrogen**	**(-)**	**V_C**	**Volume of catalyst**	**cm^3**
ΔH°_r	**Heat of i th reaction**	**J/ mole**	**W**	**Weight of catalyst**	**kg**
H_2/H.C	**Hydrogen to hydrocarbon mole ratio**	**(-)**	**WHSV**	**Weight hour space velocity**	**hr^{-1}**
iso-P	**Iso-paraffins**	**(-)**	**Y_i**	**Molar composition of species i (A, N, and P)**	**(-)**
k	**Reaction rate constant**	**hr^{-1}**	**zt**	**Length of reactor**	**cm**
r_2	**React. rate for naphthene's dehydrogenation reaction**	**mole/gcat. hr**	**Δz**	**Integration step for the reactor length**	**(-)**
ρ_c	**Density**	**Kg/m^3**	**ϵ**	**Porosity of catalyst bed**	**(-) cm^3/cm^3**

INTRODUCTION

Naphtha is transformed into reformate by catalytic reforming. This process involves the reconstruction of low-octane hydrocarbons in the naphtha into more valuable high octane gasoline components without changing the boiling point range this is achieved mainly by conversion of straight chain naphtha to iso-paraffins and aromatics over a solid catalyst. Catalytic reforming of heavy naphtha is a very important process for producing high octane gasoline, aromatic feedstock and hydrogen in petroleum-refining and petrochemical industries. [1, 2].

The purpose of catalytic reforming of naphtha is primarily to increase the octane number of the naphtha feedstock to the level that makes the reformate product suitable as a gasoline blend stock.

During catalytic reforming long chain hydrocarbons are rearranged through isomerization, hydrogenation, dehydrocyclization and dehydrogenation reactions. These reactions occur on acid and/or metal sites and they demand the use of bifunctional catalysts. The acid function is typically provided by a solid support such as chlorinated alumina (Al_2O_3–Cl) and the metal function by a noble metal. The metal component is active for the hydrogenation and dehydrogenation reactions while the support has the acid strength necessary to promote the isomerization reactions. Synergetic action of both kinds of active sites promotes other reactions such as dehydrocyclization via a bifunctional reaction mechanism. Undesirable reactions such as hydrocracking and hydrogenolysis also occur lowering the yield of valuable products and deactivating the catalyst by the formation of coke on the active sites [2, 3, 4].

The metals used with Pt/ Al_2O_3 catalyst other than Re are Sn, Ir, and Ge. These additives modify the activity, selectivity and stability of the catalyst. These metals are used as bi- and tri-metallic catalysts. This type of bi- and tri-metallic naphtha reforming catalyst makes a big leap forward in the technology of reforming catalyst and it improves its properties, Pt-Ir-Ge/ Al_2O_3-Cl, Pt-Re-Sn/ Al_2O_3-Cl, and Pt-Re-Ge/ Al_2O_3-Cl being the most remarkable followers [4, 5, 6].

The naphtha used as catalytic reforming feed stock is very complex usually consisting of about three hundred hydrocarbons with carbon number ranging from one to twelve, and each of them undergoes various reactions. Thus a detailed kinetic model considering all the components and reactions is too complex. For this reason, attempts have been made to model naphtha reactions by considering groups of components (i.e. kinetic lumps) taking part in reforming reactions. Accordingly, various lumping kinetic models to represent catalytic reforming reactions have been reported in the literature, which have different levels of sophistication. Therefore, in catalytic reforming it is very important to develop an appropriate kinetic model capable of predicting the detailed reformate composition and behaviors of catalysts in order to combine with catalytic reforming reactor model, for simulation and optimization purposes [7, 8, 9].

The aim of this work is to produce high octane aromatics from Iraqi heavy naphtha by using prepared bi- and tri-metallic catalysts in a fixed bed reactor under various ranges of temperature and weight hour space velocity. On the other hand, predict and develop a mathematical model to describe the catalytic reforming reactions, reaction rate and optimum operating conditions for the reforming catalysts.

EXPERIMENTAL WORK

Materials

Iraqi heavy naphtha with 0.733 specific gravity was supplied by Al-Dura refinery. The properties of this naphtha is shown in Table (1). Nitrogen purchased from Dijlah factory, was analyzed by GC and confirms its purity of 99%. GC analysis for purchased from Al-Mansor plant, shows that its purity of 99.9%. To reduce oxygen and water impurities a molecular sieve type (5A) has been installed on the hydrogen line.

Table (1) the properties of heavy naphtha (Al-Dura refinery).

Property	Unit	Data
Specific Gravity at 15.6 ˚C	-	0.733
API	-	61.7
Distillation		
I.B.P	°C	60
10 vol % distilled	°C	88
20 vol% distilled	°C	94
30 vol% distilled	°C	106
40 vol% distilled	°C	110
50 vol % distilled	°C	117
60 vol% distilled	°C	124
70 vol% distilled	°C	132
80 vol% distilled	°C	140
90 vol % distilled	°C	147
F.B.P	°C	178
Total distillate	vol%	98.5
Total recovery	vol%	99.5
Residue	vol%	1
Loss	vol%	0.5

Sulfur Content	**ppm**	**3**
Mwt.	**g/gmol**	**108**
Total Paraffin	**vol %**	**60**
Total naphthene and aromatic	**vol %**	**40**

Catalysts

Pt/ γ-Al$_2$O$_3$ (RG 412), Pt-Re/ γ-Al$_2$O$_3$ (RG 482) catalysts are supplied from Al-Dura refinery. The specify names of prepared catalysts two bi-metals and tri-metal catalysts were prepared in laboratory. The physical and chemical properties of all catalysts where measured and the results are shown in Table (2):

Table (2) Physical and chemical properties of commercial and prepared catalysts.

	Commercial Pt/γ-Al$_2$O$_3$	**Commercial Pt-Re/γ-Al$_2$O$_3$**	**Prepared Pt-Ir/γ-Al$_2$O$_3$**	**Prepared Pt-Ir-Sn/γ-Al$_2$O$_3$**
Pt , wt %	**0.35**	**0.3**	**0.5**	**0.35**
Re, wt %	**-**	**0.3**	**-**	**-**
Sn ,wt %	**-**	**-**	**-**	**0.3**
Ir , wt %	**-**	**-**	**0.1**	**0.1**
Form	**Extrudate**	**Extrudate**	**Extrudate**	**Extrudate**
Surface Area (m^2/g)	**220**	**220**	**219.9**	**193.5**
Pore Volume (cm^3/g)	**0..57**	**0.6**	**0.61**	**0.85**
Bulk Density (g/cm^3)	**0.66**	**0.69**	**0.67**	**0.691**

Preparation of Platinum-Iridium-Tin / Alumina Catalyst

The Pt-Ir-Sn/ Al$_2$O$_3$ catalyst was prepared by using successive impregnation by adding iridium chloride (IrCl$_3$) to platinum supported on alumina catalyst and then adding tin chloride (SnCl$_2$) in order to reach final concentration of 0.35 wt% Pt, 0.1 wt% Ir, and 0.3 wt% Sn [10].

In the first step, the bi-metal catalyst was prepared by adding iridium chloride to platinum alumina catalyst. Then, Pt-Ir supported on alumina was mixed with 0.2M HCl (37%) which was equal to (1.5 ml for each gram of catalyst) in order to assure homogeneous distribution with stirring for 1 hr at room temperature. Then an appropriate amount of tin chloride (SnCl$_2$) was prepared by dissolving in deionnized water with heating at 70 $^\circ$C for 30 min. The tin chloride solution was added to the homogenized catalyst with gently stirred for 1 hr and then heating at 70 $^\circ$C in water bath in order to evaporate the excess liquid without stirring. The catalyst was finally dried at 120 $^\circ$C for 16 hrs and calcined in air at 500 $^\circ$C for 4 hrs and then reduced in flowing hydrogen at 500 $^\circ$C for 4 hrs with hydrogen flow rate of 60 cm^3/min.

PREPARATION OF PLATINUM-IRIDIUM / ALUMINA CATALYST

The Pt-Ir/Al_2O_3 catalyst was prepared by impregnation the parent catalyst (Pt/Al_2O_3) with Iridium chloride ($IrCl_3$) in order to reach final concentration of 0.5 wt% of Pt and 0.1 wt% of Ir [10].

Iridium chloride was added to the slurry solution of HCl and support and gently stirred for 1 hr at room temperature. The slurry was left into water bath at 70 $^{\circ}$C. Then dried at 120 $^{\circ}$C overnight. The catalysts were finally calcinied in air at 300 $^{\circ}$C for 4 hrs and then reduced by flowing hydrogen at (60 cm^3/min) at 500 $^{\circ}$C for 4 hrs. Heating ramps were programmed every 10 $^{\circ}$C /min.

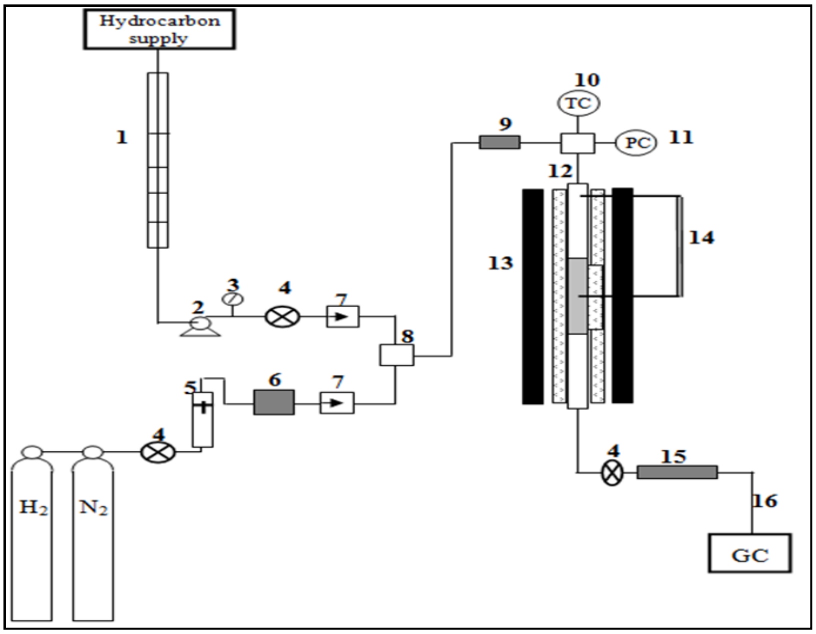
HEAVY NAPHTHA CATALYTIC REFORMING UNIT

The catalytic activities studies were carried out in a conventional continuous flow vertical tubular reactor, the dimensions were 20mm internal diameter, 30mm external diameter and 68cm height (reactor volume 214 cm^3). The reactor was charged for each experiment with 50g (catalyst bed 22 cm) of catalyst located in the middle zone, while, the upper and lower zones were filled with glass beads. Figure (1) shows the pilot plant of catalytic reforming unit.

OPERATING PROCEDURE

All the catalysts were originally in the form of extrudate. Each type was activated inside the reactor, just prior running the tests runs. The reactivation carried at 450 and 500 $^{\circ}$C for 4 hr respectively in a current of hydrogen at 1 atm pressure and flow ratio of 60 and 80 cm^3/min. Heavy naphtha pumped under pressure to the reforming unit. Hydrogen mixed with hydrocarbon prior entering the reactor. The mixture was preheated, and then admitted through the catalyst bed. The products were cooled and collected in a separator in order to exhaust the gases to the atmosphere and collect the condensed liquid from bottom of the separator. Product samples were analyzed using gas chromatography type Shimadzu 2014 GC.

The reforming process was tested at different temperatures (480, 490, 500, and 510 $^{\circ}$C), and 6 atm pressure. The weight hourly space velocities were varied at (1, 1.5, and 2 hr^{-1}), and 4:1 hydrogen to hydrocarbon molar ratio. For each run a fresh catalyst was used; therefore, the effect of catalyst deactivation was neglected.



1-Metering burette	**9- Feed preheating zone**
2-Dosing pump	**10 - Temperature controller system**
3-Liquid flow meter	**11- Pressure controller system**
4-Needle valve	**12- Stainless steel reactor**
5- H_2 flow meter	**13- Heating furnace**
6- 5A – Molecular sieve dryer	**14- Thermocouples system**
7- One way valve	**15- Cooling system**
8- Mixing section	**16- Gas chromatography**

Figure (1) Schematic diagram of the experimental apparatus of catalytic reforming pilot plant.

SIMULATION AND MATHEMATICAL MODEL

Mathematical modeling of reforming process has increasingly shown an important tool in petroleum refining industries. It because crucial in developing proper design of new reactor and revamp of existing ones. Modeling can be used to optimize operating conditions, analyze the effects of process variables, and enhance unit performance. In the present work mathematical model of catalytic reforming reactor can be of complexity which generally depends on description of reactants flow along the reactor, kinetic model of a chemical reaction and mass and energy balance (describe reformate composition).

MODEL DESCRIPTION AND ASSUMPTIONS

The main aim of the present study is to analyze the kinetics of reforming process by assessing the effect of reaction time and reaction temperature on the substrate content in the course of process which involves heavy naphtha as raw material. Therefore, three groups of compounds are found which are: paraffins (normal and iso), naphthenes (N), and aromatics (A). Then, the physical model for catalytic reforming with mass and energy balances for the element combining kinetic thermodynamic, concentration, and temperature distributions along the reactor length can be calculated. In developing the catalytic reforming reactor model the the following assumptions are taken into account:

- Steady state operation and plug flow isothermal operation.
- The pressure is constant throughout the reactor.
- The surface reaction was the limiting step.
- Density of reactant and products are constant.
- The temperature and concentration gradients along the radial direction can be neglected and only axial direction are considered.
- All the reforming reactions rates are first order (proved experimentally), all the rate equations are linear pseudo-monomolecular in nature and constant catalyst activity for calculation.

REACTION KINETICS

According to the present work investigation, analysis and monitoring of the heterogeneous reaction (consecutive and parallel) of heavy naphtha catalytic reforming, the suggested reactions network are represented schematically in Figure (2).

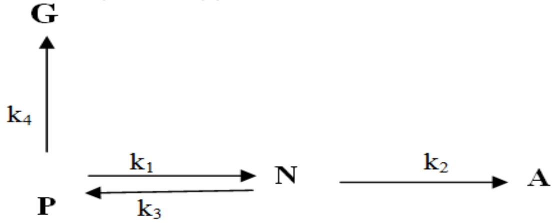


Figure (2) The suggested reactions network of heavy naphtha reforming of the present work.

$$P \leftrightarrow N + H_2 \quad \text{... (1)}$$

$$N \rightarrow A + 3H_2 \quad \text{... (2)}$$

$$P + H_2 \rightarrow 2G \quad \text{... (3)}$$

The reaction rate is considered to follow simple power law kinetic expression for above reactions [11]:

$$r_1 = k_1 C_P - k_3 C_N P_{H_2} \quad \text{... (4)}$$

$$r_2 = k_2 C_N \quad \text{... (5)}$$

$$r_3 = k_4 C_P \qquad \ldots (6)$$

In general form

$$r_i = k_i C_i^n \qquad \ldots (7)$$

where,

$$k_i = A_\circ EXP\left(\frac{-E_a}{R.T}\right) \qquad \ldots (8)$$

The reaction rate constant k_i confirms the Arrhenius expression [11]:

$$Lnk_i = LnA_\circ - \frac{E_a}{R.T} \qquad \ldots (9)$$

The reaction equilibrium constants $K_{eq} = k_1/k_3$. Therefore, equilibrium constant can be calculated by the following thermodynamic relation [9]:

$$K_{eq} = EXP\left(\frac{-\Delta G}{R.T}\right) \qquad \ldots (10)$$

the kinetic expression is to be linear (first order with respect to reactants) under the present reactions.

KINETIC REACTION MODEL

1-Mass Balance

To develop a reaction model for an integral reactor, a material balance is made over the cross section of a very short segment of the tubular catalyst bed, as shown in Figure (3):

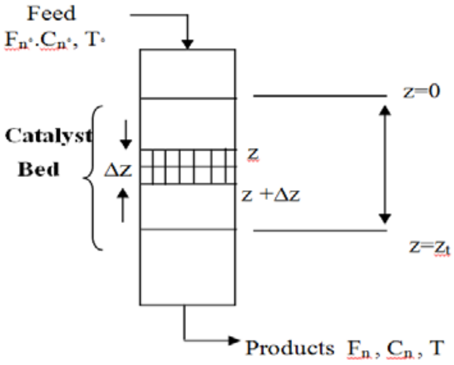


Figure (3) Segment of tubular reactor of reaction model.

Then, the resulting equation [12] is:

$$F_N\Big|_{z} - F_N\Big|_{z+\Delta z} - V_P\rho(1-€)(-r_i) = 0 \qquad ...(11)$$

As $\Delta z \longrightarrow 0$, the differential material balance reducesto:

$$\frac{dF_n}{dw} = -r_i \qquad ... (12)$$

where: $\mathbf{dw = dv\ \rho(1-€)}$

Now, the reaction rate equations can now be developed for each component in heavy naphtha feed stocks (Paraffins, Naphthenes and Aromatics) as follows:-

$$\frac{dF_P}{dw} = k_3C_N - (k_4 + k_1)C_P \qquad ... (13)$$

$$\frac{dF_N}{dw} = k_1C_P - (k_3 + k_2)C_N \qquad ... (14)$$

$$\frac{dF_A}{dw} = k_2C_N \qquad … (15)$$

A final modification to the left-hand side of equations (13) to (15) is made by defining a space time variable,

θ, as: $\theta = w/f$ …(16)

For a constant feed rate, an incremental section of catalyst bed, May expressed as:

$$dw = f.d\theta \qquad ...(17)$$

Substituting equation (17) in above equations (13, 14, and 15) gives:

$$\frac{dF_P}{d\theta} = k_3F_N - (k_4 + k_1)F_P \qquad ... (18)$$

$$\frac{dF_N}{d\theta} = k_1F_P - (k_3 + k_2)F_N \qquad … (19)$$

$$\frac{dF_A}{d\theta} = k_2 F_N \qquad \ldots (20)$$

ENERGY BALANCE

The equation used to estimate the temperature profile along the reactor is obtained from an energy balance over the differential reactor control volume [13].

$$\mathbf{f.\rho.C_p dT = r_{P\leftrightarrow N}\Delta H_{r,P\leftrightarrow N} dw + r_{N\leftrightarrow A}\Delta H_{r,N\leftrightarrow A} dw + r_{P\rightarrow G}\Delta H_{r,P\rightarrow G} dw} \ldots(21)$$

Substituting equations (17) in to above equation yield:-

$$\frac{dT}{d\theta} = \frac{1}{\rho C_P}\begin{pmatrix} r_{P\leftrightarrow N}\Delta H_{r,P\leftrightarrow N} \\ + r_{N\rightarrow A}\Delta H_{r,N\rightarrow A} \\ + r_{P\rightarrow G}\Delta H_{P\rightarrow G} \end{pmatrix} \qquad \ldots (22)$$

The above differential equation is taken to be as first order and this is improved experimentally as:-

$$-r_i = k_i C_i^n \qquad \ldots\ldots\ldots\ (7)$$

Taking natural logarithm for both side of above equation yield:

$$\ln(-r_i) = \ln k_i + n \ln C_i \qquad \ldots (23)$$

By plotting ln (-r$_i$) vs. lnC$_i$, then, the behaviors of first order must be straight line (tan 45° = 1) as shown in Figures (4 and 5) for different reaction and different catalyst. These two figures are just samples for some selected types of both catalysts.

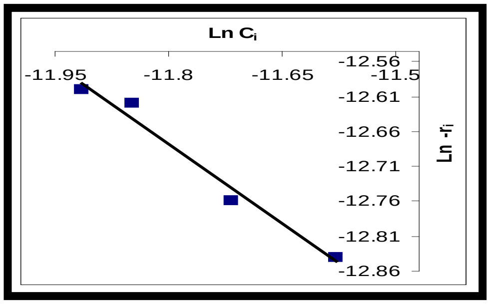


Figure (4) Plot for N+H$_2$→P for Pt-Ir catalyst at 1.5 hr^{-1}

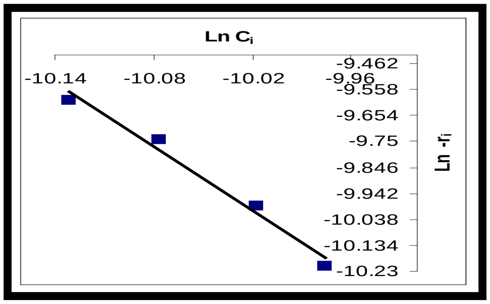


Figure (5) Plot for P→N+H$_2$ for Pt-Ir-Sn catalyst at hr^{-1}

PROCESS MODEL

The physical model for catalytic reforming axial flow reactor is shown in Figure (3). The following ordinary differential equations for mass and energy balance were integrated through each reactor bed to describe reformate composition and temperature profile along the length of the reactor. The system is numerically solved by method of finite difference approach with explicit solution of all the differential equation in the mathematical model. The schematic step of reactor models has shown in Figure (6).

For Mass balance [14]**:**

$$\frac{dY_i}{dZ} = \sum_{Ii=1}^{m} \frac{MW}{z.WHSV}\left(-r_i\right) \qquad \text{... (24)}$$

If substitute's heavy naphtha components (paraffin, naphthene, and aromatic) then, equation (24) become:

$$\frac{dY_P}{dZ} = \frac{MW}{z.WHSV}\left[r_{N\to P} - \left(r_{P\to N} + r_{P\to G}\right)\right] \qquad \text{... (25)}$$

$$\frac{dY_N}{dZ} = \frac{MW}{z.WHSV}\left[r_{P\to N} - \left(r_{N\to P} + r_{N\to A}\right)\right] \qquad \text{... (26)}$$

$$\frac{dY_A}{dZ} = \frac{MW}{z.WHSV}\left(r_{N\to A}\right) \qquad \text{... (27)}$$

For energy balance:

$$\frac{dT}{dZ} = S\,\frac{\sum_{I=1}^{m} r_i\left(-\Delta H_{r_i}\right)}{\sum_{I=1}^{m} f_i C_{P_i}} \qquad \text{... (28)}$$

$$\frac{dT}{dZ} = \frac{S}{\sum_{I=1}^{m} f_i C_{P_i}}\begin{bmatrix} r_{P\to N}\left(-\Delta H_{r,P\to N}\right) \\ + r_{N\to A}\left(-\Delta H_{r,N\to A}\right) \\ + r_{N\to P}\left(-\Delta H_{r,N\to P}\right) \\ + r_{P\to G}\left(-\Delta H_{P\to G}\right) \end{bmatrix} \qquad \text{... (29)}$$

$$\Delta H^{\circ}_{r,T} = \Delta H^{\circ}_{r,298} + \int_{298}^{T} \Delta C_P\, dT \qquad \text{...(30)}$$

The results of heat reactions estimations are represented in Table (3).

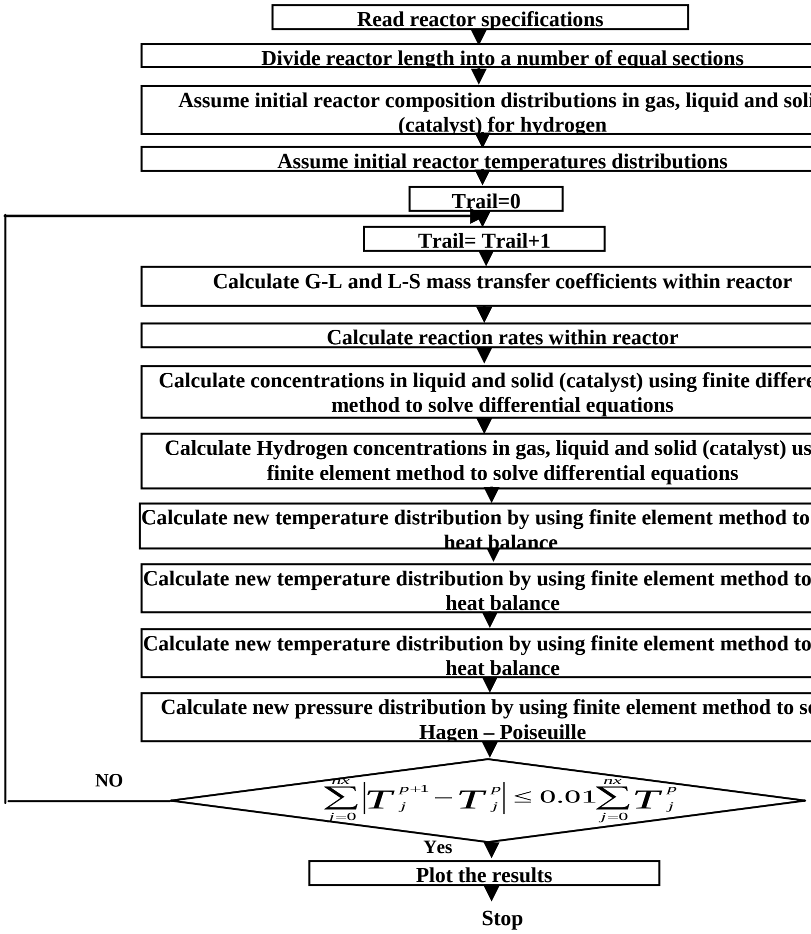


Figure (6) a schematic step of reactor models.

Table (3) Results of analysis of heat of reaction.

ΔH°_r (J/mole H_2)				
Reaction	**480 °C**	**490 °C**	**500 °C**	**510 °C**
$N + H_2 \rightarrow P$	-54393.3	-54238.5	-53903.7	-53648.5
$N \rightarrow A + 3H_2$	73119.9	73207.8	73291.5	73361.2
$P + (n-3/3)\ H_2 \rightarrow n/15(C_1-C_5)$	-52623.1	-52837.6	-53079.3	-53309.7

ESTIMATION OF REACTION KINETIC PARAMETERS

The apparent activation energy $\left(E_a\right)$ is established from Arrhenius equation that satisfies the relationships between rate constant and reaction temperature as given in equations (7, 8, and 9). From plot of $\ln(k)$ vs. (1/T) as shown in Figures (7) and (8). The values of activation energy were calculated from the slope represented by ($-E_a/R$) and the intercept represented by $\ln(A_\circ)$ let us to determine the value of pre-exponential factor. Results of each catalysts type are listed in Table (4).

Table (4) Activation energy values and pre-exponential factor for bi-metal and tri-metal catalysts.

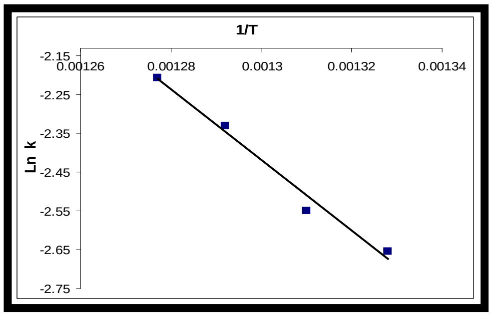


Figure (7) Arrhenius plot for the reaction + $3H_2$ for Pt-Ir-Sn/γ-Al_2O_3.

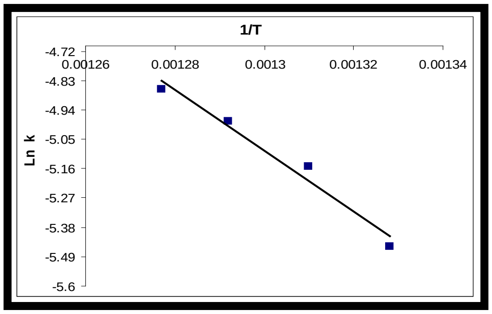


Figure (8) Arrhenius plot for the reaction N → A N + H_2 → P for Pt-Ir/γ-Al_2O_3.

Reaction	Ea/R	Ea (kcal/mol)	A∘
Pt-Ir/γ-Al_2O_3			
$P \rightarrow N + H_2$	15084	29.97	$7.927*10^8$
$N + H_2 \rightarrow P$	10674	21.21	$6.733*10^5$
$N \rightarrow A + 3H_2$	9822.2	19.52	$7.997*10^5$
$P + H_2 \rightarrow 2G$	11905	23.65	$5.803*10^6$
Pt-Ir-Sn/γ-Al_2O_3			
$P \rightarrow N + H_2$	18225	36.21	$3.626*10^{10}$
$N + H_2 \rightarrow P$	13816	27.45	$3.080*10^7$
$N \rightarrow A + 3H_2$	9131.5	18.14	$7.637*10^5$
$P + H_2 \rightarrow 2G$	15080	29.96	$2.925*10^8$

RESULTS AND DISCUSSION

Effect of Temperature

Figures (9) and (10) show that the concentrations of light components (n-P5 and n-P6) are increased with an increase in the reaction temperature and the heavier components concentration % decrease as reaction temperatures increases. This result is attributed to the dehydrocyclization reaction which is favored at higher reaction temperature and higher molecular weight of carbon number [16].

Figures (11)and 12) show that the iso-P$_6$ increases with temperature increase, but, iso-P$_7$ content increases as reaction temperature increases and then decreases at higher temperature. Also, the heavier paraffin's contents decreases with temperature increase.

Figures (13 and 14) shows that naphthenes mole % decreases as reaction temperature increases, since the conversion of naphthenes to aromatics is the primary naphthene reaction and is regarded the most favorable amongst with all other reactions in catalytic reforming. It is important to mention here that the reactivity of dehydrogenation reactions increases with an increase in naphthenes carbon number [17].

Figures (15) and (16), show that the mole percentage of aromatics components increases as the reaction temperatures increased. This behavior can be explained on the basis of that the dehydrogenation of naphthenes and dehydrocyclization of paraffin's became faster with increasing of temperature and carbon number.

The comparison between the performance of the two types of catalysts (Pt-Ir-Sn/γ-Al$_2$O$_3$, Pt-Ir/γ-Al$_2$O$_3$) shows that the first type is better than the second one because the addition of tin has enhance the selectivity of isomerization, and increases the aromatization reaction in accord with the work of Bednarova et al. [18]. Therefore, in the present investigation, it is clear that the aromatic mole% produced from the reaction is about 28.62 mole % at 510 °C and 26.56 mole% for the second type of catalyst under the same condition. Then, it can be concluded that the use of tin with platinum will lead to improvement of the dehydrogenation and dehydrocyclization reactions rather than iridium.

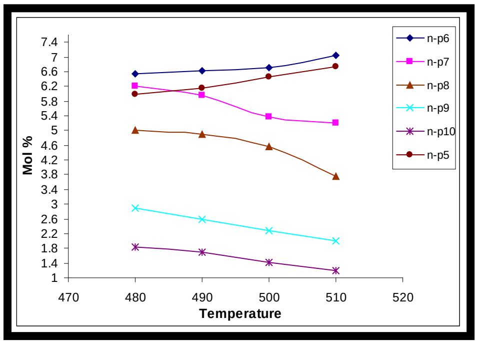


Figure (9) Effect of temperature of on the mole % of n-Paraffins components at WHSV of (1 hr^{-1}) for (Pt-Ir-Sn / γ-Al$_2$O$_3$) catalyst.

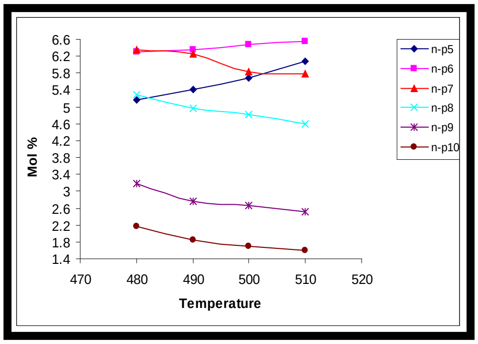
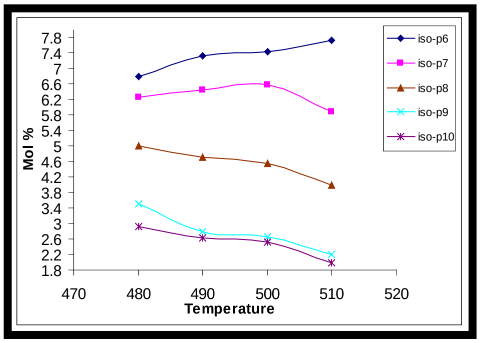


Figure (10) Effect of temperature on the mole % n-Paraffins components at WHSV of (1 hr^{-1})for (Pt-Ir / γ-Al$_2$O$_3$) catalyst.



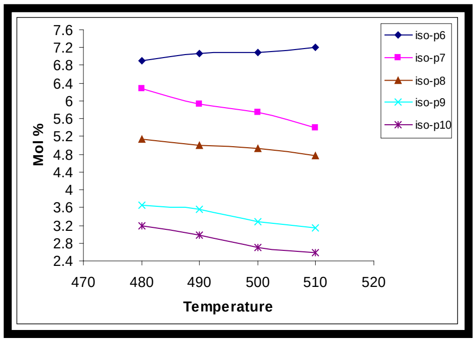
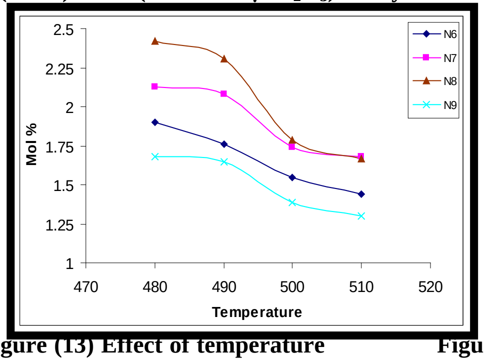


Figure (11) Effect of temperature   Figure (12) Effect of temperature on the mole % of iso-
on the mole % of   Paraffins components at WHSV of (1 hr^{-1}) iso-Paraffins components atWHSV
of (1 hr^{-1})   for (Pt-Ir-Sn / γ-Al_2O_3) catalyst.   for (Pt-Ir / γ-Al_2O_3) catalyst.



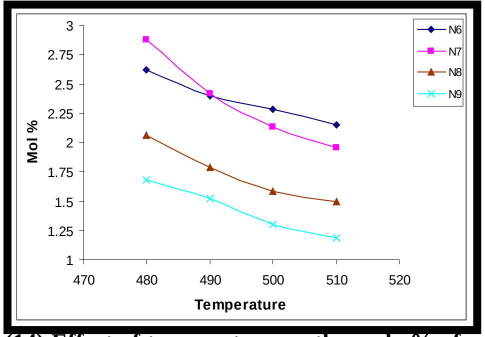
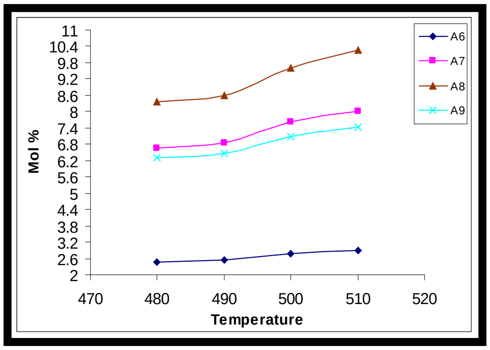


Figure (13) Effect of temperature   Figure (14) Effect of temperature on the mole % of on
the mole % of   naphthenes components at WHSV of (1 hr^{-1})   naphthenes components at
WHSV of (1 hr^{-1})   for (Pt-Ir-Sn / γ-Al_2O_3) catalyst.for (Pt-Ir / γ-Al_2O_3) catalyst.



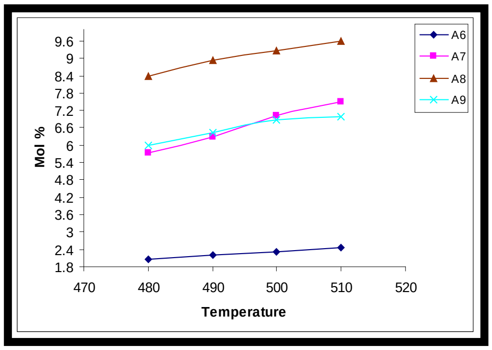


Figure (15) Effect of temperature   Figure (16) Effect of temperature on the mole % of on the
mole % of   aromatics components at WHSV of (1 hr^{-1})   aromatics components at WHSV of
(1 hr^{-1})   for (Pt-Ir-Sn / γ-Al_2O_3) catalyst.   for (Pt-Ir / γ-Al_2O_3) catalyst

EFFECT OF WEIGHT HOUR SPACE VELOCITY (WHSV)

The influence of WHSV was studied at (1, 1.5, and 2 hr^{-1}), and temperature of (510 ˚C), which gave the highest aromatics yield. Figures (17) and (18) have clearly illustrated that the mole% of light component (n-P$_5$ and n-P$_6$) decreases as WHSV increases; this behavior is due to the slow rate of hydrocracking reaction. Therefore, the increase in WHSV causes a decrease in the residence time, which offers plenty of contact time of feedstock with the catalyst inside reactor, which latter lead to an effective conversion of n-paraffins [19]. It can also observe that the heavier paraffins reactivity decreases as WHSV increases.

Figures (19) and (20) show that the iso-paraffins components decrease with increasing of WHSV, but this decrease is less than the decreases in n-paraffin. Such conclusion is attributed to the fact that selectivity of paraffin's isomerization reactions at typical reforming operating condition is relatively insignificant to space velocity. The same conclusion was noted by Jenkins et al. [20].

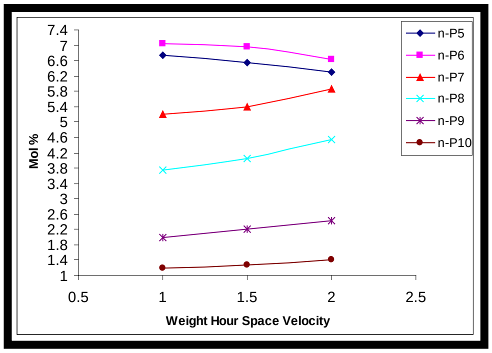


Figure (17) Effect of weight hour space velocity on the mole % of n-Paraffins components at 510 °C for (Pt-Ir-Sn / γ-Al$_2$O$_3$) catalyst.

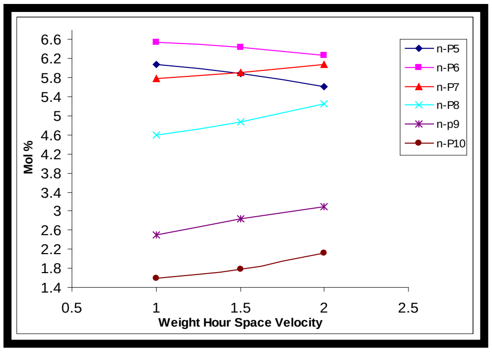


Figure (18) Effect of weight hour space velocity on the mole % of n-Paraffins components at 510 °C for (Pt-Ir / γ-Al$_2$O$_3$) catalyst.

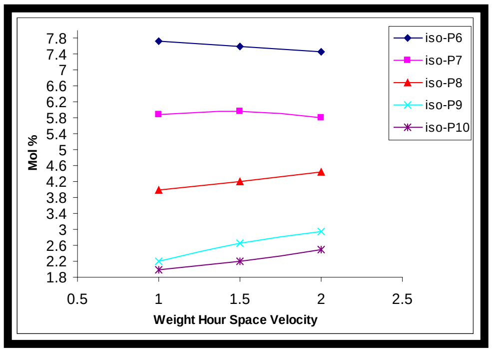


Figure (19) Effect of weight hour space velocity on the mole % of iso-Paraffins components at 510 °C for (Pt-Ir-Sn / γ-Al$_2$O$_3$) catalyst.

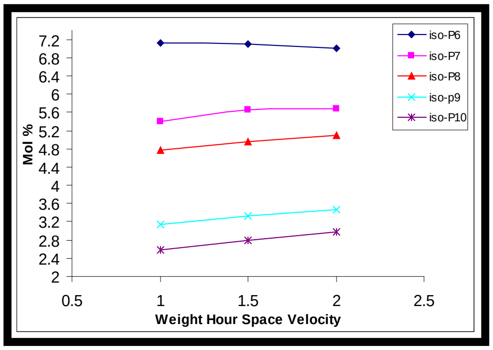
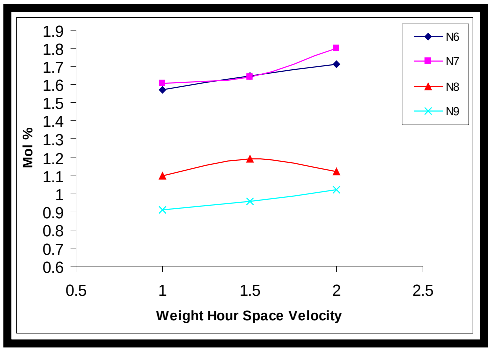


Figure (20) Effect of weight hour space velocity on the mole % of iso-Paraffins components at 510 °C for (Pt-Ir / γ-Al$_2$O$_3$) catalyst.

Figures (21 and 22) show same general trend of decreasing of naphthenes components conversion to aromatics via dehydrogenation reaction (mole % increase, means reactivity decrease) with increasing WHSV. The slights decrease in this trend is directly to the dehydrogenation reaction which is the fastest reaction among all heavy naphtha reforming reactions [3, 13].

From the results of Figures (23 and 24) it was observed that, increasing of WHSV will lead to a decrease in the aromatics yield. It is important to mention here that the aromatics components are produced from dehydrogenation of naphthenes which is not affected too much with WHSV and from dehydrocyclization reaction of Paraffins (n and iso), where, it is the slowest reaction and is affected by the increasing of WHSV and that attributed to the low contact time with the catalyst [21].



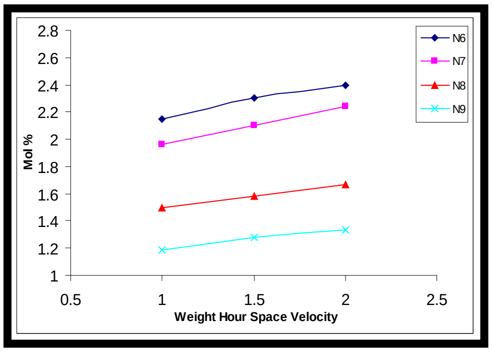
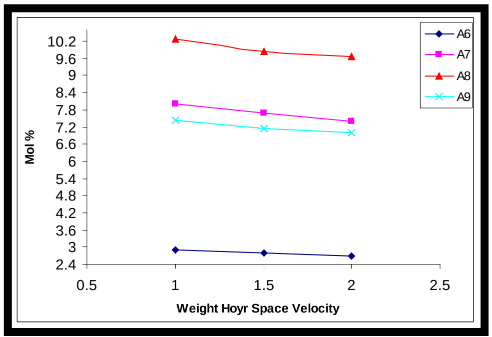


Figure (21) Effect of weight hour space   Figure (22) Effect of weight hour
space velocity on the mole % of naphthenes components at 510 °Cle % of naphthenes components
at 510 °C   for (Pt-Ir / γ-Al_2O_3) catalyst.   for (Pt-Ir-Sn / γ-Al_2O_3) catalyst.



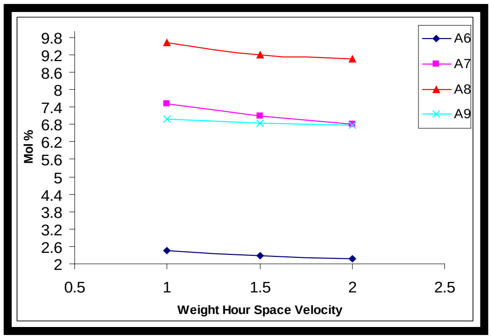


Figure (23) Effect of weight hour space Figure (24) Effect of weight hour space
velocity on the mole % of 510 °C   the mole % of aromatics components at   velocity
on aromatics components at   510 °C   for (Pt-Ir-Sn / γ-Al_2O_3) catalyst
for (Pt-Ir / γ-Al_2O_3) catalyst.

SIMULATION RESULTS OF MATHEMATICAL MODEL

Figures (25 and 26) show the concentration profiles for reactants (Paraffins and Naphthenes) and products (aromatics and gases) for all catalysts types used in the present work at 480 ˚C and WH

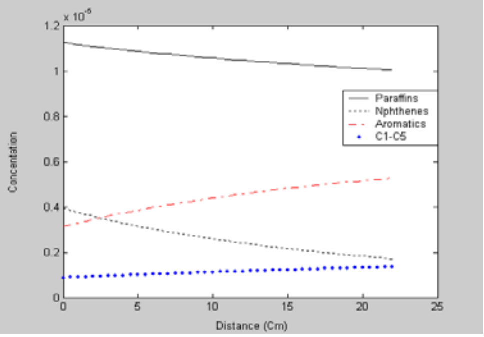
SV of 1hr^{-1} as an example.

Table (5) comparison between theoretical and experimental mol% for bi-and tri-metal catalyst at constant WHSV (1hr^{-1}) for Different reaction temperatures

Condition	Components	Pt-Ir-Sn/ γ-Al$_2$O$_3$		Relative deviation%	Pt-Ir/ γ-Al$_2$O$_3$		Relative deviation%
		Exp. Conv %	Theo. Conv%		Exp. Conv%	Theo. Conv %	
480 °C	Paraffins	46.91	51.72	6.35	48.46	55.49	14.51
490 °C	Paraffins	45.84	48.59	10.07	46.7	46.86	0.36
500 °C	Paraffins	43.54	46.63	3.47	45.25	46.28	2.28
510 °C	Paraffins	41.03	44.05	2.95	44.15	45	1.93
480 °C	Naphthenes	8.13	8.49	9.71	9.24	9.8	6.11
490 °C	Naphthenes	7.80	8.59	15.31	8.13	8.7	7.10
500 °C	Naphthenes	6.47	7.11	13.22	7.29	7.99	9.6
510 °C	Naphthenes	6.09	6.96	19.5	6.8	7.74	13.85
480 °C	Aromatics	23.79	24.84	9.77	22.14	24.59	11.1
490 °C	Aromatics	24.46	25.91	11.7	23.88	25.97	8.77
500 °C	Aromatics	27.08	27.99	6.93	25.44	27.34	7.50
510 °C	Aromatics	28.62	29.37	6.54	26.56	28.73	8.17

Figures (27 and 28) show the comparison between the experimental and predicted conversion of Naphthenes for the two catalysts types as example. Table (5) represent all the comparison between theoretical and experimental data. It was concluded that, the derived model and simulation agrees with the experimental work results according to the suggested scheme of reactions network for heavy naphtha reforming. The comparison between the model and experimental results shows that the deviation reach to 19.50%.

The predicted temperature profiles using Pt-Ir-Sn/γ-Al$_2$O$_3$ and Pt-Ir /γ-Al$_2$O$_3$ along bed length at temperatures 510 and 490 ˚C can be seen in Figures (29 and 30). The results of these figures give the trend of temperature profile which decreases along the catalyst bed length (distance), for all temperature ranges. This trend agrees with the published results for heavy naphtha catalytic reforming process. Many researches indicate that the temperature decreases along the catalyst bed, because reforming process reactions are, overall, endothermic. For this reason, commercial catalytic reformers are designed with multiple reactors and with heaters between the reactors to maintain reaction temperature at operatable levels [14, 16, 21].



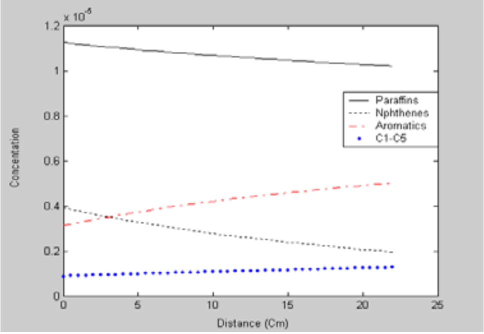
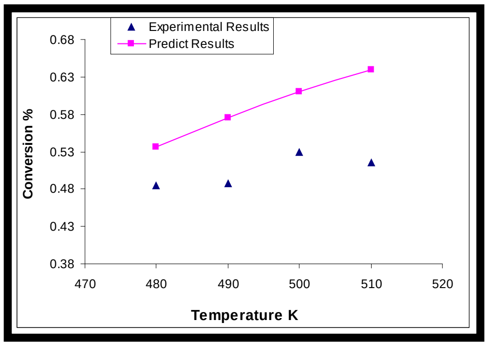


Figure (25) Concentration profiles for (Paraffins, (Paraffins, Naphthenes, Aromatics, and gases) at 480 °C 480 °C and (1 hr^{-1}) for (Pt-Ir-Sn / γ-Al$_2$O$_3$) catalyst.

Figure (26) Concentration profiles for Naphthenes, Aromatics, and gases) at and (1 hr^{-1}) for (Pt-Ir / γ-Al$_2$O$_3$) catalyst.



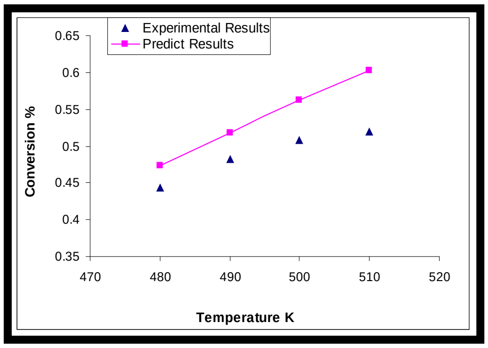
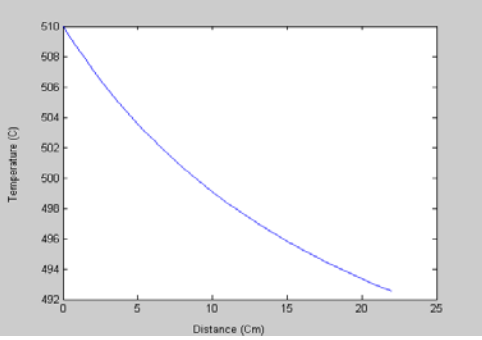


Figure (27)The comparison between the experimental experimental and predicted naphthene conversion at WHSV of (1hr^{-1}) for (Pt-Ir-Sn / γ-Al$_2$O$_3$) catalyst.

Figure (28)The comparison between the and predicted naphthene conversion at WHSV of (1hr^{-1}) for (Pt-Ir / γ-Al$_2$O$_3$) atalyst.



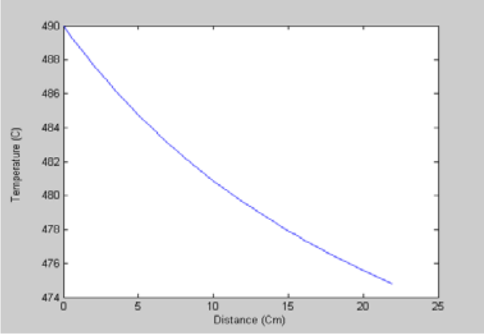


Figure (29) Simulation of temperature profile for for (Pt-Ir-Sn / γ-Al$_2$O$_3$) catalyst at 510 °C and (1hr^{-1}).

Figure (30) Simulation of temperature profile (Pt-Ir / γ-Al$_2$O$_3$) catalyst at 490 °C and (1hr^{-1}).

CONCLUSIONS

The addition of iridium (Ir) and tin (Sn) to Pt/ γ-Al$_2$O$_3$ as bi-metal (Pt-Ir/ Al$_2$O$_3$, and tri-metal Pt-Ir-Sn/Al$_2$O$_3$) improves the conversion of heavy naphtha reactants

(Paraffins and Naphthenes). On the other hand, the selectivity of catalysts toward aromatization reactions especially light aromatics (A_6, and A_7) is increased.

The conversion of heavy naphtha reactants (Paraffins and Naphthenes) increases with increasing of reaction temperature in the range (480 – 510) °C. For the (Pt-Ir-Sn/ Al$_2$O$_3$) catalyst, the % conversion increasing from (11.5 % - 22.53 %) for (Paraffins), and (56 % - 67.05 %) for (Naphthenes), while, for the (Pt-Ir/ Al$_2$O$_3$) catalyst the % conversion increasing from (8.57 % - 16.7 %) for (Paraffins) and (50 % - 63.15 %) for (Naphthenes) and decreases with increasing of weight hour space velocity above (1 hr^{-1}). The yield of the desired products (Aromatics) increases with increasing of reaction temperature in the range (480 – 510) °C. It was concluded that for (Pt-Ir-Sn/ Al$_2$O$_3$) catalyst increasing from (26.35 % - 31.7 %), while for (Pt-Ir/ Al$_2$O$_3$) catalyst increasing from (24.51% - 29.41%) and decreases with increasing of weight hour space velocity. The derived model and simulation agrees with the experimental work results according to the suggested scheme of reactions network for heavy naphtha reforming. And the comparison of the model results with experimental results shows a deviation of 19.5%.

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