Simulation and Mathematical Representation of N-Octane Aromatization on Ge-Re-Pt/Al_2O_3, Cs-Pt/ Al_2O_3, Re-Pt/ Al_2O_3 Catalysts.

Dr. Ramzy S. Hamied
Petroleum Technical Engineering Department, University of Technology/Baghdad
Email:ramze_eng@yahoo.com

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ABSTRACT

In the present study mathematical representation was used to predict the reaction kinetics of the n-octane aromatization which tested with three types of catalysts by adding (Ge, Cs, and Re) in order to improves the catalytic properties (enhanced the activity) of Pt/Al_2O_3 catalyst for n-octane aromatization. The aromatization process carried out in the range of reaction temperature varying from (425 to 500 °C) and weight hour space velocity varied from (0.6 to 1.2 hr^{-1}) with hydrogen as the carrier gas at atmospheric pressure.

The results showed that the higher conversion of n-octane aromatization increased with temperature increasing but at temperature higher than (500 °C) hydrocracking reaction is promoted. Whereas the effect of weight hourly space velocity has shown inverse impact on conversion. On the other hand the yield of aromatic increase especially benzene and toluene which produce as secondary products from the hydrogenolysis of A_8 for three types of catalysts using in the process under the same operating condition. The simulation results of the model based on proposed kinetic model was compared with the experimental results. The comparison between the predicted and commercially results shows a good agreement with error% between (6.91 – 17.87).

Key words: Simulation & Mathematical Representation; Aromatization, n-octane.

المحاكاة والتمثيل الرياضي لعملية تحويل البنتان الاعتيادي إلى مركبات عطرية باستخدام العوامل المساعدة Ge-Re-Pt/Al_2O_3, Cs-Pt/ Al_2O_3, Re-Pt/ Al_2O_3

الخلاصة

في هذا البحث تم استخدام التمثيل الرياضي للتنبؤ بحركية التفاعل لمادة البنتان الاعتيادي إلى مركبات عطرية والتي اختبرت باستخدام ثلاثة أنواع من العوامل المساعدة بإضافة (الجرمانيوم والسيزيوم والرينيوم) من اجل تحسين خواص العامل المساعد (تحسين الكفاءة) للحفاز بلاتين المحمل على الالومينا في العملية. عملية تحويل البنتان الاعتيادي إلى مركبات عطرية تمت في نطاق درجة حرارة تفاعل تتراوح

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بين (425 -500 م°) والسرعة الفراغية للغاز (6و0 – 8و1 ساعة$^{-1}$) باستخدام الهيدروجين عند الضغط الجوي. أظهرت النتائج انه كلما ازدادت درجة حرارة التفاعل تزداد معدلات التحويل للبنتان الاعتيادي إلى المركبات العطرية ولكن عند زيادة الحرارة إلى معدلات أعلى من (500 م°) تزداد معدلات التكسير ,بينما يكون تأثير السرعة الفراغية للغاز معاكس وسوف تنخفض معدلات التحويل. ومن ناحية أخرى نلاحظ إن الإنتاجية بالنسبة للمركبات العطرية (البنزين والتولوين) اكبر من البقية والتي تنتج كمركبات ثانوية من عملية تحلل للمركبات العطرية ذات 8 ذرات كربون لأنواع العوامل المساعدة المستخدمة في العملية. كذلك بينت النتائج بالنسبة للموديل الرياضي المقترح لحركية التفاعل في العملية وجود تطابق كبير عند مقارنة النتائج العملية للبحث والنتائج النظرية للموديل الرياضي حيث كانت نسبة الخطأ تتراوح بين (6.91 – 17.87).

NOMENCLATURES

Symbol	Definition	Units	Symbol	Definition	Units
A	Aromatics	(-)	mX	Meta Xelene	(-)
$A_\circ$	Pre-exponential factor	(-)	M.Wt	Molecular weight	g/gmole
BZ	Benzene	(-)	N_8	Napthene of 8 carbon number	(-)
C_i C_P	Concentration of species i Specific heat	mole/cm^3 J/mole.K	OX	Ortho Xelene	(-)
Cs	Cesium	(-)	pX	ParaXelene	(-)
C_1-C_5	Methane-Pentane	(-)	R	Gas constant	J/mole.K
E_A	Activation energy	kcal/mole	r_i	Reaction rate of species i	mole/gcat. hr
EB	Ethyl Benzene	(-)	S	Cross sectional area of reactor	m^2
F	Molar flow rate of species	mole/hr	T	Reaction temperature	°C
G Ge	Gases Germanium	(-) (-)	Tol	Toluene	-
H_2	Hydrogen	(-)	WHSV	Weight hour space velocity	hr^{-1}
ΔH°_r	Heat of i th reaction	J/ mole	Z	Length of reactor	Cm
k_i	Reaction rate constant	hr^{-1}			
K_{eq}	Reaction equilibrium constant	(-)	Sub Scribt		
α, β, γ, δ	Constant of the heat capacity polynomial	(-)	m n	6,and 7 1, and 2	(-) (-)

INTRODUCTION

The aromatization of n-alkane is a profitable reaction for the transformation to aromatics products, which are more valuable components since n-alkanes possess low-octane number (octane number of n-hexane=19; n-heptane=0 and n-octane=19) while aromatics compounds with the same carbon numbers possess much larger octane numbers (octane number of benzene=99; toluene=124 and m-xylene=145). Aromatics obtained can be used as essential raw materials for the production of a wide variety of petrochemicals industry [1, 2].

Dehydrocyclization is a process that involves both dehydrogenation and cyclization of paraffins of the corresponding carbon number leads directly to the synthesis of Benzene,

Toluene and Xylenes (BTX) the most important aromatics. This reaction could be carried out on both bi-functional (acid – metal) or mono-functional (metal only) catalysts. There are three well-known catalysts for dehydrocyclization: Pt/ZSM-5, Pt/ Al_2O_3 and Pt/ KL [3, 4].

Platinum-alumina catalysts consist of two components metallic component metal (Pt) which disperses on acidic support (Al_2O_3). Platinum is well known to promote hydrogenation-dehydrogenation type reaction and acid site is to accelerate carbonium-ion type reaction. The other metals used with Pt/ Al_2O_3 catalyst are (Ge, Cs, and Re). These additives modify the activity, selectivity and stability of the catalyst. These metals are used as bimetallic catalyst or may be used as tri-metallic catalysts (Ge), which they decrease the hydrogenolysis capacity and therefore also decrease the formation of light gases and this will leads to increase aromatics products [5].

Much of the studies on this subject, involving the paraffins, have been directed towards elucidating the reaction mechanism and not much at quantifying its kinetic parameters.Lars [6] in devising a mechanism for the aromatization over the platinum/alumina catalyst noted that the paraffin predominantly to six-membered ring intermediates is believed to occur, followed by dehydrogenation to aromatics and no isomerization occurs.

Davis , and Sang [7, and 8] compared the conversion of n-octane by addition another metal to platinum catalyst and found that greatly enhanced the activity and decreased the rate of deactivation for the dehydrocyclization since the dominant metal catalyzed pathway to produce aromatics was 1,6 –ring closure and no activity to isomerisation. bdul Halim [9] studied the aromatization of n-heptane and n-octane to toluene and xylene by using different commercial and prepared catalysts under varying temperature and space velocities, they concluded that the conversion of prepared catalysts more active than commercial catalyst.

Ako [10] studied the mechanism and the kinetics of n-octane dehydrocyclization reaction on acidic Pt/Al_2O_3 catalysts by using a Langmuir-Hinshelwood-Watson type of rate model was developed for the proposed mechanism by using a search technique employing the nelder and mead modified simplex optimization routine in order gave the best fit of the experimental data were selected. These results are in excellent agreement with the known and expected trends.

The aim of the present work is to study the kinetic model of dehydrocyclization reaction of n-octane by using different catalysts in a fixed bed reactor with various range of temperature and WHSV and to estimate the kinetics parameters (pre-exponential factors, activation energy, heat of reactions) for the proposed model of dehydrocyclization reaction.

EXPERIMENTAL WORK

Catalysts

Two types of catalysts are supplied from Al-Dura refinery (Pt/ γ-Al_2O_3, Pt-Re/ γ-Al_2O_3). The other two catalysts are prepared in Research and Development Centre University of Technology. The physical and chemical properties of all catalysts

commercial and prepared where measured and the results are shown in Table (1):

Preparation of Platinum – Cesium / Alumina Catalyst

The Cs-Pt/Al_2O_3 catalyst was prepared by impregnation the parent catalyst (Pt/Al_2O_3) with cesium nitrate solution ($CsNO_3$) in order to reach final concentration of 0.35 wt% of Pt and 1 wt% of Cs [8].

Then, to prepare 100g of Cs-Pt/ Al_2O_3 catalyst one must use 1.25g of hexachloroplatinicacid (40 wt% of Pt) and use 42g of cesium nitrate. The metal precursor was dissolved in 80 ml distilled water at 50 °C until all the solid particles are dissolved. The Cs-Pt/Al_2O_3 catalyst charged to the vacuum flask of impregnation apparatus and stay under less than 5mmHg vacuum pressure for 15min before all catalyst particles covered with the impregnation solution of cesium nitrate. The impregnation carried out at 50 °C for 4hrs, the impregnation catalyst was dried at 110 °C overnight and the catalysts were finally calcinied by heating in air at 500 °C for 6 hrs. Then reducing in flowing hydrogen of (60 cm^3/min) at 500 °C for 4 hrs. Heating Ramps were programmed at 10 °C /min.

Preparation of Platinum – Rhenium – Germanium / Alumina Catalyst

The Ge-Re-Pt/ Al_2O_3 catalyst was prepared by co-impregnation by adding germanium metal (Ge 99.999%) to platinum- rhenium supported on alumina catalyst in order to reach final concentration of 0.3 wt% Pt, 0.3 wt% Re and 0.3 wt% Ge [11].

Then to prepare 100g of Ge-Re-Pt/Al_2O_3 catalyst. A 0.75g of hexachloroplatinic acid ($H_2PtCl_6.2H_2O$) of (40% Pt) and ammonium perrhenate (NH_4ReO_4) 0.158g and germanium metals (Ge) 0.3g of (99.999% Ge) were used. Then, Pt-Re 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 germanium (Ge) was prepared by dissolving in deionnized water with heating at 70 °C for 30 min. The Germanium solution was added to the homogenized catalyst with gently stirred for 1 hr and then heating at 70 °C in water bath in order to evaporate the excess liquid without stirring. The catalyst was finally dried at 120 °C for 16 hrs and calcined in air at 500 °C for 4 hrs and then reduced in flowing hydrogen at 500 °C for 4 hrs with hydrogen flow rate of 60 cm^3/min.

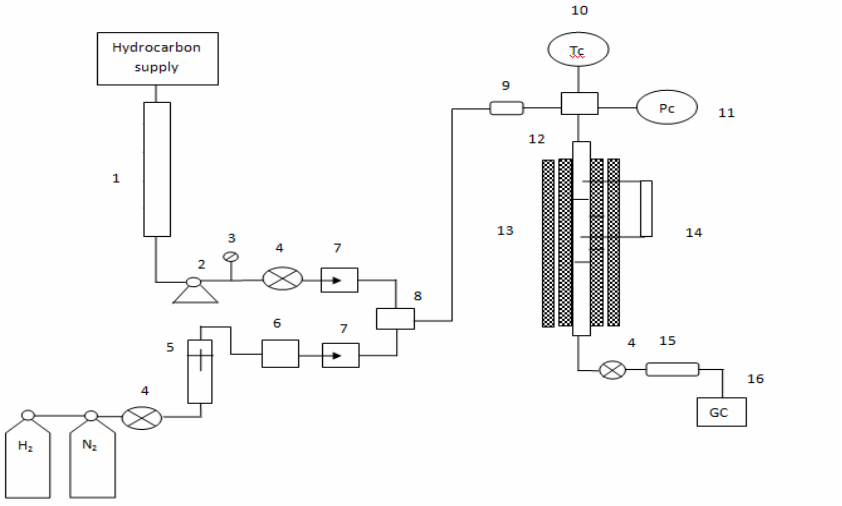
Table (1) Physical and chemical properties of commercial and prepared catalysts.

	Commercial Pt/γ-Al_2O_3	**Commercial Re-Pt/γ-Al_2O_3**	**Prepared Cs-Pt/γ-Al_2O_3**	**Prepared Ge-Re-Pt/γ-Al_2O_3**
Pt , wt %	0.35	0.3	0.35	0.3
Re, wt %	-	0.3	-	0.3
Ge ,wt %	-	-	1	0.3
Cs , wt %	-	-	-	-
Form	Extrudate	Extrudate	Extrudate	Extrudate
Surface Area (m^2/g)	215	220	215	200
Pore Volume (cm^3/g)	0..57	0.6	0.57	0.685
Bulk Density (g/cm^3)	0.66	0.69	0.66	0.69

Description of Aromatization Flow Process

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. The reactor was charged for each experiment with catalyst located in the middle zone, while, the upper and lower zones were filled with glass beads as represented in Figure (1) which shows the details of the process equipments. N-octane pumped under atmospheric pressure to the unit. Hydrogen mixed with hydrocarbon prior entering the reactor inlet. 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. Products samples were analyzed using gas chromatograph type Shimadzu 2014 GC.

The aromatization process was examined at different reaction temperature (425, 450, 475, and 500 $^{\circ}$C) and weight hour space velocity (0.6, 1.2, and 1.8 hr^{-1}) with constant pressure, and 4:1 hydrogen to n-octane molar ratio. 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 temperature was 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. And fresh catalyst was used in each run.



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 value	15- Cooling system
8- Mixing section	16- Gas chromatography

Figure (1) Schematic diagram of the experimental apparatus of n-octane aromatization pilot plant.

Mathematical Model (Description and Assumption)

The main aim of the present study is to analyze the kinetics of aromatization process by assessing the effect of reaction time and reaction temperature on the substrate content in the course of process which involves n-octane as raw material. In developing the dehydrocyclization reactor model the following assumptions are taken into account:

- Steady state operation and plug flow isothermal operation.
- 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 reactions rates are first order.
- All reactions were in homogenous phase.

The reaction mechanism of n-octane dehydrocyclization reaction of the present work shown below:

1- n-octane $\rightarrow N_8 + H_2$ …(1)
2- $N_8 + H_2 \rightarrow$ n-octane ...(2)
3- $N_8 \rightarrow$ Aromatics + $3H_2$ …(3)
4- n- octane + $H_2 \rightarrow 2G$ …(4)
5- Aromatic hydrodealkylation …(5)

The reaction rate is considered to follow simple power law kinetic expression for above reactions [12]:

$$r_1 = k_1 C_P - k_2 C_N P_{H_2} \quad \text{... (6)}$$

$$r_2 = k_3 C_N \quad \text{... (7)}$$

$$r_3 = k_4 C_P \quad \text{… (8)} \quad ;$$

$$r_4 = k_5 C_A \quad \text{… (9)}$$

In general form

$$r_i = k_i C_i^n \quad \text{… (10)}$$

The kinetic constants were expressed in equation (11):

Where

$$k_i = A_\circ EXP\left(\frac{-E_a}{R.T}\right) \quad \text{… (11)}$$

The reaction rate constant k_i confirms the Arrhenius expression [12]:

$$Lnk_i = LnA_\circ - \frac{E_a}{R.T} \quad \text{... (12)}$$

The reaction equilibrium constants $\mathbf{K_{eq} = k_1/k_2}$. Therefore, equilibrium constant can be calculated by the following thermodynamic relation [13]:

$$K_{eq} = EXP\left(\frac{-\Delta G}{R.T}\right) \quad \text{... (13)}$$

The equations of mathematical model results from application of material and energy balance principles in a differential volume [14]. The system is numerically solved by method of finite difference approach with explicit solution of all the differential equation in the mathematical model.

$$-\frac{dC_i}{dZ} = \sum_{i=1}^{m} \frac{M.Wt}{z.WHSV}(r_i) \quad \text{... (14)}$$

$$\frac{dT}{dZ} = \frac{s\sum_{i=1}^{m}(r_i)(-\Delta H_{Ri})}{\sum_{i=1}^{m} F_i.C_{P_i}} \quad \text{... (15)}$$

In order to evaluate the heat capacity the following correlation was used [15];

$$Cp_i = \alpha_i + \beta_i T + \gamma_i T^2 + \delta_i T^3 \quad \text{... (16)}$$

In order to evaluate the heat of reaction for the above reactions the following correlation was used [16]:

$$\Delta H^\circ_{r,T} = \Delta H^\circ_{r,298} + \int_{298}^{T} \Delta C_P dT \quad \ldots(14) \; ; \; \Delta H^\circ_{f,298} = n_i \Delta H^\circ_{f,\text{Products}} - n_i \Delta H^\circ_{f,\text{Reactant}} \quad \ldots(17)$$

RESULT AND DISCUSSIONS

Validation of Reaction Kinetics Parameters

The apparent activation energy (E_a) is established from Arrhenius equation that satisfies the relationships between rate constant and reaction temperature as given in equations (10, 11, and 12). From plot of $Ln(k)$ vs. (1/T). 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. The results of the analysis of the parameter estimation for each catalyst type are listed in Table (2). Also the results of heat reactions for all reaction suggested in aromatization of n-octane estimation are represented in Table (3).

Table (2) Activation energy values and pre-exponential Factor for three catalysts types.

Reaction Step	Ea (kcal/mol)	A◦ Pre-exponential factor
Ge-Re-Pt / Al_2O_3		
n-octane $\rightarrow N_8 + H_2$	28.61	$7.921*10^8$
$N_8 + H_2 \rightarrow$ n-octane	17.73	$2.121*10^6$
$N_8 \rightarrow$ Aromatics + $3H_2$	21.33	$7.55*10^5$
n- octane + $H_2 \rightarrow 2G$	24.75	$2.025*10^7$
$A_8 + H_2 \rightarrow A_m + C_n$	16.77	$3.573*10^5$
Cs-Pt / Al_2O_3		
n-octane $\rightarrow N_8 + H_2$	24.26	$2.451*10^7$
$N_8 + H_2 \rightarrow$ n-octane	13	$5.139*10^5$
$N_8 \rightarrow$ Aromatics + $3H_2$	21.13	$1.565*10^6$
n- octane + $H_2 \rightarrow 2G$	22.43	$2.260*10^6$
$A_8 + H_2 \rightarrow A_m + C_n$	16.51	$2.571*10^6$
Re-Pt / Al_2O_3		
n-octane $\rightarrow N_8 + H_2$	23.67	$2.111*10^7$
$N_8 + H_2 \rightarrow$ n-octane	14.41	$6.514*10^5$
$N_8 \rightarrow$ Aromatics + $3H_2$	19.32	$5.370*10^6$
n- octane + $H_2 \rightarrow 2G$	22.76	$1.995*10^6$
$A_8 + H_2 \rightarrow A_m + C_n$	17.61	$2.450*10^5$

Table (3) Results analysis the heat of reaction.

ΔH°_r (kcal/mole H_2)				
Reaction	425 °C	450 °C	475 °C	500 °C
n-octane $\rightarrow N_8 + H_2$	12.67	12.83	12.98	13.13
$N_8 \rightarrow$ Aromatics + $3H_2$	52.94	53.15	53.33	53.49
$P_8 + (5/3)\ H_2 \rightarrow 8/15(C_1\text{-}C_5)$ [17]	-18.31	-21.91	-22.12	-22.38
$A_8 + H_2 \rightarrow A_m + C_n$	13.24	13.42	13.62	13.81

Effect of Reaction Temperatures

The influences of reaction temperatures on the performance of n-octane aromatization process were investigated. The temperature range was between (425 - 500 ˚C). The WHSV of (0.6 hr^{-1}) for Ge-Re-Pt/Al_2O_3 Cs-Pt/Al_2O_3, and Re-Pt/Al_2O_3 catalysts.

The Figures (2, 3, 4, and 5) show that an increasing reaction temperature increases of aromatics yield. This is because that dehydrocyclization reaction is favored at high temperatures [18]. Among the aromatic hydrocarbons, the most important increase was observed in the light aromatics, such as A_6, and A_7 more than the other aromatics (A_8) which are decreased; this decrease is a accompanied by an increase in the hydrogenolysis of A_8 aromatics and this agreement with the results of Siriporn et al, [19]. Also it was found that increasing the temperature increase the cracking and this will lead to increasing light components products (C_1- C_5) also consequently the rate of coke deposition especially under atmospheric pressure, therefore fresh catalyst was used in each run.

It can be observed from these Figures when adding germanium and using as tri-metal catalyst inhibits hydrogenolysis activities since the addition of (Ge) in order to improve the catalytic properties of bi-metalic catalyst and suppresses the formation of gaseous products (C_1- C_5) and thus will increases the liquid yield.

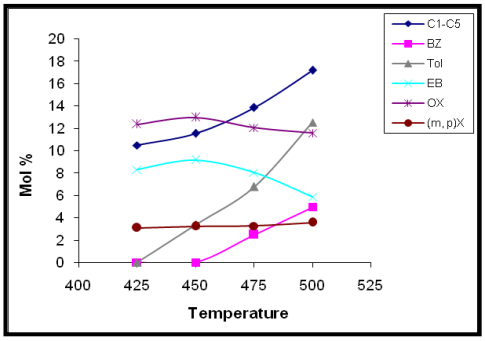


Figure (2) Effect of temperature on the mole % of products components at WHSV of (0.6 hr^{-1}) for (Ge-Re-Pt /Al_2O_3) catalyst.

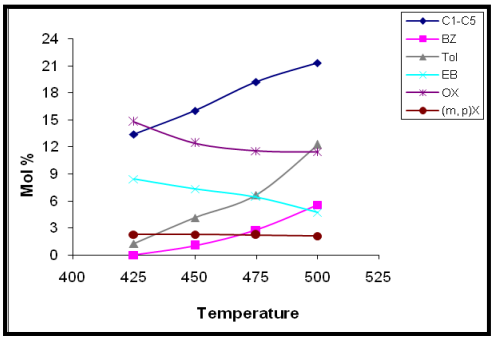


Figure (3) Effect of temperature on the mole % of products components at WHSV of (0.6hr^{-1}) for (Cs-Pt/ Al_2O_3) catalyst

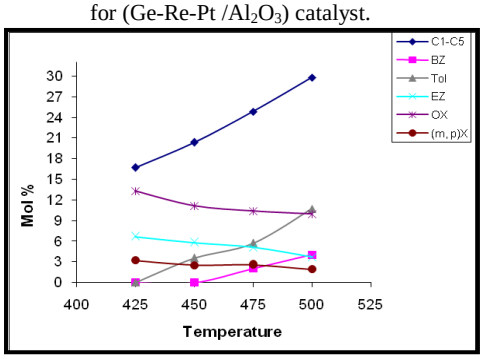


Figure (4) Effect of temperature on the mole % of products components at WHSV of (0.6 hr^{-1}) for (Re-Pt /Al_2O_3) catalyst.

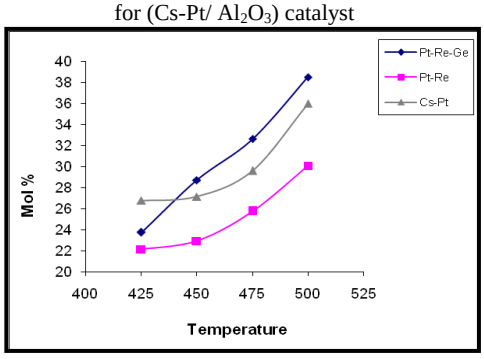


Figure (5) Effect of temperature on the mole % of total aromatics components at WHSV of (0.6hr^{-1}) for three catalysts types.

Effect of Weight Hour Space Velocity

The influence of weight hour space velocity reactions of n-octane aromatization process was studied in the range of (0.6 - 1.8 hr^{-1}), at reaction temperature of (500 ˚C). It was observed that this reaction temperature gives the highest aromatics yield for Ge-Re-Pt/Al_2O_3 Cs-Pt/Al_2O_3, and Re-Pt/Al_2O_3 catalysts.

.The results of Figures (5, 6, 7, and 8) show that, when increasing of WHSV will lead to decrease in the aromatics yield. It is important to mention here that the aromatics components are produced from dehydrocyclization reaction of Paraffins, where, it is the slowest reaction [18] and is affected by WHSV increases (low contact time of the feedstock with the catalyst inside reactor) this will affect the completed of dehydrocylization reaction [8]. The results indicate that's aromatization process

favored low WHSV. From the same Figures it is clear that the mol% of light components (C_1-C_5) also decreased with increasing WHSV, this is because hydrocracking reaction is slow.

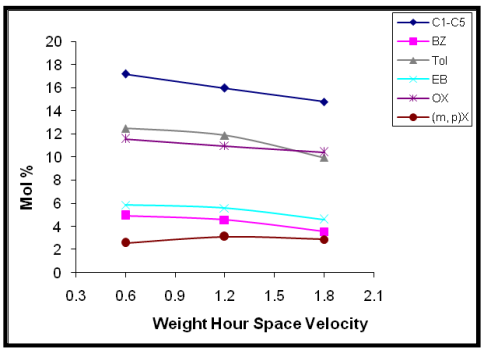


Figure (6) Effect of weight hour space velocity on the mole % of products components at 500 °C for (Ge-Re-Pt / γ-Al_2O_3) catalyst.

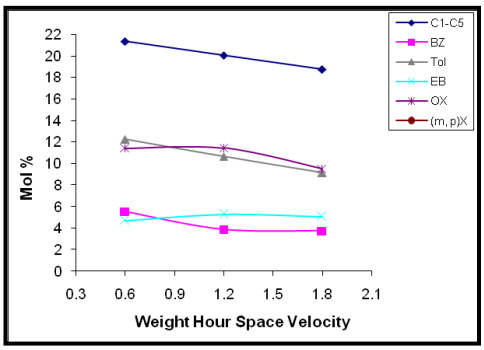


Figure (7) Effect of weight hour space velocity on the mole % of products components at 500 °C for (Cs-Pt / γ-Al_2O_3) catalyst.

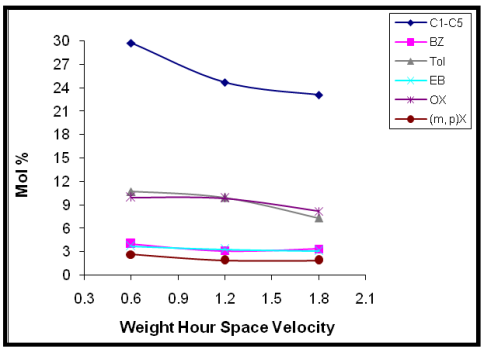


Figure (8) Effect of weight hour space velocity on the mole % of products components at 500 °C for (Re-Pt / γ-Al_2O_3) catalyst.

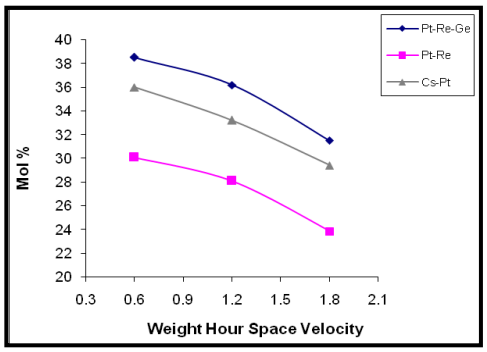


Figure (9) Effect of weight hour space velocity on the mole % of total aromatics components at 500 °C for three catalysts types.

Simulation Results of Mathematical Model

The comparison between the experimental and predicted conversion of total aromatics for three catalysts types (Ge-Re-Pt, Cs-Pt, and Re-Pt supported on γ-Al_2O_3) shown in Figures (10, 11, and 12) respectively, it can be concluded that the conversion of aromatics in the predicted results increases with increasing of operating temperature. Table (4) represents the comparison between theoretical and experimental data for all the products from the aromatization process of n-octane at different reaction temperatures for three types catalysts using in the process. It was concluded that, the derived model and simulation shows a good agreements with the experimental work results according to the suggested scheme of reactions for n-octane aromatization.

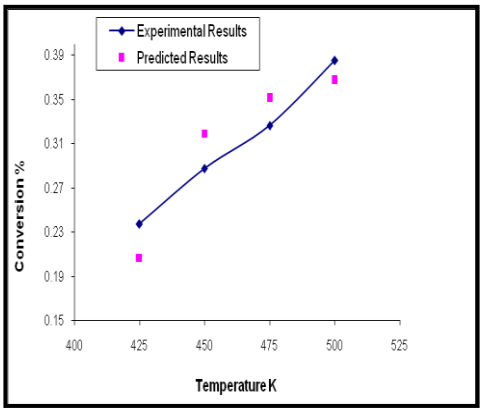


Figure (10) The comparison between the experimental and predicted conversion for total aromatics at WHSV WHSVof ($0.6hr^{-1}$) for (Ge-Re-Pt / γ-Al_2O_3) catalyst.

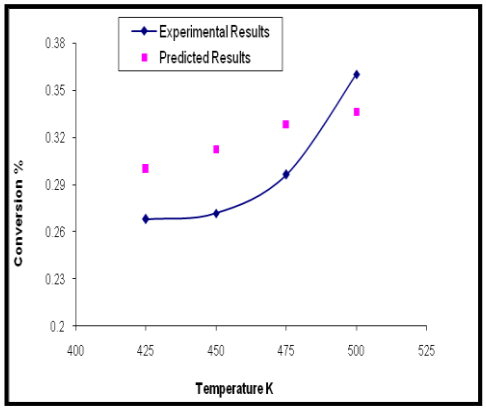


Figure (11) The comparison between the experimental and predicted conversion for total aromatics at of ($0.6hr^{-1}$) for (Cs-Pt / γ-Al_2O_3) catalyst.

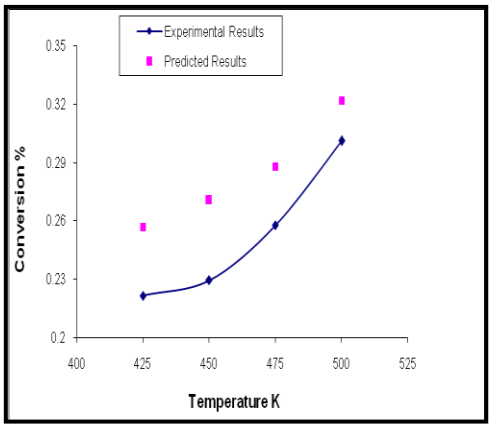


Figure (12) The comparison between the experimental and predicted conversion for total aromatics at WHSV of ($0.6hr^{-1}$) for (Re-Pt / γ-Al_2O_3) catalyst.

Table (4) Comparison between actual and simulation results of n-octane aromatization for three catalysts types.

Composition												
Ge-Re-Pt/Al_2O_3												
	425 °C			450 °C			475 °C			500 °C		
COMP	Exp.	Pred.	Abs. diff.	Exp.	Pred.	Abs. diff.	Exp.	Pred.	Abs. diff.	Exp.	Pred.	Abs. diff.
C_1-C_5	0.105	0.1113	0.0063	0.1155	0.1270	0.0115	0.1386	0.1188	0.0198	0.1721	0.151	0.0211
BZ	0.0	0.0	0.0	0.0	0.0	0.0	0.0248	0.0263	0.0015	0.0496	0.051	0.0014
Tol	0.0	0.0	0.0	0.0339	0.0345	0.0006	0.0677	0.0689	0.0012	0.1252	0.1316	0.0064
EB	0.0832	0.0797	0.0035	0.0915	0.0952	0.0037	0.0805	0.0778	0.0027	0.0588	0.0571	0.0017
OX	0.1235	0.1204	0.0031	0.1297	0.1258	0.0039	0.1206	0.1153	0.0053	0.1158	0.1123	0.0035
(P,M)X	0.0309	0.0324	0.0015	0.0323	0.0331	0.0008	0.0328	0.0315	0.0013	0.0358	0.0347	0.0011
Total Aromatics	0.2376	0.2067	0.0309	0.2874	0.3191	0.0317	0.3264	0.3508	0.0244	0.3852	0.3670	0.0182
Cs-Pt/Al_2O_3												
	425 °C			450 °C			475 °C			500 °C		
COMP	Exp.	Pred.	Abs. diff.	Exp.	Pred.	Abs. diff.	Exp.	Pred.	Abs. diff.	Exp.	Pred.	Abs. diff.
C_1-C_5	0.1393	0.1532	0.0139	0.1602	0.1346	0.0256	0.1922	0.2173	0.0251	0.2134	0.2374	0.0240
BZ	0.0	0.0	0.0	0.0103	0.0110	0.0007	0.0276	0.0293	0.0017	0.0553	0.0575	0.0022
Tol	0.0126	0.0132	0.0006	0.0410	0.0430	0.0020	0.0665	0.0692	0.0027	0.1224	0.1272	0.0048
EB	0.0848	0.0924	0.0076	0.0733	0.0682	0.0051	0.0644	0.0612	0.0032	0.0471	0.0492	0.0021
OX	0.1480	0.1378	0.0102	0.1243	0.1169	0.0074	0.1156	0.1098	0.0058	0.1144	0.1189	0.0045
(P,M)X	0.0227	0.0238	0.0011	0.0227	0.0238	0.0011	0.0222	0.0232	0.0010	0.0208	0.0215	0.0007
Total Aromatics	0.2679	0.2997	0.0318	0.2716	0.3123	0.0407	0.2963	0.3282	0.0319	0.360	0.3364	0.0236
Re-Pt/Al_2O_3												
	425 °C			450 °C			475 °C			500 °C		
COMP	Exp.	Pred.	Abs. diff.	Exp.	Pred.	Abs. diff.	Exp.	Pred.	Abs. diff.	Exp.	Pred.	Abs. diff.
C_1-C_5	0.1676	0.2015	0.0339	0.2033	0.2318	0.0285	0.2481	0.2914	0.0433	0.2976	0.3410	0.0434
BZ	0.0	0.0	0.0	0.0	0.0	0.0	0.0204	0.0218	0.0014	0.040	0.0414	0.0014
Tol	0.0	0.0	0.0	0.0351	0.0369	0.0018	0.0570	0.0597	0.0027	0.1071	0.1107	0.0036
EB	0.0664	0.0711	0.0047	0.0578	0.0612	0.0034	0.0507	0.0532	0.0025	0.0371	0.0389	0.0018
OX	0.1328	0.1394	0.0066	0.1115	0.1160	0.0045	0.1037	0.1079	0.0042	0.0996	0.1025	0.0029
(P,M)X	0.0323	0.0339	0.0016	0.0250	0.0262	0.0012	0.0257	0.0267	0.001	0.0194	0.0199	0.0005
Total Aromatics	0.2214	0.2566	0.0352	0.2294	0.2703	0.0408	0.2576	0.2877	0.0301	0.3009	0.3217	0.0208

CONCLUSIONS

In this paper new kinetic model for n-octane aromatization reactions has been developed. The addition of germanium (Ge) improves the conversion of n-octane by suppressing the hydrogenolytic activity of bi-metallic catalyst in the process by decrease the formation of light gases and this will leads to increase aromatics products. On the other hand, the selectivity of catalysts toward aromatization reactions especially light aromatics (A_6, and A_7 which is produce by hydrogenolysis of A_8) is increased with increasing of reaction temperature in the range (425 – 500) °C, and decreases

with increasing of weight hour space velocity above (0.6 hr^{-1}). The derived model and simulation result agrees with the experimental work according to the suggested scheme of n-octane reactions with error% between (6.91 – 17.87).

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