

Kinetic Models Study of Hydrogenation of Aromatic Hydrocarbons in Vacuum Gas Oil and Basrah Crude Oil Reaction

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Abstract

The aim of this research is to study the kinetic reaction models for catalytic hydrogenation of aromatic content for Basrah crude oil (BCO) and vacuum gas oil (VGO) derived from Kirkuk crude oil which has the boiling point rang of (611-833)K.

This work is performed using a hydrodesulphurization (HDS) pilot plant unit located in AL-Basil Company. A commercial (HDS) catalyst cobalt-molybdenum (Co-Mo) supported in alumina ($\gamma\text{-Al}_2\text{O}_3$) is used in this work. The feed is supplied by North Refinery Company in Baiji. The reaction temperatures range is (600-675) K over liquid hourly space velocity (LHSV) range of (0.7-2) hr^{-1} and hydrogen pressure is 3 MPa with H_2/oil ratio of 300 H_2/l of Basrah Crude oil (BCO), while the corresponding conditions for vacuum gas oil (VGO) are (583-643) K, (1.5-3.75) hr^{-1} , 3.5 MPa and 250 H_2/l respectively .

The results showed that the reaction kinetics is of second order for both types of feed. Activation energies are found to be 30.396, 38.479 kJ/mole for Basrah Crude Oil (BCO) and Vacuum Gas Oil (VGO) respectively.

Keywords: catalytic hydrogenation, hydrotreating process, hydrodearomatization process, reaction kinetic models, aromatic hydrocarbons.

دراسة نماذج حركية التفاعل لهدرجة المركبات العطرية لزيت الغاز الفراغي ونفط خام البصرة

الخلاصة

يهدف البحث الى دراسة نماذج حركية التفاعل لهدرجة المحفزة للمحتوى الأروماتي لنفط خام البصرة و زيت الغاز الفراغي المشتق من نفط خام كركوك ذو مدى الغليان (611-833) كلفن. تم أنجاز التجارب باستخدام وحدة ريادية للمعاملة الهيدروجينية لتنزع الكبريت الموجودة في شركة الباسل باستخدام عامل مساعد تجاري نوع كوبالت-موليبدينوم المحمول على الألومينا. تم تجهيز المغذي المستخدم للدراسة من قبل شركة مصافي الشمال في بييجي. كانت حدود درجات حرارة التفاعل لنفط خام البصرة من 600 إلى 675 كلفن و 583 إلى 643 كلفن لزيت الغاز الفراغي المشتق من خام كركوك، وكانت حدود سرع السائل الفراغية من 0.7 إلى 2 ساعه $^{-1}$ لنفط خام البصرة ومن 1.5 إلى 3.75 ساعه $^{-1}$ لزيت الغاز الفراغي وكانت جميع التفاعلات تحت ضغط هيدروجيني ثابت مقداره 3 ميكاباسكال لنفط خام البصرة و 3.5 ميكاباسكال لزيت الغاز الفراغي وباستخدام نسبة هيدروجين إلى المغذي 300 لتر/لتر لنفط خام البصرة و 250 لتر/لتر لزيت الغاز الفراغي المشتق من نفط خام كركوك.

بيينت النتائج أن الحركية الظاهرة لتفاعل تشبّع المركبات الاروماتية لنفط خام البصرة ولزيت الغاز الفراغي هي من الدرجة الثانية .

² تم حساب طاقات التشيط الظاهرية فكانت 30.396 و 38.479 كيلو جول/مول لتفاعل تشبّع المركبات الاروماتية لنفط خام البصرة ولزيت الغاز الفراغي على التوالي.

Notations

A :frequency factor in Arrhenius Eq. (5)

B: Boltzman's constant(1.380658×10^{-23} J/mol K)
 $C_{A_{in}}$: concentration of aromatic in feed
 $C_{A_{out}}$: concentration of aromatic in product
 E_a : activation energy
H: Plank's constant ($6.6260755 \times 10^{-34}$ J.sec)
 ΔH^* : activation enthalpy change
k : true reaction rate constant
 k_1 : reaction rate constant in Eq. (2)
 k_2 : reaction rate constant in Eq. (3)
 k_v : reaction rate constant in Eq. (1)
K : Transmission coefficient
LHSV: liquid hourly space velocity, hr⁻¹

l : liter
R : gas constant (8.314 J/mol K)
S : aromatic content in Eq.(4)
 S_1^0 : primary components of the compounds easy remove
 S_2^0 : primary components of the compounds difficult remove
 ΔS^* : activation entropy change
T: absolute temperature
Abbreviations
BCO: Basrah Crude Oil
HDA: hydrodearomatization
HYD: hydrogenation
HDS: hydrodesulphurization
VGO: vacuum gas oil

Introduction

In recent years, the catalytic hydrogenation of organic fractions has received renewed interest. The tightening of environmental regulations concerning the emission of aromatic hydrocarbons forces further upgrading of fossil fuels with a particular interest in aromatic (HYD).

The saturation of hydrocarbons takes place in multi component mixtures with simultaneous hydro-desulfurization, hydro-denitrogenation, hydro-deoxygenation [1,2] (HYD) of various feeds for the production of fuels is extensively practiced in the petroleum industry, and to some extent in coal liquefaction and in the upgrading of synthetic fuels and lubricating oils. Another promising area where (HYD) can be applied is the development of renewable non-fossil fuels (pyrolytic bio-oil) for the elimination of the oxygen-containing molecules and the improvement of the H/C ratio.

(HYD) reactions occur on the active sites of the catalysts. Also, a suitable pore size distribution of the catalysts is required to ensure the access of reactant molecules to the active sites. The catalysts used in (HYD) consist of

a molybdenum catalyst that is supported on a high surface area carrier of (100-300) m²/g, most commonly alumina, and is promoted by either cobalt or nickel.^[3]

The process is normally carried out in a trickle-bed reactor at an elevated temperature and hydrogen pressure. In the case of severe deactivation, an ebullating bed reactor might be used but this type of reactor is not suitable due to back-mixing when a high conversion is needed. The specific characteristic of a trickle bed reactor is that a part of the catalytic surface is covered by a liquid and the other part by the gas. In the common set up, the liquid phase flow down wards through the reactor concurrently with the gas phase that partly consists of vaporized compounds. The temperature and pressure ranges for the (HYD) of aromatic hydrocarbons in the liquid phase batch reactor are reported to be (450-700) K and (3.5-17) MPa, respectively^[4-7].

An important reaction in petrochemical industry and refineries is hydroconversion, which enables the change in the molecular weight and structure of organic molecules. Examples are (HYD) and (HDA). When oil is hydrotreated, the reduction of aromatic

compounds competes with the removal of sulfur and nitrogen. The purpose of hydrotreatment is to improve the stability and quality of the product. The reduction of aromatic compounds, especially polyaromatics, gives a higher stability to the product, as well as affecting the solubility and colour of the product. Aromatics in fuels not only lower the quality and produce undesired exhaust emissions, they also have potential hazardous and carcinogenic effects^[7].

In spite of the large number of articles published in recent years, the subject has been widely reviewed. The catalytic aspects of the (HYD) are discussed by Krylov and Navalikhina^[8]. Special attention to the preparation methods is discussed in more detail by P. Grange and X. Vanhaeren^[9]. A comprehensive review of the hydrodeoxygenation, with particular focus on upgrading of bio-oils, is published by Furimsky^[10]. Catalyst deactivation during hydroprocessing, including the adverse effects of the O-compounds, is reviewed by Furimsky and Massoth^[11].

Reaction Kinetic Models

In the trickl-flow regime, only part of the catalyst surface is covered by a film of liquid, and it is sometimes assumed that only this part of the catalyst is effective. Correlations for the fraction wetted area have been used to interpret trickle-bed reaction data and to predict trends. However, it is incorrect to assume that the reaction rate is directly proportional to the wetted surface^[12].

The kinetic studies used in hydrotreating process can also be used to study the kinetics of aromatics removed (HYD)^[13]. Many studies are carried out in order to determine the reaction order of hydrotreating process .

All of these studies indicated that the kinetics of hydrotreating process takes one of the following three possibilities :

1. First order reaction . Henry and Gilbert^[14] and Yui^[15] proved that kinetic of hydrotreating process for the vacuum residue derived from the Kuwait crude and for the light and heavy gas oil derived from Albetra crude followed order reaction. Also, it was found that the kinetic of hydrogen treated Jumboor and Bie-Hasan crudes followed first order reaction^[16]. Yui and Sanford^[17] found the kinetic of aromatic hydrogenation through hydrotreating of light gas oil derived from Athabasca tar followed first order reaction .
2. The reaction of hydrotreating process can be described by use of two simultaneous first order expression , one expression for easy to remove compounds and a separate expression for difficult to remove compounds. Arey et al.^[18] fitted kinetic data for heavy vacuum gas oil, atmospheric residues, vacuum residue and deasphaltened residue according to this model.
3. Second order reaction. Sok^[19] proved that kinetic of aromatic hydrogenation for middle distillate derived from Athabasca tar at diesel fuel and jet fuel production followed second order reaction, while Abbas^[16] proved that the apparent kinetic of hydrotreating process for deasphalting of Basrah crude oil followed the second order.

Mohammed et al.^[20] clarified that the reaction kinetic of hydrotreating process of Qaiara deasphaltened crude oil followed second order reaction .

Trickle bed reactors are widely used in petroleum refinery processes, particularly in residue oil hydrotreating process. The liquid wets each particle of catalyst as it flows through the catalyst

bed. The reacting gas, which is hydrogen, penetrates through liquid film on the surface of the catalyst. The reacting hydrogen may be recirculated or pressure maintained to replace the hydrogen as it reacts with out recirculation.

The following assumption must be made for the purpose of trickle bed performance analysis under ideal conditions and first order kinetic:

Plug flow of liquid, that is no dispersion in the axial or radial directions, no mass or heat transfer limitations between gas and liquid and between liquid and solid catalyst or inside catalyst particles (the liquid saturated with gas at all time), first order isothermal, irreversible reaction with respect to liquid (gases reactant present in excess), catalyst particle completely bathed with liquid, the reactant completely in the liquid phase and no vaporization or condensation.

For this case of a so-called ideal trickle bed reactor, the integrated mass balanced equation written for the reactor about a differential volume element takes the form^[21]:

$$\ln \left[\frac{C_{A_{in}}}{C_{A_{out}}} \right] = \left[\frac{3600kV}{LHSV} \right] \dots\dots\dots(1)$$

There is a mass evidence showing that the value of k_V determined from trickle bed data increased as a liquid flow rate increased. In other words, the fractional conversion increases with liquid flow rate even though Equation (1) predicts no change.

Concerning the optimum state, the predominate equation of the reactor performance of first order reaction takes the following shape^[21]:

$$\ln \left[\frac{C_{A_{in}}}{C_{A_{out}}} \right] = \left[\frac{k_1}{LHSV} \right] \dots\dots\dots(2)$$

If $\ln[C_{A_{in}}/C_{A_{out}}]$ is plotted versus $[1/LHSV]$, a straight line, is obtained, with a slope equal to k_1 which represents the reaction constant of first order.

When the reaction is of second order, the equation take the following form^[21]:

$$\left[\frac{1}{C_{A_{out}}} \right] - \left[\frac{1}{C_{A_{in}}} \right] = \left[\frac{k_2}{LHSV} \right] \dots\dots\dots(3)$$

If $[1/C_{A_{out}}] - [1/C_{A_{in}}]$ is plotted versus $[1/LHSV]$, a straight line, is obtained, with a slope equal to k_2 which represents the reaction constant of second order.

When a two simultaneous first order expression suggested, Equation (4)ow may be used^[21]:

$$S = S_1^0 \exp \left[-\frac{k_1}{LHSV} \right] + S_2^0 \exp \left[-\frac{k_2}{LHSV} \right] \dots\dots\dots(4)$$

The activation energy measures the energy which reaction must have before they can overcome the barrier between the reactants. The activation energy for the hydrogenation reaction is calculated using Arrhenius equation which satisfies the relationship between rate constants and reaction temperatures^[13]

$$k = A \exp \left[-\frac{E_a}{RT} \right] \dots\dots\dots(5)$$

The activation enthalpy and entropy for the hydrogenation reaction is calculated using equation (6), which is obtained from the absolute reaction rate theory^[22]

$$\frac{k}{T} = K \frac{B}{H} \exp \left[-\frac{\Delta S^*}{R} \right] \exp \left[-\frac{\Delta H^*}{RT} \right] \dots\dots\dots(6)$$

The aim of this work is to determine the kinetics of (HYD) for hydrotreating of (BCO) & (VGO) derived from Kirkuk crude oil using trickle bed reactor and cobalt–molybdenum supported on alumina ($\text{Co-Mo}/\gamma\text{-Al}_2\text{O}_3$) as a catalyst. The operating conditions for BCO are: 600-675K, LHSV (0.7-2) hr^{-1} ,

hydrogen pressure of 3 MPa and H₂/Oil ratio of 300 l/l. The corresponding conditions for VGO are 583-643K, LHSV (1.5-3.75)hr⁻¹, pressure of 3.5 MPa and H₂/Oil ratio is 250 l/l.

Experimental Work

Feedstock

First feed stock is (BCO) from Baiji refinery. Table (1) includes crude properties, while second feed stock is (VGO) which is obtained by vacuum distillation of atmospheric reduced crude of Kirkuk crude oil. The second feed stock preparation includes blending the following fractions: light VGO (611-650)K, middle VGO (650-690)K, heavy (VGO) (690-727)K and very heavy (VGO) (727-833)K with the following volume percentage: 13.67, 21.67, 27 and 37.66 respectively. Table (2) includes (VGO) properties.

Catalyst

Cobalt–molybdenum supported on alumina (Co-Mo/ γ -Al₂O₃) as a catalyst is used for this process. Table (3) is the catalyst properties. A 90 cm³ of catalyst is supported into the reactor (Trickle Bed Reactor) for (BCO) experiments, 120 cm³ for VGO experiments and dried at 393 K for 2 hours. 5.4 mm ceramic ball is put into two layers over and under the catalyst. Catalyst activation is performed prior to feed introduction using gas oil as splicing agent which contain 0.6% CS₂ at 477 K and 2 MPa hydrogen pressure, 2.66 hr⁻¹ LHSV for 4 hrs and at 573 K, 2 MPa, 1 hr⁻¹ LHSV and hydrogen flow 0.45 l/min for 16 hrs.

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Distillation Unit

This unit consists mainly of round bottom flask, distillation column, still head distillate receivers, reflux condenser and vacuum system.

The hydrotreated sample is charged in 1 liter round bottom flask,

with electric heating mantle 1.2 KW. The heating mantle is connected with step down transformer provide heat input adjustment. The temperature of liquid crude oil in the flask is recorded using a thermocouple through a glass jacket inside the distillation flask. The boiling point of distillated fraction is recorded by mercury thermometer located at the top of distillation column. The 15 trays distillation column has 50 mm diameter and 750 mm length. The still head includes high efficiency reflux condenser. The cooling medium is alcohol at temperature as low as 243 K to provide the necessary cooling in the early stage of distillation. The cooling medium is turned to ordinary tap water after the distillation temperature exceeds 343 K. No distillates collection before attaining equilibrium in the trays. A magnetic valve connected to the reflex timer used to obtain the desired reflex ratio. The reflex ratio is 3:1 for distillation temperature up to 611 K and 1:1 for the remainder fractions.

The vacuum system consisted of a high efficiency vacuum pump with highly tightened tube connections in order to provide a vacuum pressure as low as 0.5 mm Hg . The distillation unit is operated under atmospheric pressure till the distillation temperature reached 611K then distillation unit system is connected to vacuum pump through a vapor trap and the distillation is continued using pressure of 2 – 4 mm

Hg. Figure 1 show the distillation unit.

Hydrotreating Unit

Hydrotreating runs are performed in a laboratory continuous high pressure unit employing an up-flow co-current trickle bed reactor.

The reactor is stainless, and heat resisting steel with dimensions of 65 cm length, and 2 cm diameter. The reactor is jacketed with five separately heat-controlled block shells in order to

ascertain isothermal operation. The reactor products are cooled in a condenser-cooler and separated from unreacted hydrogen and the hydrocarbon gases by passing into a high and low pressure separators. Gases are then vented to the exterior through a gas flow meter. The unit is supplied with high pressure dosing pump to introduce the feedstock into the unit.

A calibrated micrometer is fitted in the pump to estimate the feedstock flow rate.

Hydrogen is fed to the reactor through a heated high pressure line. The unit is supplied with an electrical gas inlet flow sensor and hydrogen flow rate is estimated by standard calibrations with the electrical pulses. The catalyst bed is located between two bed of inert material with dimensions of 13.5 cm length .

Hydrotreating process is accomplished using trickle bed reactor. The reaction temperatures range is (600-675)K over liquid hourly space velocity (LHSV) range of (0.7 – 2)hr⁻¹ and hydrogen pressure of 3MPa with a H²/oil of 300 l/l for (BCO). The corresponding values for (VCO) are (583-643)K, (LHSV) (1.5-3.75)hr⁻¹ and hydrogen pressure of 3.5 MPa with H²/oil 250 l/l. Figure 2 showed the flow diagram of the (HDS) unit.

Deasphalting Unit

BCO is mixed with n-heptane as a solvent in 2-neck glass flask with an approximate volume of 250 cm³. Solvent to oil ratio is 1-15:1 (volume to weight ratio). Mixing is made by 12.5mm magnetic bar. Mixing time is varied between 0.25 to 4.0 hrs .

The studied solution temperature is (293 - 313)K. The required temperature is adjusted by water bath.

High efficiency vertical condenser operating at total reflux is

mounted on the mixing flask in order to decrease the solvent losses. The condenser coolant is alcohol at temperature of 259 K and it is circulated by cooling machine.

In order to filter the solvent-oil solution in a reasonable time, vacuum filtration unit is assembled, which consisted of filtration flask, Buchner funnel (90 mm in diameter). Vacuum system includes traps, condenser and cooling machine, in order to avoid vacuum pump damage by the high volatility solvent.

Filter paper is washed with reasonable amount of the same solvent. It is weighted after dried in an electric furnace maintained at 383 K for about 15 to 20 minutes.

Solid – Liquid Chromatography Analysis

The group composition of (VGO) and (BCO) hydrotreated products are determined by elution absorption chromatography using silica gel as absorbent. Column of about 25 mm in diameter are packed to a height of 500 mm with silica gel which had been freshly calcined at 773K over night (16hrs). About 2 grams of sample is introduced into the column and the saturation fraction is eluted from the column using 150 cm³ of n-hexane. After that the aromatics fraction was eluted with 200 cm³ of benzene. Finally the polar aromatics fraction is eluted with 150 cm³ of methanol – benzene mixture (20/80 by volumes) Figure 3.

Results and Discussion

The reaction kinetics obtained from the analysis of the results of (HYD) process of BCO & VGO indicated that the kinetic of reaction is not first order as illustrated in Figures 3 and 4. The kinetic of aromatics (HYD) followed a kinetic of second order as illustrated in Figures 5 and 6.

The reaction rate constant of kinetic (HYD) of (BCO) and (VGO) derived from Kirkuk crude oil which has the boiling range from (611–833)K is illustrated in Table (4) ranged between $0.0093 \text{ (hr . wt\%)}^{-1}$ at 600 K to $0.0287 \text{ (hr . wt\%)}^{-1}$ at 675 K for (BCO) and $0.0181 \text{ (hr . wt\%)}^{-1}$ at 583 K to $0.0463 \text{ (hr . wt\%)}^{-1}$ at 643 K for (VGO) which means that temperature increase will result in quicker aromatic saturation reactions^[23].

A plot of $\ln(k)$ versus $(1/T)$ according to Eq. (5) as shown in Figures (7) and (8) for (BCO) and (VGO) gives a straight line with a slope equal to $(-E_a/R)$ from which the activation energy is calculated. The activation energy for hydrogenation is found to be 50.461 KJ/mole for (BCO) and 48.498 KJ/mole for (VGO).

A plot of $\ln(k/T)$ versus $(1/T)$ according to Eq. (6), as shown in Figures (9) and (10) gives a straight line with a slope equal to $(-\Delta H^*/RT)$ from which the activation enthalpy can be calculated. The intercept of this line which is equal to $\ln(K_B/H) + (\Delta S^*/R)$ is used to calculate the activation entropy ΔS^* . Calculated values of ΔH^* and ΔS^* are listed in Table (4)

Conclusions

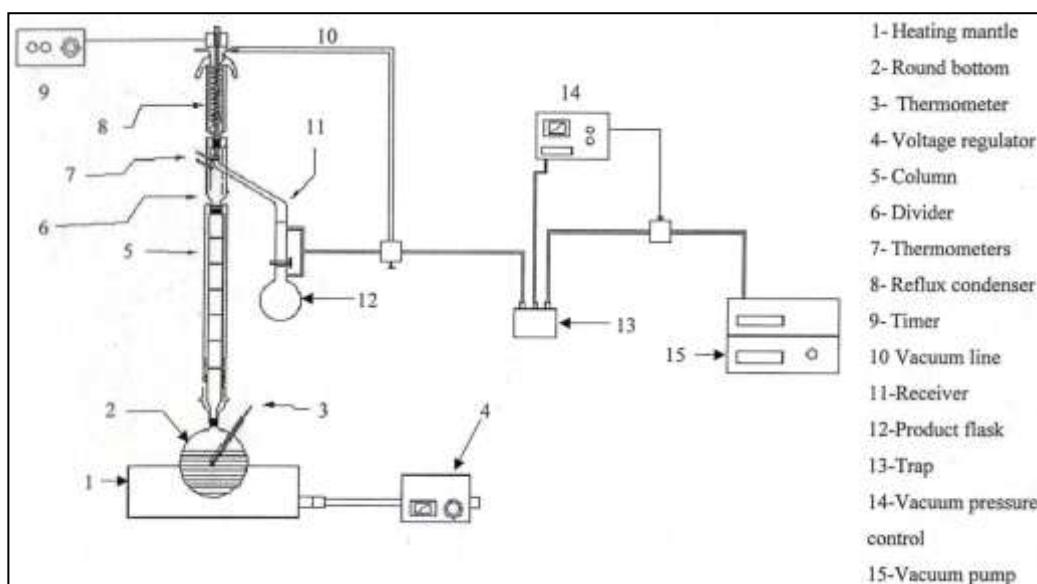
1. The Kinetic analysis shows that aromatic saturation reactions through hydrogenation of (BCO) and (VGO) followed a second order.
2. Aromatic saturation increases as the temperature of reaction increased and decreased with decreasing of the LHSV.
3. Activation energy of aromatic saturation reactions through (HYD) of (BCO) and (VGO) derived from Kirkuk crude oil are 50.461 and 48.198 KJ/mole respectively

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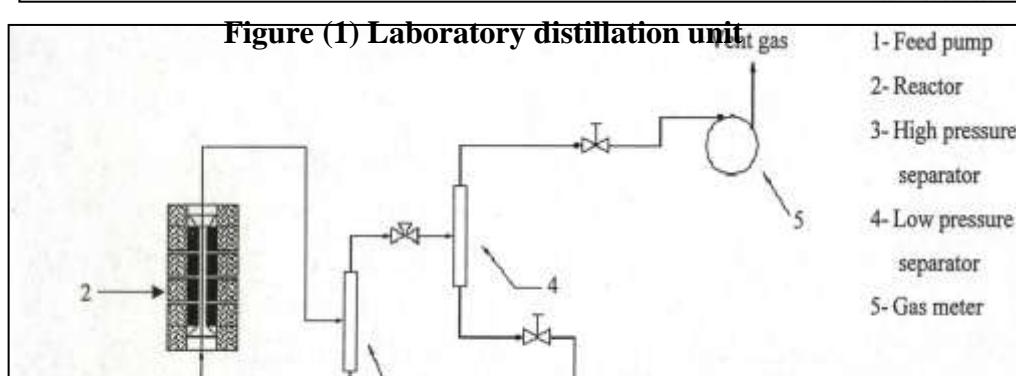


Figure (2) flow diagram of laboratory hydrodesulfurization unit

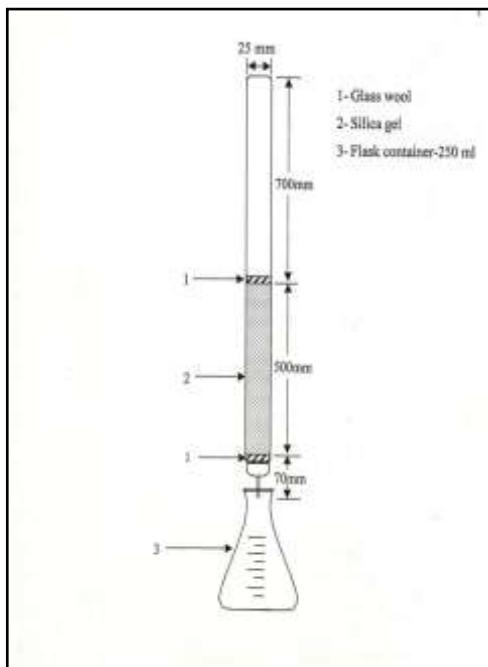


Figure (3) Solid liquid chromatographic column

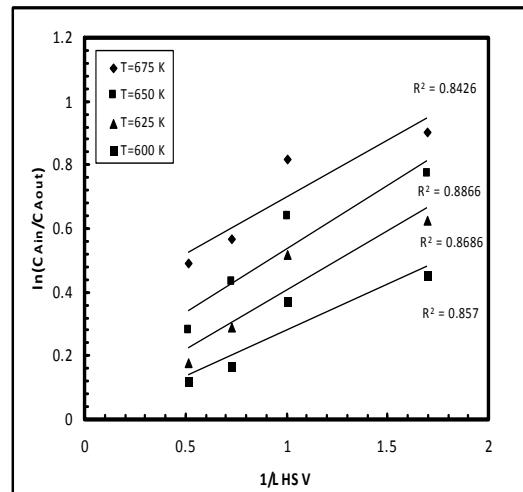


Figure (4) First order kinetic of aromatic hydrogenation of (BCO)

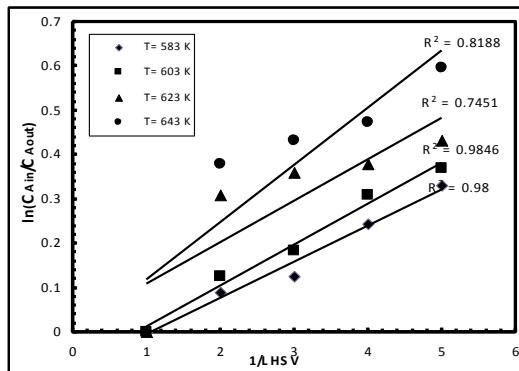


Figure (5) First order kinetic of aromatic hydrogenation of (VGO)

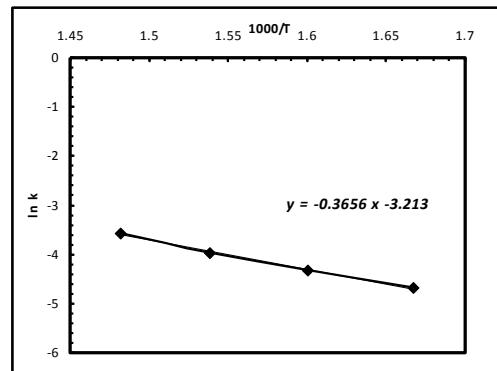


Figure (8) $\ln k$ versus $1/T(K)$ of second order kinetic model for aromatic hydrogenation of (BCO)

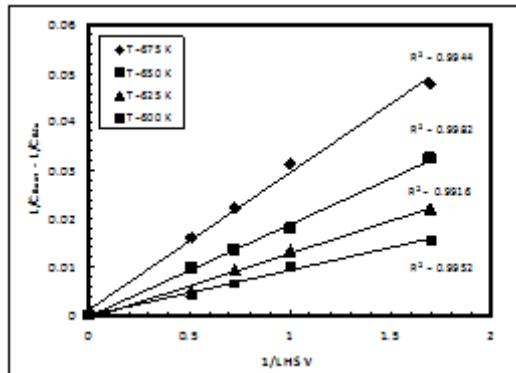


Figure (6) Second order kinetic of aromatic hydrogenation of (BCO)

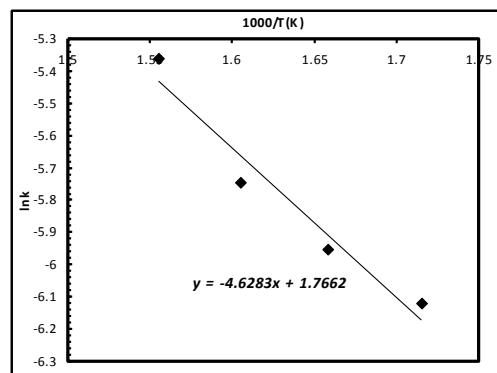


Figure (9) $\ln k$ versus $1/T(K)$ of second order kinetic model for aromatic hydrogenation of (VGO)

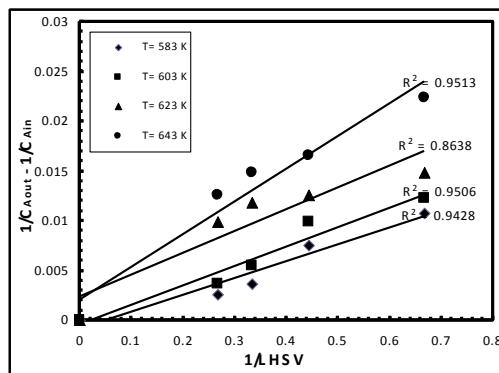


Figure (7) Second order kinetic of aromatic hydrogenation of (VGO)

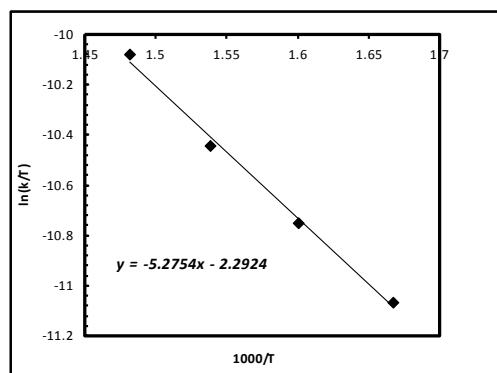


Figure (10) $\ln(k/T(K))$ versus $1/T(K)$ of second order kinetic model for aromatic hydrogenation of (BCO)

Table (1) The Properties of feed stock (BCO)

Properties	Value
Sulfur content (wt %)	1.95
Specific Gravity at 15.6 °C	0.8560
API	33.6
Viscosity at 40 °C (cSt)	6.9
Pour point °C	-36
CCR (wt %)	4.1
Vanadium content (wt. ppm)	23.90
Nickel content (wt. ppm)	16.41
Ash content (wt %)	0.009

Table (2) The Properties of feed stock of (VGO)

Properties	Value
Sulfur content (wt %)	2.5
Specific Gravity at 15.6 °C	0.911
API	23.858
Viscosity at 40 °C (cSt)	11.653
Pour point °C	29
CCR (wt %)	0.58
Flash point (K)	465
Aniline point (K)	325

Table (3) Properties of catalyst commercial catalyst (CO-MO/ γ -Al₂O₃)

Chemical specification	Value
MoO ₃ (wt %)	15
NiO (wt %)	3
SiO ₂ (wt %)	1.1
Na ₂ O (wt %)	0.07
Fe (wt %)	0.04
SO ₂ (wt %)	2
Al ₂ O ₃	Balance
Physical specification	Value
Surface area m ² /g	180
Pore volume cm ³ /g	0.5
Bulk density g/cm ³	0.67
Mean particle diameter mm	1.8
Form	Extrude
Surface area m ² /g	180
Pore volume cm ³ /g	0.5
Bulk density g/cm ³	0.67
Mean particle diameter mm	1.8

Table (4) Values of reaction rate constant and thermodynamic properties through hydrogenation aromatic of (BCO) and (VGO)

Compounds	Basrah crude oil				Vacuum gas oil				
	Temperature(K)	600	625	650	675	583	603	623	643
Rate constant (hr.wt%)⁻¹	0.009	0.012	0.018	0.028	0.018	0.025	0.033	0.046	
Thermodynamic properties									
Ea* (KJ/mole)	30.396				38.4797				
Δ H* (KJ/mole)	43.86				33.3923				
Δ S*(J/mole.K)	-216.6				-244.522				

