

KINETIC MODELS STUDY OF HYDRODESULPHURIZATION VACUUM DISTILLATE REACTION

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ABSTRACT

This study deals with kinetics of hydrodesulphurization (HDS) reaction of vacuum gas oil (611-833) K which was distilled from Kirkuk crude oil and which was obtained by blending the fractions, light vacuum gas oil (611 - 650) K, medium vacuum gas oil (650-690) K, heavy vacuum gas oil (690-727) K and very heavy vacuum gas oil (727-833) K.

The vacuum gas oil was hydrotreated on a commercial cobalt-molybdenum alumina catalyst presulfied at specified conditions in a laboratory trickle bed reactor. The reaction temperature range (583-643) K, liquid hourly space velocity range (1.5-3.75) h⁻¹ and hydrogen pressure was kept constant at 3.5 MPa with hydrogen to oil ratio about 250 lt/lt.

The conversion results for desulphurization reaction appeared to obey the second order reaction. According to this model, the rate constants for desulphurization reaction were determined. Finally, the apparent activation energy (E_a), enthalpy of activation (ΔH^*) and entropy (ΔS^*) were calculated based on the values of rate constant (k₂) and were equal 80.3792 KJ/mole, 75.2974 KJ/mole and 197.493 J/mole, respectively.

KEY WORDS: Hydrodesulphurization reaction, Vacuum gas oil, Trickle bed reactor, Reaction kinetics models.

NOTATIONS

A: frequency factor in Arrhenius eq. (10)
B: Boltzman's constant (1.380658 x 10⁻²³
J/mol K)

Cs_o : concentration of sulfur in feed

(ppm)

Cs: concentration of sulfur in product

(ppm)

E_a: activation energy

F : feed rate. (gmol/hr)

H: Plank's constant ($6.6260755 \times 10^{-34}$ J. sec).

ΔH^* : Activation enthalpy change

k : true reaction rate constant.

k' : proportional constant .

k_{app} : apparent reaction rate constant.

k_1 : reaction rate constant in eq.(4).

k_2 : reaction rate constant in eq. (9).

K : Transmission coefficient

L : liquid mass velocity

LHSV: liquid hourly space velocity, hr^{-1}

l : Reactor length.

R : gas constant (8.314 J/mole K)

ΔS^* : Activation entropy change

T: absolute temperature

V : Reactor volume

W : Mass of catalyst

x : Conversion

Greek Letters

β : exponent for velocity effect

η : effectiveness factor

ρ : density of fluid (gm/cm^3)

ρ_b : density of catalyst bed (gm/cm^3)

Abbreviations

ASTM: American society for testing of materials

CCR: Conradson Carbon Residue

HDS: Hydrodesulphurization

HDN: Hydrodenitrogenation

HVGO: Heavy Vacuum Gas Oil

LVGO: Light Vacuum Gas Oil

MVGO: Medium Vacuum Gas Oil

VHVGO: Very Heavy Vacuum Gas Oil

VGO: Vacuum Gas Oil

INTRODUCTION

Hydrodesulphurization (HDS) of heavy oils to meet rapidly increasing low sulfur fuel oil markets is one of the major technical and economic challenges facing the refining industry. One route to low sulfur oil production is vacuum gas oil (VGO) desulphurization. Atmospheric distillation tower residuum is first fractionated in a vacuum distillation tower to vacuum gas oil and residuum. The sulfur content of the vacuum gas oil is then significantly reduced by means of catalytic (HDS). This process has the advantage of being relatively inexpensive. Feedstocks to this process may include virgin and visbreaker vacuum gas oil, thermal and catalytic cycle, and cooker gas oil^(1, 2).

HDS is a catalytic process whereby a crude oil fraction as the feedstock is passed with hydrogen through a catalytic bed at elevated temperature and pressure. The basic chemical concept of the process

is to convert the organic sulfur compounds in feedstock to hydrogen sulfide. The ease of desulphurization is dependent upon the type of compound, and the lower boiling fractions are desulphurized more easily than the higher boiling fractions. The difficulty of sulfur removal increases in order ⁽³⁾:

paraffins < naphthenes < aromatics

Under the usual commercial (HDS) conditions, the various reactions that result in the removal of sulfur from the organic feedstock occur. Thiols and open-chain and cyclic sulfides are converted to saturated and/ or aromatic compounds depending on the nature of the particular sulfur compound involved. Benzothiophenes are converted to alkylated aromatics, while dibenzothiophenes are usually converted to biphenyls. In fact, the major reactions which occur as part of (HDS) process involve simple carbon-sulfur bond rupture and saturation of the reactive fragments as well as saturation of olefinic material ⁽³⁾.

Petroleum stocks are extremely complex mixtures of compounds containing, in addition to carbon and

hydrogen, significant amounts of sulfur, nitrogen, oxygen, and various metals. These compounds vary in type, molecular lubricating oil. A great deal of the published work on trickle beds has been directed to understand and improve the operation of these processes ⁽⁵⁾.

There have been many studies of the hydrodynamics of trickle beds that describe the different flow structure, molecular weight and physical properties. At the temperature at which catalyst HDS reactors are normally operated, the most important or desirable reaction is the HDS reaction of sulfur containing compounds. The HDS reaction involves the cleavage of the C-S bond according to an incompletely understood mechanism to produce an organic compound and H₂S. The various sulfur compounds react at different rates according to their reactivity ⁽⁴⁾.

Trickle-bed reactors are widely used for hydrogenations in the petroleum industry, including (HDS) of heavy oils and gasoline, hydrodenitrogenation (HDN), hydrocracking, and hydrofinishing of regimes and give empirical correlations for the pressure drop, liquid holdup, and the partial wetting of the catalyst ^(5, 6, and 7).

When gas and liquid flow downward through a bed of solids, the flow regime may be trickle flow, pulsing flow, bubble flow, or spray flow, depending on the flow rates and properties of the fluids and solid. At low gas and liquid rates, the gas phase is continuous and liquid flows in a thin laminar film over wetted portions of the particle surface. This is called the gas-continuous region or the trickle-flow region.

The present work deals with the study of kinetics of hydrodesulphurization (HDS) reaction of VGO (611-833) K which was distilled from Kirkuk crude oil by using laboratory trickle bed reactor.

REACTOR MODELS OF (HDS) REACTION

In the trickle-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, incorrect to assume that the reaction rate is directly proportional to the wetted surface ⁽⁸⁾.

In kinetic models for trickle beds, the reaction is often assumed to be first order to both reactants, but attention is focused on the liquid reactant, since the gas concentration doesn't change very much in the reactor. For HDS, and other high-pressure purification processes, the hydrogen concentration in the liquid is often as great as or greater than the hydrocarbon concentration, in contrast to slurry hydrogenations, where the dissolved hydrogen concentration is much lower than that of the other reactant. For the ideal case of plug flow and completely wetted catalyst, the conversion for a first-order reaction is given by the same equation used for gas-solid reactions and the material balance equation written for a differential mass of catalyst dW is ⁽⁸⁾:

$$FCs_o dx = k\eta C_s_o(1-x)dW \dots\dots\dots (1)$$

$$\ln\left(\frac{1}{1-x}\right) = \frac{k\eta W}{F} = \frac{k\eta V\rho_b}{F} \dots\dots\dots (2)$$

In petroleum processing, the conversion may be given as a function of the liquid hourly space velocity (LHSV), and the apparent rate constant, k_{app} , includes the effect of partial wetting as well as the effect of internal concentration gradients:

$$\ln\left(\frac{1}{1-x}\right) = \frac{k_{app}\rho_b}{LHSV} \quad \dots\dots\dots (3)$$

$$\text{or} \quad \ln\left[\frac{C_{S_o}}{C_s}\right] = \frac{k_1}{LHSV} \quad \dots\dots\dots (4)$$

where

$$LHSV = \frac{F}{V} = \frac{L/\rho}{l} \quad \dots\dots\dots (5)$$

$$k_1 = k_{app}\rho_b \quad \dots\dots\dots (6)$$

$$\text{and} \quad x = \frac{C_{S_o} - C_s}{C_{S_o}} \quad \dots\dots\dots (7)$$

The reciprocal of LHSV has the units of time, but it is not the average residence time, since the liquid occupies only a fraction of the bed volume.

Frye and Mosby⁽⁹⁾ showed that the HDS kinetic of the three compounds found in cycle oil feedstock followed a first order model. It was proposed that the HDS reactions of petroleum distillates were also first order⁽¹⁰⁾. The Kirkuk reduced kinetic follow first order model⁽¹¹⁾.

If the rate constant k_{app} in Eq. (3) is assumed to depend on a fractional power of the liquid flow rate L , as in $k_{app} = k' L^\beta$, Eq. (5) can be modified to show a fractional dependence on LHSV and on the bed length l and becomes⁽¹²⁾:

$$\ln\left[\frac{C_{S_o}}{C_s}\right] = \frac{k'l^\beta}{(LHSV)^{1-\beta}} \quad \dots\dots\dots (8)$$

Different values of β have been reported^(13, 14), Henry and Gilbert⁽¹²⁾ took $\beta = 1/3$. A similar effect of LHSV and catalyst bed length on conversion in the absence of back mixing was also predicated on the basis of catalyst wetting model of Mears⁽¹⁵⁾ and took $\beta = 0.32$.

The reaction of HDS can be described using a second-order treatment. Application of this model to Kuwait vacuum residue using two types of catalyst gives a liner relation⁽¹⁶⁾. Mohammed et al⁽¹⁷⁾ show that the HDS of Qaiyarah deasphalted reduced crud followed second order kinetic. The kinetic of the catalyst HDS of the deasphalted oil and non-asphaltenic fraction obtained from the atmospheric residue of the Greek Thasos crude oil follow second order model⁽¹⁸⁾.

And where the hydrodesulphurization reaction supposed to be second order, equation (4) becomes:

$$\frac{1}{C_s} - \frac{1}{C_{S_o}} = \frac{k_2}{LHSV} \quad \dots\dots\dots (9)$$

Equation (9) indicates that in the absence of back mixing and liquid hold up effect or incomplete catalyst wetting effects.

The activation energy measures the amount of energy which reactants must have before they can overcome the barrier between them and the product state. The activation energy for the desulphurization reactions was calculated by using Arrhenius equation which satisfies the relationship between rate constants and the reaction temperatures⁽³⁾

$$k = A \exp(-E_a/RT) \quad \dots\dots\dots (10)$$

The activation enthalpy and entropy for the desulphurization reaction was calculated by using equation (11), which was obtained from the absolute reaction rate theory⁽¹⁹⁾:

$$\frac{k}{T} = K \frac{B}{H} \exp(\Delta S^*/R) \exp(-\Delta H^*/RT) \quad \dots\dots\dots (11)$$

EXPERIMENTAL WORK

The vacuum gas oil (VGO), used in the present work, was obtained from the distillation of atmospheric reduced crude (ARC) of Kirkuk crude oil in vacuum distillation tower of Biji refinery. The feedstock used in present work is a vacuum gas oil (VGO) with boiling range (611-833K) and prepared by blending the fractions light VGO (611-650K) , medium VGO (650-690K) ,

heavy VGO (690-727K), and very heavy VGO (727-833K) with the volume percentages 13.67 , 21.67 , 27 , 37.66 respectively. The properties of the VGO used are given in Table (1).

The catalyst used is a commercial cobalt-molybdenum on alumina (Co-Mo-alumina) type and its properties are shown in Table (2). The catalyst presulfided to promote its activity by charging 120 cm³ of the fresh catalyst to the hydrodesulphurization reactor after drying at 393K for two hours and using a solution of 0.6 vol. % of CS₂ in commercial gas oil. The first 4 hours of activation carried out at 21 bar and 477K with 4 hr⁻¹ liquid space velocity and no hydrogen flow. The next step of the activation spending 16 hr with the following conditions: temperature 573K, LHSV 1 hr⁻¹, pressure 2.1 MPa and hydrogen to oil ratio of 200 lt/lt.

The hydrodesulphurization (HDS) runs performed in a laboratory continuous high pressure unit employing an up-flow co-current trickle bed reactor. The reactor made of stainless steel and its dimensions are 65cm length and 2cm diameter and jacketed with five separately

heat-controlled block shells in order to keep a certain isothermal operation. The reactor products are cooled in a condenser-cooler and separated from unreacted hydrogen, H_2S and the hydrocarbon gases passing through a high and low pressure separators. The gases then vented to the exterior through a gas flow meter. The unit supplied with a high pressure dosing pump to introduce the feedstock to the reactor. A calibrated micrometer was fitted with pump to estimate the feedstock flow rate. The hydrogen fed to the reactor from a hydrogen cylinder through a heated high pressure line. The hydrogen flow rate estimated by electrical gas inlet flow sensor using standard calibrations with the electrical pulses. The catalyst bed in the reactor was located between two beds of inert material with dimensions of 13.5cm length. Fig. (1) shows the flow diagram of the HDS unit.

The HDS experiments of the VGO were carried out with temperature range of (583-643K) over liquid hourly space velocity (LHSV) ranging from 1.5 hr⁻¹ to 3.75 hr⁻¹, hydrogen pressure kept constant at 3.5 MPa, and hydrogen to feed ratio approximately 250 lt/lt was

employed for all experiments and when the steady-state operation was established, the products were collected.

The sulfur content in the feedstock and product were determined according to bomb method ASTM: D 129-64. This method consists mainly of bomb, sample cup, firing wire, and cotton wicking. The sample is oxidized by combustion in a bomb containing oxygen under pressure 4 MPa. The sulfur as sulfate in the bomb washings is determined gravimetrically as barium sulfate. Any other details are found in ref. (20).

RESULTS AND DISCUSSION

The hydrodesulphurization of vacuum gas oil in a fixed catalyst bed reactor is a complex process and many variables affect the extent of sulfur removal. The main variables are temperature, pressure, LHSV, and hydrogen to oil volumetric ratio. Through the present study, the hydrogen pressure and the hydrogen to oil ratio kept constant.

The % sulfur removal (x) increases with increasing the temperature and decreasing the LHSV as shown in Fig. (2) and these results are in agreement with

other studies on the HDS^(21,22). The increasing % sulfur removal at high reaction temperature may be attributed to several reasons. Firstly, the unreactive sulfur compounds which most properly belong to thiophene derivatives become activated enough to react with hydrogen and secondly, the aromatic compounds are decomposed to smaller molecules which can more easily diffuse into the catalyst micro and mesopores and reach the inner active sites where the desulphurization reaction mainly occurs⁽²³⁾. Thus, the upper temperature value is limited by the undesirable side reactions such as hydrocracking and thermal cracking reactions which are expected to occur at high temperature, as well as the contact time between the reacting fluids and catalyst decreasing when increasing the LHSV and this lead to the extent of sulfur removal decrease with increasing LHSV.

Data obtained from the laboratory unit for the desulphurization of the vacuum gas oil analyzed by the available kinetics models outlined above.

The data correlated with first order kinetics equation (4) assuming ideal plug flow models including the effect of fluid

flow. The results showed that hydrodesulphurization data have a deviation from the first order kinetics models as shown in Fig. (3) where the plot of $\ln(C_{s_o}/C_s)$ versus $(1=LHSV)$ usually results in an upward-curving line. The curvature could be due in part to a reaction order higher than 1.0 or to a distribution of reactivities in the sulfur compounds. The main reason is probably a change in wetted area with flow rate, since the fraction of surface wetted was probably small at the low flow rates that were used.

Fig. (4) shows the plots of $\ln[\ln(C_{s_o}/C_s)]$ versus $\ln(1/LHSV)$ according to equation (8) and gives an upward-curving line especially at high temperature. Thus, the results of hydrodesulphurization deviate from this model and when the data are regressed according to Eq. (10), this gives straight lines with slopes equal to $(1-\beta)$. The calculated values of β range is (0.134-0.386) and are increased with temperature increasing and not far from those obtained by Henry and Gilbert⁽¹²⁾ and Mohammed⁽²⁴⁾.

Second order kinetics model (Eq.9) is also used to fit the obtained data by plotting $(1/C_s) - (1/C_{s_0})$ versus $(1/LHSV)$ as shown in Fig. (5). The plot gives straight lines with slopes equal to rate constants (k_2) at each temperature and the model is agreed very well with the experimental data. Thus, the conversion results of reaction obeyed to second order reaction and the values of rate constants calculated at different temperatures are given in Table (3) and increased with the temperature.

A plot of $(\ln k_2)$ versus $(1/T)$ according to eq. (10) as shown in Fig. (6) gives a straight line with a slope equal to $(-E_a / R)$ from which the activation energy was calculated. The activation energy for desulphurization was found to be 80.3792 KJ/mol. This value is not far from value 87.1 KJ/mol obtained by Mann et al. ⁽¹⁴⁾.

A plot of $\ln (k_2/T)$ versus $(1/T)$ according to Eq. (11), as shown in Fig. (7), gives a straight line with slope equal to $(-\Delta H^*/R)$ from which the activation enthalpy can be calculated and the intercept of this line which is equal to $\ln(KB/H) + (\Delta S^*/R)$ may be used to calculate the activation entropy ΔS^* . Calculated values of ΔH^* and ΔS^* are,

75.2974 KJ/mol, and 197.493 J/mol respectively.

CONCLUSIONS

1. The hydrodesulphurization reaction of vacuum gas oil for Krikuk crud obeys second order kinetics model.
2. The reaction rate constants for hydrodesulphurization reaction increase with increasing reaction temperature, obeys Arrhenius equation.

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Table (1): The properties of feed stock VGO.

Specification	Value
Sp.gr. at 60/60 °F	0.911
°API	23.858
Viscosity (cst) at	
323 K	11.563
373 K	2.784
Pour point (K)	302
Flash point (K)	465
Aniline point (K)	325
CCR (wt. %)	0.58
Sulfur content (wt. %)	2.5

Table (3): Values of k_2 calculated.

Temperature,(K)	k_2 (hr. wt. %)-1
583	0.4064
603	0.5866
623	1.0897
643	1.8551

Table (2): The catalyst properties.

Chemical compositions	Value wt. %
MoO3	15.0
NiO	3.0
SiO2	1.1
Na2O	0.07
Fe	0.04
SO2	2.0
Al2O3	Balance
Physical properties	Value
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
Mean particle length (mm)	4

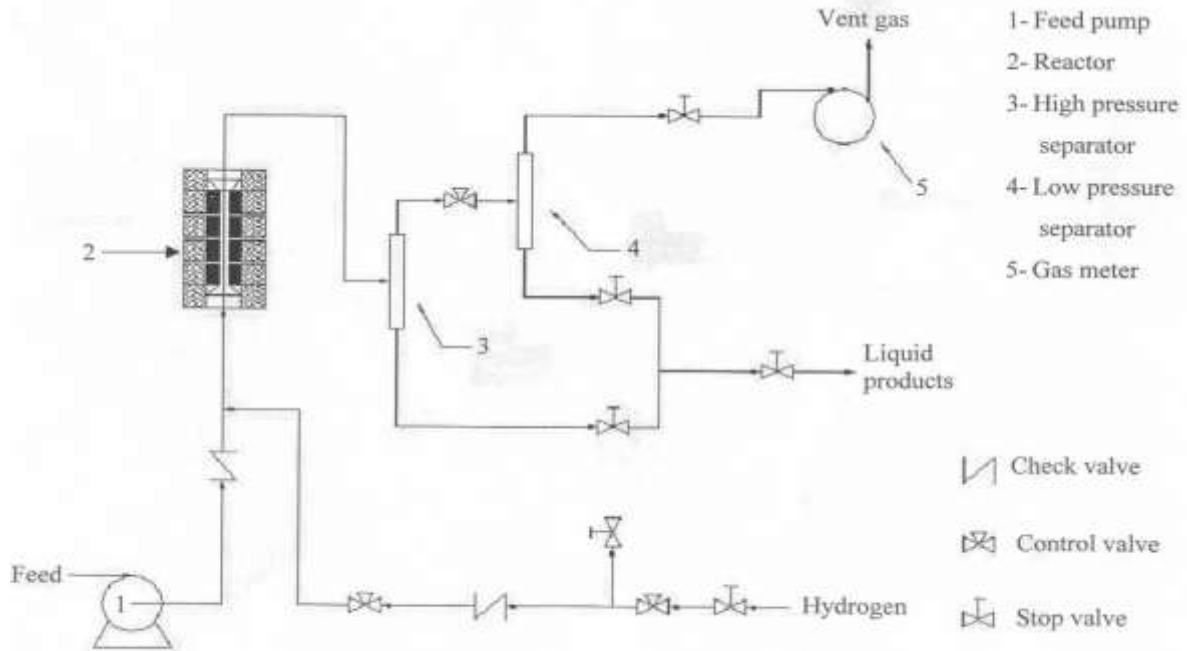


Fig. (1). Flow Diagram of Laboratory Hydrodesulphurization Unit

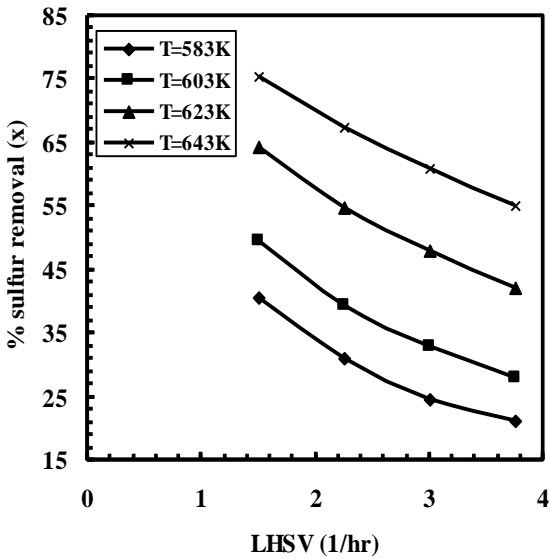


Fig.(2).Effect of LHSV on the % sulfur removal (x) from feedstock.

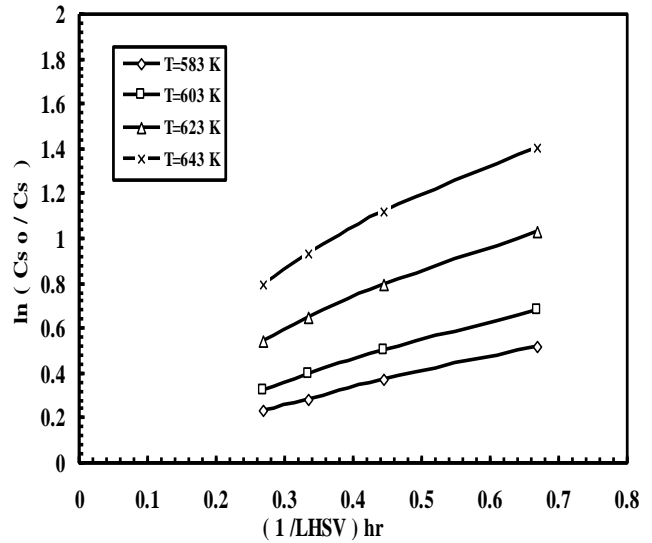


Fig.(3).The relation between $\ln(Cs o / Cs)$ and $(1/LHSV)$.

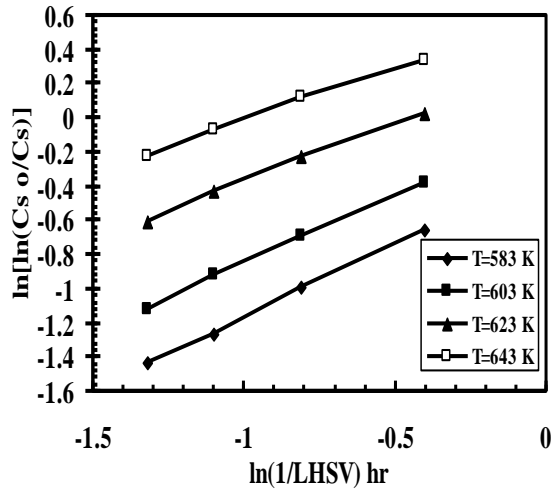


Fig.(4).The relation between $\ln[\ln(Cs o/Cs)]$ and $\ln(1/LHSV)$.

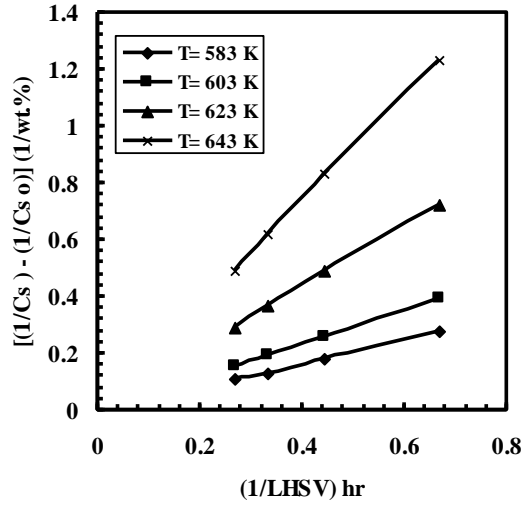


Fig.(5).The relation between $[(1/Cs) - (1/Cs o)]$ and $(1/LHSV)$.

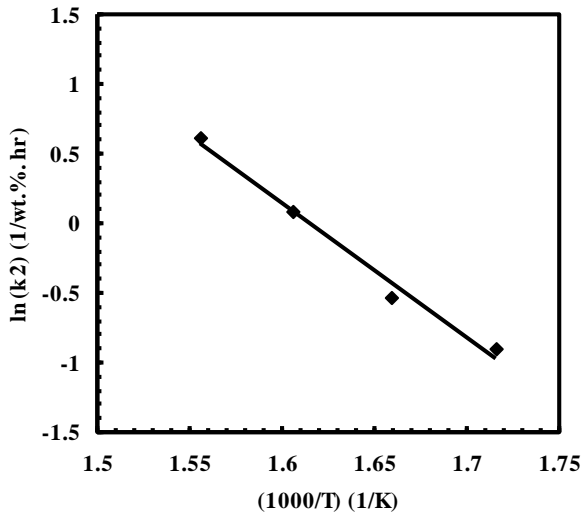


Fig.(6).The relation between $\ln(k2)$ and $(1/T)$.

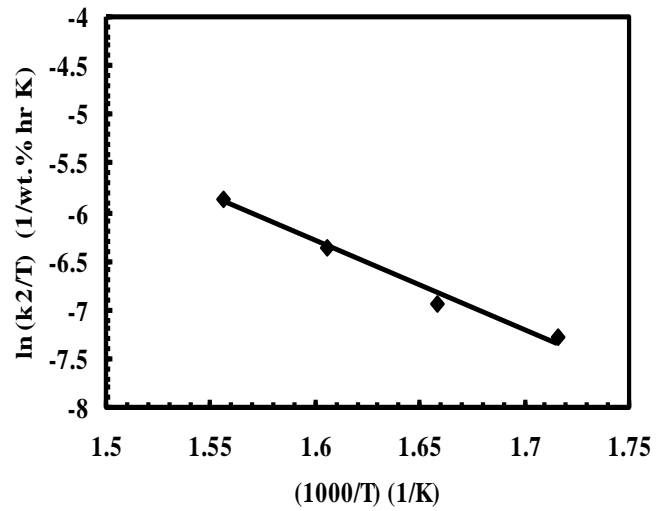


Fig.(7).The relation between $\ln(k2/T)$ and $(1/T)$.

دراسة نماذج حركية تفاعل المعاملة الهيدروجينية لنزع الكبريت من زيت الغازالفراغي المتقطر

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الخلاصة

تمت الدراسة بموجب عقد مع شركة مصافي الشمال / بيجي لدراسة حركية تفاعل عملية نزع الكبريت بوجود الهيدروجين لزيت الغاز الفراغي المتقطر من نطف خام كركوك والمستحصل عليه بمزج مقاطع زيت غاز خفيف ومتوسط وثقيل وتقليل جدا باستخدام المفاعل الخريبي المختبري (Trickle Bed Reactor) الذي يحتوي على عامل مساعد صناعي نوع كوبلت-موليبدينوم المحمل على الالومينا وقد اجري التفاعل عند مدى درجة حرارة (583-642) كلفن ومدى سرعة سائل فراغية (1.5-3.75) ساعة⁻¹ وضغط هيدروجين ثابت قدره (3.5) ميكاباسكال وان نسبة الهيدروجين إلى الزيت حوالي (250) لتر/لتر.

بينت نتائج الدراسة بان التفاعل هو من الدرجة الثانية وقد تم حساب قيم ثابت سرعة التفاعل ومن ثم حسبت طاقة التنشيط والتغير في الانتالبي والتغير في الانتروبي للتفاعل.

الكلمات الدالة: تفاعل المعاملة الهيدروجينية لنزع الكبريت ، زيت غاز فراغي ، مفاعل خريبي ، نماذج حركية تفاعل .