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Kinetic Studies of Hydrodesulfurization of Vacuum Distillate

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Abstract

Vacuum gas oil (611-833)K was distilled from Kirkuk crude oil, which was obtained by blending the following fraction, 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 condition in a laboratory trickle bed reactor. The reaction temperature varied from (583-643)K over liquid hourly space velocity ranging between (1.5-3.75)h-1 , Hydrogen pressure was kept constant at 3.5 MPa with a hydrogen to oil ratio of about 250 L/L

The conversion results for desulfurization appeared to obey the second order kinetics. According to this model rate constants for desulfurization reaction were calculated. Finally, the apparent activation energy (Ea), enthalpy of activation (ΔH^*) and entropy (ΔS^*) were calculated based on the values of rate constant (k). The calculated values of Ea, ΔH^* and ΔS^* were 74.657 kJ/mole, 74.712 kJ/mole and 167.132 J/mole.k, respectively.

Introduction

Kinetic studies using individual sulfur compounds have usually indicated that simple first-order kinetic with respect to sulfur are the predominate mechanism by which sulfur is removed from the organic material as hydrogen sulfide. However, there is still much learned about the relative rates of reaction exhibited by the various compounds present in petroleum [1].

Residue hydrodesulfurization is considerably more complex than the hydrodesulfrization of model organic sulfur compounds or, for that matter, narrow-boiling petroleum fractions. In published studies of the kinetic of residua hydrodesulfurization, one of the three approaches has generally been taken.

1-The reaction can be described in terms of simple first-order expression. Frye and Mosby [2] showed that the hydrodesulfurization kinetic of the three compounds found in cycle oil feed stock followed a first order model. It was proposed that the HDS reaction of petroleum distillates were also first order [3]. The Kirkuk reduced kinetics follow first order model [4].

2-The reaction of hydrodesulfurizatio can be described by use of two simultaneous first-order expressions, one expression for easy-to-remove sulfur and a separate expression for difficult-to-remove sulfur. The hydrodesulfurization of an Arabian lighit-atmospheric residuum could be represented as the sum of two competing first order reaction [5]. Arey et al [6] fitted kinetic data for heavy vacuum gas oil, atmospheric residues, vacuum residue and deasphaltened residue according to this model.

3-The reaction of hydrodesulfurization can be described using a second-order treatment. Application of this model to Kuwait vacuum residue using two type of catalyst gives a liner relation. Mohammed et al[7] show that the HDS of Qaiyarah deasphaltened reduced crude followed second order kinetic. The kinetic of the catalytic HDS of the deasphaltened oil and non-asphaltenic fraction obtained from the atmospheric residue of the Greek Thasos crude oil follow second order model[8]

For Completely wetting effects are negligible, the governing equation for the reaction performance and for first-order reaction may be expressed as[9].

$$\ln\left[\frac{C_{Ain}}{C_{Aout}}\right] = \left[\frac{k}{LHSV}\right] \qquad (1)$$

Where:

CA_{in}: inlet concentration, weight percent.

CA_{out}: outlet concentration, weight percent.

k: reaction rate constant,h-1

LHSV: liquid hourly space velocity.

And when the hydrodesulfurizatiopn reaction supposed to be second order the expression for second order –γ = Kc2A gives enough 2

$$\frac{1}{C_{Aout}} - \frac{1}{C_{Ain}} = \frac{k}{LHSV} \qquad (2)$$

Equation 1 and 2 indicate that in the absence of back mixing and liquid hold up effect or incomplete catalyst wetting effects,

A log-log of

$$\ln\left[\frac{C_{Ain}}{C_{Aout}}\right] and \frac{1}{C_{Aout}} - \frac{1}{C_{Ain}} vs \frac{1}{LHSV}$$

Should be straight line with slope equal to unity. Also at constant LHSV the conversion should be independent of catalyst bed length. When two simultaneous first order expression equation 3 may be used [10]

$$C_{Ain} = (S1)_0 \exp\left[-\frac{k1}{LHSV}\right] + (S2)_0 \exp\left[-\frac{k2}{LHSV}\right] \qquad (3)$$

Where:

$(S1)_0$ and $(S2)_0$: the initial compositions of easy and difficult to remove sulfur.

k_1 and k_2 : the reaction rate constant of easy and difficult to remove sulfur.

If back mixing is insignificant and conversion is highly related to liquid-hold up then modified Henry and Gilbert equation holds (9) when the desulfurization governs the first-order reaction it can be expressed as:

$$\ln\left[\frac{C_{Ain}}{C_{Aout}}\right] = \frac{kL^{\beta}}{(LHSV)^{1-\beta}} \qquad (4)$$

where:

L: length of catalyst bed

β: empirical constant

It can be shown from equation (4)that a log-log plot of

$$\ln\left[\frac{C_{Ain}}{C_{Aout}}\right] vs \frac{1}{LHSV}$$

Should yield straight line with a slope equal to (1-β).

Different values of β have been reported [11,12]. Henry and Gilbert took β = 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 (13) equation 5

$$\ln\left[\frac{C_{Ain}}{C_{Aout}}\right] = \frac{kL^{\gamma}}{(LHSV)^{1-\gamma}} \qquad (5)$$

where:

γ : empirical constant

Mears took γ = 0.32

A log-log plot of $\ln\left[\frac{C_{Ain}}{C_{Aout}}\right] vs \frac{1}{LHSV}$ gives a straight line with a slope equal to (1-γ)

Experimental Work

Feed stock

The feed stock in this investigation was the vacuum gas oil which was obtained by distillation unit of atmospheric reduced crude (ARC) of Kirkuk crude oil in Baiji refinery vacuum distillation unit. The percentage of VGO was 45vol.% of the original atmospheric reduced crude. The properties of the VGO is given in table 1.The feed stock preparation includes blending the fraction LVGO (611-650)K, MVGO (650-690)K, HVGO (690-727)K, and Very HVGO (727-833)K with the percentage volumes 13.67,21.67,27,and37.66 respectively. The resulted mixture represents actual Kirkuk crude oil vacuum distillate.

Table 1: The properties of feed stock (VGO)

Specification	**Value**
Sp.Gr. at 60/60 F	0.911
API °Gravity,	23.858
Viscosity ,cs at 323 K 373 K	11.563 2.784
Pour point, K	302
Flash point, K	465
Aniline point, K	325
CCR, wt%	0.58
Sulfur content, wt%	2.5

The catalyst

The catalyst employed for the HDS process in this investigation was the commercial Ni-Mo-alumina type catalyst .The properties of this catalyst are identified in table 2.

Table 2: The catalyst properties

Properties	**Value**
MoO_3, wt%	15.0
NiO, wt%	3.0
SiO_2,wt%	1.1
Na_2O,wt%	0.07
Fe, wt%	0.04
SO_2,wt%	2.0
Al_2O_3,wt%	*Balance*
Physical specification	**Value**
Form	*Extrudate*
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

The Hydrodesulfyrization Experiment

The HDS runs were performed in a laboratory continuous high-pressure unit employing an up-flow concurrent trickle bed reactor. The reactor is stainless, and heats resisting steel with dimensions of 65cm length, and 2cm diameter. Experiments were undertaken by varying the reactor temperature (583-643)K and ,LHSV (1.53-3.75)h-1 ,while the pressure kept constant at 2.5 Mpa. Details about the experimental procedure were described in other reference [14].

Test Methods

The sulfur content of the feed stock and products 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 4MPa. The sulfur as sulfate in the bomb washings is determined gravimetrically as barium sulfate.

Results and Discussion

Data obtained from the laboratory unit for the desulfurization of the vacuum gas oil were analyzed by the available kinetics models outlined in introduction.

Data were correlated with first order kinetics equation assuming ideal plug flow models including the effect of fluid flow :

Results show that hydrodesulfurization data have a deviation from the first order kinetics models as shown in figure 1. The results are treated accordingly to hold-up model of Henry and Gilbert (equation 4) and the incomplete catalyst-wetting model of Mears (equation 5)

As shown in figure 2 the plots according to equation (4) give straight lines with slope equal to (1-β). The calculated values of β varied from 0.135-0.39. The range of the values is not far from those obtained by Henry and Gilbert(9) and Mohammedetal(15).

Second order kinetics model equation (2) is also used to fit the obtained data by plotting

$$\frac{1}{C_{Sout}} - \frac{1}{C_{Sin}} vs \frac{1}{LHSV}$$

As shown in figure 3.

These plots give straight lines with slopes equal to rate constants. The values of rate constant calculated at different temperatures are given in table 3.

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 desulfurization reaction was calculated by using the Arrhenius equation, which satisfies the relationship between the rate of the reaction and temperature (1).

$$k = A\exp^{-(Ea/RT)} \qquad (6)$$

Where:

A: Equation constant, frequency factor or exponential factor

Ea: Activation energy (kJ/mol)

R: Gas constant (kJ/mol.K)

T: Temperature of reaction (K)

A plot of ln k vs 1/T as shown in figure 4 gives a straight line with a slope equal to –Ea/RT from which the activation energy was calculated. The activation energy for desulfurization was found to be 74.657 kJ/mol. This value is not far from value 87.1 kJ/mol obtained by Mann.at(16).

The activation enthalpy and entropy for the desulfurization reaction was calculated by using the equation (7), which was obtained from the absolute reaction rate theory [17]

$$\frac{k}{T} = K\frac{F}{h}\exp(\Delta S^{*}/R)\exp(\Delta H^{*}/RT) \qquad (7)$$

Where:

K: Transmission coefficient

F: Boltzman constant, J/K

H: Plank constant, J/S

ΔS*: Activation Entropy , J/mol.K

ΔH*: Activation Enthalpy, kJ/mol

A plot of ln k/T vs 1/T in figure 5 gives a straight line with slope equals to ΔH*/R from which the activation enthalpy can be calculated. The intercept of this line which is equal to ln(KT/h)+(ΔS*/R)may be used to calculate the activation entropy ΔS*. The values of calculated ΔH* and ΔS* are 74.712 kJ/mol, and 167.132 J/mol.K respectively.

Table 3: Results of activation energy, enthalpy and entropy calculations

Temperature K	k $(hr.Wt.\%)^{-1}$	Ea^* kJ/mol	ΔH_a^* kJ/mol	ΔS_a^* J/mol.K
583	0.421	74.657	74.712	167.132
603	0.593			
623	1.076			
643	1.856			

Conclusions

1-The hydrodesulfurization reaction of vacuum gas oil distilled from Krikuk crude obey the second order kinetics.

2- The reaction rate constants for hydrodesulfurization reaction is varying with the reaction temperature. The calculated values of reaction rate based on the reaction temperature increasing were 0.421,0.593,1.076,and 1.856 respectively

3-Activation energy , ennthalpy and entropy of hydrosulphurization reaction were calculated.

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