

HYDRODESULFURIZATION OF CRUDE OIL FRACTIONS USING Co-Mo/Al₂O₃ CATALYST *)

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ABSTRACT

Kinetic of hydrodesulfurization reaction is studied for crude oil fractions: Vacuum distillate, deasphalted oil, reduced crude oil and vacuum residue.

I. INTRODUCTION

Sulfur compounds of petroleum products must be removed to eliminate the air pollution. Hydrodesulfurization is the most modern and the most effective catalytic process for removing sulfur from oil products. Depending on the feedstock quality; desulfurization between 80 and 99 percent can be obtained. This process converts sulfur into hydrogen sulfide by reaction with hydrogen in the presence of catalyst.

Cobalt and molybdenum oxides on alumina catalysts are in most general use today because they have proven to be highly selective, easy to regenerate, and resistant to poison. Hydrodesulfurization catalysts which have a good performance, active for industrial use for hydrodesulfurization of crude oil fractions containing large amounts of catalyst poisoning material such as asphaltene and organic metallic compounds (2).

The ease of hydrodesulfurization is depended upon the type of compound. Lower-boiling compounds are more easily than higher-boiling ones. The difficulty of sulfur removal increases in order paraffins, naphthenes, aromatics (2).

In order to obtain more data about hydrodesulfurization process, and experiment has been carried out to study the hydrodesulfurization reaction rate of crude oil fractions using Co-Mo/Al₂O₃ catalyst. The operating conditions are: temperature from 360^o to 395^o and pressure

100 kg/cm². An autoclave apparatus unit with oscillation 200 rpm, has been used in these experiments.

II. EXPERIMENTAL

Crude oil fractions: i.e. vacuum distillate, deasphalted oil, reduced crude oil and vacuum residue as feedstock, purified hydrogen with a purity 99,5% by volume and typical hydrodesulfurization Co-Mo/Al₂O₃ catalyst has been used in these experiments.

The experiment has been carried out using an autoclave apparatus unit with oscillation: 200 rpm, the reactor volume: 500 cc and the inside diameter of reactor: 10 cm. The reactor temperature was regulated automatically. Liquid product samples at different in contact time have been taken for each feedstock. And sulfur content of these liquid products is analysed by ASTM D. 1551.

III. RESULTS

Hydrodesulfurization reaction of vacuum distillate, deasphalted oil, reduced crude oil and vacuum residue at the operating temperature 375^oC, is plotted as first order, i.e. $S \cdot 10^2/S_0 = f(\text{hour})$ on the Figure 1, and as second order i.e.: $(1/S - 1/S_0) = f(t, \text{hour})$ on the Figure 2. Base on the straight line of $(1/S - 1/S_0) = f(t, \text{hour})$ on this

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Figure 2, the kinetic of hydrodesulfurization reaction of these crude oil fractions is agree with the second order of reaction.

Arrhenius plot of rate constant of hydrodesulfurization reaction, i.e. $\log k = f(1/T, K)$, of vacuum distillate, deasphalted oil, reduced crude oil and vacuum residue is plotted on the Figure 3. And the activation energy (E) of hydrodesulfurization reaction of vacuum distillate, deasphalted oil, reduced crude oil and vacuum residue are obtained $E = 19.3; 23.2, 27.0$ and 29.4 kcal/mole respectively.

The reaction rate of hydrodesulfurization of those crude oil fractions are obtained as follows:

Vacuum distillate
 $(1/S - 1/S_0) = 2.53 \cdot 10^{10} e^{-19.3/RT} \times t$

Deasphalted oil
 $(1/S - 1/S_0) = 1.32 \cdot 10^{12} e^{-23.2/RT} \times t$

Reduced crud oil
 $(1/S - 1/S_0) = 1.38 \cdot 10^{15} e^{-27.0/RT} \times t$

Vacuum residue
 $(1/S - 1/S_0) = 1.16 \cdot 10^{16} e^{-29.4/RT} \times t$

Correlation between viscosity at $50^{\circ}C$ and conradson carbon number of feedstock, and the activation energy of hydrodesulfurization is plotted on the Figure 4. Observed activation energies of hydrodesulfurization reaction of those four types of crude oil fractions increase with both viscosity and conradson carbon number of feedstocks.

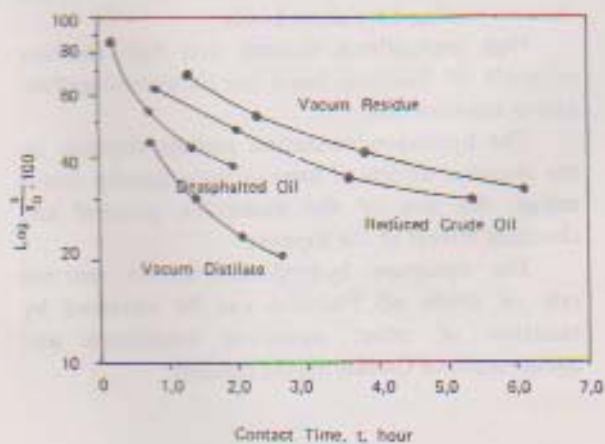


Figure 1. Influence of contact time (t) on the reaction rate of hydrodesulfurization.

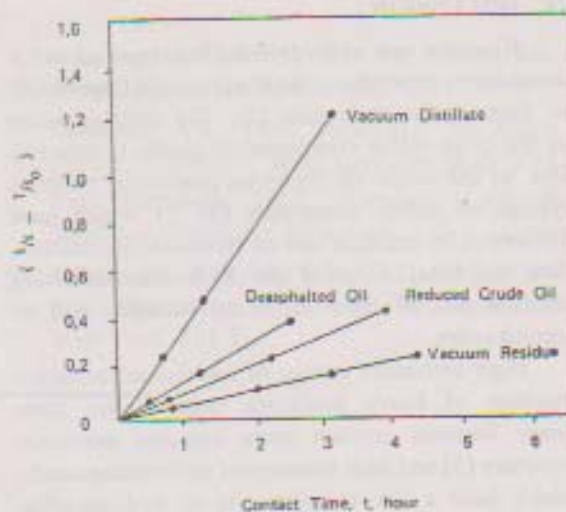


Figure 2. Influence of contact time (t) on the reaction rate of hydrodesulfurization of vacuum distillate, deasphalted oil, reduced crude oil and vacuum residue.

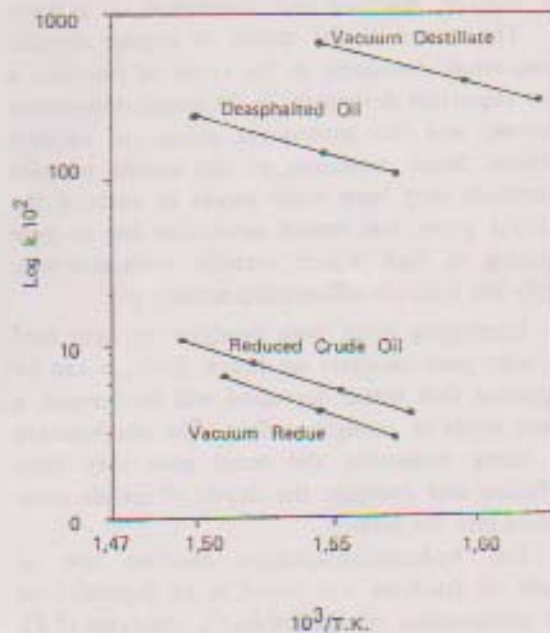


Figure 3. Hydrodesulfurization reaction of vacuum distillate, deasphalted oil, reduced crude oil and vacuum residue.

IV. DISCUSSION

Reaction rate of hydrodesulfurization of sulfur compounds depends on the structure and complexity of these sulfur molecules (3). The reaction order of the pure sulfur compound is closed to one (4). Due to the crude oil fractions, containing various typical of sulfur compounds (4) 2) which have difference in reaction rate of hydrodesulfurization, thus the total order of the hydrodesulfurization reaction rate of these crude oil fractions will be second order.

High activation energy of hydrodesulfurization reaction of heavy feedstock suggest that these heavy feedstock contain more complex molecular structure (5) and high viscosity of sulfur compounds, which have a low reaction rate of hydrodesulfurization.

As asphaltene acts as a catalyst poison, the heavy feedstock containing high asphaltene content, i.e. reduced crude oil and vacuum residue has a low reaction rate constant of hydrodesulfurization. And hydrodesulfurization reaction rate of crude oil fractions which free in asphaltene compound i.e. vacuum distillate and deasphalted oil is high.

The nature of the metals of organo metallic compounds containing in the crude oil fractions is very important determinat in the metals depositions process, and the subsequent effect on catalyst activity. Small molecules of this organo metallic compounds may have more succes in entering the catalyst pores, but metals saturation due to pore plugging of high organo metallic molecules may imply less hydrodesulfurization activity (6).

Employing small pore catalysts on light feed or large pore catalysts on heavy feeds, it can be suggested that metal deposited will be formed, a lower levels at catalyst surface. The combination of heavy molecules and small pore may limit diffusion and decrease the depth of metals penetration into the particle.

The hydrodesulfurization reaction rate of crude oil fractions was found to be depended on the composition of Co-Mo/Al₂O₃ catalysts (7,8).

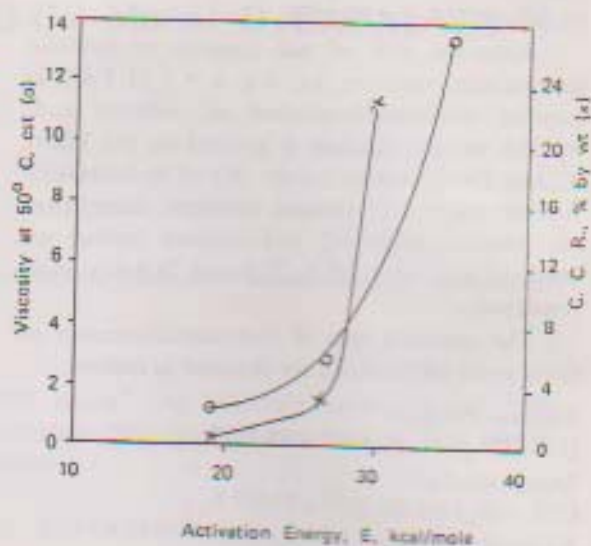


Figure 4. Correlation between viscosity at 50°C, Conradson carbon number (CCR) of feedstock and activation energy of hydrodesulfurization reaction.

V. CONCLUSIONS

Hydrodesulfurization reactions of vacuum distillate deasphalted oil, reduced crude oil and vacuum residue have second order.

High asphaltene content and high viscosity of crude oil fractions has a low its hydrodesulfurization reaction rate.

The hydrodesulfurization process depends on the chemical effects of form of the originally found sulfur, the size of the molecules, physical and chemical effects of the support.

The optimum hydrodesulfurization reaction rate of crude oil fractions can be obtained by variation of other operating conditions and composition of Co-Mo/Al₂O₃ catalyst.

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