

Estimation of activation energies during hydrodesulfurization of middle distillates

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Abstract

Hydrodesulfurization (HDS) of different petroleum distillates was carried out in a batch reactor using commercial CoMo catalyst and reaction conditions similar to industrial practice. Various experiments (agitation, particle size and amount of catalyst tests) were conducted with different hydrocarbon feeds to assure the operation under kinetic regime. Reaction orders and activation energies for each feed were determined by two approaches (linear and non-linear regressions). Both kinetic parameters (n and E_A) were found to follow a direct relationship with sulfur content in the feed. Reaction orders ranged between 1.96 and 3.36 and activation energies from 21.49 to 41.96 kcal/mol, which were within the range of those reported in the literature. High values of reaction order were attributed to contributions of HDS reaction of each individual compound exhibiting very different reaction rate constants.

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1. Introduction

The worldwide tendency is to impose more severe norms for fossil fuels due to the environmental impact of the polluting agents generated during combustion of gasoline, diesel and fuel oil. On the other hand, the increasing production of heavy crude oils and the need to incorporate them as feed to refineries, has provoked lot of problems when processing these heavy feedstocks. Particularly, the amount and type of sulfur compounds present in streams used as feed for hydrodesulfurization (HDS) processes have been adversely affected. In other words, new feeds to HDS processes possess higher sulfur content with low reactivity characteristics (the so-called

refractory compounds, e.g. dialkyldibenzothiophenes) [1].

But not only that, the future of fuels is more and more stringent, since most of the countries has announced specifications with almost “zero” level of sulfur (the so-called ultra-low sulfur fuels) [2]. This severe fuel policy represents a challenge in petroleum refineries because of the necessity for producing ultra-low sulfur fuels to protect the environment. For existing HDS plants, the options are limited to the use of more active catalysts, increase of reaction severity (e.g. increase of temperature and/or decrease of space-velocity), change of reactor internals to improve contact efficiency between hydrogen and hydrocarbons, or plainly to revamp the plant by installing more reactors in series to achieve deep hydrodesulfurization [1,3].

The complex nature of oil fractions with sulfur compounds exhibiting very different reactivities as well as the presence of other components such as nitrogen (basic and non-basic), aromatics, etc., which react at the same time and compete for the same active sites, and also the

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impossible to avoid inhibiting effect of by-products of the same reactions (e.g. hydrogen sulfide) have limited HDS experimental studies to model compounds ranging from easy-to-desulfurize (e.g. thiophene) to hard-to-desulfurize (e.g. 4,6-dimethyldibenzothiophene). These are the main reasons why few works have been reported dealing with experiments with real petroleum feedstocks under commercial conditions, since most of the times it is not simple to extract individual effects and one does not know which one to blame. However, when a catalyst formulation is almost ready for commercial application experiments with real feeds are mandatory. Testing with real feeds, not only for exploring the commercial application of new catalyst formulations but also for process design and optimization studies, is a very important step for new technology development. Consequently, kinetic data obtained from experiments with real feeds are of great interest, since they are employed for reactor modeling, simulation and optimization.

Kinetic studies for hydrodesulfurization can be divided roughly in two parts: those conducted with model compounds, and those carried out with real feeds. Kinetic studies for HDS of model compounds escape out from the scope of the present contribution, and we can only mention that different model molecules have been utilized for HDS experiments, such as thiophene, benzothiophene, dibenzothiophene (DBT), 4-methylDBT, and 4,6-dimethylDBT, and kinetics has been assumed (and confirmed) to follow first reaction order with reactivity decreasing as the sulfur atom in the molecule is more difficult to remove [4–7]. Other kinetic modeling approaches, e.g. Hougen–Watson kinetics based on the structural contribution, have also been reported [8].

In the case of HDS of real feeds n th order kinetics with respect to total sulfur concentration is usually applied, in which n value depends on several factors, such as type and concentration of sulfur compounds, catalyst properties, type of feed, operating conditions, experimental device, among others. In a previous paper [9], we have briefly reviewed information regarding the effect of type of feed on reaction orders and activation energies of hydrodesulfurization reactions, which by the way is scarce in the open literature. It was found that some authors use their experimental information to calculate reaction order which commonly ranges from 1.5 to 2.5, and others prefer to assume the value of n and then calculate the kinetic constant. Most of the values of reaction orders increases as the sulfur content in the feed also increases. However, this general increasing tendency of n with respect to sulfur in feed was not observed for activation energies, which may be due to differences in experimental conditions.

To get more knowledge about the kinetics of HDS of real feeds we have conducted systematic studies to evaluate the effect of the type of feed on reaction order and activation energy using experimental data obtained in a batch autoclave with commercial catalyst and different petroleum distillates.

2. Experimental

2.1. Materials

Four products from petroleum refining were used for hydrodesulfurization tests. Three of them were straight-run distillates (KS: kerosene, LSRGO: light straight-run gas oil, and HSRGO: heavy straight-run gas oil) and one was a cracked product from FCC unit (LCO: light cycle oil). The main properties of the four feeds are presented in Table 1. A CoMo commercial *ex situ* sulfided catalyst was employed, which properties are 119 m²/g specific surface area, 0.26 cm³/g pore volume, 0.8983 g/cm³ bulk density, 88 Å mean pore diameter, 2.42 wt% Co and 10.73 wt% Mo. All samples (hydrocarbons and catalyst) were recovered from a commercial hydrodesulfurization unit of a Mexican refinery.

2.2. Activity tests

Prior to each activity test, certain amount of fresh catalyst was first crushed and sieved to have the desired average particle size. Each catalyst sample was loaded to an atmospheric glass unit, in which activation was carried out. A 50 mL/min flow of hydrogen was passed through this unit and at the same time the temperature was increased up to 120 °C (50 °C/h). When the temperature reached 120 °C, it was kept for 0.5 h with the same H₂ flow. Next, hydrogen was passed through a container having CS₂ and the saturated mixture of H₂/CS₂ was passed through the reactor. Simultaneously the temperature was incremented up to 230 °C (50 °C/h). These conditions were maintained for 2 h. Although the catalyst is already sulfided (*ex situ*), CS₂ was used to assure complete catalyst sulfiding. Finally, the temperature was decreased to ambient conditions with a hydrogen flow of 15 mL/min. The activated catalyst was transferred very quickly into a batch reactor (1 L, Parr model) in nitrogen atmosphere in order to avoid contact with air for long time. This reactor contains the hydrocarbon feed (750 mL), in which hydrodesulfurization tests were carried out.

A schematic diagram of the reactor is shown in Fig. 1. After catalyst loading, the reactor was closed and pressurized with hydrogen to the desired value. Heating was started from room temperature to the required value. Stirring was started when temperature reaches the set point and the time was noted at that point as the beginning of the reaction. Temperature, pressure and stirring are controlled automatically using digital controller. A total of five reaction products were collected each hour.

Table 1
Properties of the feeds

	KS	LCO	LSRGO	HSRGO
Specific gravity 20/4 °C	0.8386	0.8610	0.8626	0.9007
Total sulfur (wt%)	1.047	1.326	1.436	1.831
Viscosity at 40 °C (cSt)	2.90	3.79	5.61	19.55

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