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A batch reactor study to determine effectiveness factors of commercial HDS catalyst

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Abstract

In this work we present a series of experiments in order to determine effectiveness factor of commercial hydrodesulfurization (HDS) catalysts. All the tests were carried out with straight-run gas oil (SRGO) and CoMo/γ-Al_2O_3 catalyst in a batch reactor at 54 kg/cm^2 pressure, 320–380 °C reaction temperature, 1000 rpm stirring and reaction times between 1 and 6 h. Four sizes of catalyst were employed for HDS experiments: (1) Commercial size, average particle size $d_p = 2.5$ mm, (2) $d_p = 0.833$ mm (20 mesh), (3) $d_p = 0.369$ mm (40 mesh), and (4) $d_p = 0.246$ mm (60 mesh). Before HDS tests all the samples were loaded to a continuous high-pressure reactor, then dried, soaked and sulfided with a mixture of SRGO and dimethyl disulfide (DMDS, 1 wt.% sulfur) at typical activation conditions. The effects of reaction temperature, reaction time, and catalyst particle size on hydrodesulfurization are discussed and reaction order, kinetic constants, effectiveness factors and activation energies are calculated for each particle size. The values of effectiveness factors are within those reported in the literature.

Keywords: Hydrodesulfurization; Effectiveness; Kinetic constant

1. Introduction

Before commercial application, all catalysts must be extensively studied in laboratory scale reactors. The successful design not only of the commercial catalysts but also of the industrial reactors depends primarily on the reliability of the experimentally determined parameters used in the scale-up [1].

Laboratory reactors are frequently employed for different purposes, among them for catalyst screening, evaluation of alternative feedstocks, kinetic parameters estimation, studies of the effect of operating conditions on product selectivities, prediction of the behavior of industrial scale reactors, etc. [2]. The selection of the experimental setup is related to the reacting system more than the type of industrial reactor, even when this latter is already defined. In other words, a laboratory reactor does not necessarily be a reduced scale replica of an industrial reactor [3].

Perego and Paratello [3] have published a review of experimental methods in catalytic kinetics in which some guidelines are given to select an appropriate experimental procedure and a suitable laboratory reactor for evaluating the kinetics for a given reaction system. They discussed the influence of transport phenomena due to the flow, the catalyst and the reactor geometry and the criteria for their absence. In a more recent paper, Bej [4] has also published a review of experimental techniques, but in this case, the review is focused on the performance evaluation of hydroprocessing catalysts, and the various reactors and approaches that have been used at different stages of hydroprocessing catalysis research and development are discussed. Similarly to Perego and Paratello [3], Bej [4] has also provided guidelines for selecting the appropriate reactor and methodology to evaluate hydroprocessing catalysts. Both reviews dedicate a section to highlight the characteristics and classification of batch reactors, and to discuss the advantages and disadvantages when using them for screening of catalyst, which can be summarized as follows [3,4]:

- In a batch reactor the catalyst and the reactants are charged into a vessel and brought to react as function of

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C_{As}	molar liquid phase concentration of A inside the solid
D_A	diffusion coefficient of A in the liquid phase
D_e	effective diffusivity of A in the pores of catalyst
D_K	Knudsen diffusivity
E_A	activation energy
k	intrinsic kinetic constant
k_{ap}	apparent kinetic constant
LHSV	liquid hourly space velocity
n	reaction order
MW	molecular weight
r_g	mean pore radius
S_g	specific surface area of particle
S_p	total geometric external area of particle
T	temperature
υ_A	molar volume of solute A
υ_L	molar volume of liquid solvent
V_g	pore volume per unit mass of catalyst
V_p	total geometric volume of catalyst

Greek symbols

η	effectiveness factor
θ	particle porosity
μ_L	liquid viscosity
ρ_P	particle density
τ	tortuosity
Φ	Thiele modulus

time, under specific conditions of temperature and pressure.

- The progress of the reaction is monitored by periodically analyzing the vessel content.
- Batch reactors are efficient, cheap and easy to operate.
- The catalyst can be either suspended in the liquid, the so-called slurry reactor, or kept in a spinning or static basket inside the reactor. For slurry reactors sufficient agitation is required to keep the catalyst suspended in the liquid. For spinning basket reactor the basket is rotated by suitable means having both the catalyst and the liquid with agitation, and for static basket reactor only the liquid is agitated.
- The main problem with batch reactors is the uncertainty of the reaction conditions, because bringing together reactants, catalyst, and operating conditions so that at zero time everything is as desired is not easy. For this reason, the reaction time is generally counted from the moment when the temperature of the reactor reaches the prescribed level.
- For hydrotreating experiments, the reaction pressure is controlled at the desired level during the course of the reaction by adding gaseous hydrogen to compensate its consumption.
- Ideal mixing to have global uniformity of concentrations and temperature throughout the reaction volume is easy to achieve. This means that with perfectly mixed batch reactors there are neither intrareactor nor interphase gradients. In the case of hydrotreating tests, a value of 1000 rpm stirring rate has been reported in the literature to be the minimum in which reaction rate is not limited by the external mass transfers [5].

Despite their disadvantages, batch reactors continue being utilized by researchers either for initial screening of catalyst formulations or for carrying out kinetic studies.

Catalysts are generally used in the form of crushed particles in order to operate under chemical reaction kinetic control. Although sometimes the catalysts can also be crushed to operate at an optimum level even under mass transfer control. During hydrotreating experiments carried out with model compounds, the recommended particle size to eliminate internal mass transfer limitations has been reported to be that obtained when sieving the catalyst with 60 mesh [5]. The common approach to verify this is to divide the catalyst into progressively smaller particles until further subdivision has no effect on the reactant conversion [3]. However, when a promissory catalyst formulation is obtained it needs to be tested in its probable commercially applied size and shape, which has to be eventually compared with a commercial reference catalyst. Most of the times, the available experimental information of the prototypes is different to that reported for commercial catalysts, and hence some tests at identical conditions have to be performed for that comparison.

One common test practiced by catalyst suppliers is to use the so-called standard real feed at also standard operating conditions, of course, with commercial size and shape particles. The standard feed can vary from one supplier to another, but in general they are synthetic feeds prepared by blending refinery streams to have certain concentration of contaminants. The standard operating conditions can also vary among suppliers but they should be very close or even identical to the commercial operation. In such tests, only the effect of operating conditions on conversion is frequently studied (activity test), or for the case of catalysts for heavy oils hydrotreating the effect of time-on-stream on conversion is also analyzed (stability test), and not too much attention is put on determining the kinetic behavior of the reaction with those commercial particles and real feeds.

The usual manner to represent kinetics of hydrotreating reactions when real feeds are employed is by means of power law model, since the use of more detailed models, such as Langmuir–Hinshelwood–Hougen–Watson (LHHW) model, may be difficult due to the different types of sulfur compounds present in a real feed as well as to the competitive adsorption effects on the active surface of the catalyst by aromatics and nitrogen compounds also present in the feed. In a very old paper, Weller [6] has pointed out some other reasons to use power law model instead of LHHW model, which remain relevant nowadays.

The basic kinetic information generated with power law model, such as reaction order, reaction rate constants, and activation energy, together with effectiveness factor calculation and the experimental data obtained during the common test in which the effect of operating conditions on conversion is studied, is a more complete approach to define the best catalyst formulation for a certain commercial application.

Various researchers have used power law model to describe the different hydrotreating reactions. For HDS, values of reaction order between 1 and 2.5 and activation energies in the range of 16–70 kcal/mol have been reported, which depend mainly on the type of feedstock and catalyst, operating conditions, and experimental setup [7]. Effectiveness factors of 0.4–0.6 for hydrodesulfurization reaction with commercial catalysts and real feeds have also been reported [8–11]. However, information of effectiveness factors for commercial catalyst is not abundant in the open literature. This motivated us to conduct some experiments with real feed and commercial catalyst with different particle sizes in a batch reactor at different reaction temperatures.

2. Experimental

A straight-run gas oil (SRGO) sample was employed for all HDS tests. The main properties of this gas oil are: 1.487 wt.% sulfur, 0.8632 specific gravity 20 °C/4 °C, and 208–375 °C distillation range. A commercial NiMo/γ-Al_2O_3 catalyst sample was also used, which has the following properties: 176 m^2/g specific surface area, 0.51 cm^3/g pore volume, 2.35 wt.% CoO, and 10.5 wt.% MoO_3. Both the SRGO and the catalyst were recovered from a commercial hydrodesulfurization unit of a Mexican refinery.

Prior to activity tests, the catalyst was first crushed and sieved to have samples with different average particle size (d_p): tri-lobular commercial size extrudates (2.5 mm), 20 mesh (0.833 mm), 40 mesh (0.369 mm), and 60 mesh (0.246 mm). Each catalyst sample was loaded to a high-pressure flow reactor (2.54 cm i.d., stainless steel) in which the activation was performed with the following procedure: the catalyst was dried for 2 h at atmospheric pressure and 120 °C with hydrogen flow. After drying, the catalyst was allowed for soaking with SRGO during 2 h at 150 °C and then the sulfiding agent was introduced. This sulfiding agent was a mixture of SRGO and dimethyl disulfide (DMDS, 1 wt.% sulfur). The H_2S is produced by decomposition of DMDS in situ. Sulfiding was done at 28 kg/cm^2 pressure at two different temperatures. First sulfiding was carried out at 260 °C for 3 h and finally it was done at 320 °C for 8 h.

Once the activation was finished, reactor temperature is reduced from 320 to 200 °C at a rate of 30 °C/h. When 200 °C temperature is achieved, the sulfiding feed is changed to another lighter feed (naphtha) without stopping hydrogen flow. Reactor cooling is continued from 200 to 40 °C at a rate of 20 °C/h. When temperature is of 40 °C, naphtha flow is stopped and at the same time hydrogen is changed to nitrogen to have an inert atmosphere. Pressure is then reduced from the operating value to atmospheric and temperature is decreased from 40 °C to ambient. When these conditions are reached, the catalyst is unloaded and immediately transferred to a clean and dry vessel. The reactor and the vessel have to be with nitrogen bubbling before and after catalyst unloading to prevent its oxidation.

Ten grams of sulfided catalyst is transferred in inert atmosphere to a Batch reactor (Parr 4842 model) containing 1 L SRGO. The batch reactor is then closed and pressurized with hydrogen to a value of 54 kg/cm^2 and the desired reaction temperature is achieved. The reaction was carried out at temperatures of 320, 340, 360, and 380 °C during 6 h with vigorous stirring (1000 rpm). For each temperature, fresh sample of sulfided catalyst was employed. Temperature, pressure and stirring are controlled automatically. A total of six reaction products were collected each hour and product sulfur content was analyzed by X-ray fluorescence following the ASTM D4294 method.

3. Results and discussion

3.1. Effect of reaction temperature on hydrodesulfurization

The effect of temperature on HDS was studied in the range of 320–380 °C keeping constant the reactor pressure at 54 kg/cm^2 for the different particle sizes. For each temperature six samples were taken out from the reactor, one each hour. The products were analyzed to determine the sulfur content and hence the percentage of hydrodesulfurization defined as:

$$\mathrm{HDS}\,(\%) = \left(\frac{S_{\mathrm{feed}} - S_{\mathrm{prod}}}{S_{\mathrm{feed}}}\right) \times 100 \tag{1}$$

where S_{feed} and S_{prod} are the total sulfur contents in weight percentage in the feed and in the product, respectively.

An example of the final results obtained in the batch reactor for the commercial size extrudates is shown in Fig. 1. The well-known behavior reported in the literature for this type of reactions is observed, that is the higher the reaction temperature and time the higher the sulfur removal. For the other sizes the same tendencies were obtained. In general, the percentages of HDS for the different particles sizes were: 3.4–74.0% for commercial size, 8.9–79.0% for 20 mesh, 13.2–82.3% for 40 mesh, and 15.6–85.3% for 60 mesh. It should be mentioned that these values cover a wide range of sulfur removals.

3.2. Effect of catalyst particle size on hydrodesulfurization

Fig. 2 shows the percentage of hydrodesulfurization as function of particle size represented as $1/d_p$ for different reaction temperatures. In this figure only the results obtained at 6 h time are presented. It is observed that as the particle size is diminished removal of sulfur is increased. It is also

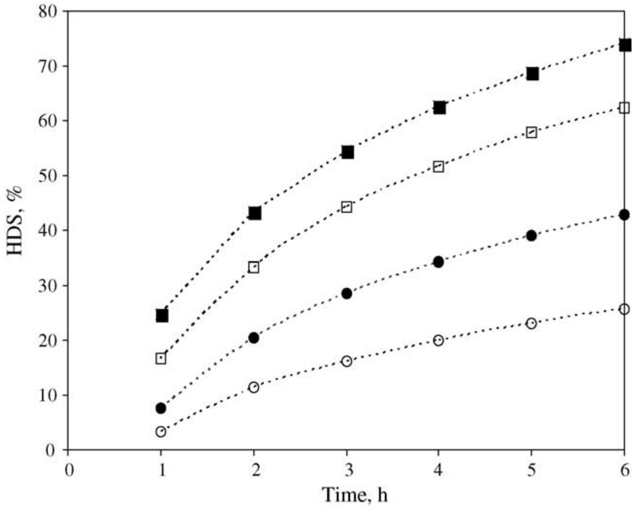

Fig. 1. Effect of time and reaction temperature on HDS for the commercial particle size: (○) 320 °C, (●) 340 °C, (□) 360 °C, (■) 380 °C.

seen from this figure that the commercial catalyst showed the lowest conversions.

3.3. Reaction order and kinetic constants

Based on the reports in the literature about the effect of stirring rate on batch reactors behavior [3–5], we can assume that the 1000 rpm stirring used in our experiments is the optimal value to have a perfectly-mixed system in which intrareactor and interphase gradients can be neglected, then the concentration of sulfur (C_S) as function of time (t) for the power-law kinetic model can be easily determined as follows:

$$C_S = [(n-1)k_{ap}t + C_{S0}^{1-n}]^{1/(1-n)} \tag{2}$$

In this equation k_{ap} represents the "apparent" kinetic constant, which may be influenced by intraparticle gradients depending on the catalyst particle size.

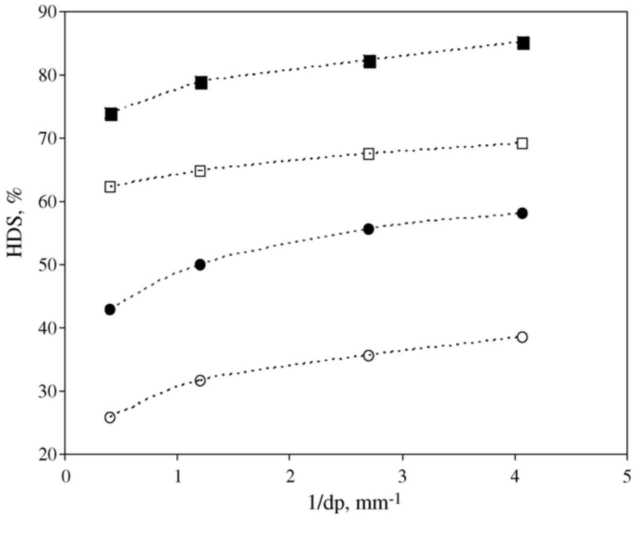

Fig. 2. Effect of particle size and reaction temperature on HDS for 6 h time: (○) 320 °C, (●) 340 °C, (□) 360 °C, (■) 380 °C.

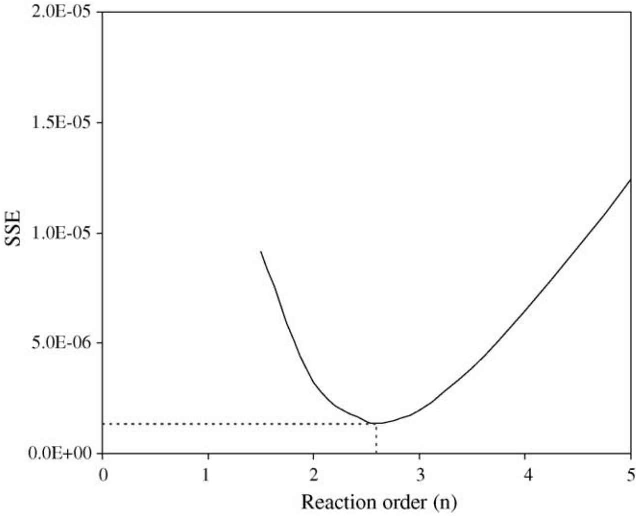

Fig. 3. Sum of square errors of the differences between experimental and calculated sulfur contents.

For the four temperatures and catalyst particle sizes the best values of n and k_{ap} were determined by minimization of the sum of square errors (SSE) between experimental sulfur concentrations and those calculated with Eq. (2). The optimization process for n is shown in Fig. 3. The optimal value of reaction order was found to be 2.6. The order of reaction with respect to total sulfur has been reported to depend on the type and composition of the individual sulfur compounds in the oil [7]. For SRGO hydrodesulfurization, reaction order has been found to be lower than that found here. However, our feed exhibits high sulfur content (1.487 wt.% S) compared with the common feeds reported in the literature. Hence, a higher value of n probably indicates a very wide spectrum of sulfur compounds of significantly different individual HDS rates.

Fig. 4 shows a lineal transformation of Eq. (2) for $n = 2.6$ for the case of commercial catalyst size at different temperatures in which the good fit is clearly demonstrated with values of r^2 higher than 0.978. The slope of each straight line gives directly the value of k_{ap}. All the values of kinetic constants calculated by this means are summarized in Table 1. It is observed that the lower the particle size and the higher the temperature the higher the kinetic constant values.

3.4. Effectiveness factor

Because of the commercial catalyst crushing and sieving process the smallest particle size (60 mesh) studied in this work was assumed to have sphere shape and then the effectiveness factor (η) can be determined as function of Thiele modulus (Φ) with the following equation valid for sphere particles [12]:

$$\eta = \frac{3(\phi \coth \phi - 1)}{\phi^2} \tag{3}$$

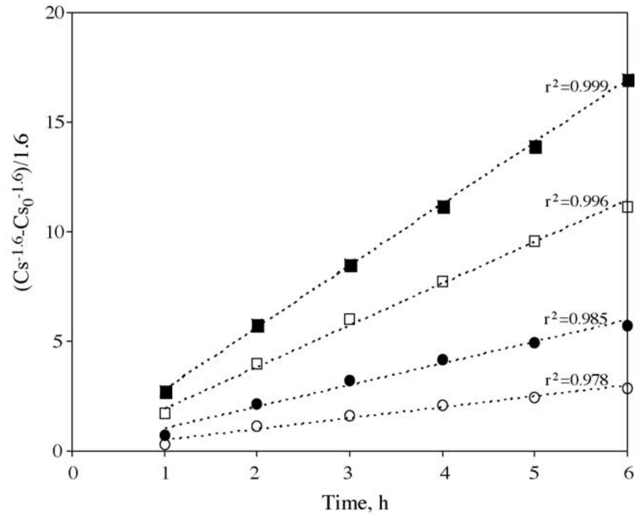

Fig. 4. Power-law model for $n = 2.6$ for commercial catalyst at different reaction temperatures: (○) 320 °C, (●) 340 °C, (□) 360 °C, (■) 380 °C.

The generalized Thiele modulus for *n*th-order irreversible reaction is [12]:

$$\phi = \frac{V_\mathrm{p}}{S_\mathrm{p}}\left[\left(\frac{n+1}{2}\right)\frac{kC_\mathrm{As}^{n-1}\rho_\mathrm{P}}{D_\mathrm{e}}\right]^{0.5} \tag{4}$$

Effective diffusion (D_e) was determined with the following equation [12]:

$$D_\mathrm{e} = \frac{\theta}{\tau}\left(\frac{1}{\frac{1}{D_\mathrm{A}}+\frac{1}{D_\mathrm{K}}}\right) \tag{5}$$

The molecular diffusivity of solute A in the liquid and Knudsen diffusion are [12,13]:

$$D_\mathrm{A} = 8.93\times10^{-8}\,\frac{\upsilon_\mathrm{L}^{0.267}T}{\upsilon_\mathrm{A}^{0.433}\mu_\mathrm{L}} \tag{6}$$

$$D_\mathrm{K} = 9700 r_\mathrm{g}\left(\frac{T}{\mathrm{MW}}\right)^{0.5} \tag{7}$$

where υ_L and υ_A are molar volume of solute and liquid solvent respectively, and μ_L is the dynamic liquid viscosity which were estimated with correlations reported in the literature [14,15].

Catalyst porosity (θ) and mean pore diameter (r_g) were calculated with the following equations from experimental data of specific surface area (S_g), total pore volume (V_g), and particle density (ρ_P). Tortuosity factor (τ) was assumed to be 4 according to literature reports [11].

$$\theta = \rho_\mathrm{P} V_\mathrm{g} \tag{8}$$

$$r_\mathrm{g} = \frac{2\theta}{S_\mathrm{g}\rho_\mathrm{P}} \tag{9}$$

For 60 mesh particle size, effectiveness factors at the different temperatures were virtually one.

To be sure that with 60 mesh particle size the reaction is kinetically controlled we conducted some experiments at 360 °C reaction temperature with particle sizes smaller than 60 mesh. The results are given in Fig. 5 in which it is clearly observed that a further reduction of particle size gives the same hydrodesulfurization level than 60 mesh. It has been shown that if the conversion varies by decreasing the particle size, intraphase mass transfer is limiting, whereas a constant conversion indicates that the system is under chemical kinetic control [3,5]. Therefore, it is demonstrated that this particle size is small enough to eliminate internal mass transfer limitations and then effectiveness factor calculated with the above procedure is correct.

Once the particle size for eliminating intraparticle gradients has been defined, effectiveness factor for other shapes can be evaluated with the following equation, which employs values of intrinsic kinetic constant (*k* determined with 60 mesh particle size) and apparent kinetic constant (k_ap determined with the other particle sizes) [12]:

$$\eta = \frac{k_\mathrm{ap}}{k} \tag{10}$$

Effectiveness factors calculated by this means are shown graphically as function of catalyst particle size and temperature in Fig. 6. It is seen that the higher the temperature the lower the effectiveness factor, and the lower the catalyst

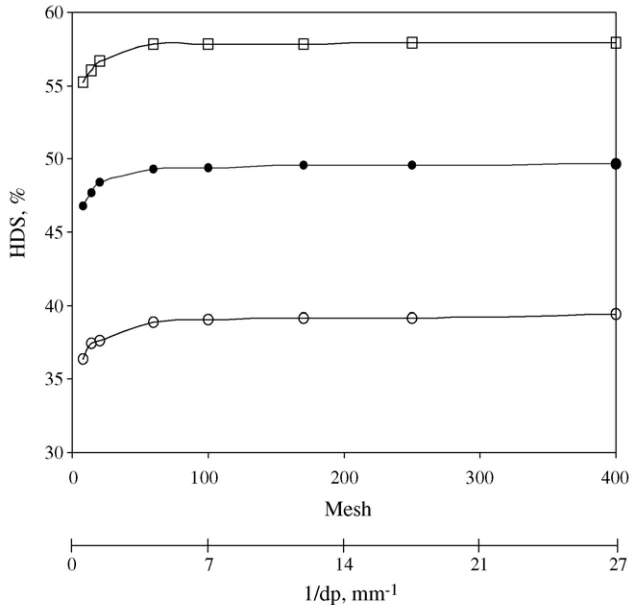

Fig. 5. Effect of particle size on HDS at 360 °C for different times: (○) 2 h, (●) 4 h, (□) 6 h.

Table 1
Kinetic constants for different catalyst particle sizes $(\mathrm{g/cm^3})^{-1.6}\,\mathrm{s^{-1}}$

Temperature (°C)	Commercial catalyst size	20 mesh	40 mesh	60 mesh
320	0.0180	0.0406	0.0653	0.1684
340	0.0290	0.0653	0.1138	0.2659
360	0.0380	0.0851	0.1401	0.3632
380	0.0443	0.1017	0.1780	0.4696

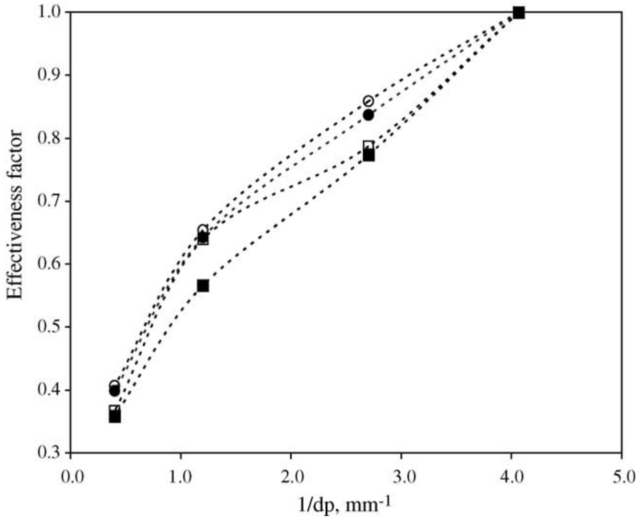

Fig. 6. Effect of particle size and reaction temperature on catalyst effectiveness factor: (○) 320 °C, (●) 340 °C, (□) 360 °C, (■) 380 °C.

particle size the higher the value of effectiveness factor. This behavior has also been reported by others [16,17]. For commercial particle size values of effectiveness factors of 0.4–0.55 were obtained which are within the range reported in the literature [8–11].

3.5. Activation energy

Activation energies for each catalyst particle size were determined with Arrhenius equation and are shown in Fig. 7. The expected behavior when internal mass transfer limitations are eliminated is observed, that is as the catalyst particle size is reduced the activation energy increases [18]. For commercial catalyst and 20 and 40 meshes there is no significant difference in activation energies (27.59–27.93 kcal/mol), however, 60 mesh exhibited a higher value of activation energy (29.37 kcal/mol).

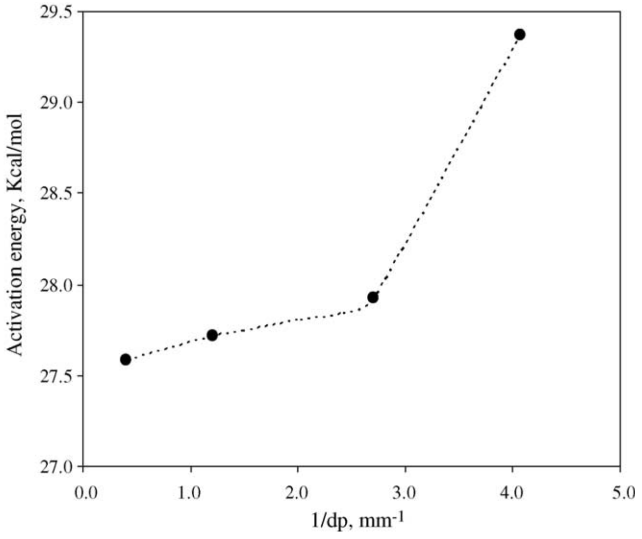

Fig. 7. Activation energy as function of catalyst particle size.

4. Conclusions

Values of effectiveness factors between 0.40 and 0.55 were obtained in the present work when employing typical hydrodesulfurization catalyst in industrial size and shape, which indicates that intraparticle mass transfer limitations are present during HDS reaction with commercial catalyst size.

Activation energy showed an increase when reducing particle size which also supports the fact that internal mass transfer gradients are found in commercial catalyst size.

Catalyst particles crushed and sieved with 60 mesh (0.246 mm average particle size) are small enough to conduct experiment under kinetic control. This means that the commercial catalyst size has to be reduced by about ten times to eliminate internal mass transfer limitations.

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