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Testing of hydrodesulfurization process in small trickle-bed reactor

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Abstract

The influence of some reaction parameters on hydrodesulfurization (HDS) in the experimental trickle-bed reactor (Andreas–Hofer apparatus) was investigated. A mixture of two gas oils (atmospheric gas oil and light cyclic oil from FCC) was used as feed. The investigations were performed at 300 °C, under space velocity from 1.0 to 2.5 $m^3\,m^{-3}\,h^{-1}$, hydrogen pressure of 40 and 65 bar, at H_2/CH ratio from 100 to 500. A simple reactor and a kinetic model were used, yielding good agreement between experimental and theoretical values of sulfur concentrations. Simulation experiments were performed by changing H_2/CH ratio, pressure and LHSV. The correlation recorded between the changed parameters and sulfur content was in that with higher pressure and ratio of H_2/CH the percentage of removed sulfur increased. Increased space velocity produced opposite effect. These experimental results and the change of either one or more process parameters or of the catalyst type enabled performance of the industrial reactor.

Keywords: Hydrodesulfurization; Gas oil; Process conditions

1. Introduction

Hydrodesulfurization (HDS), a fundamental step in the production of petroleum fuels [1–5], is of particular importance for the improvement of both feed and process products properties. This results from the basic role of hydrotreatment, the process aimed at removal of sulfur, nitrogen, and aromatics and of other undesired compounds from oil fractions. Apart from protecting the catalyst in the processes where sulfur and nitrogen compounds act as catalytic poisons, hydrodesulfurization is performed to improve products quality in terms of their chemical stability, color, odor, cetane number, etc. [6–16].

The problem of excessive sulfur in motor fuels is basically related to catalytic cracking, bringing total sulfur content in motor gasoline to up to 95%. In other words, quality parameters of petroleum fuels are directly associated with the process in question [17–24]. Because of this, hydrodesulfurization of gas oils is a very important process, as these oils are used as feedstocks in catalytic cracking.

Pollution problems are forcing changes in fuel specifications. Motor fuel quality in future need to be modified to improve combustion quality and exhaust gas clean-up performance.

Sulfur content in fuels must be eliminated to very low value (below 50 ppm) required by the new regulations expected in the near future and several proposals can be made, for example:

- increase of catalyst activity with new types of catalysts;
- increase the process severity mainly higher hydrogen pressure and/or ratio hydrogen/oil;
- development of new non-catalytic processes.

The main goal of article is to show how the experiments conducted in Andreas–Hofer apparatus can be utilized for real predictions of the process conditions in industrial plant. We tried to illustrate how the severe process conditions (increasing pressure and ratio H_2/CH) influence on decreasing of sulfur content in products.

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Nomenclature

A_s	cross-sectional area (m^2)
C_S	dimensionless sulfur concentration
H_2/CH	hydrogen/feed ratio
k	kinetic constant (s^{-1})
L	reactor length (m)
LHSV	liquid hourly space velocity, v/(v catalyst h) ($m^3\,m^{-3}\,h^{-1}$)
n	exponent in kinetic model
P	pressure (bar)
r_S	reaction rate ($mol\,m^{-3}\,s^{-1}$)
SD	normalized mean square deviation
T	temperature (°C)
u	linear velocity ($m\,s^{-1}$)
V_u	total volumetric flow rate ($m^3\,s^{-1}$)
X_S	conversion of sulfur compounds
X_{Se}	experimental conversion
X_{St}	theoretical conversion
z	axial distance along a reactor

Greek letter

τ	dimensionless space time

It is obvious that the knowledge of kinetic constant in the rate equation is important for the prediction and the simulation of an existing industrial plant by changing the process conditions, for example, the pressure, temperature or ratio H_2/CH. All results were obtained from the real experiments and can be valuable for process design of industrial plant.

So, knowing the estimated kinetic constants, we were be able to change the given process variables (parameters) like pressure, ratio H_2/CH and LHSV without conducting new experiments. On the basis of proposed and verified reactor and kinetic model, simulation was performed to see how the changed process variables change the sulfur content in the product.

The experiments in this study were performed with the mixture of two gas oils as a feedstock and with two hydrotreating catalyst components (85 vol.% HDS and 15 vol.% hydrodenitrification (HDN)) as a catalyst. Based on the experimental results, a kinetic model was designed and tested [25–28]. Also, the process was simulated under changing key variables.

2. Experimental

2.1. Feed and the catalyst

A test was performed with the mixture of gas oils as feed and by applying the appropriate catalyst for hydrodesulfurization (85%) and hydrodenitrification (15%). The feed and catalyst properties are shown in Table 1.

Table 1
Physico-chemical properties of the feedstock and catalyst

	HDN	HDS
Catalyst		
NiO (%)	3.0	–
CoO (%)	–	3.1
MoO_3 (%)	13.0	12.4
Extrudate diameter (mm)	1.6	1.3
Bulk density (g/cm^3)	0.81	0.71
Specific area (m^2/g)	155	265
Pore volume (cm^3/g)	0.45	0.54
Crushing index (%)	99	98
Feedstock		
S (ppm)	13200	
Density (15 °C) (g/cm^3)	0.8630	
Viscosity (40 °C) (mm^2/s)	3.7	
Cetane index	49	
ASTM distillation (°C)		
IBP	225	
10%	250	
30%	270	
50%	288	
70%	314	
90%	359	
FBP	400	

2.2. Methods

Hydrodesulfurization was performed in a high-pressure test plant (‘Andreas–Hofer’) (Fig. 1).

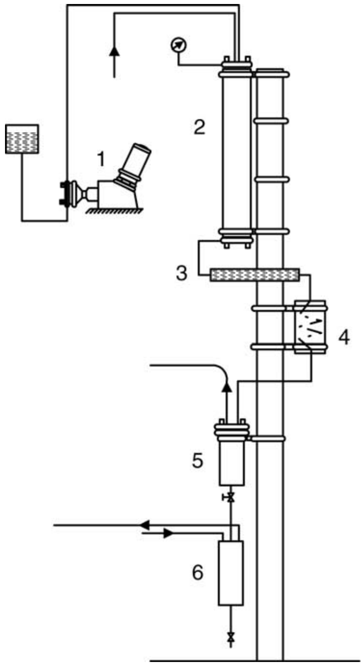

Fig. 1. Schematic presentation of the hydrodesulfurization device.

Physical properties of the tested feed and samples were determined by standard methods: density (EN ISO 3675), viscosity (EN ISO 3104), ASTM distillation (ISO 3405) and cetane index (EN ISO 4264).

Chemical properties were determined using automatic analyzer LECO CHNS-932 for carbon and hydrogen content. Sulfur content was determined with METOREX X-MET 920 (X-ray) fluorescent spectrometer.

2.2.1. *Process description*

The mixture of gas oils was carefully dosed, using the pump from the dispensing vessel, and mixed with hydrogen at the reactor inlet. In the reactor gas oil and hydrogen were heated to the operating temperature and under operating pressure, and passed through the catalyst layer, where the reactions proceeded. After the reactor, the hydrotreated product was cooled with water in the pre-cooling and cooling section. To separate gas, the condensed hydrotreated product was transferred to a high-pressure separator. The separated gas contained unreacted hydrogen and smaller volumes of hydrogen sulfide, compounds of hydrocarbons and ammonia, and other gases and vapors. A liquid product was periodically released into a low-pressure separator to be rinsed with argon under higher temperature by which gas leftovers and low volatility components were removed. A finished hydrotreated product was released into the receiving vessel for the stripped product. Gaseous products were released into the atmosphere, through a dedicated pipeline.

2.2.2. *Experimental equipment*

The mixture of gas oils was treated in the high-pressure test plant, comprising: (1) dosing pump for hydrotreatment mixture; (2) pipe reactor; (3) pre-cooler; (4) serpentine cooler; (5) high-pressure separator; and (6) section for stripping of the hydrotreatment mixture.

2.2.3. *Process conditions*

Hydrotreatment was performed under the following process conditions:

1. $H_2/CH = 0.118$, 0.354 and 0.590 N m^3/kg;
2. LHSV = 1.0, 1.5, 2.0, 2.5 m^3 m^{-3} h^{-1};
3. pressure = 40 and 65 bar;
4. temperature = 300 °C.

3. Results and disscusion

Hydrodesulfurization (HDS) and hydrodenitrification (HDN) of the mixture of gas oils were carried out in the test plant under conditions approximating those in industrial processes. Also, the conventional feedstock and the catalyst were used. The purpose was to determine how change of a particular reaction parameter effected removal of sulfur from feedstock. A series of experiments was carried out under different pressure (40 and 65 bar), space velocity (1.0; 1.5; 2.0 and 2.5 m^3 m^{-3} h^{-1}), H_2/CH ratio (0.118, 0.354 and 0.590 N m^3/kg) and temperature of 300 °C. Each sample of gas oil was analyzed for sulfur content, density, viscosity and cetane index. Also, ASTM distillation and ^{1}H NMR spectroscopy were made to determine composition of the products with respect to the initial composition of feedstock. The examples are shown in Tables 2 and 3.

Table 2
Hydrodesulfurization product properties under the following process conditions: $P = 40$ bar, LHSV = 1.0 m^3 m^{-3} h^{-1}, $T = 300$ °C, H_2/CH ratio 0.118, 0.354 and 0.590 N m^3/kg

	H_2/CH ratio (N m^3/kg)		
	0.118	0.354	0.590
S (ppm)	671	223	210
X_{HDS} (%)	94.92	98.31	98.41
Density (15 °C) (g/cm^3)	0.850	0.848	0.849
Viscosity (40 °C) (mm^2/s)	3.4	3.5	3.5
Cetane index	52	53	53
ASTM distil (°C)			
IBP	222	224	212
10%	245	246	244
30%	265	265	265
50%	283	284	284
70%	308	308	310
90%	354	354	355
95%	380	382	378
FBP	390	390	382

The results show the influence of process parameters on physico-chemical properties of the products and on the conversion of sulfur compounds. All experiments show the reduction of sulfur content, density and viscosity, as well as increase of cetane number values compared with the initial feedstock. ^{1}H NMR spectroscopy showed characteristic changes developed during hydrodesulfurization. Decrease in the content of aromatic rings hydrogen ($H_{arom.}$) was caused by their hydrogenation. Increase in monoaromatic rings protons with regard to the condensed aromatic rings protons showed predominance of hydrogenation of the condensed aromatic compounds.

3.1. *A reactor model*

Mathematical models for a trickle-bed catalytic reactor can be very complex due the many micro and macro effects occurring inside the reactor: flow patterns of both phases, size and shape of a catalyst particles, wetting of the pores of a catalyst with liquid phase, pressure drop, intraparticle gradients, thermal effects and, of course, kinetics on the catalyst surface.

It seems preferable to reduce complexity of the system, taking into account the importance of various processes. This suggests construction of a simpler model that incorporates all main features of many processes, but with fewest parameters possible.

The reactor was considered in steady-state operation with plug flow of gas and liquid phase.

Table 3
The results of gas oils ^{1}H NMR spectroscopy before and after hydrodesulfurization under the following process conditions: $P = 65$ bar, LHSV = 1.0 m^3 m^{-3} h^{-1}, $T = 300$ °C and H_2/CH ratio = 0.354 N m^3/kg

Gas oils mixture	Before hydrotreatment	After hydrotreatment
Protons of monoaromatic rings (6.5–7.05 ppm) (%)	32	59
Protons of condensed aromatic rings (7.05–9.0 ppm) (%)	68	41
Aromatics (total) (wt.%)	37.1	21.8
Nonaromatics (wt.%)	62.9	78.2

Table 4
Estimated parameters k and n in the kinetic model, Eq. (2)

H_2/CH ratio (N m^3/kg)	$P = 40$ bar[a]			$P = 65$ bar[a]		
	k	n	SD × 10^3	k	n	SD × 10^3
0.118	0.120	1.63	3.120	1.473	2.762	4.564
0.354	0.135	1.44	1.329	1.880	2.796	2.053
0.590	0.245	1.66	2.563	1.821	2.523	4.792

[a] At $T = 300$ °C.

The catalyst particles were assumed to be isothermal and homogeneously distributed inside the reactor. That was acceptable due to low concentration of the gas oil in the inlet mixture. The highest ratio between hydrogen and gas oil was 0.590 N m^3/kg. The assumed pseudohomgeneous reactor space allowed calculation of the mean reaction rate based on the reactor's volume. Taking into account all aforesaid considerations, a simple reactor model was derived:

$$\frac{dC_S}{d\tau} = -r_S \tag{1}$$

The kinetics of real feed desulfurization was complex due to various sulfur compounds in the gas oil requiring different rate and reactivity for each reaction. In practice, all desulfurization reactions are usually lumped into a single reaction of sulfur with hydrogen giving hydrogen sulfide as the end product. In the present study, the applied empirical correlation was

$$r_S = kC_S^n \tag{2}$$

with the apparent reaction order between 1 and 3.

3.2. Estimation of kinetic parameters

Unknown values of kinetic parameters, k and n, in the kinetic model were experimentally estimated in the test plant. Final sulfur concentrations were compared with the model values using nonlinear least-squares analysis. These values are presented in Table 4 for all series of the experiments. Experimental and theoretical values of the unconverted amount of sulfur are plotted against the reactor dimensionless space time, in Figs. 2 and 3, showing fairly good agreement. Due to high reaction rate in the initial part of the catalyst bed, sulfur concentration decreased rapidly. The values of the kinetic constant k were higher with increase of pressure and H_2/CH ratio. The exponent n remained almost unchanged, varying the reaction conditions. It is true that after deep desulfurization, overall reaction order is expected to decline to 1, but

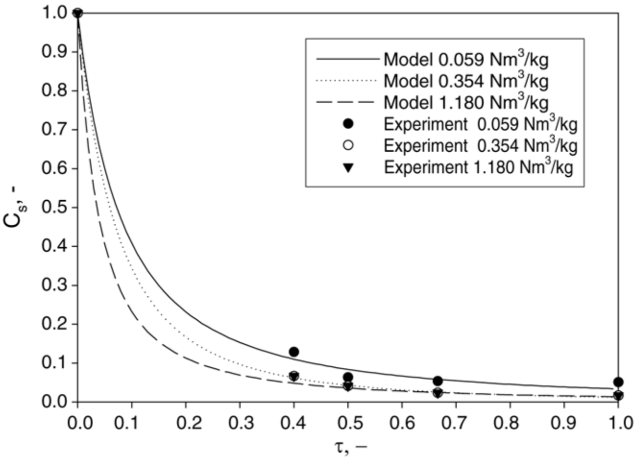

Fig. 2. Sulfur concentration (dimensionless) as the function of dimensionless space time, τ for three H_2/CH ratios at $T = 300$ °C and $P = 40$ bar.

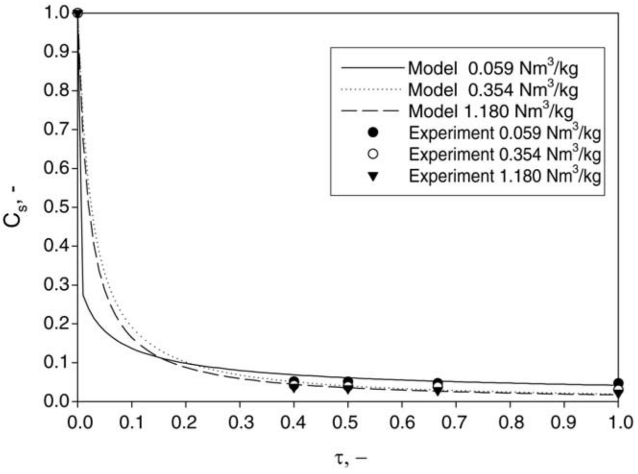

Fig. 3. Sulfur concentration (dimensionless) as a function of dimensionless space time, τ for three H_2/CH ratios at $T = 300$ °C and $P = 65$ bar.

contrary, as shown in Table 4, reaction order increases with decreasing of the sulfur content in product. It can be explained by the increasing role of inhibitors and the larger reactivity scale of various sulfur compounds in the feedstock. Similar results have been reported [29,30].

3.3. Process simulation

Hydrodesulfurization can be simulated with known reactor configuration, kinetic model, feed and catalyst characteristics, and by changing key variables, such as feed rate, pressure and hydrogen/feed ratio. Eq. (2) can be transformed by using the reactor length, z as a variable and by introducing the cross-sectional area, A_s and inlet concentration of sulfur, C_S, Eq. (3),

$$\frac{dX_S}{dz} = \frac{A_s C_S^{n-1}}{V_u} k(1 - X_S)^n \tag{3}$$

Simulation was performed by changing process parameters (the ratio H_2/CH, pressure or LHSV) keeping other parameters constant. The influence of these parameters on decrease of sulfur content was investigated in the range outside the experimentally given values.

Some simulation tests are presented in Figs. 4 and 5. The results obtained by changing the LHSV were in agreement with the role of the pronounced residence time in the reactor—the smaller LHSV the better desulfurization. As expected, H_2/CH ratio increased, while other operating parameters remained constant, slightly smaller sulfur content was recorded in the exit stream. As expected, similar effects showed increase of the process pressure as can be seen in Fig. 6. However, severe process conditions mean higher production costs, and other possibilities, mentioned earlier, must be taken into consideration.

These results can be used in the industrial practice, for prediction of the expected sulfur content in products. However, one should not overestimate such results, because other variables and the reaction conditions need to be equal or similar to the experimental ones.

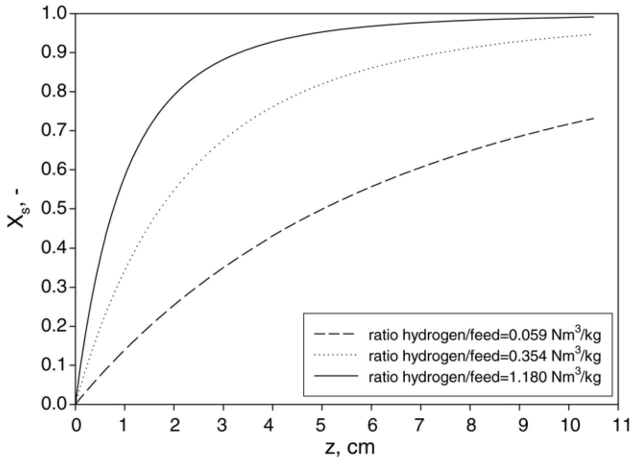

Fig. 4. Simulation of the reactor by changing H_2/CH ratio. Conversion against the reactor length (LHSV = 1 $m^3\ m^{-3}\ h^{-1}$, T = 300 °C, P = 40 bar).

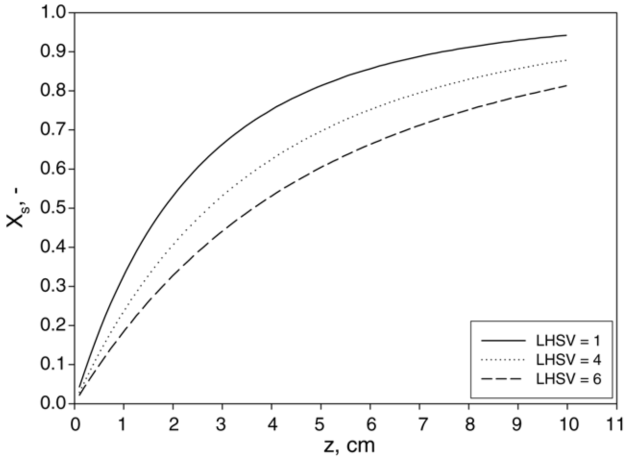

Fig. 5. Simulation of the reactor by changing LHSV. Conversion against the reactor length (H_2/CH = 0.118 N m^3/kg, T = 300 °C, P = 40 bar).

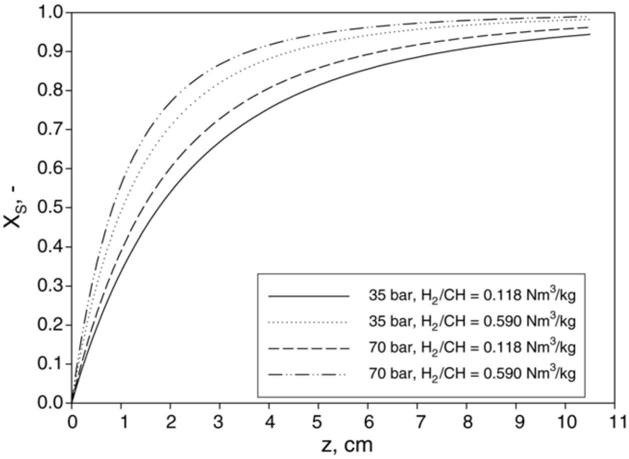

Fig. 6. Influence of pressure and H_2/CH ratios on the percentage of removed sulfur. Conversion against the reactor length. LHSV = 1 $m^3\ m^{-3}\ h^{-1}$, T = 300 °C.

4. Conclusion

A steady-state model for a trickle-bed catalytic reactor (test plant) was developed to model hydrodesulfurization of vacuum gas oil containing considerable amounts of sulfur compounds.

The kinetic parameters were estimated on the basis of experimental results of sulfur content in the exit reaction mixture. The agreement between the experimental and theoretical values was satisfactory.

The experiments revealed that increase of pressure and H_2/CH ratio as well as decrease of LHSV had positive effect on the removal of sulfur compounds from the gas oil, while other process parameters were kept constant. Also, the analysis of physico-chemical characteristics of the products showed their improved quality compared with the initial feedstock, i.e., reduction of density and viscosity, as well as the increase of cetane index values.

Theoretical simulations were performed by changing pressure, H_2/CH ratio and LHSV and keeping other parameters constant. High number of design parameters offers the possibility of accepting such process conditions that are optimal for a given feedstock.

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