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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).

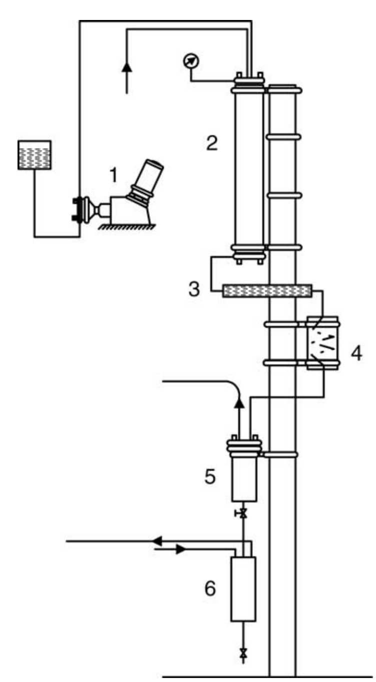

Fig. 1. Schematic presentation of the hydrodesulfurization device.