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Testing the Impact of Hydrodesulphurisation Process Parameters on Diesel Fuel Properties

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In this work the influence of changes in hydrodesulphurisation (HDS) process parameters (space velocity and temperature) on efficiency of sulphur compounds removal was tested. The feedstock, straight run gas oils (STGO) from Croatian crude oil used for diesel fuel production have been subject to the hydrodesulphurisation process with Co-Mo/Al_2O_3 commercial catalyst in a trickle bed reactor in high-pressure apparatus at the following conditions: total reactor pressure of 500 kPa, reactor inlet temperature in the range 330 - 355 °C, liquid hourly space velocity (LHSV) in the range 2.0, 2.5 and 3.0 h^{-1} and hydrogen/hydrocarbons ratio of 120.
The laboratory high-pressure apparatus was upgraded by implementation of a modern computer-based control system. Control system supports experimentation aiming better process conditions monitoring and control with the purpose of improved repeatability and achievement of safe operation.

1. Introduction

Ever stricter environmental protection requirements for all types of motor fuels require a content reduction of certain hydrocarbons (aromatics and olefins), and particularly of sulphur. Sulphur level in diesel fuel in Croatia is currently 50 mg/kg and it has met the EURO IV requirements in accordance with EN 590:2004 standard.
A higher demand for diesel and surplus of petrol quantity has occurred in Croatia, as in the rest of Europe. The new diesel fuel specification (EURO V requirements, 10 mg/kg sulphur level) requires the optimal use of the existing refinery units and construction of new hydro-treatment process units in Croatian refineries.
Hydrodesulphurisation process is the most widely spread process used in petroleum industry for elimination of undesirable sulphuric, nitrogen, polyaromatics, olefins and

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metal compounds, thus considerably improving the quality of motor fuels, as well as feedstock used in further refinery processing (Leprince, 2001).

2. Laboratory set-up

Laboratory high-pressure apparatus is intended for operating conditions and catalyst activity testing. It emulates a real production process, and consists of reactants feed container, reactor, heat exchanger, separation unit and low pressure tanks for products as can be seen from Figure 1. On the existing apparatus usual hydrodesulphurization process could be tested allowing broad ranges of changes in operating conditions (temperature, pressure, hydrogen/ hydrocarbons ratio, and different types of catalysts).
Laboratory apparatus is automatized by installation of sensors, transmitters, mass flow controllers, and controller with the purpose of increased accuracy, repeatability and reliability of the experimentation. Several control loops are implemented and advanced process control is established. Installed Honeywell HC900 Hybrid Controller is an integrated loop and logic controller that is designed specifically for small and medium-scale unit operations. It comprises a set of hardware and software modules that satisfy any of a broad range of process control applications. The HC900 Controller uses the latest state of the art technology and utilizing cutting edge control solutions. The controller provides many of the features and functions which require a combination of logic and loop control.
All measurements and control actions are provided continuously, and are shown on the operator panel and SCADA system *Spec View 32* interface. Control loops are operated automatic or manual. In the case of emergency there are alarms which serve for easily registration of process equipment malfunction or violating specified values. All data are continuously stored in database for later analysis. The communication between hybrid controller and graphic interface is based on Modbus TCP/IP protocol.

3. Experimental

3.1 Catalyst and feed

The commercial HDS catalysts by Haldor Topsoe were used in the experiments. At the top of the reactor there is a layer of glass balls, followed by a layer of catalyst A (total amount 6.3 % m/m, chem. composition, %: MoO_3 4-8, NiO 1-3, Al_2O_3 80) and catalyst B (total amount 93.7 % m/m, chem. composition, %: CoO 3-6, MoO_3 20-25, Al_2O_3 70-80) at the bottom. In the experiments highly active fresh catalysts were used. The reactor includes with 80 cm^3 of catalyst.
Straight-run gas oil (SRGO) from Croatian crude oil (mixtures of Moslavina and Slavonija crude oils and gas condensate) from atmospheric distillation was investigated in the work. Properties of the feed were determined by standard test methods. Physical and chemical feed properties: density, 15 °C: 0.8331 $kgdm^{-3}$, sulphur: 4875 mg/kg, PAH: 4.9 % m/m, olefins: 2.77% m/m, distillation, °C, ASTM D 1160: IBP 157.6, 50 % v/v 262.0, 90 %v/v 338.5, FBP 355.5.

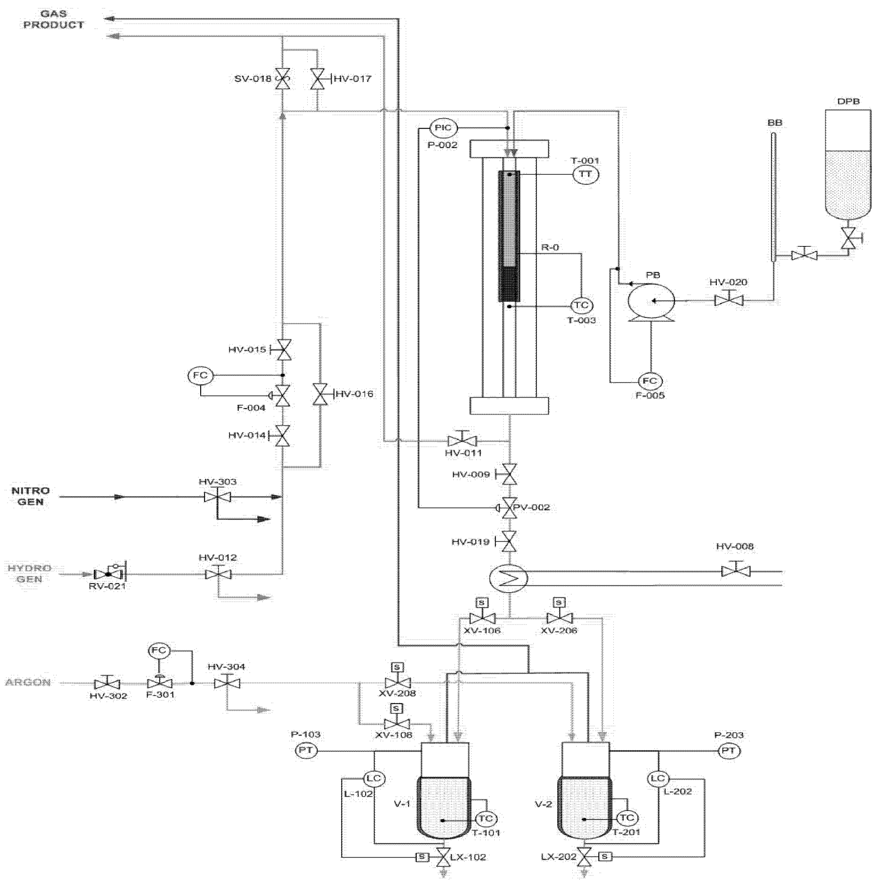

Figure 1. Simplified P&I diagram of the laboratory apparatus

3.2 Operating conditions

In this study, three sets of experiments were performed with changes of liquid hourly space velocity (LHSV) in the range of 2.0, 2.5, and 3.0 h^{-1}. The temperature was varied from 330 °C to 355 °C. Other parameters like pressure and hydrogen/hydrocarbons ratio were kept constant (Table 1). During the experiments hydrogen of the 3.0 purity was used.

4. Result and Discussion

The aim of research was to find the optimal process parameters at which the sulphur content would satisfy the EURO IV specification, i.e. to obtain 50 mg/kg of sulphur in hydrodesulphurisation products.

Figure 2 shows the influence of temperature and LHSV on the sulphur content in products after the hydrodesulphurisation process. With the temperature increase from

330 °C to 355 °C at the constant LHSV=2.0, 2.5 and 3.0, constant pressure and hydrogen/hydrocarbon ratio, a considerable reduction in the sulphur content was observed. The highest sulphur reduction is achieved at LHSV=2.0 h^{-1}. The data on sulphur quality in the obtained products indicate that with LHSV=2.0 h^{-1} and T=345 °C, 350 °C and 355 °C, sulphur level is under 50 mg/kg as with LHSV=2.5 h^{-1} at T=350 °C and 355 °C (table 3). These data meet the EURO IV specification requirements.

By increasing LHSV from 2.0 to 3.0, increase in the content of sulphur occurred, due to a shorter feed retention time in the reactor (Figures 3 and 4).

The poly-aromatic hydrocarbons (PAH), like unsaturated hydrocarbons, are very important compounds of diesel fuel limited at 11 m/m % in the EN 590:2004 standard. The content of PAH increases with an increase of the feed's boiling temperature. During the hydrodearomatisation reaction occurring simultaneously with the hydrodesulphurisation reaction, the polycyclic aromatics are converted in mono-aromatics or saturated compounds (Christolini B.A et al., Maples R.E., Meyers R. A.).

The content of PAH in the initial feed is 4.9 m/m %. With the increased LHSV, content of PAH has increased too. The content of PAH rises with the temperature increment. In this way, a lower PAH content is realised at T= 330 °C (Figure 5).

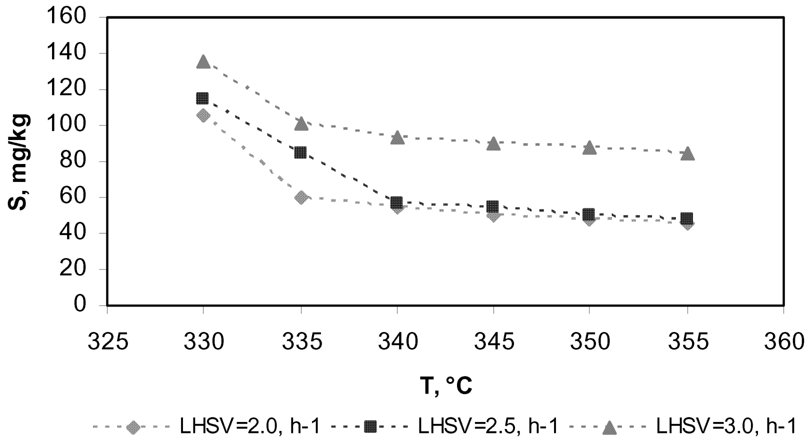

Figure 2. Dependence of sulphur content on temperature (p=500 kPa, hydrogen/hydrocarbons ratio of 120)

Table 1. Process condition and sulphur quality in products of high pressure apparatus (p= 500 kPa, hydrogen/hydrocarbons ratio=120)

T, °C	LHSV, h^{-1}	S, mg/kg
330	2.0	114
335	2.0	60
340	2.0	55
345	2.0	50
350	2.0	48
355	2.0	46
330	2.5	106
335	2.5	84
340	2.5	57
345	2.5	54
350	2.5	50
355	2.5	48
330	3.0	136
335	3.0	101
340	3.0	93
345	3.0	90
350	3.0	88
355	3.0	85

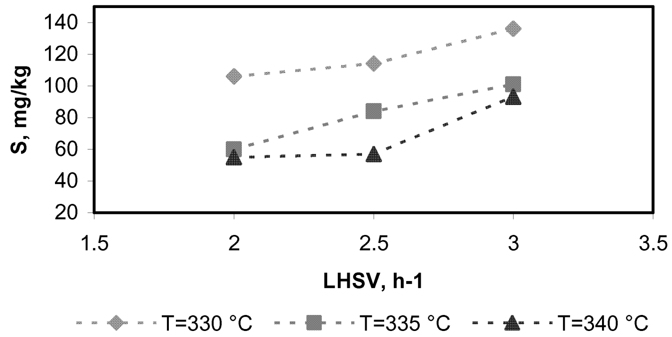

Figure 3. Dependence of sulphur content on LHSV (p=500 kPa, hydrogen/hydrocarbons ratio of 120)

5. Conclusions

The satisfactory elimination of sulphur compounds meeting the EURO IV requirements have been achieved by higher temperature and lower space velocity of the catalysts used.

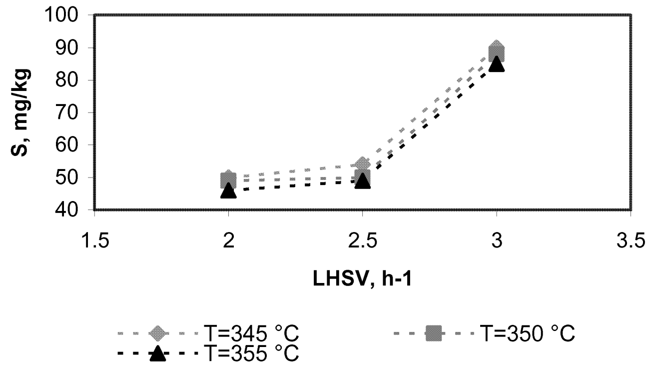

Figure 4. Dependence of sulphur content on LHSV (p=500 kPa, hydrogen/hydrocarbons ratio of 120)

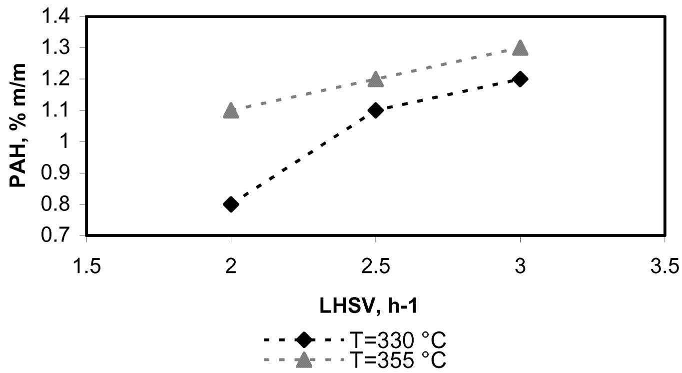

Figure 5. Dependence of PAH content on LHSV (p=500 kPa, hydrogen/hydrocarbons ratio of 120)

The quantity of poly-aromatic hydrocarbons, as expected, has significantly decreased during the hydrodesulphurisation process.
The automatization of laboratory high-pressure apparatus for hydrodesulphurization has improved accuracy, repeatability and reliability of performed experiments.

6. Literature

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