

INVESTIGATION OF THE DEEP HYDRODESULPHURIZATION OF GAS OIL FRACTIONS

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The sulphur content of automotive diesel fuels was tightened all over the world, for example a sulphur content limit of 350 ppm came into force in the European Union in the year 2000 and this value will be 50 ppm in the year 2005, even 10 ppm from the end of this decade. One of the reasonable solutions for refineries to satisfy these strict requirements is deep hydrodesulphurization of the gas oils fractions. In this paper the experimental results of the hydrodesulphurization of gas oils with different sulphur, nitrogen and aromatic contents on NiMo/Al₂O₃/promoter catalyst are presented. Effect of the key process parameters and composition of the feeds on the yield and the quality of products are discussed. In addition to this, hydrogenation reactions of aromatic compounds taking place during the hydrodesulphurization are covered. On the basis of experimental results the advantageous process parameters were determined for producing diesel fuel blending components of sulphur content lower than 50 ppm and lower than 10 ppm.

Keywords: hydrodesulphurization, hydrodearomatization, NiMo/Al₂O₃, feed quality

Introduction

The quality requirements of diesel fuels became stricter and stricter all over the world in the last years and this tendency will continue in the near future, too. The most pronounced changes were introduced in the maximum allowable sulphur content, for example its value was limited to 350 ppm in 2000 and 50 ppm from 2005, furthermore fuel having maximum 10 ppm sulphur content should be regionally available from this date and all automotive diesel fuels must be sold with less than 10 ppm sulphur content after January, 2009 [1].

Reduction in the sulphur content of diesel fuels contributes to the decrease of SO₂ (acid rain precursor) sulphate particles and emission of particulate matter, but the most important reason for this reduction is to preserve the efficiency of modern exhaust gas treating systems e.g. NO_x traps, NO_x converters, particulate filters for a long

time, because these systems are greatly sulphur sensitive [2].

Production of diesel fuels with lower than 50 ppm and mainly 10 ppm sulphur content gave a headache for the refining industry and initiated extensive research and development activities on both the conventional hydrodesulphurization technology and the alternative methods e.g. desulphurization by selective adsorption (Phillips 66 Co. "S Zorb Process"), chemical oxidation followed by extraction (Uni-Pure and Texaco "ASR-2 Process"), biological desulphurization and production of Fischer-Tropsch diesel fuel [3-5].

The main difficulty in producing low sulphur (< 50 ppm sulphur content) and practically sulphur-free diesel fuels (< 10 ppm) arises from the sterically hindered dibenzothiophenes content of gasoil fractions. It is known that there are two possible reaction pathways for the removal of sulphur. The first is direct extraction of the sulphur atom from the molecule, and the second, hydrogenation of aromatic rings followed by extraction of the sulphur atom. The sterically

hindered heterocyclic sulphur compounds contain one or two alkyl groups adjacent to the sulphur atom (4 and/or 6 position) which restricts the vertical adsorption of molecules to the hydrogenolysing active sites of the catalyst and promote the flat adsorption to the hydrogenating active sites of the catalyst, see *Figure 1* [4]. Hence it follows that the removal of these compounds requires the application of catalysts having relatively high hydrogenating activity, for example NiMo/Al₂O₃.

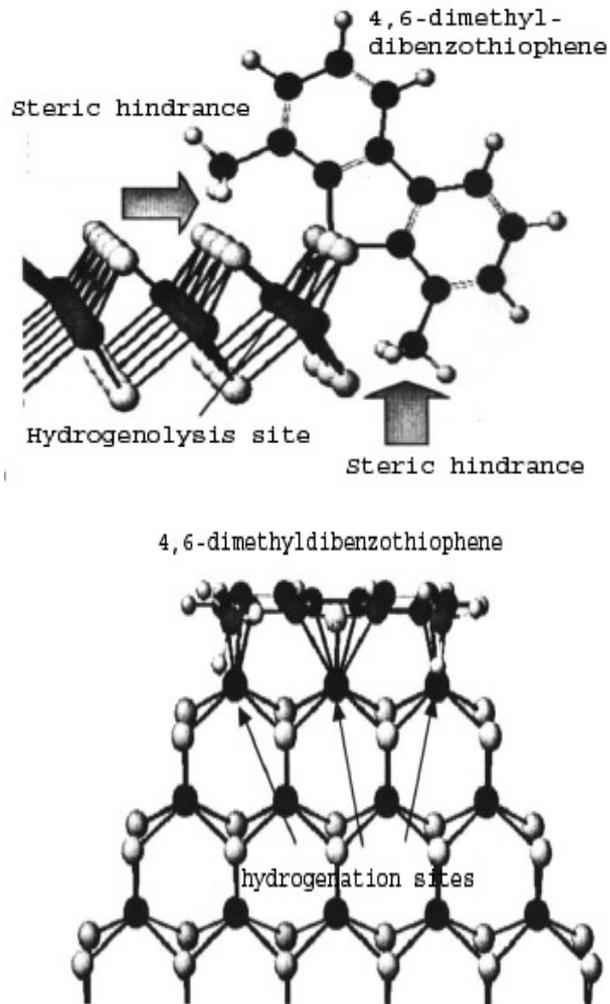


Figure 1 Adsorption of a sterically hindered dibenzothiophene to the active sites of catalyst

Beside proper selection of the catalyst optimization of process parameters contribute to the successful implementation of hydrodesulphurization too. The optimal parameters are the following:

- Higher partial pressure of hydrogen, especially in case of applying NiMo/Al₂O₃ type catalyst.

- Lower partial pressure of hydrogen sulphide, because this compound inhibits hydrodesulphurising reactions.
- Lower liquid space velocity corresponding to longer residence time, and higher volume ratio of hydrogen-to-hydrocarbon.

The aim of this present study was to identify and quantify the key process parameters for the hydrodesulphurization of gas oils of different sulphur, nitrogen and aromatic content on NiMo/Al₂O₃/promoter catalyst. Effect of the key process parameters (temperature, pressure, LHSV, hydrogen/hydrocarbon volume ratio) and composition of the feeds on the yield and quality of products were investigated. In addition, hydrogenating reactions of aromatic compounds taking place during the hydrodesulphurization were studied as well. On the basis of experimental results the advantageous process parameters were determined for producing diesel fuel blending components of sulphur content lower than 50 ppm and lower than 10 ppm. Possible applications of the obtained diesel fuel blending components in themselves or together with others were examined with the objective of satisfying standard specifications of commercial products.

Experimental

The hydrodesulphurizing experiments were carried out at the University of Veszprém, Department of Hydrocarbon and Coal Processing.

Apparatus

The experiments were carried out in a high pressure reactor system. This system consists of a tubular reactor of 100 cm³ efficient volume free from back-mixing, as well as equipment and devices applied in the reactor system of hydrotreating plants (pumps, separators, heat exchangers, temperature and pressure regulators and gas flow regulators).

The experiments were carried out on a catalyst of constant activity and in continuous operation. Repeatability of the experimental results was higher than 95% considering the total errors of both the technological experiments and the tests methods.

Materials

Catalyst

The hydrodesulphurizing experiments were carried out on a commercially available NiMo/Al₂O₃/promotor type catalyst which was pre-treated according to the recommendation of the supplier.

Feedstock

The feeds were two straight run light gas oils ("A1" and "A2") and two straight run heavy gas oils ("B1" and "B2"). Feeds "A1" and "B1" were derived from crude oil exploited in Hungary while feeds "A2" and "B2" were produced from Russian crude oil. Their main properties are given in Table 1. These data show that the quality of gas oil produced from domestic source ("A1" and "B1") is better compared to those derived from Russian crude, regarding especially sulphur, nitrogen and aromatic contents of which properties influence the efficiency of hydrodesulphurization in a large extent.

Table 1 Main properties of the feeds

Property	Feed			
	A1	A2	B1	B2
Density at 15 °C, kg/m ³	797.1	835.2	820.0	860.0
Sulphur, ppm	600	5100	1200	9300
Nitrogen, ppm	5	9	114	217
Aromatics, %				
mono	8.9	16.6	8.5	18.9
di	4.2	8.0	3.9	8.1
tri+	0.7	1.0	2.1	3.2
Total	13.8	25.6	14.4	30.2
CFPP, °C	<-24	-23	8	5
Flash point, °C	52	59	64	70
Distillation, °C				
Initial boiling point	169	154	172	188
10 vol. %	197	233	248	284
30 vol. %	215	254	275	309
50 vol. %	224	266	291	324
70 vol. %	237	278	307	336
90 vol. %	263	284	336	354
95 vol. %	278	301	354	366
End boiling point	291	306	361	369
Cetane index	57.2	52.8	68.2	58.5

Methods

Properties of the feeds and products were determined by standard test methods which are summarized in Table 2. For example sulphur and nitrogen content was measured by oxidative combustion and electrochemical detection (APS-35 equipment) and aromatic content by high performance liquid chromatography (HPLC) (EN 12916:2000).

Table 2 Applied test methods

Properties	Standards
Density, at 15°C	MSZ EN ISO 12185
Cetane Index	MSZ 13166
Flash point	MSZ EN 22719
Sulphur content	ASTM D 6428
Nitrogen content	ASTM D 6366
Aromatic content	EN 12916:2000
Distillation data	ASTM D86-97

The experiments were carried out on a catalyst of constant-state activity, in continuous operation.

Hydrodesulphurising (HDS) and aromatic saturating (HDA) activities of the catalyst were determined on the basis of Equations 1-2.

$$\text{HDS activity: HDS\%} = 100 (S_{\text{feed}} - S_{\text{product}}) / S_{\text{feed}} \quad \text{Eq. 1}$$

where S_{feed} : sulphur content of the feed, ppm
 S_{product} : sulphur content of the product, ppm

$$\text{HDA activity: HDA\%} = 100 (A_{\text{feed}} - A_{\text{product}}) / A_{\text{feed}} \quad \text{Eq. 2}$$

where A_{feed} : total aromatic content of the feed, %
 A_{product} : total aromatic content of the product, %.

Process parameters

The applied process parameters are summarized in Table 3.

Table 3 Applied process parameters

Parameters	
Temperature, °C	300-360
Pressure, bar	40-60
Liquid hourly space velocity, (LHSV), h ⁻¹	1.0-2.0
H ₂ to hydrocarbon volume ratio, m ³ /m ³	400

Results and discussion

Hydrodesulphurizing (HDS) experiments

After each experiment we determined first the yield of the stabilized liquid products. The yield was higher than 98% in every case. However, the amounts of the gas and gasoline fractions were higher at higher temperatures and lower liquid hourly space velocities (LHSV), due to the stricter process parameters.

Experiments applying straight run light gas oils (Feed "A1" and "A2")

Results of HDS experiments applying straight run light gas oils (Feed "A1" and "A2") are summarized in *Figures 2-5*, showing the change of sulphur content of the products and the variation of HDS activities of the catalyst as a function of temperature at a lower and a higher value of pressure (40 bar and 60 bar) and of LHSV (1.0 h^{-1} and 2.0 h^{-1}) in case of both feeds, respectively.

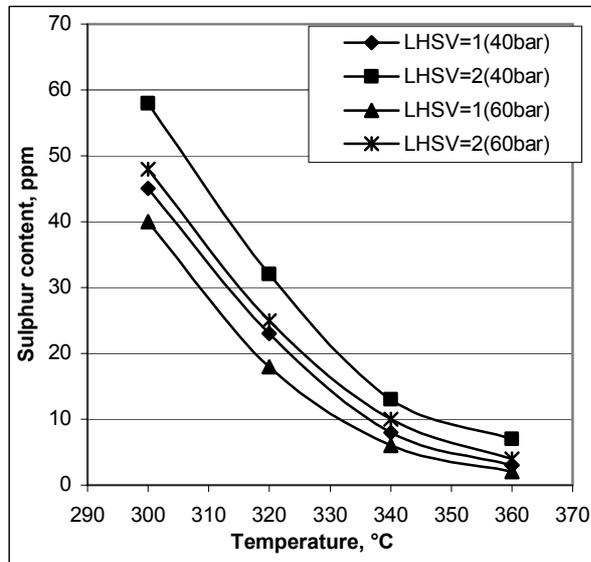


Figure 2 Effect of temperature on the reduction of sulphur content (Feed "A1")

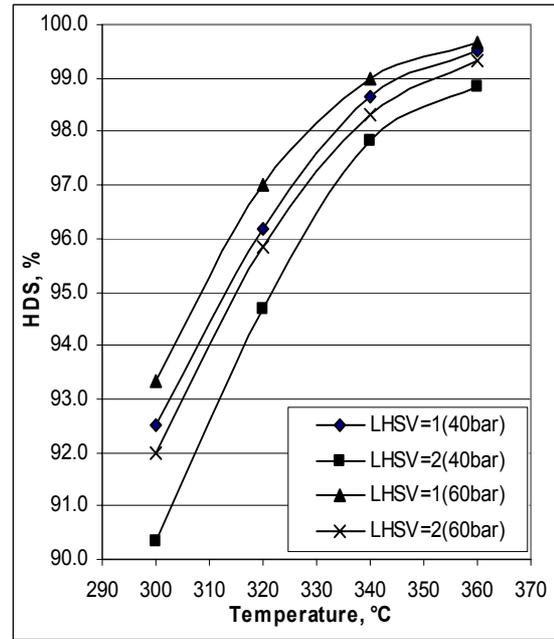


Figure 3 Effect of temperature on the HDS activity (Feed "A1")

The highest rate of the reduction of sulphur content occurred in the temperature range of 300-340°C in case of both feeds and at every process parameter applied, where it decreased practically linearly with increasing temperature; above this range the sulphur content further decreased, but the rate of reduction decreased in a large extent. *Figures 3 and 5* show that HDS activities exceed 98% (even 99% in case of feed "A2") at 340°C suggesting that most sulphur compounds were converted at this temperature, and only the most refractory ones remained in the products.

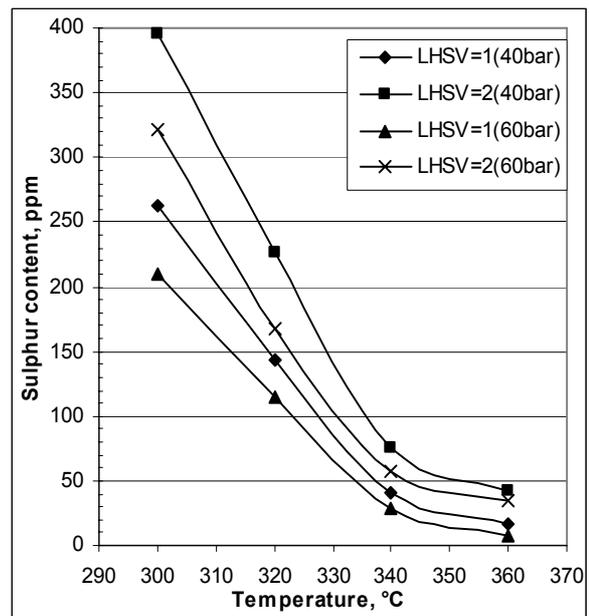


Figure 4 Effect of temperature on the reduction of sulphur content (Feed "A2")

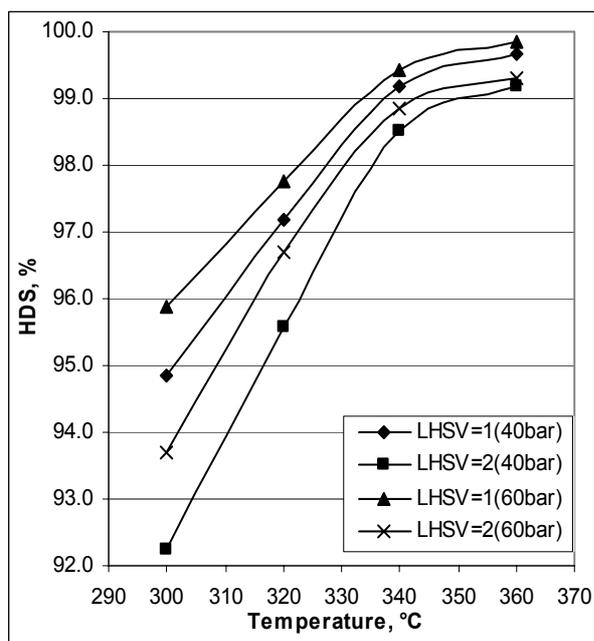


Figure 5 Effect of temperature on the HDS activity (Feed "A2")

Figures 2 and 4 show the pressure and LHSV effects and the attainable sulphur content. Increasing the pressure and decreasing the LHSV (longer mean residence time) had advantageous effect on the sulphur content of the products at a given temperature, especially in case of feed "A2" and lower temperatures (300°C and 320°C). Effect of decreasing the LHSV from 2.0 h⁻¹ to 1.0 h⁻¹ was more pronounced than that of the increasing the pressure from 40 bar to 60 bar. This suggests that the applied feeds contain such types of heterocyclic sulphur compounds (probably alkyl benzothiophenes) which are preferably converted by direct desulphurization route. This reaction pathway is influenced by the partial pressure of H₂ (P_{H2}) in a less extent than the hydrogenating route. Besides the increase of P_{H2} is essentially favourable for "direct" reaction route because it decreases the partial pressure of H₂S which compound exerts negative effect on the rate of the reaction.

Concerning values of maximum allowable sulphur content of diesel fuels coming into force in year 2005 (50 ppm) and in year 2009 (10 ppm) it

can be stated that products having sulphur content lower than 50 ppm can be obtained even at a temperature as low as 300°C and LHSV = 1.0 h⁻¹ at 40 bar and LHSV = 1.0 h⁻¹ and 2.0 h⁻¹ at 60 bar applying feed "A1". Products below 10 ppm sulphur content can be produced at 340°C and in all cases, except pressure of 40 bar and LHSV of 2.0 h⁻¹. On the contrary, products below 50 ppm sulphur can only be produced at significantly higher temperature (at 340°C and above) in case of feed "A2" and product below 10 ppm sulphur content can only be obtained at the highest temperature and pressure (360°C and 60 bar) and the lowest LHSV (1.0 h⁻¹). The reason of this is that feed "A2" contains sulphur in higher concentration originally, and it is postulated fact that sulphur compounds exert self-inhibition effects on the desulphurising reactions, and higher amount of sulphur leads to the formation of more H₂S. Besides the feed "A2" contains significantly more aromatics (see Table 1) which also inhibit the desulphurizing reactions (especially direct desulphurization) by competitive adsorption. In consequence of all these effects the attainable reduction in sulphur content is less.

Experiments applying straight run heavy gas oils (Feed "B1" and "B2")

Figures 6-9 show the results of HDS experiments carried out applying straight run heavy gas oils (Feed "B1" and "B2"), that is the change of sulphur content of the products and variation of HDS activities of the catalyst as a function of temperature at a lower and a higher pressure (40 bar and 60 bar) and of LHSV (1.0 h⁻¹ and 2.0 h⁻¹) for both feeds, respectively. Figures 7 and 9 show that significant reduction in the sulphur content took place even at the temperature of 300°C in case of Feed "B1" (above 90% HDS activity) and a further increase of temperature resulted in a relatively low improvement (about 6%). On the contrary, in case of Feed "B2" significant improvement on HDS activity (between 18% and 30% depending on process conditions) was experienced in the applied temperature range.

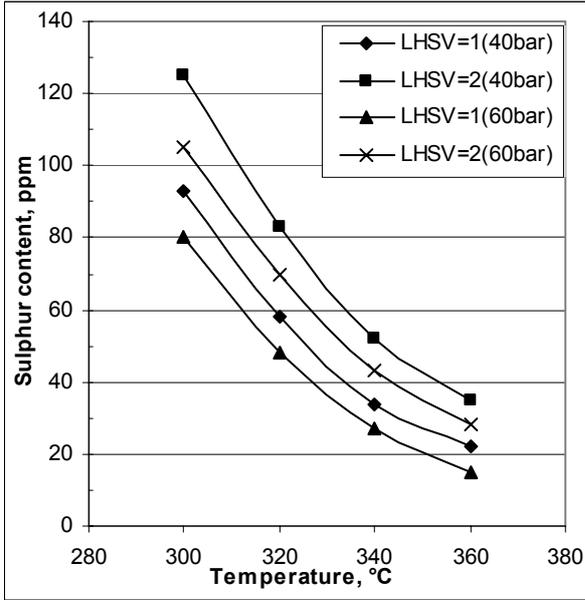


Figure 6 Effect of temperature on the reduction of sulphur content (Feed "B1")

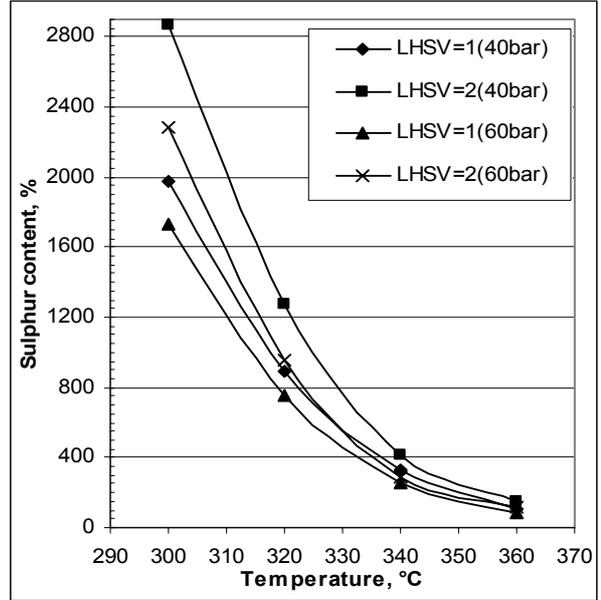


Figure 8 Effect of temperature on the reduction of sulphur content (Feed "B2")

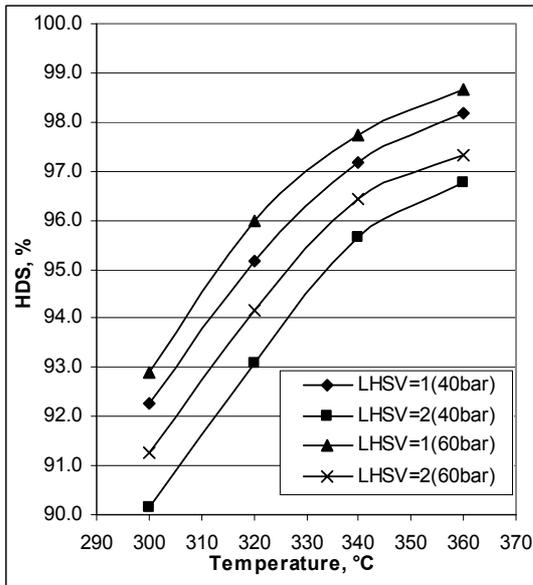


Figure 7 Effect of temperature on the HDS activity (Feed "B1")

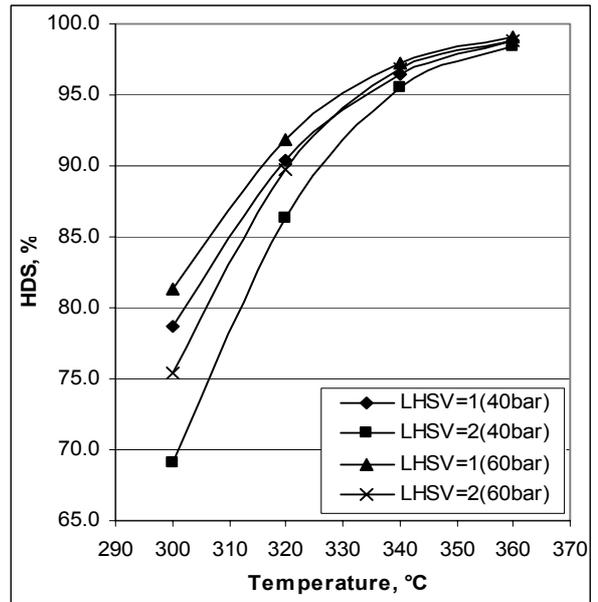


Figure 9 Effect of temperature on the HDS activity (Feed "B2")

Regarding other process parameters (pressure and LHSV) it can be stated that the increase of pressure and the decrease of LHSV exerts advantageous effect on the attainable sulphur reduction at a given temperature, especially in case of Feed “B2” and at lower temperatures. Studying the effects of pressure and LHSV showed an interesting picture. Namely, the decrease of LHSV from 2.0 h⁻¹ to 1.0 h⁻¹ caused higher improvement on the reduction of the sulphur content than the increase of the pressure from 40 bar to 60 bar at constant temperature in case of Feeds “A1”, “A2” and “B1”. On the contrary, in case of Feed “B2” the advantageous effect of the increase of the pressure was higher than that of the reduction of LHSV above 330°C. This suggests that distribution of the sulphur compounds greatly differs in the latter one compared to the former ones. Feed “B2” contains presumably higher amount of sterically hindered heterocyclic sulphur compounds (e.g. dibenzothiophenes alkylated in 4 and 6 positions) and the conversion of these refractory sulphur compounds takes place mainly in the “indirect” reaction route involving hydrogenation of the aromatic ring in the first step. This is an equilibrium reaction and exothermic process, and the increase of the pressure, especially of the partial pressure of hydrogen, shifts the equilibrium towards saturation of aromatics which implies higher reduction in sulphur content, too.

Concerning present (350 ppm) and future (50 ppm from 2005 and 10 ppm from 2009) sulphur content regulations of diesel fuels it can be stated that products having sulphur content lower than 350 ppm can be produced even at less severe operating conditions (300°C, 40 bar and LHSV = 2.0 h⁻¹) applying feed “B1”. Products having sulphur content below 50 ppm can be produced at 340°C and in all cases except at pressure of 40 bar and LHSV of 2.0 h⁻¹. On the contrary, products having sulphur content below 350 ppm can only be produced at significantly higher temperature (at 340°C and above) in case of feed “B2”, and products below 50 ppm sulphur content could not be obtained even at the highest temperature and pressure (360°C and 60 bar) and the lowest LHSV (1.0 h⁻¹) applied. The main reason of this is probably that this feed contains considerable amount of sterically hindered heterocyclic sulphur compounds. Besides the heavy gas oil obtained from Russian crude contains originally higher sulphur which would contribute to the evolvement of strong self-inhibition effect on the desulphurising reactions, furthermore, the higher amount of sulphur leads to the formation of more

H₂S which inhibits these reactions, too. The high amount of nitrogen and aromatics (see Table 1) contained in feed “B2” also inhibits the desulphurising reactions.

Experiments for hydrodearomatisation (HDA)

The reduction of the aromatic content taking place collaterally with the hydrodesulphurization was investigated as well. Since the primary purpose of this study was to investigate the reduction of the sulphur content, the results of only those HDA experiments are presented which are obtained at process conditions required for the production of gas oils having sulphur content meeting the present (350 ppm) and future (50 ppm from 2005 and 10 ppm from 2009) quality requirements. These results are summarized in Table 4.

Table 4 Aromatic contents of selected products

Properties	Feeds			
	A1	A1	A2	A2
Sulphur, ppm	45	6	41	7
Pressure, bar	40	60	40	60
Temperature, °C	300	340	340	360
LHSV, h ⁻¹	1	1	1	1
Aromatics, %				
mono	12.7	8	19.7	16.0
di+	0.8	1.2	3.0	2.7
total	13.5	9.2	22.7	18.7
HDA, %	2.2	33.3	11.3	27.0
Properties	Feeds			
	B1	B1	B2	B2
Sulphur, ppm	43	34	100	81
Pressure, bar	60	40	60	60
Temperature, °C	340	340	360	360
LHSV, h ⁻¹	2	1	2	1
Aromatics, %				
mono	10.2	10.7	18.8	16.0
di+	3.3	3.1	3.1	2.7
total	13.5	13.8	21.9	18.7
HDA, %	6.2	4.2	27.5	38.1

The valid standard regarding the commercial type diesel fuel (EN 590) contains regulation of aromatics only for the polyaromatic content with maximum allowable value of 11%. This value will not change in 2005 counter to sulphur content and it will be tightened presumably from 2009.

Comparing the polyaromatic content of feeds (Table 1) to the required value it can be stated that both light gas oils and one of the heavy gas oils that is produced from domestic crude satisfy this value, and only the other heavy gas oil contains polyaromatics in a little bit higher concentration.

Data of *Table 4* show that products manufactured to satisfy different requirements of sulphur content have low polyaromatic content even in case of Feed "B2", and all values meet the requirement of the standard EN 590. This indicates that satisfying the requirement of polyaromatic content can be reached more easily than that of the sulphur content.

These data also demonstrate that HDA activity of the catalyst was relatively low (between 2.2% and 11.3%) at process conditions for obtaining products of lower than 50 ppm (Feed of "A1", "A2" and "B1"), and this is advantageous from the point of view of hydrogen consumption. These results also show that mainly the reduction of the polyaromatic content took place in these conditions, and the products contain mono aromatics in higher concentration than the feeds, which means that saturation of the mono aromatics to naphthenes takes place with a lower rate of reaction than their formation from di- and polyaromatics by consecutive ring opening hydrogenation.

On the basis of the experimental results presented it can be seen that products having sulphur content lower than 10 ppm can only be produced from Feed "A1" and "A2" at strict process conditions (high pressure and temperature, as well as low LHSV). The HDA activity of the catalyst was relatively high in these conditions (27.0% and 33.3%) and not only the reduction in polyaromatic content but the decrease in mono aromatic content took place. The reduction of the aromatic content of gas oils is advantageous from the aspects of environmental protection and engine operation. However, if the primary purpose of the hydrotreatment is the reduction of the sulphur content, high HDA activity involves growing hydrogen consumption that is not beneficial from the point of view of economy. Besides, the use of more hydrogen causes more fuel consumption consequently higher flue gas emissions in the steam-reforming process, so some parts of the emissions are shifted from the cars to the refinery.

Quality parameters of Feed "B2" are the worst of all examined feeds (high aromatic, sulphur and nitrogen contents), and to obtain products with relatively low sulphur content strict process conditions (high temperature and pressure low

LHSV) should be applied. The degree of the saturation of aromatics was high in these conditions (from 27.5% to 38.1%, depending on process parameters), which is unfavourable from the point of view of hydrogen consumption and it leads to the problems mentioned before. One of the possible solutions of processing this feed can be the application of the two-step HDS. In the first step of this process more selective desulphurising catalyst (e.g. CoMo) can be applied for converting a predominant part of sulphur compounds, and in the second step the remaining sulphur compounds can be removed on a type of catalyst having high hydrogenating activity (for example noble metal/zeolite) in mild process conditions.

Summary

The sulphur content of automotive diesel fuels was tightened all over the world, for example sulphur content limit of 350 ppm came into force in the European Union in the year 2000 and this value will be 50 ppm in the year 2005, even 10 ppm from the end of this decade.

This paper summarized the results of experiments of hydrodesulphurizing of feeds having different qualities (sulphur, nitrogen and aromatic content, boiling point range, etc.) on NiMo/Al₂O₃/promoter catalyst. The feeds were two straight run light gas oils ("A1" and "A2") and two straight run heavy gas oils ("B1" and "B2"). Feeds "A1" and "B1" were derived from crude oil exploited in Hungary while feeds "A2" and "B2" were produced from Russian crude oil.

The highest rate of the reduction of sulphur content occurred in the temperature range of 300-340°C in case of both feeds and in all cases, where it decreased practically linearly with increasing temperature, above this range the sulphur content decreased further, but the rate of the reduction decreased in a large extent. Pressure and LHSV also influence the attainable sulphur content. Increasing pressure and decreasing the LHSV (longer mean residence time) had advantageous effect on the sulphur content of products at a given temperature. Studying the effects of the pressure and LHSV showed an interesting picture. Namely, decreasing LHSV from 2.0 h⁻¹ to 1.0 h⁻¹ caused higher improvement on the reduction of the sulphur content than the increase of the pressure from 40 bar to 60 bar at constant temperature in case of Feeds "A1", "A2" and "B1". On the

contrary, in case of Feed "B2" the advantageous effect of the increase of pressure was higher than that of the reduction of LHSV above 330°C. This suggests that distribution of the sulphur compounds greatly differs in the latter one compared to the former ones.

Concerning values of maximum allowable sulphur content of diesel fuels coming into force in year 2005 (50 ppm) and in year 2009 (10 ppm) it can be stated that products having sulphur content lower than 50 ppm can be obtained even at a temperature as low as 300°C and LHSV = 1.0 h⁻¹ at 40 bar and LHSV = 1.0 h⁻¹ and 2.0 h⁻¹ at 60 bar applying feed "A1", products below 50 ppm sulphur can only be produced at significantly higher temperature (at 340°C and above) in case of feed "A2". Applying feed "B1" products having sulphur content below 50 ppm can be produced at 340°C and in all cases except at pressure of 40 bar and LHSV of 2.0 h⁻¹, but in case of feed "B2" product below 50 ppm sulphur content could not be obtained even at the highest temperature and pressure (360°C and 60 bar) and the lowest LHSV (1.0 h⁻¹) applied. Products below 10 ppm sulphur content can be produced at 340°C and in all cases, except pressure of 40 bar and LHSV of 2.0 h⁻¹ in case of Feed "A1", on the contrary, product below 10 ppm sulphur content can only be obtained at the highest temperature and pressure (360°C and 60 bar) and the lowest LHSV (1.0 h⁻¹) in case of Feed "A2". However, products containing lower than 10 ppm sulphur could not be obtained applying heavy gas oils even at highest temperature and pressure and the lowest LHSV applied.

The reduction of the aromatic content taking place collaterally with the hydrodesulphurization was investigated as well. The polyaromatic content of products was well below the required value (11%) of EN 590 standard, which indicates that satisfying the requirement of polyaromatic content can be reached more easily than that of the sulphur content.

The HDA activity of the catalyst was relatively high in conditions to be applied to obtain products having the lowest sulphur content for every applied feeds, and not only the reduction in polyaromatic content but the decrease in mono aromatic content took place. The reduction of the aromatic content of gas oils is advantageous from the aspects of environmental protection and engine operation. However, if the primary purpose of the hydrotreatment is the reduction of the sulphur content, high HDA activity involves growing hydrogen consumption that is not beneficial from the point of view of economy. Besides, the use of more hydrogen causes more fuel consumption consequently higher flue gas emissions in the steam-reforming process, so some parts of the emissions are shifted from the cars to the refinery.

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