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DEEP HYDRODESULPHURISATION OF GAS OILS

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Abstract. *The 350 ppm limit of sulphur content came into force in the European Union in the year 2000, and this value will be 50 ppm in the year 2005 and 10 ppm at the end of this decade. In this paper the possible routes for meeting these strict requirements are summarized. The experimental results of the hydrodesulphurisation of gas oils obtained on Ni-Mo/Al_2O_3/promoter catalyst are presented. Effect of the key process parameters (temperature, pressure, LHSV) and of composition of the feeds on the yield and quality of the products are discussed. In addition to these hydrogenating reactions of aromatic compounds taking place during hydrodesulphurisation are covered. On the basis of the experimental results the advantageous process parameters for producing diesel fuel blending components of different sulphur content were determined.*

Key words: *deep hydrodesulphurisation, gas oil, diesel fuel, aromatic saturation*

Introduction

Meeting the limits of increasing severity of exhaust emission for Diesel vehicles requires a complex approach. This includes improved engine construction e.g. “common rail” fuel injection system, cooled exhaust gas recirculation, use of improved exhaust emission treating systems e.g. NO_x traps, NO_x converters, particulate filters and in addition to these use of sulphur-free fuels [1, 2, 3, 4, 5, 6]. The European Union made by its new regulations the necessary legislative actions to ensure improved fuel quality for the improved engine performance. Among Diesel fuel quality parameters the sulphur limit level changed to the largest extent in the last years, and this will be the key parameter in the near future. The present and expected Diesel fuel quality parameters are summarized in Table 1. Many European countries apply tax incentives to extend the use of Diesel fuels having sulphur content of 10 ppm, for example Germany (2003), Finland (2002), Sweden (2001) [7].

Table 1. Present and planned quality parameters of Diesel fuels

Requirements	MSZ EN590 (2000)	EU (2005)	EU (2009)
Cetane number, min.	51	51	[a]
Density kg/m^3, 15°C, max.	820–845	820–845	[a]
Polyaromatics, %, max.	11	11	[a]
Distillation of 95lv%, °C, max.	360	360	[a]
Sulphur content ppm, max.	350	50/10[b]	10

[a] Until the end of 2005 the European Commission will carry out a comprehensive review

[b] Fuel must be geographically available

Meeting the maximum sulphur content of 50 ppm (10 ppm) coming into force from 2005 and in particular of 10 ppm from 2009, initiate extensive research and development activities both on the conventional hydrodesulphurisation technology and on alternative methods which are summarized on Figure 1.

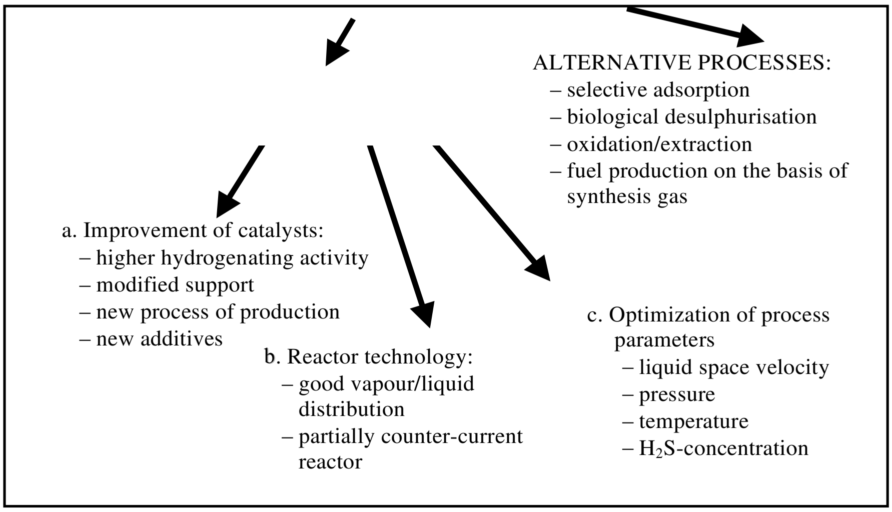

Figure 1. Ways for processing low sulphur diesel fuels

Conventional Hydrodesulphurisation, HDS

Improvement of catalysts. To improve performance of the catalyst, all steps in the preparation of catalyst - choice of a precursor of active species, selection of support, synthesis procedure and post-treatment of the synthesised product - should be taken into account. Some examples for these different approaches are summarized in the following.

- By applying new synthesis procedure, 20-30% increase of activity can be achieved with higher dispersion, improved utilisation of molybdenum and greater conversion of active metals to their sulphided form. Good examples are for this the AKZO Nobel Catalyst STARS (Super Type II Active Reaction Sites) and the Criterion Catalyst CENTINEL catalyst family [8, 9].
- Noble metals (e.g. Pt, Pd) on acidic supports (e.g. amorphous silica-alumina: ASA, zeolite) can also advantageously be applied beside the conventional transition metal sulphide catalysts, because they have higher hydrogenating activity. Production of practically sulphur-free Diesel fuels (below 10 ppm) needs application of a catalyst being able to remove even sterically hindered sulphur compounds, such as 4- and/ or 6-methyl dibenzothiophenes. In case of these compounds the first step is hydrogenation of the aromatic ring followed by the elimination of sulphur atom. Catalysts having higher hydrogenating activity are preferred for this reaction. It should be mentioned, however, that feeds need to be partially desulphurised to sulphur level below 500 ppm before applying these types of catalysts [10, 11].
- Change of the nature of active sites by addition of P, F, B_2O_3 [12, 13, 14].
- Post-treatment of the synthesised catalysts by nitrilo triacetic acid, ethylene diamine, etc. [15].

Reactor technology. Beside improving the activity of catalysts, upgrading of hydroprocessing equipment is inevitable to produce fuels of low sulphur content. The most important developments carried out in this area in the last years are summarized as follows [16-18]:

- By applying dense catalyst loading instead of sock catalyst loading 15% higher catalyst volume in the same equipment can be achieved.
- Maximum catalyst utilization can only be achieved if the gas and liquid reactants are uniformly distributed both volumetrically and thermally before they are introduced into the top of each catalyst bed. Many types of vapour/liquid distributor trays were commercialized in the last years. Some examples from these are Haldor Topsoe's „Dense Pattern, Flexible Distribution Tray" and „Vapour-Lift Distribution Tray"; AKZO Nobel's „Duplex vapour/liquid distribution tray"; Shell Global Solutions' „High Dispersion" and „Ultra Flat Quench" trays.
- The use of counter-current reactor system, in which the hydrocarbon stream is fed into the top of the reactor and hydrogen is supplied partially at the bottom of the reactor, provides more favorable concentration profiles of H_2S and H_2 than the conventional co-current reactors. The partially counter-current reactor designed by ABB Lummus being applied in the SynSat technologies is an example for this conception.

Optimization of process parameters. Optimization of process parameters means [16, 18, 19, 20]:

- higher partial pressure of hydrogen, especially in case of applying $NiMo/Al_2O_3$ type catalyst;
- lower partial pressure of hydrogen sulphide, because this compound inhibits HDS reactions;
- lower liquid space velocity corresponding longer residence time, and higher volume ratio of hydrogen-to-hydrocarbon.

Alternative Processes

Although alternative methods for desulphurising of gas oil such as desulphurisation by selective adsorption (Phillips 66 Co. "S Zorb Process"), chemical oxidation followed by extraction (Uni-Pure and Texaco "ASR-2 Process"), biological desulphurisation and production of Fischer – Tropsch Diesel fuel are under development recently [21-23]. For most refineries upgrading of their existing HDS units remains the most reasonable solution.

Increase of pressure of hydrotreating units is not relevant in many refineries, because the existing equipments are designed for lower pressures (generally 40-50 bar) than those used in the new hydrotreating units (above 60 bar). In this case one of the possible solutions is the application of a second reactor in the downstream of the existing one.

The aim of the present study was to identify and quantify the key process parameters for hydrodesulphurisation and hydrodearomatisation of two previously hydrotreated gas oil fractions being similar as if they would have been produced in a low pressure hydrotreater. The experiments were carried out using $NiMo/Al_2O_3$ catalyst of steady-state activity, by continuous operation. We studied the effects of key process parameters on the removal of sulphur and nitrogen as well as saturation of aromatics. On the basis of the experimental results process parameters for producing low sulphur (below 50 ppm) and sulphur-free (below 10 ppm) Diesel fuel blending components, respectively, were determined.

Experimental

Apparatus. The experiments were carried out in a high-pressure reactor system. This consists of a tubular reactor of 100 cm^3 efficient volume without back-mixing, and of equipments similar to those of a commercial unit (pumps, separators, heat exchangers, as well as temperature, pressure and gas flow regulators).

Catalyst. The hydrogenating experiments were carried out on a commercially available presulphided $NiMo/Al_2O_3$ catalyst.

Feeds. Two hydrotreated gas oil fractions were used, representing characteristic types of refinery Diesel blending components. Feed A was a lighter distillate containing significantly more normal paraffins, while Feed B was heavier, contained more aromatics and less paraffin hydrocarbons. Their important properties are summarized in Table 2.

Process parameters. The applied process parameters are summarized in Table 3.

Methods. Properties of the feeds and products were determined by standard test methods (Table 4). For example, sulphur content was measured by the pyro-fluorescence method (ASTM

Table 2. Important properties of the feeds

Parameters	Feed A	Feed B
Density, 15°C, kg/m^3	825	840
Sulphur content, ppm	294	271
Nitrogen content	44	80
Aromatic content, %		
total	28.0	34.4
mono	23.3	27.6
di	4.2	6.3
poly	0.5	0.5
n-Paraffin content, %	19.5	10.4
Distillation data, D86, °C		
Initial boiling point	175	200
10 vol.%	200	227
50 vol.%	248	277
90 vol.%	329	339
Final boiling point	359	364
Flash point, °C	60	67
Kinematic viscosity, 40°C, mm^2/s	2.34	3.24
Cetane index	51.9	54.0

Table 3. Applied process parameters

Parameters	
Temperature, °C	290-350
Pressure, bar	40-50
Liquid hourly space velocity, (LHSV), h^{-1}	0.8-1.5
H_2 to hydrocarbon volume ratio, m^3/m^3	400

Table 4. 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 5453
Nitrogen content	ASTM D 4629
Aromatic content	EN 12916:2000
n-Paraffin content	ASTM D 5442
Distillation data	ASTM D86-97

D 5453) and aromatic content by high performance liquid chromatography (HPLC) (EN 12916:2000).

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

$$\text{HDS activity: HDS\%} = 100\,(S_{feed} - S_{product}) / S_{feed} \qquad (1)$$

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

$S_{product}$: sulphur content of the product, ppm

$$\text{HDA activity: HDA\%} = 100\,(A_{feed} - A_{product}) / A_{feed} \qquad (2)$$

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

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

Results and Discussion

Experiments applying feed "A". 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 gas and gasoline fractions were higher at higher temperatures and lower liquid hourly space velocities (LHSV), due to the stricter process parameters.

Figure 2 displays the change of sulphur content of the products as function of temperature and LHSV at 40 bar and with LHSV = 0.8 and 1.0 h^{-1} at 50 bar. This shows that increase of temperature and decrease of LHSV reduce sulphur content of the products. The highest rates of the reduction of sulphur content were in the temperature range of 290-330°C at every applied LHSV and the values decreased, although in less extent, when the temperature was increased above 330°C. Sulphur content below 50 ppm can be achieved even at a temperature as low as 290°C and LHSV = 1.2 h^{-1}, while at LHSV = 1.5 h^{-1} higher than 305°C is needed. Products below 10 ppm sulphur content could only be produced at the lowest applied LHSV and above 340°C at 40 bar, while above 340°C with LHSV= 1.0 h^{-1} and above 320°C in case of LHSV= 0.8 h^{-1}, respectively, at 50 bar.

Increase of pressure is advantageous for the reduction of sulphur content of the products, too, especially at lower temperatures. One explanation could be that sulphur compounds remaining in the gas oil after the previous hydrodesulphurization could mainly be heterocyclic species having one or more alkyl chains. Conversion of these refractory sulphur compounds takes mainly place by "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 pressure, especially the partial pressure of hydrogen, shifts the equilibrium towards saturation of aromatics what implies higher reduction in sulphur content, too. Additionally, the increase of pressure is favorable for "direct" reaction route, too, because the partial pressure of H_2S, that exerts negative effect on the rate of reaction, decreases.

Figure 2 shows that sulphur content of the products obtained at 40 bar and LHSV= 0.8 h^{-1} and at 50 bar and LHSV= 1.0 h^{-1} were similar. This suggests that 20% reduction in the LHSV

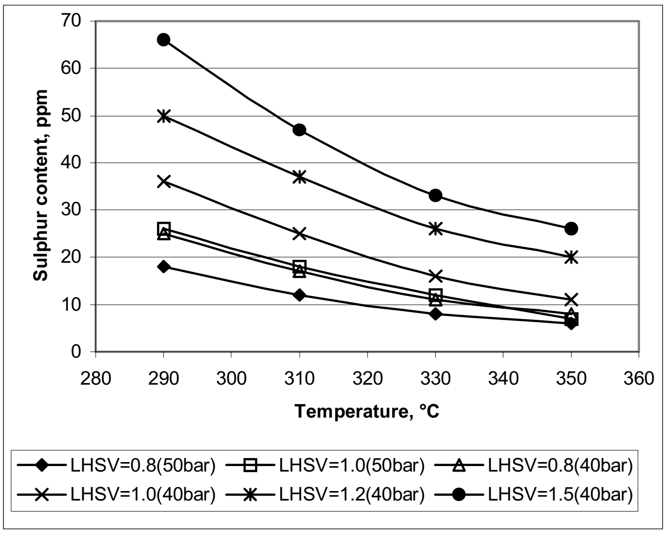

Figure 2. Effect of temperature and LHSV on the reduction of sulphur content (feed "A"; sulphur content: 294 ppm)

(from 1.0 h^{-1} to 0.8 h^{-1}) exerts same effect as the increase of total pressure by 10 bars. So, products having lower than 10 ppm sulphur can be produced either by increasing the total pressure which implies higher operational costs or decreasing the LHSV that leads to loss of attainable yield. The economically reasonable solution depends on the local process and economical conditions.

Figure 3 shows the change of HDS activity of the catalyst as function of temperature and LHSV at 40 bar and with LHSV = 0.8 and 1.0 h^{-1} at 50 bar. This displays that HDS activity changes in a wide range (e.g. from 77.6% to 98.0%), depending on the process parameters applied. It can also be seen that the attainable HDS activity was considerably influenced by pressure and LHSV, by the latter especially at lower temperatures, showing importance of the selection of proper LHSV.

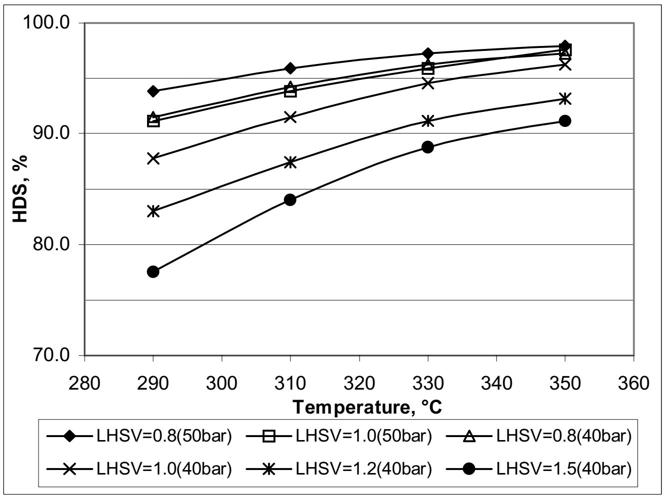

Figure 3. Effect of temperature and LHSV on the HDS activity of the catalyst (feed "A")

Reduction of nitrogen content of gas oils is important, too, because the heterocyclic nitrogen compounds exert negative effect on the conversion of sulphur and aromatic compounds by competitive adsorption on the surface of catalysts, the basic nitrogen compounds behave as poisons for acidic catalysts applied in the refining industry, and they decrease the storage stability of petroleum products.

Figure 4 shows the change of nitrogen content of the products of feed "A" in function of temperature and pressure at LHSV= 0.8 h^{-1}. It displays that the nitrogen content was reduced in a large extent and the product obtained at 350°C and 50 bar contain nitrogen less than 1 ppm or it is practically nitrogen-free. The highest rate of reduction of nitrogen content occurred in the temperature range of 290-330°C, where the concentration of nitrogen compounds decreased almost linearly. The increase of pressure was advantageous for reducing the nitrogen content, too, especially at lower temperatures.

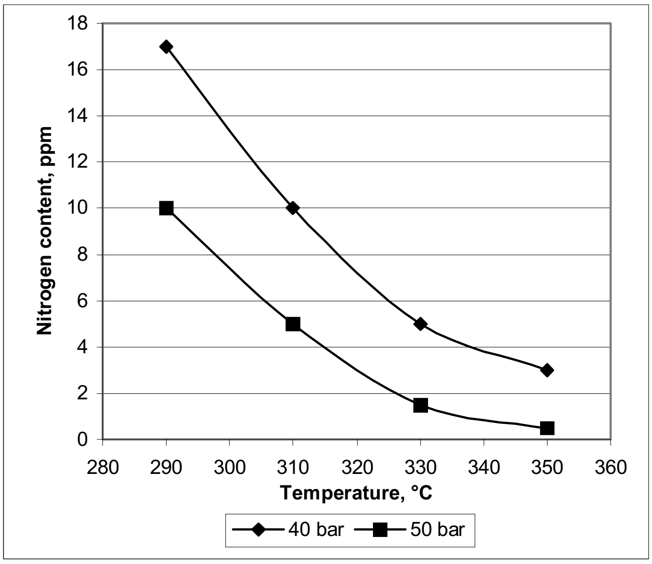

Figure 4. Effect of temperature and pressure on reduction of the nitrogen content (feed "A", nitrogen content: 44 ppm; LHSV= 0.8 h^{-1})

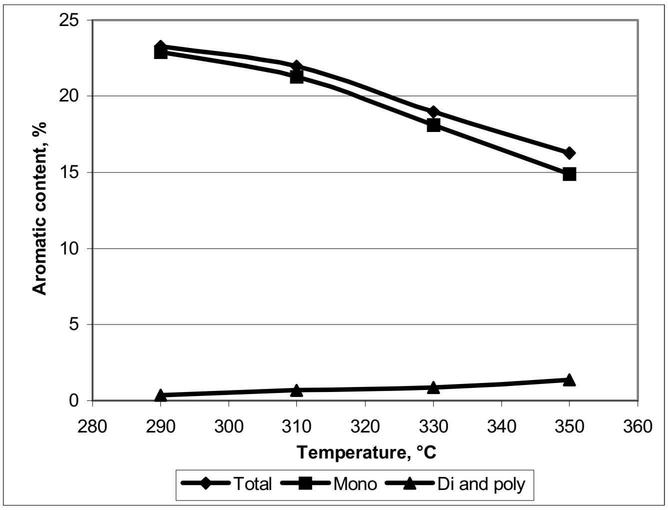

Figure 5. Effect of temperature on the reduction of aromatic content (feed "A"; mono aromatics: 23.3%, di- and polyaromatics: 4.7%, total aromatic content: 28.0%; pressure: 50 bar; LHSV: 0.8 h^{-1})

Reduction of the aromatic content taking place parallelly to hydrodesulphurisation was investigated, too. Similarly to the decrease of sulphur content, highest reduction of aromatics was obtained at 50 bar. For this reason only the results of experiments carried out at this pressure are presented. Figure 5 displays the change of total-, mono- and polyaromatic contents of the products in case of feed "A" as function of temperature and applying LHSV of 0.8 h^{-1}. Figure 5 shows that mono and total aromatic contents of the products were steadily reduced by increasing the temperature, while di- and polyaromatic content shows a slight increase, maybe due to a shift in hydrogenation/dehydrogenation equilibrium. The mono and total aromatic content of the products was lower than that of the feed in every investigated case what proves that not only the ratio of aromatic compounds changed, but also saturation of mono aromatics occurred on the catalyst.

The HDA activity of the catalyst was calculated, too, the values change between 17% and 42%. This relatively high HDA activity supports, too, that the applied catalyst has significant hydrogenating activity.

Reduction of the aromatic content is advantageous from the point of view of environmental protection and engine operation. Higher aromatic content in the fuel causes namely higher flame temperature in the engine which contributes to higher NO_x concentrations in the exhaust gases. Besides, polyaromatics in the fuel affect the formation of particulate matters and polyaromatic hydrocarbon emissions of the engine. Aromatic hydrocarbons have relatively low cetane number, and conversion of these compounds to saturated hydrocarbons having higher cetane number improves the operation characteristics of the engine, for example better ignition, shorter start-up period, etc.

Experiments applying feed "B". Like feed „A", liquid yields using feed „B" were above 98% in each run. Whereas the main object of the study was to produce products of low sulphur content (< 10 ppm) and this type of products could only be obtained at low LHSV in case of feed "A", which can be hydrogenated easier than the feed "B", therefore the experiments applying this latter were carried out only at low values of LHSV (0.8 and 1.0 h^{-1}). Figure 6 displays the change of sulphur content of the products as function of temperature at 40 and 50 bar and at the chosen values of LHSV. Considering set sulphur levels from 2005 and 2009, respectively, we can conclude that low sulphur products (below 50 ppm) can be produced at a temperature as low as 290°C, but sulphur-free products (below 10 ppm) can only be obtained at 50 bar and at the applied highest temperature and lowest LHSV.

The highest rate of reduction of the sulphur content occurred in the temperature range 290-310°C at 40 bar and LHSV= 1.0 h^{-1}, where it decreased practically linearly with increasing temperature, while it was in the range of 290-330°C in other cases, and above this the rate of the reduction of sulphur content decreased. Increase of the pressure is advantageous for the reduction of sulphur content of the products and the correlation between the increase of pressure and reduction of LHSV was similar to the mentioned in case of feed "A".

Comparing the sulphur content of the products obtained from feed "A" and feed "B" at similar process conditions (see Fig. 2 and 6) it can be stated that the products obtained from feed "B" containing aromatics and nitrogen compounds in higher concentration showed higher sulphur content than those produced from feed "A", in spite of the fact that the latter contain sulphur in something higher concentration. This indicates that higher aromatic and nitrogen content exerts negative effect on the desulphurising reactions but this effect decreases with increasing temperature which is the result of the growing activity of the catalyst.

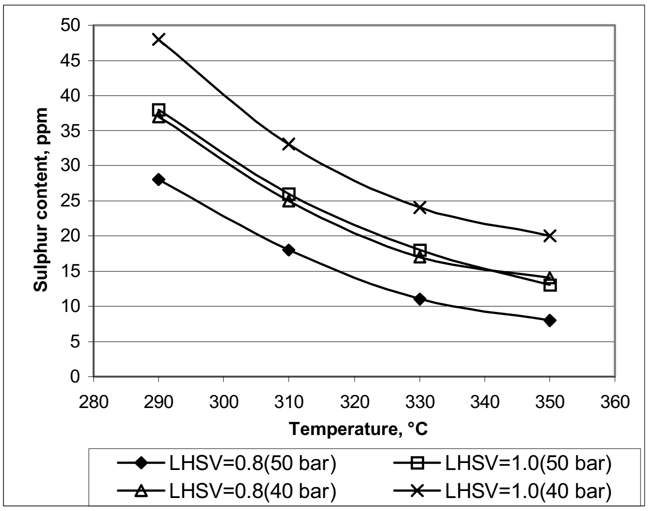

Figure 6. Effect of temperature on the reduction of sulphur content (feed "B"; sulphur content: 271 ppm)

Figure 7 displays HDS activity as function of temperature at 40 and 50 bar and LHSV = 0.8 and 1.0 h^{-1}. This shows that the values of HDS activity were in a wide range (e.g. from 82.3% to 97.0%) depending on the process parameters. Activities of 95% or higher could only be obtained at 330°C and above at LHSV= 0.8 h^{-1} and at 350°C with LHSV= 1.0 h^{-1} in case of 50 bar, and at 350°C applying LHSV= 0.8 h^{-1} in case of 40 bar.

The change of nitrogen content of the products was investigated, too, Figure 8 shows the results of experiments carried out in the temperature range of 290-350°C, at pressures of 40 and 50 bar and LHSV= 0.8 h^{-1}. The shape of curves is similar to those obtained in case of feed "A", but the nitrogen content of the products of feed "B" produced at same technological parameters is slightly higher.

Reduction of aromatic content taking place parallelly to hydrodesulphurisation was also investigated. Figure 9 displays the change of total-, mono- and polyaromatic content of the products in function of temperature at 50 bar and LHSV = 0.8 h^{-1}. It is to be seen that mono and total aromatic contents of the products steadily decrease with increasing temperature. The

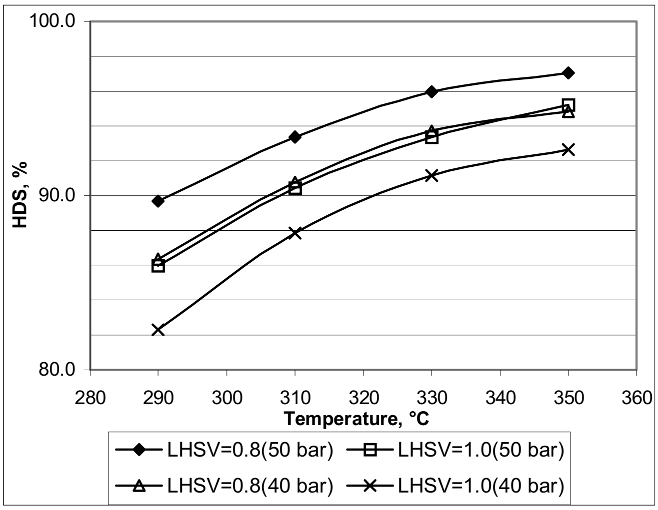

Figure 7. Effect of temperature on the HDS activity (feed "B")

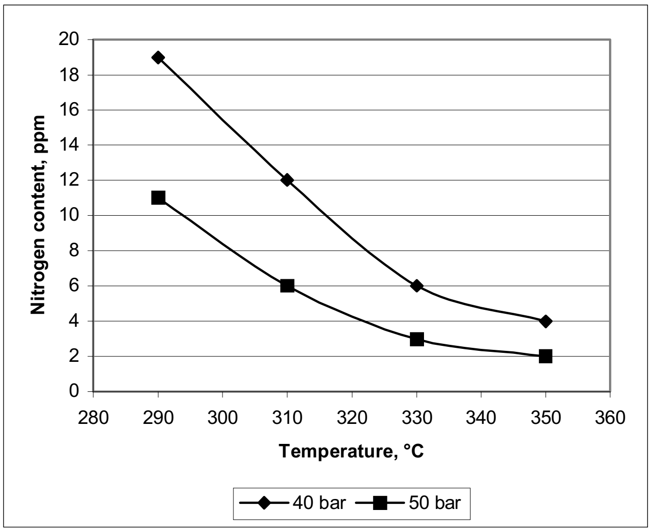

Figure 8. Effect of temperature and pressure on the reduction of nitrogen content (feed "B", nitrogen content: 80 ppm; LHSV= 0.8 h^{-1})

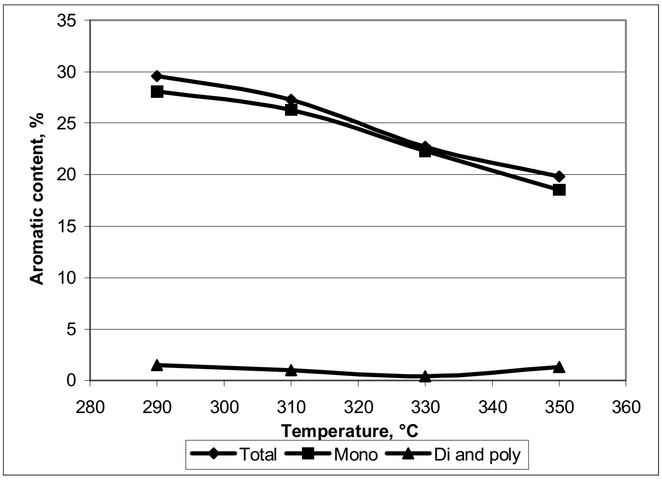

Figure 9. Effect of temperature on the reduction of aromatic content (feed “B”; mono aromatics: 27.6%, di- and polyaromatics: 6.8%, total aromatic content: 34.4%; pressure: 50 bar; LHSV: 0.8 h^{-1})

di- and polyaromatic contents first decrease by increasing the temperature then they go through a minimum point at 330°C and increase gradually again.

However, the significant part of di- and polyaromatic content of the feed is removed even at 290°C. As regards to mono aromatic content of the products, it can be stated that they are higher than that of the feed at 290°C. This 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. However, the increase of temperature effected that mono aromatic content of the products became lower than that of the feed, namely saturation of the mono aromatics being present originally in the feed takes place, too, which indicates that the investigated NiMo type catalyst has considerable hydrogenating activity.

The HDA activity of the catalyst was calculated as well, this increases in a considerable extent (from 14.0% to 42.4%) with the rise of temperature. These results support, too, that the investigated catalyst has significant hydrogenating activity.

Reduction of the aromatic content of gas oils is advantageous from aspects of environmental protection and of engine operation which are summarized previously. However, primary purpose of the hydrotreatment is reduction of the sulphur content, the high HDA activity involves growing hydrogen consumption that is not beneficial from the point of view of economy. Besides, use of more hydrogen causes more fuel consumption consequently higher flue gas emissions in the steam-reforming process, so some part of emissions is shifted from the cars to the refinery.

Conclusions

Production of Diesel fuels of lower and lower sulphur contents requires continuous development of HDS processes. We summarized some examples of these in the Introduction.

Investigation of the reduction of sulphur content of a highly aromatic and a more paraffinic feed on $NiMo/Al_2O_3$ catalyst showed that we are able to produce gas oils having sulphur content less than 50 ppm (EU limit from 2005), as well as less than 10 ppm sulphur content (EU limit from 2009) from both feeds on the applied catalyst. Highest rate of the reduction of sulphur content occurred in the temperature range 300-330°C in case of both feeds, but further increase of temperature reduced it largely. The increase of pressure was advantageous for the reduction of sulphur content, especially at lower temperature. It can also be seen that the attainable HDS activity is influenced by the LHSV, showing the importance of selecting proper values of it. Correlation between about 20% reduction of LHSV and increase of pressure by 10 bars (from 40 to 50 bar) was noticed in case of both feeds. On the basis of experimental results it can be stated that higher aromatic and nitrogen content exerts negative effect on the attainable reduction of sulphur, especially at the applied lower temperatures.

The nitrogen content of feeds was reduced in a large extent on the applied catalysts, too, even we can produce practically nitrogen-free product at advantageous process parameters.

The mono and total aromatic content of the products was steadily decreased by increasing the temperature. Mono aromatic content of the products was lower than that of the feeds at the applied lowest temperature in case of feed “A” and above 310°C in case of feed “B”, showing that the catalyst provides hydrogenating activity enough to saturate not only mono aromatics originating from polyaromatics but also those being originally present in the feeds. Significant part of the di- and polyaromatic content of the feed is removed even at 290°C, while the change of di- and polyaromatic contents in function of temperature increases steadily in case of feed “A” and shows a curve with minimum point in case of feed “B”. Reduction of the aromatic content of gas oils is advantageous from aspects of environmental protection and of engine operation, but it is not beneficial from the point of view of economy, in consequence of increasing hydrogen consumption. HDA activity of the applied NiMo type catalyst is relatively high compared to that of CoMo type one.

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