Quality Improvement of Heavy Gas Oil with Hydroprocessing

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Abstract

Quantity requirement for diesel fuel of low sulphur and aromatic content is increasing worldwide; meantime the quality of available crude oils has declined causing challenges in hydroprocessing of gas oils. Results of quality improvement of heavy gas oil are presented, it was carried out in one stage on NiMo/Al_2O_3 catalyst and in two stages on NiMo/Al_2O_3 and PtPd/USY-zeolit catalysts. In one stage hydroprocessing sulphur and polyaromatic contents of the products met the requirements of the standard only if strict process parameters were applied which resulted in operation problems and product loss, moreover the advantageous process parameters of hydrodesulphurization and hydrodearomatization did not coincide. In two stages hydrotreating a partially hydrogenated product obtained on NiMo catalyst was further hydroprocessed on PtPd/USY at moderate process conditions. Results showed that the advantageous process parameters for reduction of sulphur and aromatics coincided. Quality parameters of products regarding to aromatics met not only the requirements of the standard but the stricter requirements of engine manufacturers also.

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1 Introduction

The quantity requirements for high quality middle distillates (diesel fuel and JET) continuously increased in the last decade, especially in the European Union. Figure 1 shows that the increase in consumption of diesel fuel was more than 30% in the time period of 1999-2007, and this tendency was interrupted by the world economy crisis [1]. At the same time, the consumption for motor gasoline considerably decreased.
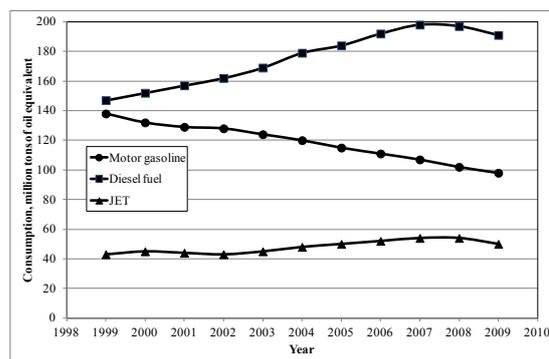
Fig. 1. Change of the consumption of the motor gasoline, diesel fuel and JET in the European Union [1]

Additionally, the quality specifications of diesel fuels became more and more stricter everywhere [2-4]. The most important quality changes that occurred in the standard regarding to diesel fuels along with requirements of engine manufacturers given in the World Wide Fuel Charter are summarized in Table 1. Data show that the most pronounced changes occurred in the maximum allowable sulphur content, which decreased from 350 mg/kg to 10 mg/kg. Polyaromatic content of diesel fuels was also decreased, and further tightening in its value is expected in the near future. Requirements of engine manufacturers for diesel fuels are even stricter compared to the standard values. In the light of these expectations the polyaromatic content should be decreased to 2% whereas the total aromatic content to 15%, respectively.

The main reasons that led to introduction of restrictions in sulphur content of diesel fuels were the following: decrease in the risk of acid rain formation caused by the SO_X content of exhaust gases, and preserve the efficiency of exhaust gas treating catalysts for longer period [5-7].

Aromatics, especially polyaromatics, contribute to formation of particulate matters as well as to increase in the NO_x concentration of exhaust gases due to the high flame temperature on burning them. Aromatic compounds have low cetane number, which indicates unfavourable combustion characteristics causing irregular engine operation and increased emission [5-7].

It is well known that the reaction between an aromatic compound and hydrogen is reversible and at normal hydrotreating conditions, complete conversion may not be possible due to equilibrium limitations [8]. Since industrial feeds contain mixtures of tri-, di- and monoaromatics, and hydrogenation proceeds via consecutive reversible reactions the determination of kinetic and thermodynamic parameters is difficult task and requires some empirical considerations. Yui [9] applied the following equation to calculate the fractional degree of hydrogenation of aromatics at equilibrium (X_{Ae}).

$$X_{Ae} = \left(k_f p_{H2}^{\beta} - k_r M\right) / \left(k_f p_{H2}^{\beta} - M\right) \qquad (1)$$

where k_f and k_r are the forward and reverse rate constants, p_{H2} is hydrogen partial pressure, β is the power term and M is the ratio of naphthenes and aromatics in the feed C_{N0}/C_{A0}.

They considered that k_f and k_r follow an Arrhenius type equation, so

$$k_f = k_{f0} exp\left(-E_f / RT\right) \qquad (2)$$

and

$$k_r = k_{r0} exp\left(-E_r / RT\right) \qquad (3)$$

where k_{f0} and k_{r0} are frequency factors, E_f and E_r are activation energies, R is the gas constant and T is the absolute temperature.

Results for feed containing 41.1% aromatics and M=1.20 summarized on Figure 2. Parameters of equations 1-3 were determined based on data obtained with hydrotreating of this feed at various process conditions. They were β=1.73, E_f= 125.3 kJ/mol, E_r = 210.0 kJ/mol, k_{f0}= 2.79x10^8 h^{-1}MPa$^{-\beta}$ and k_{r0}= 2.432x10^{16} h^{-1}.
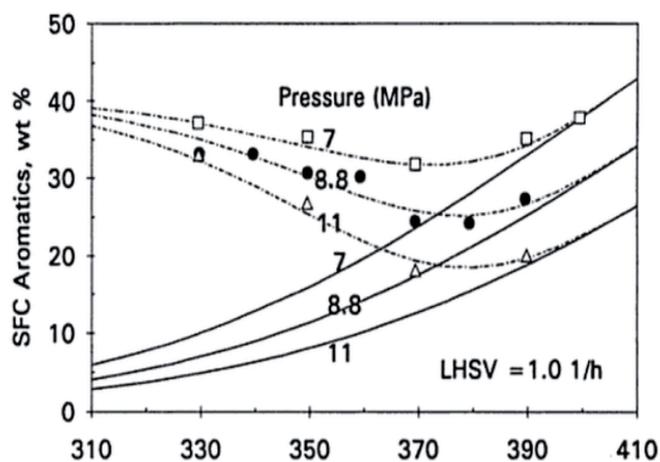

Fig. 2. Observes and calculated aromatics at various pressures, solid lines indicate the equilibrium limit [9]

At the same time, the quality of available crude oil stocks continuously declined giving tough challenges for refineries to produce high quality diesel fuels in increasing quantity [10-13]. The economic and political events occurred recently highlight the attention of the refining industry to diversify the crude oil sources and to increase the flexibility of the whole petroleum processing train [14-16].

The aim of the present study was to determine the optimal process route and operating parameters (temperature, pressure and liquid hourly space velocity in the following: LHSV) for producing gas oil blending components with specifications that correspond to the standard of automotive diesel fuel from a heavy gasoil applied as feed. This investigation contributed to elaborate technology alternative for hydrotreating gas oils produced from heavy crude oils.

2 Experimental

To improve the quality of the selected heavy gas oil two alternatives were investigated. Hydroprocessing in one step using a transition metal sulphide catalyst supported on alumina, and in two steps where partially hydrogenated product on transition metal sulphide catalyst was produced at first then it was hydrogenated on noble metal/zeolite catalyst further.

Tab. 1. Change of the quality requirements of diesel fuels

Properties	EN590 (2000)	EN590 (2004)	EN 590 +A1 (2009)	WWFC* Category 4 (2006)
Density, at 15°C, kg/m³	820–845	820–845	820–845	820-840
Sulphur content, mg/kg,	350	50/10	10	10
Polyaromatic content, %	11	11	8	2
Total aromatic content, %	-	-	-	15
Distillation of 95lv%, °C	360	360	360	340

*WWFC – World Wide Fuel Charter

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2.1 Apparatus

The experiments were carried out in a high-pressure reactor system, which consists of a tubular reactor (100 cm^3 efficient volume and free from back-mixing) and the usual equipments and devices applied in the reactor system of hydrotreating plants (pumps, separators, heat exchangers, and temperature, pressure and gas flow regulators). The experiments were carried out on catalysts of stable activity and in continuous operation.

2.2 Materials
2.2.1 Catalyst

A commercial type NiMo/Al$_2$O$_3$ catalyst promoted with phosphorus (Ni/(Ni+Mo) atomic ratio 0.274, surface area 182 m^2/g and pore volume 0.55 cm^3/g) was used in the one step process and in the first step of two steps process. The catalyst was pretreated as recommended by the supplier. The details are confidential therefore we can not write more about the procedure.

In the second step of two steps process, a PtPd/USY-zeolite catalyst was applied containing 0.6% Pd and 0.3% Pt. The main properties of the support are the following: SiO$_2$/Al$_2$O$_3$ ratio 33.5, total and mesopore surface areas 592.5 m^2/g and 51 m^2/g calculated using BET-plots and t-plots, respectively. Metal dispersion of the Pt-Pd bimetallic catalyst was 0.48 determined by CO chemisorption measurement.

2.2.2 Feed

Heavy gas oil fraction derived from Russian crude oil applied as feed in the one step process as well as in the first step of two steps process and its partially hydrogenated product in the second stage. Their main properties are given in Table 2. Data show that the quality of selected gas oil fraction is very poor especially with respect to sulphur, nitrogen and aromatic contents, which considerable influence the efficiency of the hydrodesulphurization.

Tab. 2. Important properties of feeds

Property	Value	
	1st step	2nd step
Density, @15°C, kg/m^3	860.0	853.1
Sulphur content, mg/kg	9910	187
Nitrogen content, mg/kg	286	81
Aromatic content, %		
Mono aromatics, %	21.4	19.1
Polyaromatics, %	14.5	7.6
Total aromatics, %	35.9	26.7
Boilingpoint range, °C	188-376	195-368

2.3 Methods

Properties of feeds and products were determined by standard test methods, for example sulphur and nitrogen content was measured by oxidative combustion followed by UV (ultraviolet) and CLD (chemi-luminescence) detection (multi EA 3100 equipment), and the aromatic content by high performance liquid chromatography (HPLC) (EN 12916:2000).

2.4 Process parameters

The applied process parameters were selected considering the industrial practice. In case of one stage hydroprocessing they were as follows: temperature 300-380°C, total pressure 50-80 bar, LHSV 1.0-3.0 h^{-1} and hydrogen to feed volume ratio 400 Nm^3/m^3. In the first step of two stages hydrotreatment: temperature 360°C, total pressure 60 bar, LHSV 1.5 h^{-1} and hydrogen to feed volume ratio 400 Nm^3/m^3. In the second step: temperature 280-340°C, total pressure 60 bar, LHSV 1.5 h^{-1} and hydrogen to feed volume ratio 400 Nm^3/m^3.

3 Results and discussion
3.1 One stage hydrotreating

Each sample was purged with nitrogen to make it free from dissolved H$_2$S and stabilized before the analytical measurements. Effect of the change of temperature and LHSV on the sulphur content of products at 80 bar is displayed on Figure 3. In accordance with literature data both the increase of temperature and decrease of LHSV, especially their combined effect, favourably influenced the efficiency of hydrodesulphurization of the selected gas oil. Our aim was to determine the extent of hydrodesulphurization and compare the two alternative routes.

90% of the sulphur in its compounds were converted at the mildest process conditions applied (9910→921 mg/kg at 300°C and 3.0 h^{-1}). In order to obtain such product quality which is a sulphur content fulfilling the specification of the standard (10 mg/kg) the temperature should be increased and the LHSV decreased significantly. The slope of curves of sulphur content vs temperature was the steepest in the temperature range of 300-340°C then it became minor as the temperature increased further.
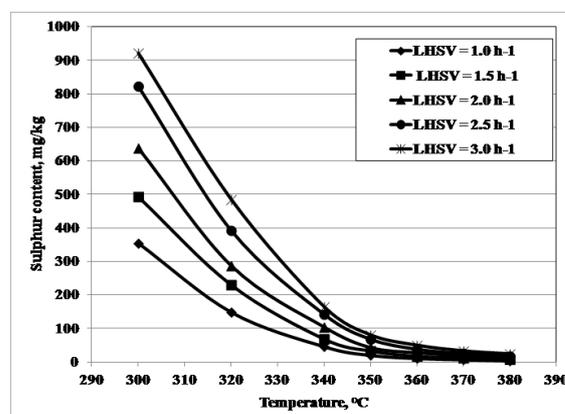

Fig. 3. Change of the sulphur content of the products in function of temperature and LHSV (liquid hourly space velocity, cm$^3_{feed}$/cm$^3_{catalyst}$ h) (pressure: 80 bar)

Fig. 4. Change of the sulphur content of the products in function of temperature and LHSV(liquid hourly space velocity, $cm^3_{feed}/cm^3_{catalyst}$ h) (pressure: 80 bar)
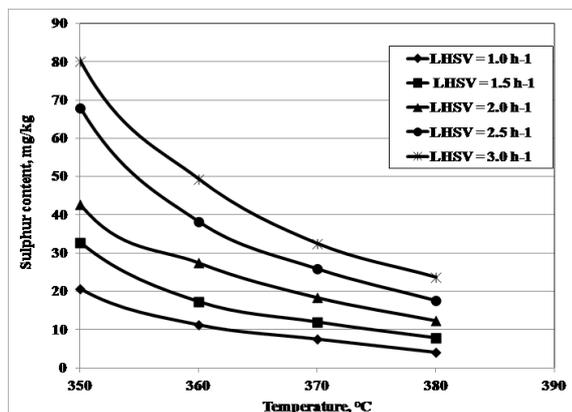

Fig. 5. Change of the sulphur content of the products in function of pressure and LHSV (liquid hourly space velocity, $cm^3_{feed}/cm^3_{catalyst}$ h) (temperature: 380°C)

Figure 4 highlights the change of sulphur content in the deep hydrodesulphurization range. Relatively high temperatures and long residence time (low LHSV) required to remove the last tens of mg/kg of sulphur remaining in products. The explanation is known, it is due to the high final boiling point of the selected gas oil, it contains relatively high amount of substituted heterocyclic sulphur compounds (e.g. alkyl dibenzothiophenes) those contain one or two alkyl groups adjacent to the sulphur atom (e.g. 4 methyl or 4,6 dimethyl dibenzothiophene) [16-18]. These alkyl groups sterically hinder the connection of the sulphur atom to the active centre of the catalyst and the conversion of this type of sulphur compounds referred as hindered dibenzothiophenes, requires high temperature and pressure, and low LHSV [3,15,19].

The decrease in LHSV (meaning longer residence time) at constant temperature improves degree of hydrodesulphurization, even at lower temperatures. Reduction of LHSV from 3.0 h^{-1} to 1.0 h^{-1} resulted in 570 mg/kg (920 mg/kg → 350 mg/kg) decrease of sulphur content at 300°C, while this was only 118 mg/kg (164 mg/kg → 46 mg/kg) at 340°C.

Figure 5 displays the effect of the pressure on the hydrodesulphurisation of selected gas oil at 380°C and LHSV of 1.0, 1.5 and 2.5 h^{-1}. Data show that sulphur content of products decreased with increasing pressure, especially at higher LHSV, meaning that the shorter residence time could be partially compensated.

Reasons of this advantageous effect are well known. The higher total pressure means larger hydrogen partial pressure and smaller partial pressure of H_2S, which exerts negative effect on the rate of hydrotreating reactions. The higher hydrogen partial pressure is advantageous for saturation reactions of aromatics. The conversion of the refractory sulphur compounds takes mainly place by "indirect" reaction route, which involves the hydrogenation of the aromatic ring in the first step [3,13,15,19]. This is an equilibrium reaction so, the increase of partial pressure of hydrogen, shifts the equilibrium towards saturation of aromatics which implies higher reduction rate of sulphur content, too. The higher pressure is also favourable for dealkylation reactions resulting removal of the alkyl groups are adjacent to sulphur atom.
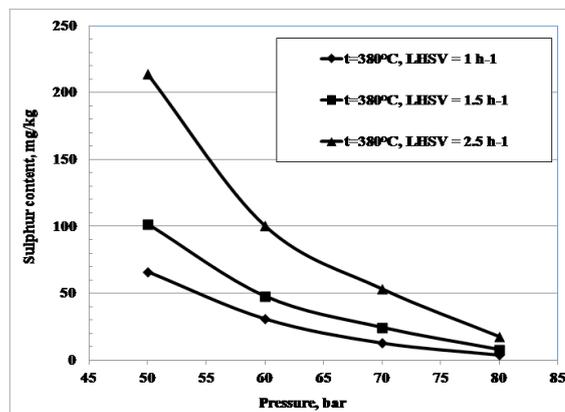
Products of sulphur content less than 10 mg/kg could only be produced at pressure of 80 bar and temperature of 370°C and LHSV of 1.0 h^{-1}, or temperature of 380°C and LHSV of 1.0, 1.5 h^{-1}. These strict operating conditions decrease the yield of valuable liquid products by increasing the rate of hydrocracking reactions, and shorten the lifetime of the catalyst. Additionally, the low LHSV reduces the productivity, too.

Reduction of aromatic content taking place parallel to hydrodesulphurisation was also investigated. Figure 6-8 display the effect of temperature and pressure on total, mono and polyaromatic contents of products at LHSV of 1.0 h^{-1}.

Figure 6 shows the total aromatic content was lower than that of the feed at every applied temperature and pressure, at 360°C the curve has a minimum point due to thermodynamic reasons. At given temperature increase of total pressure also contributed to reduce the total aromatic content. The saturation of aromatics was remarkable in the pressure range of 60-80 bar and around the temperature of 340°C. An explanation for this is the higher rate of ring opening reactions at elevated pressures and temperatures, which take place parallel with aromatic saturating reactions and are irreversible. Product having the lowest total aromatic content of 20.8% can be obtained at temperature of 360°C, pressure of 80 bar and LHSV of 1.0 h^{-1}. Unfortunately this value is considerable higher than the requirement of the engine manufacturers given in the WWFC (15%).

Figure 7 shows the products obtained at 50 and 60 bar at temperature of 320°C contained more mono aromatics than the feed has. The rate of saturation of mono aromatics to naphthenes is smaller than that of their formation from di- and polyaromatics by consecutive ring opening at these process conditions. However, the mono aromatic content of products was lower than that of the feed at higher temperatures and pressures. This means that the saturation of mono aromatics being present originally in the feed or formed from the polyaromatics by consecutive ring hydrogenation takes place on the catalyst, which indicates that the investigated NiMo type catalyst has considerable ring saturation activity.
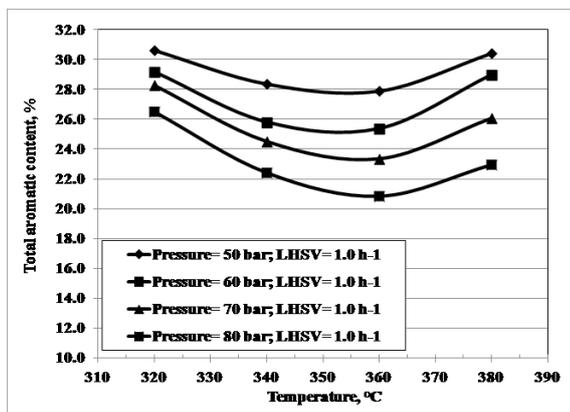
Fig. 6. Change of the total aromatic content of the products in function of temperature and pressure (liquid hourly space velocity, LHSV: 1.0 h⁻¹)

Fig. 7. Change of the mono aromatic content of the products in function of temperature and pressure (liquid hourly space velocity, LHSV: 1.0 h⁻¹)

Product having the lowest mono aromatic content (14.5%) can be obtained at the temperature of 360°C, pressure of 80 bar and LHSV of 1.0 h⁻¹.

Figure 8 shows that the shape of curves regarding to change of polyaromatic content is similar to those obtained with monoaromatics, however, the minimum of polyaromatic content was shifted to lower temperatures. Polyaromatic content of the applied gas oil (14.5%) was higher than the value specified in the standard (8%), and significantly higher comparing to the requirement of the WWFC (2%). Polyaromatic content of products corresponds the requirement of the standard at every applied pressure and various temperatures but not to that of the requirement of the WWFC.

In comparison of the advantageous process parameters of the hydrodesulphurization and the hydrodearomatization the following could be assessed. Products of low aromatic content can be obtained in the temperature range of 340-360°C at every applied pressure, but the sulphur content of products obtained at these process conditions did not satisfy the requirement of the standard. Additionally, the process conditions required to obtain product of sulphur content to be met with the requirement of the standard, were unfavourable for the saturation of aromatics. Only one combination of process parameters was found on the applied NiMo catalyst that can be used to produce product of quality parameters being satisfied both the sulphur and polyaromatic requirements of the standard.

The results clearly showed that the advantageous process parameters of the hydrodesulphurization and the aromatic reduction did not coincide on the catalyst applied in the one step hydroprocessing.

3.2 Two stages hydroprocessing

A possible solution to resolve the above mentioned problems is to carry out the hydrotreating of the gas oil in two stages. In the first step partially desulphurised gas oil was produced at mild process conditions on NiMo catalyst selected according to the following criteria the temperature to be in the advantageous
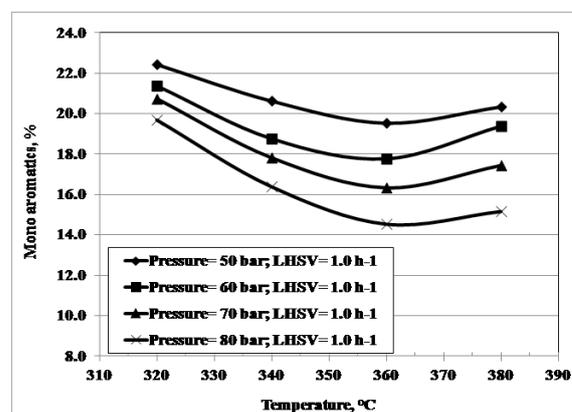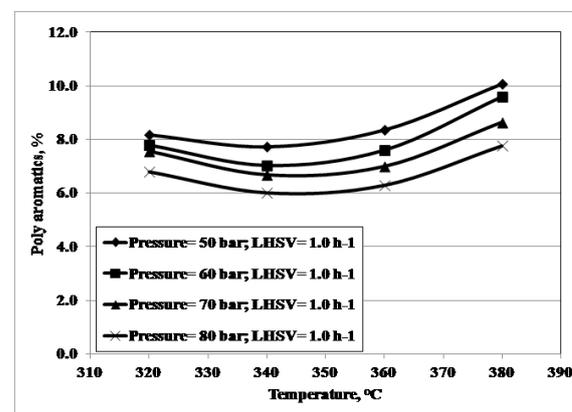

Fig. 8. Change of the polyaromatic content of the products in function of temperature and pressure (liquid hourly space velocity, LHSV: 1.0 h⁻¹)

region of aromatic saturation (340-360°C), the pressure lower than 68 bar and LHSV at least 1.5 h⁻¹ (suitable for industrial practice). Additionally, the sulphur content of the prehydrogenated product has to be maximum 200 mg/kg, because the sulphur tolerancy of PtPd/USY catalyst to be applied in the second step is in this region [20, 21, 22]. The selected process parameters were: temperature 360°C, total pressure 60 bar, LHSV 1.5 h⁻¹ and hydrogen to feed volume ratio 400 Nm³/m³.

Properties of the obtained product named as feed for 2ⁿᵈ step are shown in Table 2. Comparing the heavy gas oil feed with this partially hydrogenated product 98% of the sulphur content of the feed was removed and almost 50% of polyaromatics saturated in the first step, so it could further processed on PtPd/USY catalyst in the second one. Selection of process parameters was done that they should correspond those applied in the 1ˢᵗ step, namely pressure was 60 bar and LHSV 1.5 h⁻¹.

Change of the sulphur content in function of temperature on the PtPd/USY catalyst showed that products of sulphur content lower than 10 mg/kg can be processed at temperature as low as 310°C (Figure 9). The explanation is again the faster hydrogenation of hindered dibenzothiophenes. Conversion of these refractory sulphur compounds takes mainly place in two
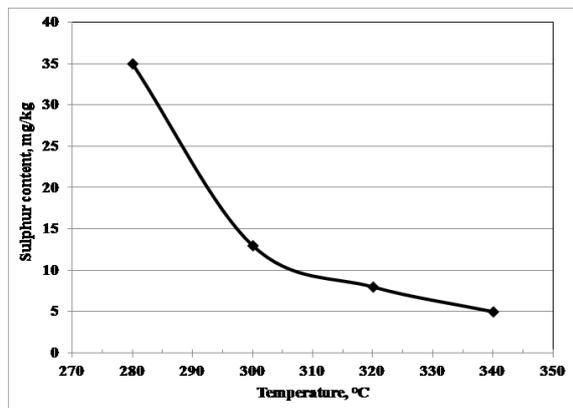
Fig. 9. Change of the sulphur content of the products in function temperature on PtPd/USY catalyst

Fig. 10. Change of the aromatic content of the products in function temperature on PtPd/USY catalyst

steps: first the aromatic ring is hydrogenated then the hydrodesulphurization takes place. Therefore the higher hydrogenation activity of precious metals results in higher hydrodesulphurization activity also. Additionally, the higher acidity of USY zeolite comparing to the Al_2O_3 promotes reactions e.g. transalkylation, shift of alkyl groups or dealkylation [21,22].

The aromatic content of products in function of temperature is displayed on Figure 10. The mono- and polyaromatic contents of the product obtained even at lowest temperature (280°C) were significantly lower than those of the feed was proving the high hydrogenation activity of PtPd/USY catalyst.

Figure 10 shows that both mono and polyaromatic content changes according to a curve with a minimum again. The minimum point for mono- and polyaromatics did not coincide meaning that optimal temperature of saturation of mono and polyaromatics is different.

Reduction of the aromatic content is advantageous from the point of view of environmental protection and engine operation. In relation to the decrease of aromatic content: products of lower than 14% total and 2% poly aromatic contents can be obtained in the temperature range of 300-340°C. This clearly showed that the advantageous process parameters for the hydrodesulphurization and reduction of aromatics coincided in case of the PtPd/USY catalyst.

The applied PtPd/USY catalyst kept its activity for a long time (350 in hours) despite the feed contained 187 mg/kg sulphur. The products obtained at the advantageous process parameters satisfy the strictest quality requirements and are applicable as good quality diesel fuel blending components.

4 Summary

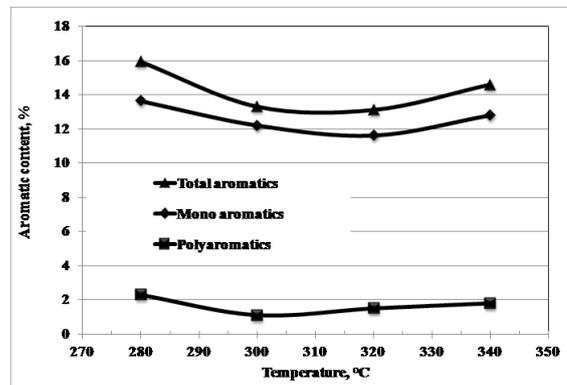The optimal process route and operating parameters (temperature, pressure and LHSV) were determined for producing gas oil blending components of quality meeting the specifications of standard of automotive diesel fuel and applying a heavy gasoil as feed.

Hydroprocessing was carried out in one (on NiMo/Al_2O_3 catalyst) and in two stages (on NiMo/Al_2O_3 catalyst and on PtPd/USY catalyst).

In one stage process products of sulphur content lower than 10 mg/kg can only be produced at high temperature (380°C) and pressure (80 bar), and at low LHSV (1.0 h^{-1}). These strict operating parameters decrease the yield of the valuable liquid product by increasing the rate of the hydrocracking reactions, and shorten the lifetime of the catalyst. Additionally, the low LHSV reduce the productivity. Low aromatic content can be obtained in the temperature range of 340-360°C. The results clearly showed that the advantageous process parameters of the hydrodesulphurization and the aromatic reduction don't coincide in the one step hydroprocessing.

In the two stages hydrotreating of the heavy gas oil at first a partially hydrogenated product was produced on NiMo catalyst at moderate process conditions. This product was hydroprocessed on PtPd/USY catalyst at various operating parameters. Products of lower than 10 mg/kg sulphur content can be processed above 310°C at 60 bar and LHSV of 1.5 h^{-1}. Products of lower than 14% total and 2% poly aromatic contents can be obtained in the temperature range of 300-340°C. The advantageous process parameters for the hydrodesulphurization and reduction of aromatics coincided in case of the PtPd/USY catalyst. Quality parameters of products obtained at advantageous process conditions satisfied the sulphur and polyaromatic requirements of the standard of diesel fuel, even more the stricter requirements of engine manufacturers regarding to the total and polyaromatic contents.

Acknowledgement

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