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PRODUCTION OF ENVIRONMENTALLY FRIENDLY DIESEL FUELS

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This paper examines options for reducing emissions by improving fuel quality. In the scope, the importance of deep hydrodesulphurization and hydrodenitrogenation is discussed which reduce the formation of acid rains and sulphate particles. The experimental results of the hydrotreating of a gas oil on Ni-Mo/Al_2O_3/promoter catalyst are presented. The effect of the key process parameters (temperature, pressure, LHSV, hydrogen/hydrocarbon volume ratio) on the yield and quality of products are discussed. Based on experimental results, the advantageous process parameters were determined for producing diesel fuel blending components of 500, 400, 300, 200, 150 and 50 ppm sulphur content. The possible applications of the obtained diesel fuel blending components in themselves or together with others are examined to satisfy the standard specifications of commercial products.

Keywords: hydrodesulphurization; diesel fuel; emission reduction

Introduction

The exhaust gases of diesel engines pollute the environment to a significant extent due to containing CO, CO_2, NO_x, SO_2 and particulates. Therefore, these contribute to the formation of acid rains, green house effect and the reduction of ozone level in the higher atmosphere, which may damage both the environment and human health [1-3].

The emissions of diesel engines which may cause cancers, are 25-35 times higher as compared to gasoline engines. The particles of smallest size are especially harmful; the effects of these were investigated by epidemology and breathing studies, and established to cause asthma, allergies and lung cancer [4].

For this reasons the sulphur and aromatic, mainly polyaromatic, content of automotive diesel fuels was tightened all over the world. For example sulphur content limit of 350 ppm will come into force in the European Union in the year 2000 and 50 ppm in the year 2005, respectively (*Table 1*) [5-8].

The emissions of diesel engines can be reduced partly by developing engine constructions, improving the quality of fuels and using exhaust gas treating systems (oxidising catalysts, particle filters, NO_x-trap) [9-13].

The aim of the present study was to identify and quantify the key process parameters for the hydrotreating of a gas oil to produce diesel fuel blending components of various sulphur contents which meet the requirements of the year of 2000 and the following years.

Table 1 Diesel fuel quality requirements at present and in the future

Properties	EN-590	MSZ-1627	Requirements in the European Community						
			EC	EP	E CA	ET	EP	E CA	ET
			January 2000			January 2005			2010
Density at 15°C, kg m^{-3}, max.	820-860	850-860	845	845	845	845	825	-	825
Distillation									
85 vol.% point, °C, max.	350	350	-	-	-	-	-	-	-
95 vol.% point, °C, max.	370	-	350	350	360	350	340	d	330
Cetan number, min.	49	48	51	51	51	53	58	d	58
Sulphur content, ppm, max.	500	500	350	200	350	200	50	50	50
Total aromatic content, %, max.	-	-	-	-	-	-	-	-	-
Polycyclic aromatic content, %, max.	-	-	11	11	11	8	1	d	1

EC: European Council; EP: European Parliament; E CA: EU Conciliation Agreement on fuels and vehicles;
ET: European Community Amendment; d: debated

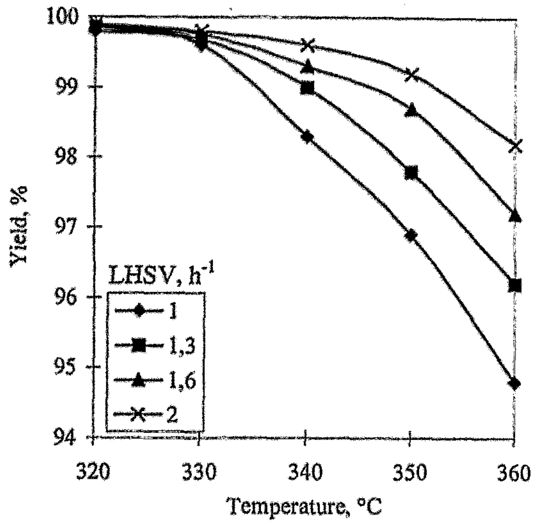

Fig.1 Effect of temperature and LHSV on the yield of the stabilized liquid product

We also studied the rate of hydrodenitrogenation (HDN) reactions, taking place parallel to the deep hydrodesulphurization (HDS). We considered this particularly important because only little information is available in the literature about the connection between the change of sulphur and nitrogen contents of the gas oil under the conditions of deep HDS, when the sulphur content of the products is 50-500 ppm [14-18]. However, from environmental aspects the reduction of the nitrogen content of diesel fuels is similarly important, because nitrogen oxides, which are also formed during the burning of the organonitrogen compounds, may cause pollution of the environment (acid rains, ozone formation), corrosion in the parts of the engine and its exhaust system, furthermore they decrease the base content of the engine oil.

Experimental

The experiments were carried out in the high pressure twin reactor system at our department. This system consists of a tubular reactor of 100 cm^3 efficient volume, as well as equipments and devices applied in the reactor system of hydrodesulphurization plants (pumps, separators, heat exchangers, temperature and pressure regulators, gas flow regulators).

The feedstock was a heavy gas oil fraction having sulphur content of 9300 ppm, nitrogen content of 217 ppm and total aromatic content of 27.5%. Its detailed properties are given later together with those of the products obtained in the case of using advantageous process conditions.

The experiments were carried out on a Ni-Mo/Al_2O_3/promotor type catalyst, which was available in presulphided form.

The temperature range of the experiments was 320-360°C, the pressure 40 bars; the liquid hourly space velocity (LHSV) varied between 1.0 h^{-1} and 2.0 h^{-1} and the volume ratio of hydrogen-to-hydrocarbon was 200 dm^3 dm^{-3}.

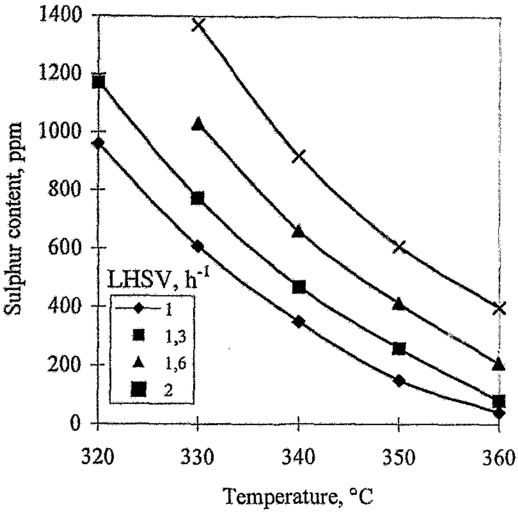

Fig.2 Effect of temperature and LHSV on the reduction of the sulphur content

The properties of the feedstock and products were determined by standard tests methods: sulphur content by X-ray fluorescence spectrometry, aromatic content by HPLC (MSZ 10907/1998) and nitrogen content by the ASTM D 4629 method.

The experiments were carried out on catalyst of permanent activity and by continuous operation. The repeatability of the experimental results was higher than 95% considering the ensemble errors of the technological experiments and tests methods.

Results and Discussion

We plotted the yields of the stabilised liquid product as a function of temperature and LHSV. *Fig.1* demonstrates that both the increase in temperature and decrease in LHSV results in the reduction of the yields of liquid products. The effect of the change in temperature is more significant than that of LHSV.

The decrease of the yield can be explained therewith that the rate of HDS, HDN and hydrocracking reactions increases with stricter process parameters. Above 340°C, the yield loss can be placed mainly to the account of the hydrocracking reactions. This is supported by the fact that the amounts of the gas and the gasoline fraction (boiling point < 200°C) increase above this temperature.

Fig.2 displays the change of the sulphur content of the products as a function of temperature and LHSV. This demonstrates that both increase in temperature and decrease in LHSV reduces the sulphur content of the products. The effect of the change in temperature is in this regard, too, more significant than that of LHSV. In the case of LHSV values of 1.6 h^{-1} and 2.0 h^{-1} the sulphur content decreases exponentially in the temperature range of 320-350°C and gradually above this. Applying LHSV values of 1.0 h^{-1} and 1.3 h^{-1} the rate of sulphur content decreases nearly exponentially with increasing temperature.

Table 2 Process parameters for producing products of various sulphur contents

Sulphur content, ppm	Process parameters Temperature, °C	 LHSV, h^{-1}
<500	340	1.0 and 1.3
	350	1.0; 1.3 and 1.6
	360	1.0; 1.3; 1.6 and 2.0
<400	340	1.0
	350	1.0 and 1.3
	360	1.0; 1.3 and 1.6
<300	350	1.0 and 1.3
	360	1.0; 1.3 and 1.6
<200	350	1.0
	360	1.0 and 1.3
<100	360	1.0 and 1.3
<50	360	1.0

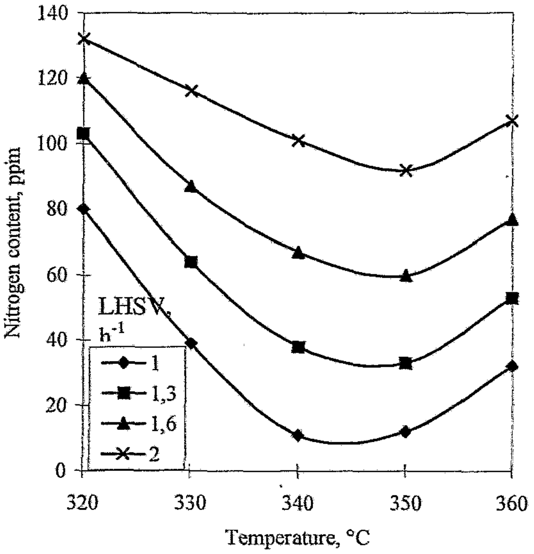

Fig.3 Effect of temperature and LHSV on the reduction of the nitrogen content

Products having sulphur content of max. 350 ppm (EC limit in 2000) can be obtained only above 340°C. The possible key process parameters for producing products of various sulphur contents are summarised in *Table 2*.

We also studied the change of nitrogen content of the products as a function of temperature and LHSV. The results are plotted in *Fig.3*, which displays that in contrast to the change of sulphur content that of the nitrogen content has a minimum point. The nitrogen content of the products decreases with rising temperature to 340-350°C, then it increases gradually. One explanation for this can be that the nitrogen content of the gas oil fraction is present in aromatic compounds, and the saturation of the rings occurs in the first step of the HDN reaction, before the nitrogen splits from the molecule in the second one. From the point of view of kinetics, the increase of temperature is advantageous for the saturation of the rings until a point where thermodynamic hindrance begins to exert a significant effect on the rate of reaction. Consequently, the rate of the HDN reactions is determined by the rate of the saturation of the rings.

Table 3 Summary of the results of the advantageous experiments

Properties	Feed stock	Experiment VZ/1	 VZ/2	 VZ/3	 VZ/4	 VZ/5
		Process conditions				
Temp., °C		340	350	350	360	360
Press., bar		40	40	40	40	40
LHSV, h^{-1}		1.0	1.3	1.0	1.3	1.0
H_2/HC, $dm^3\ dm^{-3}$		200	200	200	200	200
Yield, %						
Gas		1.6	2.2	3.2	3.8	5.3
Liquid						
<200°C		both	0.7	1.4	3.3	4.9
>200°C		98.4	97.1	95.4	92.9	89.8
		Product quality				
Density, kg m^{-3}	860	850	855	853	848	846
Sulphur cnt., ppm	9300	350	260	150	80	40
Nitrogen cnt., ppm	217	11	33	12	53	32
Aromatics, %						
mono	16.9	20.5		22.6	23.1	23.4
di	8.1	6.6		6.1	5.5	5.2
poly	2.4	1.6		1.4	1.3	1.2
total	27.5	28.7		30.1	29.9	30.0
Assay						
ibp.	188	180	193	188	186	191
10 vol.%	284	268	274	272	269	267
30 vol.%	309	303	307	305	301	299
50 vol.%	324	320	322	321	319	322
70 vol.%	336	333	335	335	331	334
90 vol.%	354	351	352	353	351	350
fbp.,	369	362	363	365	362	361
Flash point, °C	70	58	79	70	62	66
Cetan index	55	56	56	56	61	61
CFPP,°C	0	2	2	2	1	1

From the aspect of the environmental protection the reduction of both the sulphur and the nitrogen content of diesel fuels is very important. Therefore, we plotted the HDS and HDN activity in one diagram to determine the optimal process parameters for producing diesel fuel blending components of low sulphur and nitrogen contents (*Fig.4*). However, we assessed that the optimal process parameters for the HDS and HDN reactions differ from each other. In consequence, a compromise is necessary concerning the sulphur and nitrogen content of the products. For the time being only the sulphur content of diesel fuels is limited, we determined the process parameters for obtaining products, which can meet the present and the expected requirements. The results of the advantageous experiments are summarised in *Table 3*. These data display that the properties of the products meet the demands of EN 590 and MSZ 1627 standards, except CFPP. However, the CFPP requirements can be satisfied by blending the improper products with light gas oil or/and applying flow improving additives. The data concerning the distribution of the aromatic content support that saturation of aromatics also takes place parallel with the HDS and HDN reactions, though not to a considerable extent.

We estimated the emissions of the products of the experiments. The equations approved by the EPEFE were used to determine the potential of emitting CO,

Table 4 Emission potential of the products and feedstock

Emission, g km^{-1}	Feed stock	Experiment			
		VZ/1	VZ/3	VZ/4	VZ/5
CO	1.341	1.312	1.322	1.307	1.301
HC	0.093	0.083	0.086	0.066	0.065
NO$_x$	0.943	0.942	0.942	0.942	0.942
PM	0.159	0.060	0.060	0.0582	0.057

hydrocarbon (HC), NO$_x$ and particulate matter (PM) [19].

$$CO\ (\mathrm{g\ km^{-1}}) = -1.3250726 + 0.003037d - 0.025643c_{PA} - 0.015856CN + 0.0001706T_{95} \quad (1)$$

$$HC\ (\mathrm{g\ km^{-1}}) = -0.293192 + 0.0006759d - 0.0007306c_{PA} - 0.0032733CN - 0.000038T_{95} \quad (2)$$

$$NO_x\ (\mathrm{g\ km^{-1}}) = 1.0039726 - 0.0003113d + 0.027263c_{PA} - 0.0000883CN - 0.0005805T_{95} \quad (3)$$

$$PM\ (\mathrm{g\ km^{-1}}) = [-0.3879873 + 0.0004677d + 0.0004488c_{PA} + 0.0004098CN + 0.0000788T_{95}] \cdot [1 - 0.00016(450 - c_S)] \quad (4)$$

where d - density, kg m^{-3}; c_{PA} - polyaromatic content, %; CN - cetan number; T_{95} - back-end volatility, °C; c_s - sulphur content, ppm.

The data concerning the products and the feedstock are summarised in *Table 4*. Based on these data we established that reduction of the sulphur content significantly contributes to the decrease of the particulate matter emission. However, the values of the other emissions change little or not at all.

Conclusions

We were able to produce diesel fuel blending components on the applied catalyst which satisfy the present (year 2000) and the expected (year 2005) requirements.

The sulphur content of the feedstock can be reduced in one step to a great extent, and this decreases significantly the emission of SO$_2$ and sulphate particles of the diesel engine, in addition the products are less poisonous for the oxidising and NO$_x$ converting catalysts used in the exhaust gas system that leads to further reduction of diesel engine emissions.

The optimal process parameters of the HDN and HDS reactions do not coincide, so the products of low sulphur content have relatively high nitrogen content and this may result in emission problems in the future.

The obtained product is applicable as diesel fuel blending component in itself or together with others in order to suit the standard specifications of commercial products that contributes to the reduction of particulate emission of diesel engines.

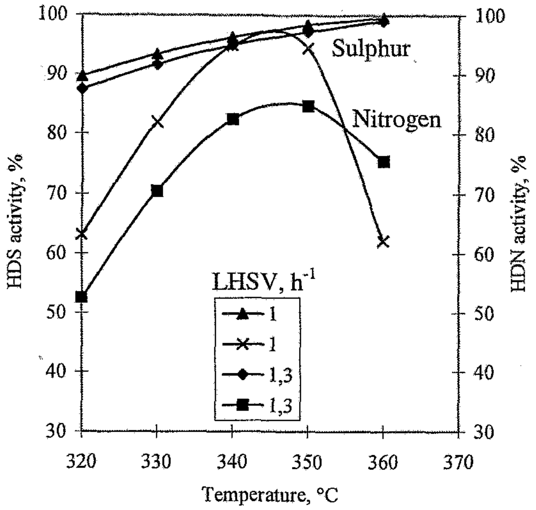

Fig 4 Effect of temperature and LHSV on the HDS and HDN activities

SYMBOLS

LHSV	liquid hourly space velocity
HDS	hydrodesulphurization
HDN	hydrodenitrogenation
CFPP	cold filter plugging point
HC	hydrocarbon
PM	particulate matter
d	density
c_{PA}	polyaromatic content
c_s	sulphur content, ppm
CN	cetan number
T_{95}	back-end volatility

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