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TESTING THE IMPACT OF FEEDSTOCK COMPOSITION AND PROCESS PARAMETERS OF HYDRODESULPHURIZATION ON DIESEL FUEL PROPERTIES

Abstract

The impact of composition of blends of potential feedstock for hydrodesulphurisation on main characteristics of diesel fraction - cetane number, sulphur content, quantity of polycyclic aromatic hydrocarbons (PAH) and flash point was tested. Blends for hydrodesulphurisation were prepared from real refinery streams and the diesel fraction was prepared by fractioning the hydrodesulphurisation products into petrol and diesel fraction.

Prepared blends can be used as input feedstock at the reconstructed process units for hydrodesulphurisation of gas oils and coking petrol at Sections 200 and 500 at Sisak OR.

Sulphur removal efficiency dependency on process parameters, temperature, space velocity and hydrogen/feedstock ratio was determined for two gas oil and sulfex extract blends.

Basic physical and chemical characteristics were determined for the obtained hydrodesulphurisation products and separate diesel fraction.

1. INTRODUCTION

Increasingly stringent environmental protection requirements prescribe reduction of sulphur, aromatics and olefin content in all kinds of motor fuels. Until the final modernization of the oil refinery Sisak, i. e. until the construction of a new hydrodesulfurization unit, the existing refinery processes have to produce diesel fuel meeting the standard EN 590:2004. Maximum permissible volume of sulphur: 50mg/kg, maximum volume of polycyclic aromatics: 11 % m/m and minimum cetane number of 51 are the main properties requiring either increase in the efficiency of individual processes, or the building in of new process units.

In order to obtain as large volumes of diesel fuel matching the requirements of standard EN 590 :2004 as possible, process units at the OR Sisak were reconstructed of section 300-Platforming at HDS of gas oils, and section 500-Unifining gasoline at HDS of gas oils and coking naphtha. It was therefore necessary to investigate the possibility of optimal use of the existing refinery processes, in order to obtain as large volumes as possible of diesel fuel matching the EN 590:2004 standard.

As regards real components produced at oil refinery Sisak, primary diesel fuel, light catalytic gas oil, sulfex extract, bottom splitter FCC gasoline and coker naphtha, several compounds were prepared of different volumetric composition, to be used in section 500. After determining the physico-chemical properties of initial compounds, the compounds were subjected to the process of hydrodesulfurization on high pressure A. Hofer test rig. Investigations were performed using the same process conditions and the same catalyst used at reconstructed HDS units of OR Sisak.

After the process of compounds hydrodesulfurization on a high pressure semi-industrial test rig, the obtained product was fractionated into gasoline and diesel fraction. Diesel fraction was determined its physico-chemical properties, including cetane number.

Dependence of the efficiency of hydrodesulfurization process on process parameters: temperature and space velocity of the feed, was tested on two compounds made of primary diesel fuel and sulfex extract, to be used in section 300. The obtained results shall contribute to an optimal choice of process parameters and obtaining fuel with maximum cetane number, with as low additive consumption as possible.

2. THE EXPERIMENTAL PART

2.1. Selection of Optimal Compound for Section 500

2.1.1 Catalysts

Experiments for section 500 used commercial HDS catalyst by Haldor Topsoe. The fixed catalyst layer in the reactor was formed after the reactor at HDS of unit 500 at OR Sisak. At the top of the reactor, there is a layer of glass balls, followed by the layer of catalyst TK-711; in the medium layer TK-551, and at reactor bottom TK-574 catalyst, Table 1. In both tests, fresh catalyst was used, being highly active.

Table 1: Characteristics of HDS catalyst for Section 500

Name	Quantity, % m/m	CHEMICAL COMPOSITION, %					Bulk density kg/l
		CoO	MoO_3	NiO	Al_2O_3	$AlPO_4$	
TK-711	3,15		4-8	1-3	80		0,5
TK-551	1,79		12-18	2-5	60-80	5-11	0,6
TK-574	95	3-6	20-25		70-80		0,8

2.1.2 Feeds

Table 2 provides the physico-chemical composition of components: primary diesel fuel (DG), light catalytic gas oil (LKPU), sulfex extract, bottom splitter FCC gasoline and coker naphtha, used for the preparation of six compounds, to be used at section 500. Table 3 provides the volumetric composition of prepared compounds, and Table 4 physico-chemical properties of the six prepared blends before the process of hydrodesulfurization.

Table 2: Physical and chem. properties of the components for testing in section 500

PROPERTIES	Diesel fuel	LCGO	Sulfex extract	FCC naphtha	Coker naphtha
Density, 15 °C	830,7	843,9	845,0	852,3	715,2
Distillation, IBP, °C	162,8	205,0	49	162	29
50 % v/v, °C	260,8	263,0	123	181	97
FBP, °C	361,4	322,0	155	219	158
Cloud point, % v/v	-4	+6	-	-	-
Aromatics, % m/m	27,3	82,1	80,64	57,9	5,2
Olefins, % m/m	-	-	-	0,7	33,1
Parafins, % m/m	72,7	17,9	20,09	41,4	61,7
Sulphur, % m/m	0,43	0,88	0,41	0,35	0,50

Table 3: Volume composition of prepared mixture for section 500

MIXTURE	Diesel fuel % v/v	LCGO, % v/v	Sulfex extract, % v/v	FCC naphtha, % v/v	Coker naphtha % v/v
B	58	10	3,5	20	8,5
E	65	10	3,5	15	6,5
F	65	10	3,5	10	11,5
G	70	15	3,5	6	5,5
H	70	10	3,5	10	6,5
I	70	10	3,5	6,5	10

Table 4: Physical and chem. properties of the mixt. before HDS proc. for section 500

MIXTURE PROPERTIES	B	E	F	G	H	I
Density, 15 °C	838,2	838,2	837,6	848,6	842,6	832,7
Distillation IBP, °C	61,5	69,5	58,9	73,9	53,6	58,2
50 % v/v, °C	224,6	233,6	237,7	250,4	243,3	241,5
FBP, °C	352,9	355,4	371,3	372,1	371,4	372,7
Cloud point,% v/v	-11	-9	-9	-7	-8	-7
PAH, % m/m	9,4	9,6	11,1	13,6	10,4	11,2
Aromatics, % m/m	48,5	45,1	41,6	44,4	44,1	43,97
Non-aromatics, % m/m	51,5	54,9	58,4	55,6	55,9	56,03
S, % m/m	0,47	0,48	0,56	0,58	0,57	0,56

2.1. 3 Operating Conditions

When testing prepared blends, process operating conditions of section 500 were used, Table 5. During the experiments, hydrogen of purity 3.0 was used.

Table 5: Process conditions of high pressure apparatus for section 500

Section	500
Reaction temperature, °C	350
Pressure, bar	55
LHSV, h^{-1}	2,5
Ratio H_2/CH	120
H_2 flow, ml/min	400
Feed flow, ml/min	3,3

2.2. Testing Process Parameters for Section 300

In the second part of testing, two blends were prepared with 14 and 22% sulfex extract in primary diesel respectively (blend 1 and blend 2). Such concentrations of sulfex extract enable its optimal use at the HDS unit 300.

2.2.1 Catalysts

The composition of catalysts used in tests was shown in Table 6.

Table6: Characteristics of HDS catalyst for Section 300

Name	Quantity, % m/m	CHEMICAL COMPOSITION, %					Bulk density kg/l
		CoO	MoO_3	NiO	Al_2O_3	$AlPO_4$	
TK-711			4-8	1-3	80		0,5
TK-574		3-6	20-25		70-80		0,8

2.2.2 Feeds

Table 7 shows physico-chem. properties of the prepared blends' components 1 and 2.

Table 7: Physical and chem. properties of the compounds and mixt. for section 300

PROPERTIES	Diesel fuel	Sulfex extract	MIXTURE 1	MIXTURE 2
Density, 15 °C	832,6	821,0	831	830,4
Distillation IBP, °C	169	49	80	70
50 % v/v, °C	266	122	250	241
FBP, °C	369	159	366	366
Cloud point % v/v	-2	-8	-6	-7
Aromatics % m/m	25,25	80,64	36,04	39,25
Olefins, % m/m	-	-	-	-
Parafins, % m/m	75,10-	20,09	-	-
PAH, % m/m	-	-	10,3	9,7
S, % m/m	0,442	0,411	0,426	0,432

2.2.3 Operating Conditions

Compounds 1 and 2 were tested with two sets of process parameters. In the first set of experiments (experiments 1, 2, 3, 4, 5 i 6), space velocity was ranging from 1.86 to 2,5 h^{-1}, while temperature, pressure and hydrogen/hydrocarbons ratio were constant (T=330 ℃, p=30 bar, ratio H2/CH= 125).

In the second set of experiments (experiments 7, 8, 9, 10, 11 and 12), the temperature of the process was changed (T=330, 340 i 350 ℃), whereas pressure, space velocity and the hydrogen/hydrocarbons ratio were constant (p=30 bar, LHSV=2,2 h^{-1} and ratio H2/CH= 125).

3. RESULTS

3.1 Selection of an Optimal Compound for Section 500

Products obtained from prepared blends after HDS process were separated into gasoline and diesel fraction at T=160 ℃. The amount of gasoline fraction for all blends was ranging from 5.84-8.50 % m/m. Table 8 shows the properties of diesel fraction obtained after HDS process and separation of gasoline fraction.

Table 8: Physical and chemical properties of diesel fraction after HDS process and separation from naphtha fractions at T= 160 ℃ for s ection 500

MIXTURE PROPERTIES	B	E	F	G	H	I
Distillation IBP, °C	171,4	173,4	176,5	183,7	178,9	177,6
50 % v/v, °C	234	242,6	248,5	254,3	250,5	252,8
FBP, °C	351,4	354,3	328,2	368,7	367,4	366,1
S, mg/kg	<10	<10	<10	<10	<10	<10
Aromatics, % m/m	44,90	41,05	39,49	39,60	39,06	37,93
Non-aromatics, % m/m	55,10	58,95	60,51	60,40	60,94	62,07
PAH; % m/m	3,1	2,7	3,0	3,6	2,8	3,2
Cetane number	42,9	47,1	45,9	47,4	47,2	48,1

Efficiency of sulphur removal in HDS process was extremely high, so that sulphur content went below 10 mg/kg. The volume of polycyclic aromatics was considerably reduced, as results from comparing values for PAHs from Table 5.

Compound B with volumetric share of DG and LKPU below 70 % and high FCC naphtha content of 20 % v/v had the lowest cetane number (42,9). The compound is not suggested for use due to the need for too much additives for cetane n. increase.

Compounds G, H and I, whose volumetric share of primary diesel fuel was 70 % v/v, had the highest cetane number values.

3.2 Testing Process Parameters for Section 300

Table 9 presents physico-chemical properties of prepared blends after the process of hydrodesulfurization for section 300, while Table 10 indicates physico-chemical properties of diesel fraction obtained after the process of hydrodesulfurization and separation of the gasoline fraction at 160 ℃ for s ection 300.

Table 9: Physical and chemical properties of the mixures after HDS process for section 300

MIXTURE	MIXTURE 1			MIXTURE 2		
PROPERTIES/EXPERIMENT	1	2	3	4	5	6
Density, 15 °C	831,5	831,3	831,1	831,9	832,1	832,3
Cloud point, % v/v	-3	-3	-3	-4	-4	-4
CFPP, % v/v	-4	-3	-3	-5	-5	-4
Ignition point, °C	43	43	40	36	35	40
Coking residue% m/m	0,036	0,018	0,030	0,009	0,008	0,012
PAH, % m/m	8,3	8,2	8,3	9,3	9,1	9,3
Cetane index	45,3	45,2	45,7	41,8	42	42,1
S % m/m	55	47	78	32	46	51

Table 10: Physical and chemical properties of diesel fraction after HDS process and separation from naphtha fractions at T= 160 ℃ for s ection 300

MIXTURE	MIXTURE 1			MIXTURE 2		
PROPERTIES/EXPERIMENT	1	2	3	4	5	6
Density,15 °C	833,0	833,6	832,3	832,9	833,6	833,7
Distillation IBP, °C	172	181	165	162	154	156
50 % v/v, °C	265	267	263	264	261	262
FBP, °C	369	369	369	366	363	337
Ignition point,°C	64	67	55	55	46	45
Aromatics, % m/m	28,59	26,99	29,26	30,91	31,83	31,38
Non-aromatics, % m/m	71,41	73,01	70,74	69,09	68,17	68,62
PAH, % m/m	6,3	5,0	7,2	7,0	8,3	7,9
Cetane number	54,2	57,2	55,2	53,6	52,7	56,4

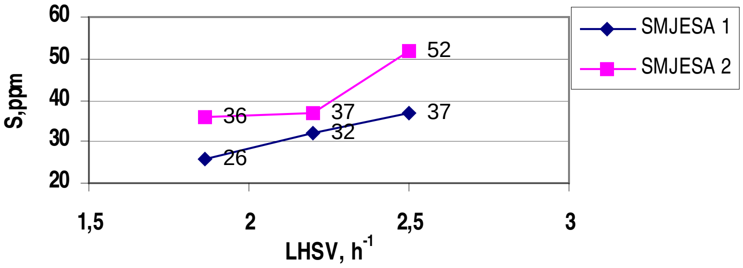
By comparing values for aromatic hydrocarbons in perpared compounds and diesel fractions obtained after the process of hydrodesulfurization and separation of gasoline fraction, it may be concluded that there was a 20 % reduction in the content of aromatics.

The highest impact on the reduction of values of polycyclic aromatics is that of space velocity. By increasing space velocity, there occurs a lower reduction of the content of polycyclic aromatics and increase in the content of sulphur, due to lesser time of feed keeping during its contact with the catalyst (Table 10, Figure 1).

With temp. increase from 330 to 350 ℃; constant sp ace velocity, pressure and ratio H_2/CH there occurs a considerable reduction in the content of sulphur (Fig. 2).

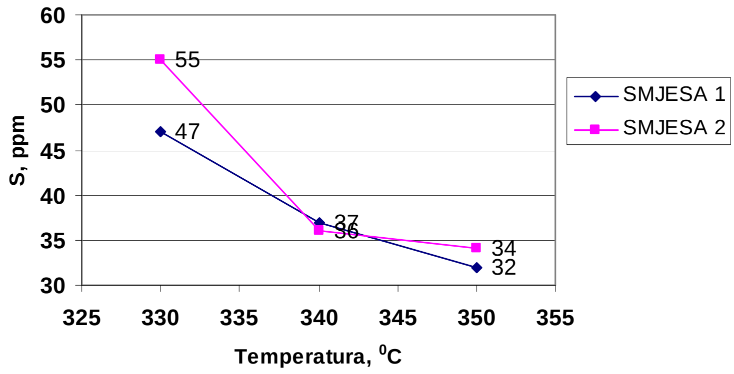
Flash point measured on diesel fraction obtained from blend 2 does not meet the standard for diesel fuel (above 55 ℃), indicating that the said compound contains too much sulfex extract. Cetane number values (CB=53-57) under all experimental conditions in both blends exceed values from the diesel fuel standard (at least 51).

Figure 1: Dependence of sulphur quantity on LHSW



T=330°C, Tlak= 30 bar, H_2 / HC = 125

Figure 2: Dependence of sulphur quality on temperature



Tlak=30 bar, LHSV=2,2 h^{-1}, Omjer H_2/CH=125

It is well known that sulphur bonded to one or more aromatic rings, such as compounds of benzotiophene and dibenzotiophene is most difficult to be removed in the process of hydrodesulfurization. Using the technique of gas chromatography, shot were initial feeds and obtained hydrodesulfurized products, detecting in them compounds of benzotiophene and dibenzotiophene, and their substituents.

Confirmation of efficient removal of sulphur compounds with selected catalysts is shown on mass chromatographs of C1-dibenzotiophene and C4-benzotiophene in initial feed and hydrodesulfurized products (Figures 3, 4, 5, and 6).

Figure 3: Quantity of C1-dibenzotiophene in feed

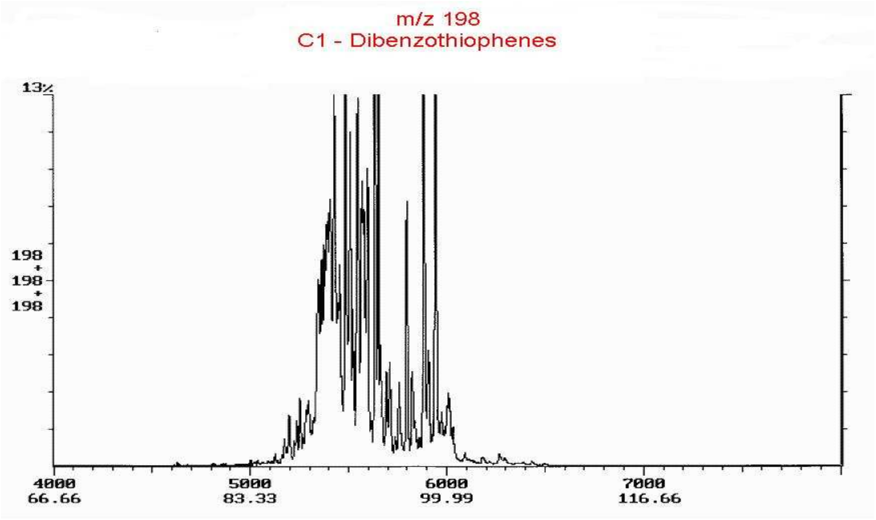


Figure 4: Quantity of C1-dibenzotiophene in products

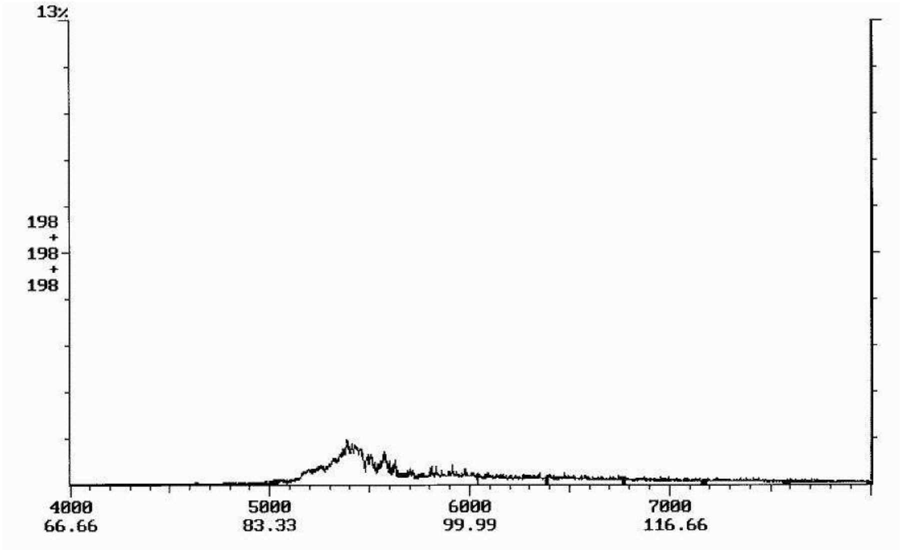


Figure 5. Quantity of C4-benzotiophene in feed

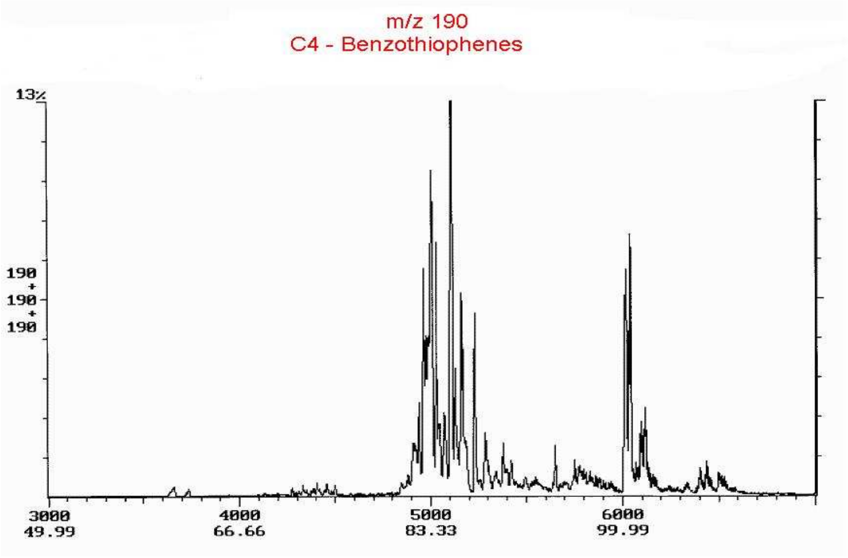
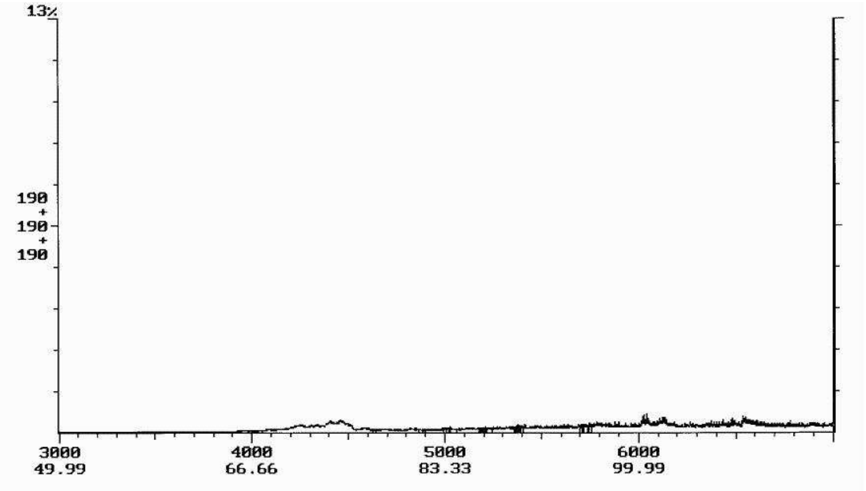


Figure 6. Quantity of C4-benzotiophene in products



4. CONCLUSION

- The results obtained for high efficiency of the process of hydrodesulfurization (98 %) enable a wide choice of refinery processes with high sulphur content, that may be useda as input feeds for reconstructed HDS sections 300 and 500.
- Diesel fractions from products of the process of hydrodesulfurization out of compounds prepared for section 500 through their content of sulphur and polycyclic aromatics meet the standard for diesel fuels EN 590:2004. Cetane number values of diesel fractions obtained from compounds for section 500 are somewhat lower and range from 46-48.
- Dependence of sulphur removal on temperature for section 300 reveals that already at the temperature of 335 ℃, sulphur content was reduced below 50 mg/kg for both compounds.
- By increasing space velocity up to 2,5 h^{-1}, with constant temperature of diesel fraction, compounds 1 and 2 for section 300 have met the standard for diesel fuels EN 590:2004. In all diesel fractions, measured were high cetane number values (CB=53-57), low PAH values, and satisfactory flash point.
- The chosen HDS catalysts have shown high efficiency in reducing the content of hardly removable sulphur compounds.

5. References

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665.658.62	hidrodesulfurizacija plinskog ulja	gasoil hydrodesulfurization
66-977	procesi po visini temperature	processes according height of temperature
66-946.3	proces po prostornoj brzini tokova	process according space velocity
665.64.033	kemijski sastav međuprodukata prerade nafte	chemical constituents of petroleum processing intermediate
.002.3	gledište sastava sirovine	raw material constituents viewpoint
.002.64	gledište svojstava produkta	product properties viewpoint

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