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IMPROVING THE QUALITY OF LOW-SULPHUR DIESEL FUEL

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Abstract. The physico-chemical and operation properties of diesel fuels containing up to 0.05 % sulphur were studied. It was proved that they meet all the requirements of the European standard EN 590-93 but their electroconductivity has to be increased by using additives. It was found that the termooxidizing stability of this type of fuels is low. It was proved that 0.05% of the additives ionol and MAP-2 increase the chemical stability of the samples under study. When using a composition of both additives, a better stabilizing effect is achieved.

Keywords: diesel fuel, physico-chemical and operation properties, oxidation stability, thermooxidation stability, additives.

AIMS AND BACKGROUND

It is known that exhaust gases from diesel engines have a considerable higher amount of sulphur oxides and smoke than the gases from engines with forced ignition[1,2]. Therefore, the increasing use of diesel fuels in motor transport will inevitably lead to an increase in smoke and gas emissions on roads and particularly on streets with heavy traffic[3,4]. One possibility of doing away with such pollution is to use high-quality diesel fuels with optimized properties[1]. It was found that decreasing the temperature at which boiling stops results in a decrease in smoke emissions. This, however, decreases cetane number, which worsens the starting parameters and the operation regime of the engine[1,2].

Investigations have shown that in order to obtain the high-quality diesel fuels it is nessesary to decrease the amount of arene hydrocarbons (up to 20%) and sulphur (up to 0.05%)[1,4]. Such fuels can be produced by hydrocracking or by using only hydropurified components. Deep hydropurification, however, may lead to complete removal of natural surface-active heteroorganic substances and worsening the antiwear properties[1,5-7].

Therefore, it is necessary to carry out thorough investigations in order to optimise the properties of low-sulphur diesel fuels by using suitable components for their production or special additives[5-11].

The aim of the present work is to study the physico-chemical and operation properties of low sulphur diesel fuels and the possibility of improving their quality by additives.

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EXPERIMENTAL

Hydropurified light diesel fraction (HLDF), 180-240°C, and hydropurified heavy diesel fraction (HHDF), 240-360°C, were used for the present study. From these components 2 samples of low-sulphur diesel fuels were obtained, designated as sample A and sample B.

Sample A contains 30% HLDF and 70% HHDF, and sample B contains 40% HLDF and 60% HHDF, respectively. The main physico-chemical and operation properties of the fuel samples were determined according to EN 590-93 standard requirements to diesel fuels. Oxidation stability was determined according to ASTM 2274 standards and thermooxidizing stability was determined according to ES 15894-85 at 150°C for 5 h in the presence of a metal lamella. In order to clarify the oxidation processes taking place, the amount of insoluble products and oxidation products was determined as well as a number of other parameters characterising the chemical stability of fuels, such as soluble gum, acidity of the oxidised fuel and the amount of peroxide oxygen.

The investigations made by a number of companies and particularly those of Adibis show the substantional influence of sulphur on the lubricating properties of the fuel. However, other parameters, such as viscosity, fraction composition and arene hydrocarbons, which depend on the type of the processed oil and the technological regime for obtaining the components, should not be neglected. The problems with the lubricating properties can be solved by using special additives called antiwear agents. In this case, the additive Kerokorr 3245 was used. It is a mixture of amines and amides dissolved in benzine fraction. The amount added according to the producer's instructions is 100 g/t.

In order to avoid dangerous accumulation of static electricity in low-sulphur diesel fuels, antistatic additives should be used. The additive Stadis (Du Pont) was experimented in this study. It is used only in summer (1.5 g/t), and in other seasons it is added only if the depressant additive does not have antistatic properties.

When studying the possibilities of increasing the chemical stability of low-sulphur diesel samples, the additives ionol and MAP-2 were used. Ionol is an antioxidant which is used in practice to increase the chemical stability of both petrol and middle-distillate fuels. The additive MAP-2 is a product suggested by the authors[10] and it contains higher fatty alcohols and ethers boiling at 240-300°C.

RESULTS AND DISCUSSION

Analysis of the data in Table 1 shows that the samples of diesel fuel meet all the requirements of the European standard EN 590-93. Besides, a number of parameters, such as cetane number, coke residue, ashes, etc. have a considerable quantitative and, therefore, qualitative reserves.

262

Table 1. Characteristics of low-sulphur diesel fuels – samples A and B

Parameters	Values for sample A	Values for sample B
Density at 15°C (g/cm³)	0.8310	0.8301
Viscosity at 40°C (mm²/s)	2.59	2.40
Cetane number	52	52
Cetane index	50	50
Distillation characteristics:		
at 250°C it distillates (% vol.)	43	46
at 350°C it distillates (% vol.)	91	93
at 370°C it distillates (% vol.)	97	97
Sulphur (%)	0.038	0.036
Flash point (°C)	75	73
Coke residue per 10 % vol. of distillation residue (%)	0.01	0.01
Ashes (%)	0.001	0.001
Water (mg/kg)	108	106
Mechanical impurities (mg/kg)	3	3
Corrosion of copper lamella (3 h at 50°C), class	1	1
Cold filter plugging point (°C)	-1	-2
Electroconductivity (μS/cm)		
– without additive	31	27
– with 1.5 g/t additive	120	110

It is proved, however, that electroconductivity of low-sulphur diesel fuels is very low (about 30 mS/cm, while the requirement is over 50 μS/cm). The results show that the use of 1.5 g/t antistatic additive Stadis 450 increases electroconductivity of both samples by almost 4 times.

The results in Table 2 show that when determining the oxidation stability of the fuel samples, a small quantity of insoluble substances is formed. It should be noted that the amount of insoluble substances is greater in sample A, containing more HHDF. According to the data in Table 2, the amount of insoluble gum in the oxidised fuels is great. This shows that at the oxidation of low-sulphur diesel fuels a great part of the oxidation products remains dissolved. However, the activity of the oxidised fuels is low, which means that the amount of acid products in the dissolved state is not great.

All these facts show that the low-sulphur diesel fuels under study have a satisfactory stability at low temperatures. In modern diesel engines, however, the fuel is heated up to temperatures considerably higher than 100°C (up to 200°C) and, therefore, diesel fuels should have high thermooxidation stability.

263

Table 2. Oxidation stability of samples A and B

Parameters	Sample A		Sample B
	–	0.025% ionol and 0.025% MAP-2	
Insoluble substances	5.25	3.38	5.04
– inc. filtered	2.82	2.46	2.61
– stuck	2.46	0.92	2.43
Soluble gum (mg/100cm³)	124.3	68.7	132.4
Acidity of oxidised fuel (mg KOH/100 cm³)	3.15	1.47	2.94
Amount of peroxide oxygen × 10³ (mmol/kg)	58.23	36.75	56.47

The results obtained for thermooxidation stability (Tables 3 and 4) show that a great amount of oxidation products is obtained: sediment, insoluble and soluble gum. Obviously, the metal surface (copper lamella) and the high temperature have a strongly negative effect on chemical stability. The investigation shows that sample A forms a greater amount of sediment.

Table 3. Thermooxidation stability of sample A

Parameters	Values for sample A			
	–	0.025% ionol	0.025% MAP-2	0.025% ionol and 0.025% MAP-2
Oxidation products (mg/100 cm³)	801.4	581.2	520.3	480.6
– incl. sediment	556.6	419.1	328.4	321.7
– insoluble gum	84.6	64.5	62.3	67.6
– soluble gum	160.2	97.6	129.6	101.3
Acidity of oxidized fuel (mg KOH/100 cm³)	5.46	3.49	4.28	3.64
Amount of peroxide oxygen × 10³ (mmol/kg)	60.08	38.75	46.20	34.32

Table 4. Thermooxidation stability of sample B

Parameters	Values for sample B			
	–	0.025% ionol	0.025% MAP-2	0.025% ionol and 0.025% MAP-2
Oxidation products (mg/100 cm³)	720.4	531.3	470.5	435.3
– incl. sediment	488.0	390.2	292.4	282.5
– insoluble gum	67.2	42.6	42.4	47.5
– soluble gum	165.2	98.5	135.7	105.4
Acidity of oxidized fuel (mg KOH/100 cm³)	5.11	3.41	4.35	3.64
Amount of peroxide oxygen × 10³ (mmol/kg)	51.54	28.34	36.10	26.35

264

Acidity and the amount of peroxides in the oxidised fuels are also high. This means that there are conditions for further formation of high-molecular oxidation products. These results show that ecological diesel fuels have low thermooxidation stability and in order to meet the high requirements of modern diesel engines they should be stabilised.

The present study shows that the additives ionol and MAP-2 increase the chemical stability at both low and high temperatures (Tables 2-4). The two additives, however, probably have a different mechanism of action because their effect on the parameters characterising chemical stability is different. Ionol is known to act as an antioxidant which interrupts the oxidation chains, mostly by reacting with peroxide radicals and thus exhausting itself. Due to this reason, its presence leads to a decrease in acidity and in the amount of peroxides, sediment, insoluble and soluble gum. The increase in the temperature increases oxidation rate and, consequently, the rate of ionol consumption. This is the main reason for its insufficient efficiency at high temperatures.

The additive MAP-2 also decreases the above parameters and it even has better efficiency than ionol as far as the total amount of oxidation products goes (Tables 3 and 4). It should be noted that it decreases the amount of sediment to a much higher degree and that of the soluble gum to a lower degree. Probably, the additive MAP-2 acts as a solubilizer. It is absorbed on the surface of the insoluble particles formed, thus preventing oxidation reactions taking place on the surface of these particles.

It was found that when a composition of both additives is used, a better stabilising effect is achieved than when they are used separately. There is a sinergetic effect, although it is not so strongly expressed.

CONCLUSIONS

1. It was found that diesel fuels containing up to 0.05% sulphur meet all the requirements of the European standard EN 590-93 but their electroconductivity should be increased by using additives.

2. It was proved that oxidation stability of low-sulphur fuels is high, and the greater part of the gum substances formed at oxidation remains dissolved.

3. It was found that the thermooxidation stability of diesel fuels containing up to 0.05% sulphur is low.

4. It was proved that 0.05% ionol and MAP-2 increase thermooxidation stability of the fuels under study, the additive MAP-2 having higher efficiency. When a composition of both additives is used, a better stabilizing effect is achieved.

265

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266