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CURRENT PROBLEMS

LOW-SULFUR DIESEL FUELS: PLUSES AND MINUSES

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One of the basic factors that negatively affect the ecological properties of diesel fuels is the content of sulfur compounds in the fuel. Calculations show that in burning 50-54 million tons of diesel fuel (average production volume of this fuel in Russia in recent years) containing 0.2% (2000 ppm) sulfur (more than 70% of the diesel fuel produced in Russia has this content), approximately 200,000 tons of sulfur oxides, a significant portion in large cities, is emitted into the atmosphere. In addition, sulfur compounds together with polycyclic aromatic hydrocarbons are a source of solid particles in diesel engine exhaust gases.

The requirements for the sulfur content of diesel fuels abroad have been gradually stiffened from 500 ppm in 1996 to 50 ppm in 2005. In some countries, the standards are even more severe. A standard for a maximum sulfur content of 10 ppm is already in effect in Sweden. In mid-2006, a maximum level of 15 ppm will be introduced in the USA, and 80% of the oil refineries (OR) in this country are ready to produce so-called ultralow-sulfur diesel (ULSD) [1] and 20% will convert to manufacture of ULSD by 2010.

The trend toward decreasing the sulfur content in diesel fuels in the USA is confirmed by the data published in [2]. In 2004, the supply of low-sulfur diesel increased by 7% with a simultaneous more than 4% decrease in the supply of fuel with a higher sulfur content.

Beginning in 2009, the sulfur content in diesel fuel in all EEC countries will be set at a maximum of 10 ppm and in 2010, the entire diesel automobile fleet will be converted to fuel with near-zero sulfur content – NZSD (near-zero sulfur diesel) [3]. These severe standards are not only imposed on fuels for high-speed automobile diesel engines but similar requirements are also beginning to spread to diesel fuels for off-road machinery [4].

The projection for diesel fuel sulfur content in different countries is shown in Fig. 1 [5].

In Russia, the diesel sulfur content according to GOST 305–82, which does not satisfy current requirements, was set at 2000 ppm and was only standardized at 350 ppm in TU 38.401.58-296–01 for an insignificant amount of diesel basically for export. In 2004, of the 54.2 million tons of diesel produced, the sulfur content in 37.4 million tons (70%) was 2000 ppm and was 350 ppm in only 2.6 million tons (4.9%).

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However, we note that in comparison to 2003, production of the latter increased by almost 1.6 times. But 5.4% of the fuel contained 5000 ppm sulfur. An important amount of diesel with a 2000 ppm sulfur content is for export in the form of intermediate products. In Western Europe, it is added as a diluent to reduce the sulfur content in feedstock for hydrotreating units [6].

Our country is thus on the level of such countries as China, India, Cambodia, and Vietnam and higher than Bangladesh, Indonesia, and some others with respect to diesel sulfur content. The lack of a positive projection for Russian diesel fuels in Fig. 1 probably indicates the lack of the same on the federal level.

This situation arose because the capacity of hydrotreating plants in Russia was only 25% of the primary oil refining capacities in 2002. Then 50% of this capacity was for obsolete plants built in 1963-1975 and 25% was for units built in 1975-1986 and 1980-1995 [7]. Of the 35 hydrotreating units operating in Russia, only 25 can produce diesel with a sulfur content under 500 ppm if the catalyst is replaced and the pressure is increased to 5 MPa [6].

In the USA, the capacity of hydrotreating units is twice as high: in 2001, it was 47.2% of the primary oil refining capacity. According to projections by the former RF Energy Ministry, by 2010 the capacity of hydrotreating

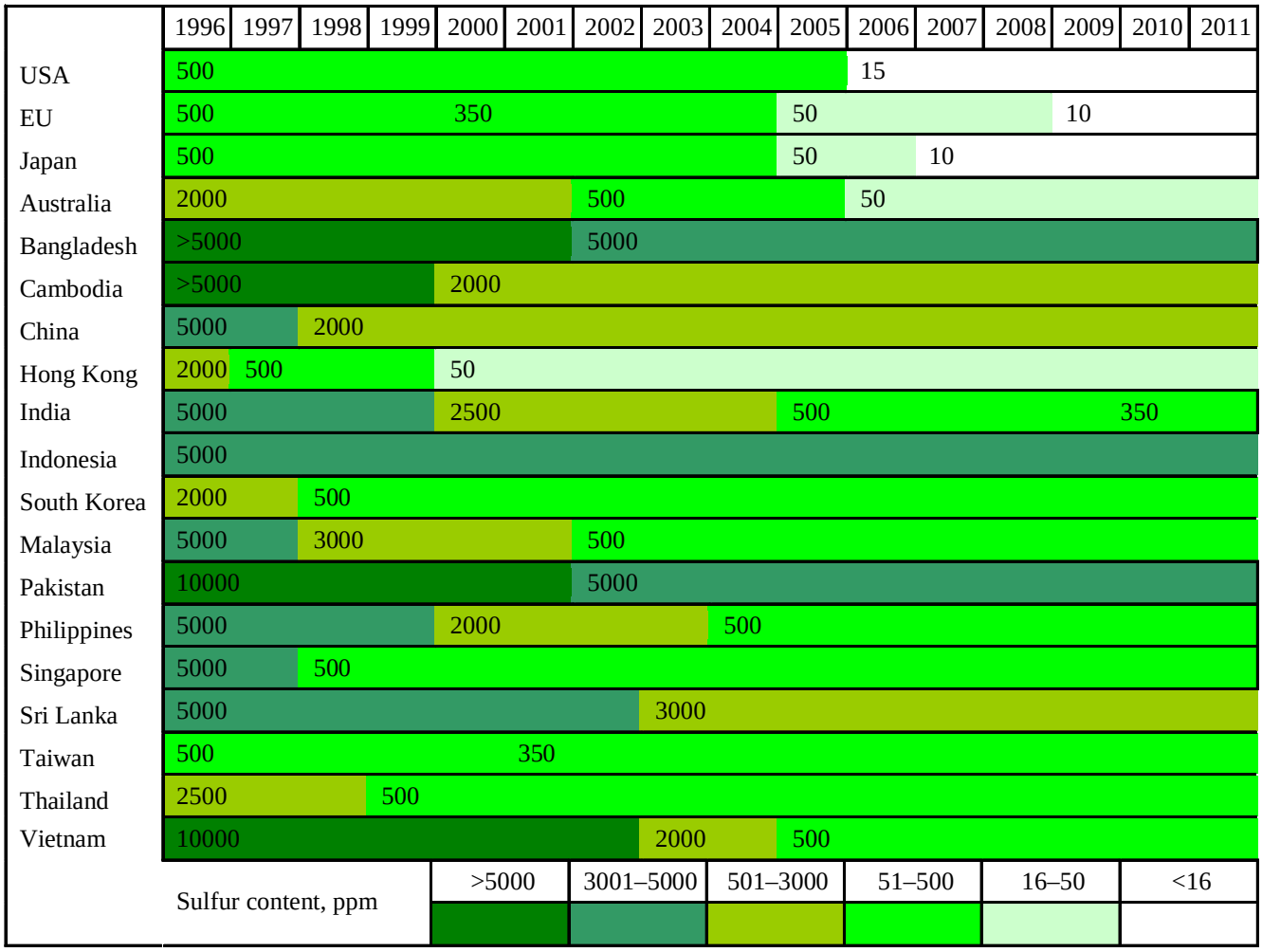

Fig. 1. Projection for sulfur content in diesel fuels in different countries.

units will only reach 38.5% of primary refining, which is clearly insufficient for satisfying current sulfur content requirements.

The possibility of organizing production of diesel that would satisfy the latest requirements was demonstrated in domestic OR by Lukoil Oil Co., which started up an exhaustive oil refining complex (EORC) at Permenefteorgsintez OJSC in 2004; this plant can produce diesel fuel with a 10 ppm sulfur content [8].

The necessity of organizing mass production of diesel with a sulfur content at the 50 ppm level and lower in Russia in the near future is undisputed and is not only determined by environmental requirements. After becoming a member of the WTO, which will probably take place in 2006-2007, our country must observe the standards of this organization, including the ISO series 1400 environmental management standards.

The fundamental role in the latest solution of this problem should in our opinion be assigned to legislative and governmental agencies (primarily the State Duma and RF Government) which can force independent oil companies to produce diesel fuels that satisfy current requirements for environmental characteristics by passing appropriate standards and specifications. Governmental agencies must also take up the problem of economic stimulation of motor fuel production (primarily automotive gasolines and diesel fuels) with a low sulfur content..

The tax on diesel fuel (regardless of the quality) is 1000 rubles/ton. This caused the selling prices of all Russian OR for diesel fuels with 350-2000 ppm sulfur content to be on the same level in February-March 2005 [9]. Although the difference in company wholesale prices for diesel fuel containing 0.2% (2000 ppm) and 0.5% (5000 ppm) sulfur was still 6.5-7% in 1982 [10].

Table 1

Diesel fuel		Additive	Concentration of additive*, ppm	Wear spot diameter after addition of additive, mm	Decrease of wear spot diameter per 100 ppm of additive
sulfur content, ppm	wear spot diameter, mm				
340	549	DIPEN **	300 (150)	353	65.3
320	553	DIPEN	300 (150)	400	51
320	553	DIPEN	500 (250)	316	47.4
—	584	DIPEN	500 (250)	361	45
100 (GShZ)	720	DIPEN	250 (125)	448	108.8
340	492	SV –59***	150 (75)	379	75.3
340	492	SV –58	150 (90)	419	48.7
340	492	SV –60	150 (75)	438	36
300	563	Kerokor LA99	200	403	80
100 (GShZ)	563	Kerokor LA99	500	460	52
320	553	Lubrisol–539	150	342	140.7
500	556	ADN ****	150	446	73.3
500	556	Lubrisol–539	200	434	61

Notes. * In parentheses: content of active substance, ppm.

** According to data in [18].

*** According to data in [17].

**** According to data in [19].

In Western Europe, tax advantages have been established for diesel fuels with 50 and 10 ppm sulfur contents. In Poland, they are $0.03/liter for fuels with a 50 ppm sulfur content and $0.056/liter for fuels with a 10 ppm sulfur content. Similar tax advantages have been established in England, Germany, and other countries [11].

Certain shifts in this direction are also occurring in our country. According to the standard approved by the Moscow Government, beginning on January 1, 2005, diesel fuel with a maximum sulfur content of 350 ppm and beginning on January 1, 2006, a 50 ppm maximum sulfur content must be supplied to Moscow [12].

At the opening of the EORC in Perm', the president of Lukoil, V. Alekperov, announced his intention to initiate the introduction of new standards for motor fuels in Russia which would stimulate production of environmentally clean petroleum products [8]. TNK-VR Co. is also examining the question of developing its own standards aimed at production of motor fuels that satisfy current requirements.

Production of low-sulfur diesels, however, will make it necessary to improve their antiwear properties, since many sulfur compounds (sulfides, disulfides, benzothiophenes, etc.) removed in hydrotreating are responsible for the fuel's necessary lubricating properties [13].

Many experiments and results of operating engines using low-sulfur (£350 ppm) diesel fuels abroad showed very fast wear of high-pressure pumps. For fuel with 2000 ppm sulfur, the lifetime of these pumps is 200,000 km and more, while catastrophic mechanical damage is observed at 3200-12,800 km for fuel with 10 ppm sulfur, and these problems arise in 4800-30,000 km for a 50 ppm sulfur content.

Tests also showed that pumps previously operating on ordinary fuel are less subject to damage than new pumps [14, 15]. Worsening of the lubricating properties of low-sulfur diesels results in wear of not only the friction couples in the high-pressure pump, but also the nozzles. As a result of their wear, the injection pressure decreases, the geometry of the sprayed jet changes [13], and as a consequence, the size of the fuel drops in the combustion chamber increases, the vaporizability and completeness of combustion worsen, and the carbon oxide and hydrocarbon content in exhaust gases and formation of carbon in the combustion chamber increase.

In view of this, a standard for the antiwear properties of diesel fuels determined with the ISO 12156 method on a HFRR (High Frequency Reciprocating Rig) was established in EN 590 and TU 38.401.58-296–01: the wear spot diameter should not exceed 460 mm. The recommendations of the International Petroleum Charter limit this index to 400 mm.

The studies conducted at the ASRI OR showed that the antiwear properties of low-sulfur diesels produced in the Russian OR of different oil companies do not satisfy these requirements. The wear spot diameter for diesel fuels produced at Novokuibyshev OR Co. is at the level of 572 mm (for a 290 ppm sulfur content), 533 mm (340 ppm) at Slavneft'–Yaroslavnefteorgsintez Co., and 537 m m (340 ppm) at Kirishinefteorgsintez LLC. Similar results were obtained for diesel fuels from other oil refineries [16].

It is fundamentally impossible to improve the antiwear properties of low-sulfur diesels by changing the production technology. In our opinion, there are realistically two ways of solving this problem:

• changing the system of feeding the diesel to the combustion chamber – stopping use of the high-performance pump or making this pump out of materials that do not require lubricants;

• using special antiwear additives.

The second way is widely used abroad. Almost all low-sulfur diesel fuels there contain antiwear additives. The line of additives includes several score of compositions whose active substances are in most cases higher carboxylic acids and products made from them – amides, esters, etc. [14].

For domestic diesel fuels primarily for export, the antiwear properties can be brought to the required foreign specifications in the standards by using foreign additives; a list of those approved for use in the RF is given in [13].

Work has begun on the synthesis and study of antiwear additives for low-sulfur diesel fuels. Some results of these studies are published in the proceedings of the III International Scientific and Practical Conference "New Fuels with Additives" [15, 17-19].

Data on the efficacy of the different antiknock additives are reported in Table 1. Tests of several additives in different organizations in different samples of diesel, including gas-condensate (GShZ), demonstrated the satisfactory reproducibility of the results in consideration of the accuracy of the HFRR method. Most of the additives investigated are relatively effective: the wear spot diameter decreases by 50-100 mm per 100 ppm of incorporated additive. They include the additives; foreign Kerokor LA 99 and Lubrisol-539, domestic DIPEN, SV-59, and ADN.

In addition to the additives in Table 1, the domestic additives PPDT-1, Al'ta, and Kaskad-5, as well as BV-01 (Belarus' Republic) have been developed and ensures the required wear spot value (maximum of 460 m) at a concentration of 50-100 ppm and when added with additives for another application (pour depressants, cetane-raising additives, etc.), at a concentration of 150-250 ppm [15, 20].

The urgency of the problem of developing antiwear additives for low-sulfur diesel fuels is also determined by the fact that introduction of different additives for motor fuels in domestic conditions has occupied a relatively long (measured in years) period.

REFERENCES

1. *Neftegaz. Tekhnol.*, No. 4, 46 (2004).
2. *Oil Gas J.*, 34 (Feb. 17, 2005).
3. V. A. Khaki, *Current Trends in Oil Refining in Russia* [in Russian], Neft' i Gaz, Moscow (2003).
4. T. N. Mitusova and M. V. Kalinina, *Mir Nefteprod. Vestn. Neftyan. Kompanii*, No. 2, 5-7 (2005).
5. Iraj Isaac Rahmin, *Oil Gas J.*, 14, No. 3, 18-28 (2005).
6. A. I. Bocharov, in: *Proceedings of the Industry-Wide Conference* [in Russian], Perm' (October 29-31, 2002), pp. 8-14.
7. E. F. Kaminskii and V. A. Khavkin, *Exhaustive Refining of Crude Oil. Process and Environmental Aspects* [in Russian], Tekhnika, Moscow (2001).
8. *Sovremennya AZS* , 23 (September 2004).
9. *Ibid.*, 96-97 (March 2005).
10. S. N. Enikolopov, *Effectiveness of Increasing the Quality of Petroleum Fuels* [in Russian], Khimiya, Moscow (1983).
11. E. F. Kaminskii, V. V. Bulatnikov, and V. A. Khaki, *Mir Nefteproduktov*, No. 5, 20-21 (2004).
12. *Mosk. Toplivn. Rynok*, No. 18, 5 (2004).
13. A. M. Danilov, *Use of Additives in Fuels* [in Russian], Mir, Moscow (2005).
14. T. N. Mitusova, E. V. Polina, and M. V. Kalinina, *Trudy NIIAT*, 30, 81-92 (2003).
15. V. Yu. Mavrin, G. Yu. Klimentova, A. M. Danilov, et al., in: *Proceedings of the III International Conference "New Fuels with Additives, St. Petersburg, June 1-3, 2004"* [in Russian], OOO KOPI-R, St. Petersburg (2004), pp. 212-215.
16. T. N. Mitusova, E. V. Polina, and M. V. Kalinina, see [14], pp. 93-101.
17. T. N. Shabalina, S. V. Kotov, and G. V. Timofeeva, See .15], pp. 217-221.

18. E. A. Nikitina, V. E. Emel'yanov, I. F. Krylov, et al., *Ibid.*, pp. 223-228.
19. G. N. Novatskii, S. V. Vodolazhskii, and B. G. Sokolov, *Ibid.*, pp. 201-207.
20. A. M. Danilov, in: *Proceedings of the 5th International Forum "The Fuel and Energy Complex in Russia: Regional Aspects"* [in Russian], St. Petersburg (April 4-7, 2005), pp. 181-183.