OXYGENATED COMPOUNDS — PETROCHEMICAL PRODUCTION WASTES — AS COMPONENTS OF AUTOMOTIVE GASOLINES

O. P. Lykov, N. V. Frolova, G. V. Kitashova, I. V. Korotkov, and L. G. Klimochkina

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Oxygen-containing compounds from non-petroleum sources (alcohols and ethers) are being used in automotive gasolines primarily to conserve petroleum raw materials, since the primary criterion of automotive vehicle economy is considered to be the distance traveled per unit volume of crude oil consumed [1]. In addition, these compounds offer a means for improving certain service characteristics of gasolines such as the octane number and anti icing properties, for reducing the amount of carbon deposition in the engines, and for reducing the content of carbon monoxide in the exhaust. However, when methanol is added to gasolines, it is noted that the alcohol-gasoline mixture will separate into layers when even traces of water are present; other problems include vapor lock due to the high vapor pressure of methanol, as well as higher corrosivity with respect to a number of materials. Compounds such as methyl tert-butyl ether (MTBE) are expensive and have only a limited raw material base.

Petrochemical plants produce considerable amounts of oxygenated compounds as waste materials in various processes; these compounds can be used as automotive gasoline compounds [2]. Utilization of these wastes as boiler fuel components has an adverse effect on the flash point and heat of combustion. For use in automotive gasolines, however, problems are created by the fact that parameters of the oxygenated waste materials such as chemical stability and boiling range may differ significantly from the properties required for gasolines.

We have evaluated the effects of complex mixtures of oxygenated compounds obtained as waste materials on the service properties of automotive gasolines. The materials that we investigated were obtained as still bottoms in the production of alcohols at the Industrial Association "Angarsknefteorgsintez," the composition of these materials including C_4-C_8 higher alcohols, ethers, esters, butyrals, butyrates, monoglycol ethers, and other compounds. In Table 1 we have listed the physicochemical property indexes included in the Plant Standard for alcohol still bottoms as a component of automotive gasolines, in comparison with the actual values obtained on two samples of this material.

As automotive gasoline samples we used a straight-run naphtha cut from the Orsk refinery and a commercial A-76 gasoline from the Industrial Association "angarsknefteorgsintez" (Table 2). The A-76 gasoline meets all requirements of GOST 2084-77. The straight-run cut from the Orsk refinery is considerably lower-boiling; it meets the distillation requirements for A-72 gasoline and all of the basic quality indexes with the exception of the octane number.

The physicochemical characteristics of these two gasolines containing 1.5-5% (wt.) of still bottoms from alcohol production are listed in Table 3. It will be seen that the addition of the alcohol still bottoms gives a higher distillation curve for the gasoline (both overall and for individual fractions); also, the acidity is increased. The gasolines containing 1.5-2% still bottoms meet all requirements of GOST 2084-77. When 5% still bottoms are added, even the low-boiling naphtha cut from the Orsk refinery fails to meet the GOST end point requirement, but does meet all other requirements.

We have also investigated the chemical stability of gasolines containing the alcohol still bottoms [3]. Tests were performed to determine the contents of existent gum, acetone-soluble gum, residue, and sum of oxidation products (Table 4). It will be seen that the addition of 2% alcohol still bottoms to the gasolines gives slight increases in the contents

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TABLE 1

Index	Plant Standard	Actual values	
		Sample 1	Sample 2
Appearance	Homogeneous, mobile liquid; color from light yellow to brown	Homogeneous, mobile liquid with a light yellow color	
Water content, wt. %	Trace	None	
Density at 20°C, kg/m³	830-880	870	866
Solid contaminants, wt. %	None		
Final boiling point, °C	275 Max.	262	266
Acid number, mg KOH/g	2 Max.	1.1	1.3

TABLE 2

Index	Limits according to GOST [All-Union State Standard] 2084-77		Actual property indexes	
	A-72 (Grade L)	A-76 (Grade L)	straight-run naphtha from Orsk refinery	A-76 gasoline from Industrial Association
Octane number (MM), Min.	72	76	65,4	77,8
Lead concentration, g/dm³, Max.	19	0,17	None	0,13
Distillation, °C				
IBP, Min.	35	35	40	38
10%, Max.	70	70	50	55
50%, Max.	115	115	66	94
90%, Max.	180	180	113	157
EP, Max.	195	195	153	190
residue, %, Max.	1,5	1,5	0,7	1
residue + loss, %, Max.	4	4	1,3	4
Vapor pressure, kPa, Max.	66,5	66,5	48,9	63,4
Acidity, mg KOH/100 cm³, Max.	3	3	None	0,15
Existent gum content, mg/100 cm³, Max.				
at production site	5	5	—	2
at consumption site	10	10	--	—
Induction period, min, Min.	600	900	900	900
Sulfur content, %, Max.	0,12	0,1	0,06	0,04

Note. All samples pass copper strip corrosion test and do not contain any water-soluble acids or alkalis, solid contaminants, or water.

TABLE 3

Index	Straight-run cut from Orsk refinery with sample 1 of still bottoms		A-76 gasoline from IA "Angarsk-nefteorgsintez" with 1.5% (wt.) sample 2 of still bottoms
	2% (wt.)	5% (wt.)	
Octane number (MM)	65.5	65.7	77.8
Lead concentration, g/dm³	None		0.15
Distillation, °C			
H. K.	41	43	37
10%	51	52	56
50%	66	67	95
90%	115	121	162
K. K.	155	200	203
residue, %	1	2.5	1.25
residue + loss, %	2	2	4
Acidity, mg KOH/100 cm³	1	2.5	1.25
Existent gum content (at site of consumption), mg/100 cm³	3.8	4.2	3.8
Sulfur content, %	0.06	0.06	0.03

Note. All samples pass copper strip corrosion test and do not contain any water-soluble acids or alkalis, solid contaminants, or water.

of existent and acetone-soluble gum, residue, and total quantity of high-molecular-weight oxidation products.

When 4-5% of the still bottoms are added, the quantities of existent gum, alcohol-soluble gum, and residue are greatly increased, indicating that extended storage of these gasolines would be accompanied by severe oxidation processes. Even with the addition of 5% still

TABLE 4

Gasoline	Content, mg/100 cm³			
	gum			
	existent	acetone-soluble	residue	sum of oxidation products
Straight-run, Orsk refinery				
without additive	None	1,9	7	8,9
with 2% sample 1 of still bottoms	3,4	2,4	35,6	41,4
with 5% sample 1 of still bottoms	4	4	90	98
A-76, Moscow refinery				
without additive	6	1	4	11
with 2% sample 1 of still bottoms	9	1,5	1	11,5
with 4% sample 1 of still bottoms	20	1,7	3,2	24,9

bottoms, the total quantity of high-molecular-weight oxidation products did not exceed the current standard (100 mg/100 cm^3). However, since gasoline base stocks with lower chemical stability may be used in practice, the content of alcohol still bottoms should obviously be limited to 1.5-2% by weight.

Thus, we have demonstrated the feasibility of compounding gasolines with such complex mixtures of oxygenated compounds as the still bottoms obtained in alcohol production (1.5-2% by weight), obtaining gasoline samples that will meet all requirements of GOST 2084-77 (with Amendments 1-3) for automotive gasolines. These samples have been tested with favorable results in the complete set of qualification test methods for automotive gasolines.

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