Quality Enhancement of Straight-Run Petroleum Fractions from High-Wax Mongolian Oils

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(Received April 13, 2007; revised June 3, 2007)

Abstract

The effect of ozonation and dewaxing of Mongolian high-wax oils on the hydrocarbon type composition of petroleum fractions has been studied. The evolution of composition and properties of straight-run petroleum fractions (IBP 180 °C) during reforming on a zeolite catalyst has been examined. It has been demonstrated that after ozonation followed by oil thermolysis the petroleum fractions are enriched with aromatic hydrocarbons while the content of naphthenic ones diminishes. Dewaxing of high-wax oil with liquefied gas has been shown to remove predominantly normal alkanes from petroleum fractions. It has been demonstrated that on catalytic thermal refining of straight-run petroleum fractions the products obtained are depleted of normal paraffin and naphthenic hydrocarbons by 2–5 times, enriched with aromatics by 2–4 times, octane rating of gasoline is enhanced by 18–40 points.

INTRODUCTION

Motor-vehicle transport gasoline should satisfy to a wide range of requirements defined in corresponding standards (GOST R 51313–99, GOST R 51855–2002). Knock rating of gasolines depends on the content of low-octane (*n*-alkanes) and high-octane components (strongly branched paraffins and aromatics) [1, 2]. Virtually all straight-run petroleum fractions are characterized with low octane rating.

Current practice of improvement of antiknock properties, *i.e.*, increasing the octane rating of petroleum fractions, is the use of octane boosters, blending with high-octane components (oxygen-containing, alkylates, reformats, *etc.*), secondary processing such as reforming, platforming zeoforming, izomerisation, *etc.* Actually, all these techniques have practical limitations imposed by standards determining fractional compositions of produced gasolines, the content of oxygen-containing compounds and additives [3].

Therefore, the development of alternative approaches to enhancement of straight-run petroleum fractions using non-conventional technological processes is highly topical.

The purpose of this study is investigation of the effect of ozonation and dewaxing of oil on the composition and properties of petroleum fractions, examination of transformations of petroleum fractions of high-wax Mongolian oils on a zeolite catalyst.

EXPERIMENTAL

Ozonation and dewaxing were applied to a high-wax oil from Tamsagbulag field (Mongolia) having the following composition: petroleum fraction – 15 vol. %, the fraction with IBP 350 °C – 51 vol. %, solid paraffin – 16.87 mass %, tar – 4.67 mass %, asphaltenes – 0.26 mass %. The oil is characterized as heavy (ν_{30} = 17.06 cSt), high pour point ($T_{p/p}$ = 20 °C), and sweet (sulphur content 0.06 mass %).

Oil samples were treated with ozone-oxygen mixture in a laboratory set-up equipped with an airlift reactor. The ozonation was performed at 40 °C to provide lower oil viscosity and enhance gas barbotage through the liquid.

The amount of consumed ozone was varied from 1.5 to 30 g per 1 kg of oil and was monitored by Tsiklon-5 analyser. Decomposition of the products obtained (according to [4, 5], ozonides dominate) was achieved by thermal cracking of the ozone-treated oils at 360 °C during 1 h at ambient pressure in a flask equipped with a reflux condenser and a trap for volatile fractions and gases. Hydrocarbon type composition of petroleum fractions obtained by fractional distillation of the ozonized and thermally treated oils at normal pressure and temperatures up to 200 °C was determined by gas chrom-atography [6].

Dewaxing was carried out with liquefied household gas having the following composition, vol. %: propane – 84.04, n-butane – 14.95. Dewaxing was performed in a laboratory setup comprising a mixer-extractor (reactor), liquefied gas tank, filter and receiver-separator. In the mixer-extractor the oil was mixed with the liquefied gas under oil/solvent (propane-butane) ratio 1 : 4, and heated to 50 °C. Further, the mixture was cooled to −25 °C, kept for 30 min and filtered at −20 °C [7]. The purified oil was fractionated in a distillation apparatus, gasoline and diesel fractions being collected.

Catalytic reforming was applied to straight-run petroleum fractions (IBP 180 °C) from Tamsagbulag and Zuunbayan fields (Mongolia). Physicochemical characteristics of straight-run petroleum fractions of the oils are listed in Table 1. One can see that the Tamsagbulag oil is richer with the petroleum fraction than the Zuunbayan one, although both oils have practically the same density. These fractions does not match the automobile gasoline standard GOST R 51105–97 [8] both in fractional composition and octane rating. Straight-run petroleum fractions are almost sulphur-free.

Hydrocarbon composition of the petroleum fractions of the oils in question is predominantly presented by aliphatic hydrocarbons. The straight-run petroleum fraction of the Tamsagbulag oil is 10 % richer with isoalkanes than that of the Zuunbayan oil, but, in contrast, contains less aromatic hydrocarbons. Due to low content of aromatics the petroleum fractions of both oils are characterized with low octane rating.

High silica zeolite (HSZ) with silica modulus 60 (Table 2) was used as the catalyst, which was obtained by hydrothermal crystallization of alumosilica gel at 175 °C during 4–6 days.

TABLE 1

Physicochemical characteristics of straight-run petroleum fractions (IBP 180 °C) of Mongolian oils

Parameter	Petroleum fractions of oils		GOST R 51105–97
	Tamsagbulag	Zuunbayan	
Mass percentage, %	16.53	10.33	–
Density d_4^{20}, g/cm^3	0.745	0.746	0.700–0.780
Initial boiling point, °C	71	78	≥35
Fractional composition (boils off at the temperature, °C):			
10 % by volume	107	112	≤75
50 % by volume	136	148	≤120
90 % by volume	174	191	≤190
Final boiling point, °C	195	214	≤215
Hydrocarbon type composition, mass %:			
n-Paraffins	26.8	30.0	–
Isoparafinns	41.8	31.9	–
Naphtenes	13.9	8.9	–
Aromatics	17.5	29.2	–
Octane number (RON)	52	56	≥80

TABLE 2

Physicochemical characteristics of high silica zeolite M60

T_{max}, °C		Concentration, μmol/g			E_a, kJ/mol		Crystallite size (d), μm	Crystallinity (α), %	Specific surface (S), m^2/g
T_I	T_{II}	C_I	C_{II}	C	E_I	E_{II}			
210	425	304	280	584	34	127	5.4–8.1	96.4	453

Note. T_{max} is temperature of maximums of the peaks of ammonia desorption for forms I and II; C_I, C_{II} and C are concentrations of acidic centres in the forms I, II, and overall concentration, respectively.

According to powder XRD and IR spectroscopy, the crystallization of the HSZ approaches 100 %. The powder diffraction pattern and IR spectrum of the prepared HSZ are similar to those observed for the ZSM-5 zeolite. To convert the zeolite in the H-form, alkali metal cations were removed: HSZ was treated with 25 % solution of NH_4Cl, then dried at 110 °C and calcined in air at 540 °C for 6 h (Na_2O content in H-HSZ was less than 0.02 %) [9].

Refining of straight-run petroleum fractions of the oils was carried out in a flow reactor with stationary catalyst bed (V = 5 cm^3) at 280–400 °C, ambient pressure, and feedstock WHSV 2.0 h^{-1}.

Reaction products were analysed by gas chromatography.

RESULTS AND DISCUSSION

Fractional composition of the petroleum fractions (IBP 200 °C) of the ozonized and thermally treated oils practically does not depend on the amount of consumed ozone. As evident from Table 3, with increasing ozone concentration the content of normal alkanes and isoalkanes shows very little variation, the concentration of naphtenes decreases from 26.1 to 17.8 wt %, while the fraction of aromatic hydrocarbons rises from 4.6 to 8.0 mass %. The amount of unidentified hydrocarbons essentially increases (from 3.8 to 8.0 mass %), apparently, due to formation of unsaturated hydrocarbons and oxidized compounds. However, the presence of unsaturated hydrocarbons and oxidized compounds in motor gasolines is undesirable as it worsens their stability.

As follows from the data obtained, oil ozonation increases the content of aromatic and olefin hydrocarbons in the distilled petroleum fractions as compared to the straight-run fraction of the original oil, thus resulting in better octane rating.

Physical chemical characteristics and hydrocarbon composition of the petroleum fractions of the original oil and the oil purified with liquefied gas are given in Table 4. On oil dewaxing with the liquefied gas at −20 °C normal alkanes (C_3–C_{16}) entirely dissolve in the propane-butane mixture and on separation of the solid residue by filtration are removed from the petroleum fraction with the liquefied gases. This results in the decrease of weight content of n-alkanes in the petroleum fraction from 26.8 to 2.0 %. The concentration of isoalkanes is only slightly affected by dewaxing because of different solubility or normal and isoalkane hydrocarbons in the propane-butane mixture.

TABLE 3

Hydrocarbon type composition of petroleum fractions (IBP 200 °C) obtained from the Tamsagbulag oil after ozonation followed by thermolysis

Amount of consumed ozone, g O_3/kg	Mass percentage, %					Octane number
	Paraffins	Isoparaffins	Naphtenes	Arenes	Unidentified compounds	
0	41.58	23.96	26.06	4.60	3.80	42
1.5	40.98	23.59	24.03	6.28	5.12	43
10	39.90	23.26	23.84	7.33	5.67	43
30	41.95	24.20	17.79	7.98	8.08	44

TABLE 4

Type composition of petroleum fractions (IBP 180 °C) or the crude and purified oil from Tamsagbulag field

Hydrocarbons	Mass percentage, %	
	Crude	Purified
n-Alkanes		
Pentane	0.7	0.0
Hexane	2.6	0.6
Heptane	0.2	0.0
Octane	5.7	0.0
Nonane	7.4	1.0
Decane	10.2	0.4
Total	26.8	2.0
Isoalkanes		
Isopentanes	0.4	0.5
Isohexanes	1.1	0.7
Isoheptanes	3.4	6.3
Isooctanes	9.3	8.0
Isononanes	8.8	11.7
Isodecanes	18.7	18.6
Total	41.7	45.8
Naphtenes		
Cyclopentane	0.2	0
Cyclohexane	6.5	4.3
Methylcyclohexane	4.8	1.6
Alkylcyclenes C_{8+}	2.4	2.0
Total	14.0	7.9
Arenes		
Benzene	0.8	8.9
Toluene	1.6	8.0
Ethylbenzene	2.0	1.5
p-, *m*-Xylenes	3.8	12.1
o-Xylene	1.7	1.9
Isopropylbenzene	1.4	1.7
Propylbenzene	0.6	0.2
Ethyltoluene	2.2	1.1
Mesitylene	2.0	8.3
Pseudocumene	1.1	0.4
Durol	0.3	0.2
Total	17.5	44.3

Note. Properties of petroleum fractions of crude and purified Tamsagbulag oil: mass percentage 16.5 and 13.6 %, density 0.7447 and 0.7538 g/cm^3, octane number 52 and 90, respectively.

Due to the increase in content of aromatics from 17.5 to 44.3 mass % and depletion of *n*-alkanes of the petroleum fraction, its octane number rises to 90 points. After dewaxing, the density of the petroleum fraction obtained only slightly increases, although the mass percentage of the petroleum fraction in the purified oil is decreased by 2.9 %.

As evident from Table 5, the increase in the reaction temperature affects the hydrocarbon composition of liquid products. In the composition of catalysates of Tamsagbulag and Zuunbayan oils mass fraction of *n*-alkanes diminishes (from 26.8 to 8.9 % and from 30.0 to 7.2 %, respectively), and the mass fraction of aromatic hydrocarbons increases (from 17.5 to 65.1 % and from 29.3 to 65.5 %, respectively). Among aromatics, an essential increase in content is observed for benzene, toluene and xylenes.

European standards Euro-2, Euro-3 and Euro-4 strictly regulate the content of aromatic hydrocarbons and, particularly, of benzene, although these compounds have high octane numbers. Figure 1 illustrates that in the catalysates obtained from the straight-run petroleum fraction of the Zuunbayan oil the content of benzene increases with the reaction temperature from 2.0 (in the original fraction) to 7.6 mass % (at 300 °C), and further shows little evolution. In the catalysates obtained from the straight-run petroleum fraction of the Tamsagbulag oil it rises from 0.8 (the original fraction) to 5.7 mass% (at 320 °C), and does not change anymore.

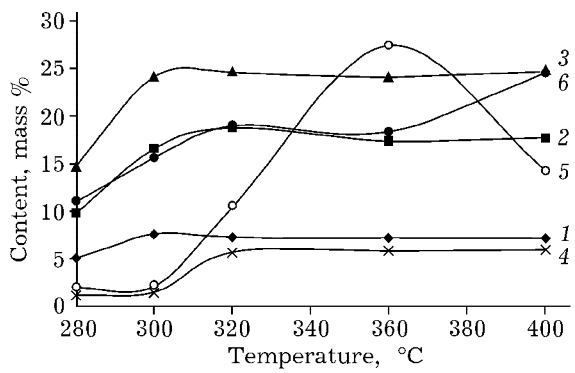

Fig. 1. Effect of reaction temperature on the percentage of benzene (*1*, *4*), toluene (*2*, *5*) and xylenes (*3*, *6*) in the gasolines obtained on processing of straight-run petroleum fractions of the Zuunbayan (*1–3*) and Tamsagbulag (*4–6*) oils on the zeolite catalyst.

TABLE 5

Hydrocarbon type composition of liquid products of processing of straight-run petroleum (IBP 180 °C) of Mongolian oils on the zeolite catalyst

Products	Mass percentage of petroleum fractions, %, for the oils										
	Tamsagbulag					Zuunbayan					
	at the reaction temperature, °C										
	Initial	300	320	360	400	Initial	280	300	320	360	400
n-Alkanes	26.8	19.3	12.9	9.9	8.9	30.0	5.5	7.6	7.3	7.5	7.2
Alkenes	0.0	1.0	1.0	1.2	1.1	0.0	0.8	1.1	1.0	0.9	1.0
Isoalkanes	41.8	30.7	26.9	18.8	22.1	31.9	27.5	20.9	21.0	20.7	21.1
Naphtenes	13.9	12.9	8.6	5.0	4.5	8.9	4.9	6.1	5.2	6.1	7.0
Arenes	17.5	36.1	50.6	65.1	63.4	29.2	61.3	64.3	65.5	64.8	63.7

Within temperature range 300–400 °C the major liquid products are aromatic hydrocarbons and isoalkanes, while the concentration of olefins is small. Further temperature rise (>400 °C) is unpractical, for intensive cracking reactions yield large amounts of side products and gaseous hydrocarbons.

The data on the composition of gaseous products formed during processing of the straight-run petroleum fractions of the oils on the zeolite catalysts are presented in Table 6. As one can see, the dominating gaseous products are alkanes C_1–C_5 with mass percentage from 74.7 to 81.7 %. Propane and butane prevail among the lowest alkanes. Alkenes are formed at different temperatures of the process (mass fraction 2.7–10.6 %), basically ethylene and propylene. The gaseous products resulting from the processing of the straight-run petroleum fraction of the Zuunbayan oil are essentially richer with C_2–C_4 olefins as compared to the tail gases originating from processing of the straight-run petroleum fraction of the Tamsagbulag oil.

The influence of the process temperature on the yields of gaseous and liquid products arising from the processing of the straight-run petroleum fractions of the Mongolian oils on the zeolite catalyst is illustrated in Table 7 and Fig. 2.

The increase in the temperature of the catalytic process diminishes the yield of catalysates resulting from processing of petroleum fractions of the Zuunbayan and Tamsagbulag oils. This indicates that at high temperatures *n*-alkanes present in the original petroleum fractions are cracked on the zeolite catalyst, and light hydrocarbons are produced. As shown above, hydrocarbon type composition of the gases formed in the reaction only slightly changes with temperature rise, and their yield increases to 47–49 mass %.

The octane number of the catalysates obtained on processing of the straight-run petroleum fraction of the Zuunbayan oil at 280–300 °C sharply grows to 94 points, and then shows little variation (see Fig. 2, curve *5*). The octane number of the catalysates obtained on processing of the straight-run petroleum fraction of the Tamsagbulag oil at 280–360 °C increases to 95 (see Fig. 2, curve *6*). Therefore, for production of high-octane gasoline the catalytic reforming of the straight-run petroleum from the Tamsagbulag oil should be started at

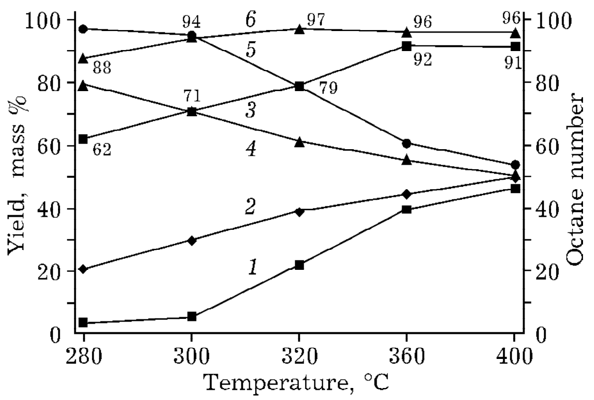

Fig. 2. Temperature dependencies of yields of gases (*1*, *2*) and catalysates (*3*, *4*) obtained on processing of straight-run petroleum fractions of the Tamsagbulag (*1*, *3*, *5*) and Zuunbayan (*2*, *4*, *6*) oils, as well as the octane number of the produced gasoline.

TABLE 6

Composition of gaseous products of processing of straight-run petroleum fractions (IBP 180 °C) of Mongolian oils on the zeolite catalyst

Products	Mass percentage of petroleum fractions, %, for the oils								
	Tamsagbulag				Zuunbayan				
	at the reaction temperature, °C								
	300	320	360	400	280	300	320	360	400
				n-Alkanes					
Methane	0.9	0.7	0.3	0.7	1.9	2.3	3.1	3.0	2.8
Ethane	2.7	2.4	1.4	2.4	5.3	5.4	6.5	6.7	6.4
Propane	59.4	63.2	58.6	61.7	57.9	64.7	61.6	61.3	58.2
Butane	12.1	12.8	13.6	11.8	10.9	8.9	8.6	7.5	9.4
Pentane	1.7	1.5	0.5	0.7	0.8	0.4	0.8	0.9	0.8
Total	76.8	80.6	74.4	77.3	76.8	81.7	80.6	79.4	77.6
				Alkenes					
Ethylene	1.5	0.9	0.7	1.2	3.4	2.6	3.6	4.2	4.2
Propylene	1.8	1.4	1.4	1.8	4.8	3.1	4.3	4.9	5.0
Butenes	0.4	0.5	0.6	0.7	1.1	0.9	0.7	0.5	1.4
Total	3.7	2.8	2.7	3.7	9.3	6.6	8.6	9.6	10.6
				Isoalkanes					
Isobutanes	16.4	14.1	20.9	16.9	12.2	10.6	9.4	9.4	9.0
Isopentanes	3.1	2.5	2.0	2.1	1.7	1.1	1.4	1.6	2.8
Total	19.5	16.6	22.9	19.0	13.9	11.7	10.8	11.0	11.8

TABLE 7

Product yields and octane number of the original and processed petroleum fractions

Reaction temperature, °C	Product yield, mass %		Octane number of the catalysate
	Gas	Catalysate	
	Tamsagbulag oil		
Initial	–	–	52
280	3.5	96.5	62
300	5.2	94.8	71
320	21.6	78.5	79
360	39.6	60.4	92
400	46.2	53.8	91
	Zuunbayan oil		
Initial	–	–	56
280	20.5	79.5	88
300	29.5	70.5	94
320	38.9	61.1	97
360	44.5	55.5	96
400	49.8	50.2	96

the temperature of 300–320 °C, while for the straight-run petroleum from the Zuunbayan oil the temperature should be 280–300 °C. With decay of the catalytic activity during the reaction, the temperature of the process should be increased at a certain rate up to 400–440 °C.

CONCLUSION

It has been found that after ozonation of high-wax oil followed by thermolysis, the content of aromatic hydrocarbons in the straight-run petroleum fraction increases with the amount of consumed ozone. Dewaxing of high-wax oil with liquefied gas at −20 °C has been shown to remove 92 mass % of *n*-alkanes from the petroleum fractions, resulting in rising of octane rating from 52 to 90 points. It has been demonstrated that catalytic refining of straight-run petroleum fractions of Mongolian oils on the zeolite catalyst decreases the content of normal paraffins by 2–5 times, increases the fraction of aromatic hydrocarbons by 2–4 times, and rises the octane number by 18–40 points.

High-octane gasolines can be obtained from high-wax Mongolian oils both by catalytic reforming and by removal of normal alkanes by liquefied hydrocarbon gases.

Acknowledgement

The authors are indebted to A. V. Vosmerikov and L. M. Velichkina for assistance in experiments on catalytic refining of straight-run petroleum fractions and helpful discussions.

REFERENCES

1 A. A. Gureev, Yu. M. Zhorov, E. V. Smidovich, Proizvodstvo vysokooctanovykh benzinov, Khimiya, Moscow, 1981.
2 A. S. Safonov, F. I. Ushakov, I. V. Chechkenev, Avtomobilnye topliva, St. Petersburg, 2002.
3 V. G. Stepanov, *Khim. i Tekhnol. Topliv i Masel*, 1 (2005) 3.
4 V. F. Kamyanov, A. K. Lebedev, P. P. Sivirilov, Ozonoliz komponentov nefti, Izd-vo TPU, Tomsk, 1997.
5 A. K. Lebedev, L. V. Gorbunova, V. F. Kamyanov, *Neftekhim.*, 20 (1980) 918.
6 V. K. Solodkov, E. I. Talalaev, V. F. Kamyanov, Gazozhidkostnaya khromatografiya gazov, gazokondensatov i neftey, Ylym, Ashkhabad, 1983.
7 A. K. Golovko, V. G. Surkov, V. F. Kamyanov, L. A. Kosheleva, VI Mezhdunar. konf. “Khimiya nefti i gaza” (Proceedings), Tomsk, 2006, p. 230.
8 G. A. Lastovkin, T. D. Radhenko, M. G. Rudin (Eds.), Spravochnik neftepererabotchika, Khimiya, Leningrad, 1986.
9 L. M. Velichkina, L. L. Korobitsyna, A. V. Vosmerikov, *Neftepererab. i Neftekhim.*, 10 (2005) 32.