



Initiated Low-Temperature Cracking of Ozonized Petroleum and Heavy Petroleum Ends

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Abstract

New way to produce greater amounts of distillate motor fuels from crude petroleum, petroleum residues and natural bitumens by an ozonization of raw material followed with thermal treatment of the product formed under the conditions similar to ones characteristic of common petroleum atmospheric rectification process is proposed. About half of heavy petroleum components boiling above 350°C can be converted into light hydrocarbons constituting the gasoline and diesel fractions and total yield of the lasts can be accordingly increased by means of described new method of oil processing. Ultimate products contain up to 16 wt.% olefins and lesser amounts of sulfur compounds and have noticeably improved principal operational properties in comparison with analogues straight-run motor petroleum distillates.

Introduction

The processing of heavy petroleum components into additional amounts of light distillates, especially, motor fuels, is one of principal tasks of petroleum refining.

The thermal and catalytic cracking processes of petroleum residues (mazuts) are the most significant secondary ways to produce gasoline and diesel fuels at petroleum refineries. The first of these processes is technologically simpler than the second one but it demands the use of very high temperatures (490-540°C) and pressures (up to 5 MPa) [1].

We have found that thermal cracking of petroleum heavy components proceeds deeper and at lesser temperatures if occurring radical-chain destruction reactions are initiated by introducing of special additives into the raw material. It was shown that effective initiators of these reactions could be obtained by an ozonization of heavy petroleum residua [2].

The ozone with the great reaction rates interacts with petroleum sulfides and condensed polycycloaromatic compounds forming the sulfoxides and ozonides, respectively [3,4]. These thermally unstable substances destroying readily by heating above 110-120°C serve as initiators of subsequent cracking reactions.

Inasmuch as oil residues ozonizing have to be di-

luted in some suitable solvent, in many cases the more handy method is direct ozonization of crude petroleum [5,6].

The main results of our investigations on application of ozone techniques for increasing distillate fuel yields by refining petroleum and petroleum residues are described in present short communication.

Experimental

An ozonization of petroleum stocks was conducted in many-sectional straight-through reactor (hydrodynamic mixer) of the laboratory pilot installation at the temperature of 20-80°C chosen with taking into account that the viscosity of liquid should not be above 15-20 cs [6]. Too viscous sorts of raw materials were diluted, if necessary, with straight-run kerosene distillate.

The initial liquid raw material and ozone-air mixture produced by the "Ozon-2M" generator ("Kurgankhimash", Kurgan, Russia) were introduced into lower section of the reactor. The sudden changes of flow rates at diaphragms delimited the sections provided fine dispersing of the liquid. The duration of gas passing through reaction zone did not exceed 2 s, stay period of petroleum in this zone being no more than 3 min. The noticed short duration of the ozonization process was necessary for preventing oxi-

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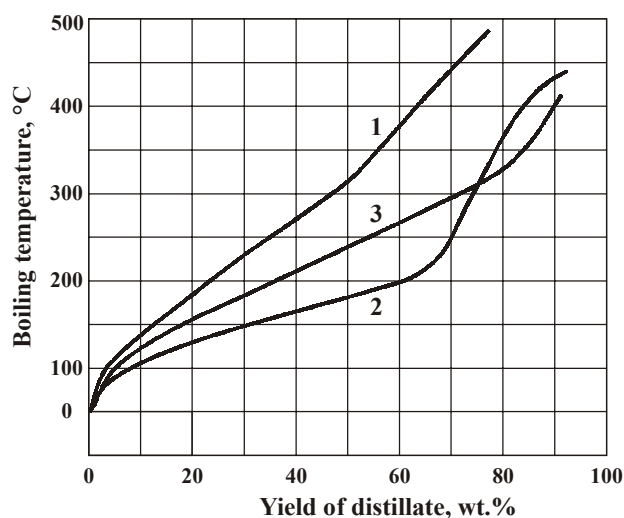
dizing destruction of generated ozonides, but it was sufficient for the complete consumption of ozone introduced into reactor. The two-phase mixture leaving the reactor was divided in the separator, waste air was exhausted to atmosphere, and liquid reaction product was heated up to 340-350°C, sustained in the reaction chamber during 30-60 min to the completion of cracking gas generation, and rectified.

Results and Discussion

The results obtained for many different raw materials had demonstrated essential advantages of low-temperature initiated cracking process proposed in comparison with the non-initiated, much more high temperature process performing at refineries.

Thus, the sum yield of IBP-350°C distillate reached 82 wt.% when gently sulfurous (1.28 wt.% of S, mainly in the thiophene rings), resinous (12.7 wt.% of resins and asphaltenes) West-Siberian commercial petroleum was subjected to the ozonization followed with thermal treatment of reaction product, while initial crude oil contained only 52 wt.% of the analogues straight-run fractions (see Fig. 1) [5,6]. It is obvious that the installation scheme must include necessarily the reaction chamber similar to one using at the cracking units of traditional petroleum refineries. Otherwise, destruction reactions of oil components will proceed in the rectification tower simultaneously with physical separation process; as a result, the efficiency of hydrocarbon fractionation can

become worse significantly (compare, for instance, lines 2 and 3 in Fig. 1).



1 – crude petroleum; 2 – ozonized petroleum; 3 – product of thermal treatment of ozonized petroleum at 350°C. Fig. 1. TBP-curves for West-Siberian commodity petroleum before and after its ozonolysis.

The cracking initiated by ozonides leads to the noticeable decrease of sulfur content of all distillates and to the appearance up to 16% of olefins in their compositions (see Table 1). It should be noted that common industrial thermal cracking products contain even greater amounts of olefins, up to 25 wt.%.

Though by the ozonation the significant amount of oxygen (1.0-1.5 wt.%) is introduced into stock

Table 1

Characteristics of distillate fractions of crude West-Siberian oil and of its thermally treated ozonization product

Boiling Interval, °C	Yield, wt.%	MM, a.e.m	ρ_4^{20}	n_D^{20}	v_{20} , cs	Content, wt.%, of		
						S	olefins	COOH
Products from crude petroleum								
IBP-50	0.18	---	---	---	---	0.00	0.00	0.00
50-100	3.06	---	0.7200	1.4038	1.56	0.00	0.00	0.00
100-150	9.20	110	0.7669	1.4310	1.84	0.10	0.00	0.00
150-200	11.36	134	0.8142	1.4566	2.50	0.21	0.00	0.00
200-250	9.27	164	0.8415	1.4710	2.91	0.41	0.00	---
250-300	13.87	205	0.8534	1.4760	5.60	0.55	0.00	---
300-350	6.59	252	0.8737	1.4885	13.4	1.04	0.00	---
350-400	9.41	312	0.8836	1.4989	28.1	1.30	0.00	---
400-450	7.78	384	0.9136	1.5114	---	1.56	0.00	---

Table 1
Continued

Boiling Interval, °C	Yield, wt. %	MM, a.e.m	ρ_4^{20}	n_D^{20}	v_{20} , cs	Content, wt.%, of		
						S	olefins	COOH
Products from ozonized petroleum								
IBP-50	0.80	---	0.6726	1.3850	---	0.00	10.9	0.00
50-100	4.08	---	0.7267	1.4060	0.67	0.00	16.0	1.02
100-150	10.58	111	0.7555	1.4246	0.91	0.09	11.6	0.30
150-200	20.86	136	0.7953	1.4458	1.39	0.13	10.5	0.15
200-250	16.18	166	0.8270	1.4648	2.30	0.26	12.4	0.04
250-300	19.03	204	0.8502	1.4779	4.75	0.40	14.9	0.01
300-350	10.67	250	0.8690	1.4868	8.50	0.69	12.6	0.008
350-400	7.20	315	0.8875	1.4940	15.0	0.88	12.5	0.006
400-420	2.14	362	0.8984	1.4995	23.1	1.31	11.0	---

composition in addition to the O-atoms presented at first, its content in destruction products was proved to be very small. Only lighter gasoline components obtained contained noticeable amounts of COOH-groups in the molecules; the concentrations of these groups in the cracking distillates reduced rapidly with the rise of their boiling points and became hardly fixing (< 0.01 wt.%) in the fractions boiling above 300°C . Evidently, oxygen atoms are removed during the cracking process in CO , CO_2 , SO_2 , NO_x and H_2O forms.

In spite of evident compositional alterations of petroleum distillates their physical constants - densities ρ_4^{20} , refractory indices n_D^{20} , average molecular masses (MM) - changed to only a small extent.

Qualitatively similar results were obtained by the ozonization of heavy ($\rho_4^{20} = 0.9266$) high-sulphurous (4.6 wt.% S, mainly in the tiocyclanic structures), high-resinous (17.4 wt.% of resins and asphaltenes) crude petroleum produced at Ulianovsk region oil-fields [6]. This petroleum was ozonized at different ozone expenditures from 6 to 40 g per 1 kg of stock. It was found that the last was able to join up to 58 g of O_3/kg , but at ozone expenditures above 12 g/kg increases in light distillate yields became inessential (see Table 2).

After an ozonization of Ulianovsk petroleum at this commercially optimal ozone expenditure and following thermal treatment at 350°C , the yields of all distillates rose, the growth of gasoline IBP- 200°C yield being comparatively faint and most significant

Table 2

The changes of Ulianovsk petroleum fractional composition after its ozonization and subsequent thermolysis depending on ozone expenditure (distillation in Engler apparatus, GOST 2177)

Fraction boiling interval, °C	Content (vol.%) in the product, obtained at O_3 expenditure, g/kg				
	0.0	6.0	12.0	30.0	40.0
IBP-100	2.5	2.6	2.8	2.8	2.8
100-150	6.5	6.8	7.3	7.5	7.6
150-200	5.5	6.2	6.7	6.9	6.9
IBP-200	14.5	15.6	16.8	17.2	17.3
200-250	6.5	7.4	8.3	8.7	8.9
250-300	8.0	9.1	10.7	11.2	11.6
300-350	8.5	9.9	12.3	12.9	12.8
IBP-350	37.5	42.0	48.1	50.0	50.6
350-400	8.5	10.3	11.9	12.5	12.6
IBP-400	46.0	52.3	60.0	62.5	63.2

increases observing for the yields of diesel $200-350^\circ\text{C}$ and oily fractions boiling above 350°C (see Table 3). More than 79 wt.% of final reaction products were distilled at 480°C instead of only 59 wt.% of the similar fractions presented in the crude oil composition.

As a result of operations performed, sharply diminished was sulfur content of all petroleum distil-

Table 3

Characteristics of distillates from ozonized and thermally treated Ulianovsk petroleum (rectification in ARN-2 apparatus, GOST 11011)

Fraction boiling interval, °C	Yield, wt.%	ρ_4^{20}	n_D^{20}	Content, wt.%, of		
				S	olefins	COOH
IBP-100	4.82	0.6927	1.4013	0.01	4.6	0.53
100-150	4.88	0.7504	1.4222	0.08	10.8	0.26
150-200	6.03	0.7912	1.4430	0.14	11.0	0.11
IBP-200	15.73	0.7484	1.4238	0.08	9.0	0.29
200-250	7.82	0.8224	1.4616	0.28	12.3	0.05
250-300	9.33	0.8443	1.4735	0.40	13.4	0.01
300-350	11.11	0.8650	1.4828	0.66	15.1	0.007
200-350	28.26	0.8464	1.4739	0.47	13.8	0.02
IBP-350	43.99	0.8114	1.4551	0.33	12.1	0.12
350-400	12.40	0.8825	1.4940	0.87	12.5	0.005
IBP-400	56.39	0.8270	1.4636	0.45	12.2	0.09
400-450	13.38	0.8964	1.5072	1.36	11.1	0.004
450-480	9.37	0.9014	1.5129	1.84	9.2	0.002
IBP-480	79.14	0.8475	1.4768	0.77	11.7	0.065

lates, e.g. from 0.51 to 0.07 wt.% in gasoline and from 3.57 to 0.43 wt.% in diesel fractions.

Unsaturated hydrocarbons (olefins) appeared in all distillates at the amounts up to 15 wt.%.

Concentrations of COOH-groups were very small in all thermally treated ozonolysis products boiling above 200-250°C.

We found that using the same technological approach it could be processed both crude petroleums and the residues producing by their distillation at the oil refineries. As it is shown in Table 4, where the compared are the yields of the distillates IBP-300°C after ozonization and subsequent thermolysis of crude commodity West Siberian oil and of the residuum > 350°C obtained by distillation of the same petroleum depending on specific ozone expenditure. Owing to greater concentrations of readily ozonizing heteroatomic and polycycloaromatic compounds in the residuum accordingly some larger amounts of ozone were necessary for its processing in comparison with the case of initial crude oil. It is seen that optimal ozone expenditure when the mazut served as raw material was about 17 g/kg. At that case approximately 53 wt.% of mazut components can be con-

verted into light gasoline and gas-oil hydrocarbons.

Table 4

Yields of IBP-300°C distillates from West Siberian petroleum and from its residuum boiling above 350°C (mazut) after their ozonization and following thermolysis depending on ozone expenditure (distillation in Engler apparatus, GOST 2177)

Ozonized raw material	Ozone expenditure, g/kg	Yield of distillate, vol.%
Crude petroleum	0	51
	7	66
	12	76
	15	74
	17	72
Petroleum residuum	0	0
	12	31.5
	17	53.3
	22	49.5
	27	42.2

Prospective sorts of stocks for production of distillate motor fuels by the method described are natural bitumens.

We studied the possibilities of this new hydrocarbon processing process by the example of natural bitumen extracted from bituminous sands of Mortuk field (West Kazakhstan). The fractional compositions of the products, obtained by usual distillation of the bitumen, by thermal cracking of bituminous rock at 450°C performed by kazakhstanian investigators without preliminary isolation of organic matter ("synt-

oil" [7]) and by the ozonolysis process are compared in the Table 5.

It is seen that total yield of motor distillates IBP-350°C after the ozonolysis of natural bitumen reached 60 wt.% though it was only 24 wt.% when the same bitumen was distilled as usual and 48 wt.% after thermal cracking the same stock at 450°C. The losses of the crude owing to gas and coke formation decrease by approximately four times due to the lesser thermal treatment temperature of bitumen ozonization product.

Table 5

Fractional compositions of crude natural bitumen and the products of its thermal cracking at 450°C [7] and ozonolysis followed by thermal treating at 350°C

Fraction boiling interval, °C	Content of the fraction, wt.%, in the		
	initial crude bitumen	thermal cracking product	ozonolysis product
IBP-150	0.0	4.0	5.0
150-200	3.6	2.8	8.1
200-250	7.0	---	23.7
250-300	4.4	---	10.9
200-300	11.4	16.8	34.6
300-350	9.2	24.4	12.3
IBP-350	24.2	48.0	60.0
Residuum > 350°C	75.8	52.0	36.5
350-400	15.2	---	9.6
Residuum > 400°C	60.6	---	26.9
400-450	---	---	9.9
Residuum > 450°C	---	---	17.0
Gas + losses	---	14.0	3.5

The effects of the desulfuration and destruction of condensed polyarenic nuclei are observed for bitumen ozonization with subsequent thermolysis of reaction product similar to petroleum ozonolysis process. The decomposition of large condensed aromatic nuclei is clearly confirmed by the results of structural group analysis of ultimate distillates obtained from crude and ozonized bitumen; the values of structural group parameters given in Table 6, namely the portions of carbon atoms in aromatic (C_a), naphthenic (C_n), paraffin (C_p) structures and in olefinic double

bonds (C_{oi}), as well as total amount of rings in mean molecule (K_t) and its content of aromatic (K_a) and naphthenic (K_n) rings, were calculated using generally known n-d-M method proposed by van Ness and van Westen.

The above-mentioned differences of cracking distillates from straight-run fractions by composition must favor an improvement of operation properties of the products.

Thus, the appearance of olefins and the rise of aromatic hydrocarbon content in gasoline fractions must

Table 6

Compositional and structural-group characteristics of distillates from initial crude bitumen and its ozonolysis product

Fraction boiling interval, °C	Content, wt.%, of			Structural group parameters						
	S	olefins	COOH-groups	C _a , %	C _n , %	C _p , %	C _{ob} , %	K _t	K _a	K _n
Fractions of crude bitumen										
IBP-200	0.06	0.0	0.00	---	---	---	---	---	---	---
200-250	0.14	0.0	0.00	11.2	67.8	21.0	0.0	1.84	0.22	1.62
250-300	0.32	0.0	0.02	7.8	70.7	21.5	0.0	2.58	0.19	2.39
300-350	0.75	0.0	0.05	7.6	59.1	33.3	0.0	2.86	0.24	2.62
350-400	1.02	0.0	0.08	15.2	49.0	35.8	0.0	3.38	0.57	2.81
Fractions of bitumen ozonolysis product										
IBP-200	0.025	9.0	0.62	---	---	---	---	---	---	---
200-250	0.08	12.5	0.05	7.4	65.5	24.9	2.2	1.72	0.15	1.57
250-300	0.19	13.8	0.012	8.6	58.4	31.1	1.9	2.07	0.21	1.86
300-350	0.33	12.8	< 0.01	9.0	52.3	37.3	1.4	2.46	0.27	2.19
350-400	0.48	12.4	< 0.01	11.0	47.8	40.1	1.1	3.10	0.41	2.69
400-450	0.81	11.5	< 0.01	12.4	44.8	41.9	0.9	3.81	0.56	3.25

cause an increase of their octane numbers, which was confirmed by means of direct experimental measurements.

The reduction of the content of aromatic components, especially of condensed polyarenes, and the enrichment of molecules in paraffin fragments must cause the rise of cetane numbers of diesel fractions and the lowering of their scale forming ability. For the same reasons the viscosity indices of oily distillates must increase considerably.

From a position of improving the operational qualities of motor fuels and the reducing environment pollution by their combustion products, the low sulfur content of obtaining cracking distillates is also of no small importance.

However, the distillates obtaining by initiated low-temperature cracking process as well as the products of usual thermal cracking, pyrolysis and coking of hydrocarbons can be insufficiently stable when storing due to the presence of easily tarring unsaturated compounds. It must be noted that the content of the last ones in industrial cracking products is still higher and reaches 20-25 wt.% and more.

It should be noted, nevertheless, that hydrogenization methods to eliminate these defects were mastered and are used in the petroleum refining industry

long ago.

Conclusions

The ozonization that followed with subsequent thermal treatment of reaction product under the conditions typical for the industrial atmospheric petroleum distillation units is new prospective way to essentially soften and, at the same time, to deepen oil refining processes. The described method permits (1) to increase significantly the yields of distillate motor fuels from crude petroleum, (2) to lessen the concentrations of sulfur and condensed polyaromatic compounds in these products, (3) to improve accordingly their principal operational qualities without using catalysts, hydrogen and abundantly high temperatures and pressures and (4) to produce large amounts of valuable oil products from heavy petroleum residues and natural bitumens.

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