

High Technology of Production of Bitumen from Highly Paraffinic Crude

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Abstract

Background: The problem of manufacturing bitumen of high quality from oil residues is quite actual problem, as under conditions of depletion of oil reserves it is needed expansion of raw materials base. **Methods:** The analysis of oil processing state in the world determines the necessity of complex approach to solve the problem of using heavy oils, oil residues and natural bitumen, combining the further working the known processes and generating new alternative technological processes. The prospects of new effective processes development in oil processing are possible with application of different chemical and physical phenomena (mechano-chemical, plasma-chemical, ultrasonic actions and the others). **Results:** Currently, in practice in Russia, for refinement of final product of highly paraffinic crudes, which is production of high-octane benzine, diesel fuels, there are used pour-point depressants and inhibitors, compounding with highly paraffinic crudes, processing by secondary processes – reforming, zeoforming, isomerization, viscosity breaking and coking. Practically, all these methods have restrictions on application of processing heavy oil stock. Therefore, the main objective is searching to find alternative methods on the basis of nontraditional technological processes¹. Facilities of bitumen production from goudron with paraffin carbohydrates about 15% of masses are considered^{2,3}. It is rather problematic to obtain quality product from such raw materials. **Conclusion:** Therefore, the process of oxidation of goudron to bitumen is conducted in the presence of a catalytic complex, the action of which consists in reduction of paraffin carbohydrates and in reduction of process, So its presence is 2 times reducing preparation time of bitumen road marks. Also, results demonstrate that the reduction in the content of paraffinic hydrocarbons occurs by 2 times.

Keywords: Bitumen, Catalytic Complex, Goudron, Highly Paraffin Petroleum Residue

1. Introduction

The basic technological process of obtaining bitumen in petroleum refining industry is oxidation of heavy petroleum residues¹. Air oxidation is applied in production of bitumen, when feed stock contains few asphaltic-resinous matters and it is essential to increase their. Depending on the composition of feedstock, the quality of oxidized bitumen changes¹⁻³. By oxidation, monocyclic and bicyclic aromatic compounds undergo major modification. Group structure of paraffin-naphthenic carbohydrates in the process of oxidation changes little.

It is known^{4,5} that wide fluctuations in composition of paraffin-naphthenic carbohydrates negatively effect on the quality of bitumen. Optimum raw materials for

obtaining bitumen are the residues of highly resinous and low paraffin oils.

Residues of oil, which contain great quantity of paraffin carbohydrates, are hardly oxidized, impede the production of oxidized bitumen properties required, the stronger the higher their concentration is and if the content of paraffin is more than 3% by mass, in the structure of bitumen there occurs the formation of a new supra molecular structure of straight chain alkane type⁵⁻⁷. Hard block paraffins as crystalline substances do not have plastic properties and their presence increases bitumen brittleness, decreases bond to mineral additive and internal constraint between its particles. The stated above indicates that the production of bitumen from highly paraffin and low-resinaceous oil residues is a problem task. The produced bitumen from

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such stock is characterized in particular by low extensibility and poor low-temperature properties⁸⁻¹¹. The analysis of up-to-date methods of production of paving bitumen from highly paraffin stock shows that all methods come to maximum fractional distillation of paraffin and further let down with highly resinous goudron of the residual waxy portion to acceptable characteristics of bitumen^{8,9}. The stated above indicates that the production of bitumen from highly paraffin and low resinous residues of oil is awkward and actual task^{7,12-14}.

The objective of the work consisted in investigation of possibilities of bitumen production from highly paraffin residue of oil in presence of the catalytic complex developed by us.

2. Materials and Methods

As oxidized oil residue, it was used goudron of Yelkhovskoye Tar Refinery Management (YTRM), with high content of paraffin-naphthenic carbohydrates. Physicochemical properties of goudron of YTRM are presented in Table 1.

The process of oxidation of unmodified and activated goudron (that is in presence of catalytic complex) was conducted in the oxidation reactor cube with 1.5 l capacity with loading of feedstock of 1l at the process temperature of 250° C and the airflow of 3 l/min*kg of feedstock^{2,4,5,11}. Feed goudron was oxidized during 18 hours with sampling at intervals of 3, 6, 10, 14 and 18 hours since start of the process, activated goudron – within seven hours with sampling at intervals of an hour.

With the aim of quantitative determination of chemical group composition, the methods of RRI of PP was used^{11,12}, being based on the principles of liquid absorption chromatography? According to it, malthenes of

Table 1. Physicochemical properties of goudron of YTRM

Values	Goudron of YTRM
Density, kg/m ³	0,9878
Relative viscosity, RV ₈₀	51,76
Content, %wt.:	
- CAB	28,23
- sulphurs	0,887
-paraffins	15
Asphaltenes/tars	0,45

heavy oil fractions are divided into Paraffin-Naphthenic (PN), Monocyclo Aromatic (MCA), Bicyclo Aromatic (BCA), Polycyclo Aromatic Carbohydrates (PCA), forming a total oil group; resin-intobenzene (B) and Alcohol Benzene (AB), preliminarily removing asphaltene by precipitation with hexane. The content of hydro carbonaceous groups is determined by n-d-m method.

The melting point was determined according to the methods described in SSS 11506. The analysis of tensile strength (shortness of ink) was conducted using the ductility machined uktilometr DB-2 in accordance of SSS 11505. Penetration (the depth of needle) was determined according to SSS 11501. Mass variation (melting point) after heat penetration on SSS 18180 (the method is used to determine bitumen stability in long-term storage at elevated temperatures, estimated according to qualitative variables). To test brittle temperature, it was used the method described in SSS 11507. Flash temperature was tested according to SSS 4333-87. By analyzing bitumen, the central place is taken by the problem of adhesion bond of bitumen with mineral surface, that is, the study of capacity of bitumen covering the particles of mineral material to resist displacement or separation under the influence of external forces. The adhesion index of bitumen was defined according to methods specified in SSS 11508.

3. Results

Intensity of oxidation process is presented by dependences of softening temperature on duration of oxidation of both activated and non-activated original goudron (Figure 1 and Figure 2).

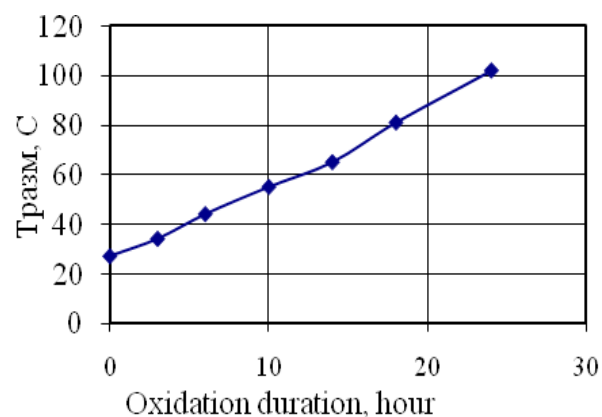


Figure 1. Dependence of softening temperature on duration of feed goudron oxidation.

From the analysis of data presented in Figure 1 and Figure 2, it is seen, that in presence of catalytic complex residence of feed stock in reaction zone reduces by 3, 5 times.

Table 2 and Table 3 represent chemical group composition in the dynamics of oxidation of original and activated goudron in YTRM PLC «Tatneft», respectively.

As it is seen from Table 2 and Table 3, oxidation of goudron in the presence of a catalyst complex is most intense and accompanied by a significant decrease in the amount of oils, including all their constituent structure. For example, for the first six hours of oxidation without the additives in goudron PCA, they are

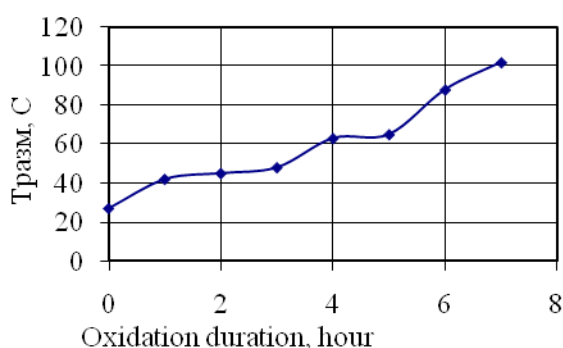


Figure 2. Dependence of softening temperature on duration of oxidation of activated goudron.

reduced by 15.6%, with additive –23.2%. BCA in two cases vary in waves, MCA reduces lightly. For three hours of oxidation with the additives, the content of PN is reduced by 3.4%, for the six hours by 6.5%, without the additives by 2.8 and 3.8%, respectively. These results show that in the presence of a catalytic complex, the conversion of paraffinic-naphthenic hydrocarbons is much faster and their relative contents in the dispersion medium (oils and resins) decrease. The dynamics of the formation of asphaltenes: for six hours of oxidation of goudron-1, they increase by 12.5%, with a modifier by 28.2% is observed especially clear⁵. Changes in physical and chemical properties of oxidized goudron of YTRM together with the catalyst complex and without are presented in Table 4 and Table 5.

According to the data from Table 2 and Table 3, the depth of needle penetration is decreased, the softening point by ring and ball increases, extensibility first increases for the first ten hours for original goudron (goudron-1), for the activated goudron (goudron-2) for the first three hours, then decreases, i.e. in the oxidation process, the percentage of asphaltenes increases, by reducing oils and resins. And for goudron-1, asphaltenes are increased by an initial accumulation of resins (as demonstrated by the indicators of the extensibility of bitumen), then the reaction rate constant increases rapidly toward the formation of asphaltenes¹⁵.

Table 2. Change of chemical group composition in the dynamics of oxidation of original goudron of YTRM

Oxidation dynamics		Oils				In all	Resins		In all	Asphaltens	Total
		Paraffin-naphthenic	Light aromatic hydrocarbon	Average aromatic hydrocarbons (bicyclic)	Heavy aromatic hydrocarbons		Benzol	Alcohol benzene			
Goudron		21	14	6,4	34,6	76	6,6	11,4	18	6,0	100
Time of oxidation, h	3	18	19	10	21	68	7,4	14,6	22	10,0	100
	6	17	14	8	19	58	7,7	15,8	23,5	18,5	100
	10	15	13	7,2	17,4	52,6	7,8	16,3	24,1	23,3	100
	14	15	13	6,5	17	51,5	7,9	16,5	24,4	25,1	100
	18	15	12	6	16,2	49,2	8	16,7	24,7	26,1	100

Table 3. Changes in the chemical composition of the group in the dynamics of oxidation of the activated goudron YTRMPLC «Tatneft»

Oxidation dynamics	Oils				In all	Resins		In all	Asphaltenes	Total	
	Paraffin-naphthenic	Light aromatic hydrocarbon	Average aromatic hydrocarbons (bicyclic)	Heavy aromatic hydrocarbons		Benzol	Alcohol benzene				
Goudron	20,8	14,2	6,4	34,6	76	6,6	11,4	18,0	6,0	100	
Time of oxidation, h	1	19,9	16,3	4,9	24,4	65,5	7,9	14,0	21,9	12,6	100
	2	18,4	13,0	5,6	21,4	58,4	7,2	17,0	24,2	17,4	100
	3	17,4	11,3	5,9	17,6	52,2	6,6	14,0	20,6	27,2	100
	4	16,5	11,5	6,4	16,5	50,9	7,3	8,0	15,3	33,8	100
	5	16,7	11,9	6,5	16,9	52	8,0	6,3	14,3	33,7	100
	6	14,3	11,9	7,1	11,4	44,7	6,6	14,5	21,1	34,2	100
	7	11,7	11,9	8,7	9,0	41,3	8,6	10,1	18,7	40,0	100

Table 4. Physico-chemical properties of oxidized non-activated goudron in accordance with SSS22245-90 “Viscous bitumen for roads”, SSS9548-74 “Roofing petroleum bitumen”, SSS9812-74 “Insulation petroleum bitumen”, SSS6617-76 “Petroleum bitumen for construction”

Indices	Time oxidation of original goudron, h						SSS 22245-90			SSS T 9548-74		SSS 9812-74		SSS 6617-76	
	0	3	6	10	14	18	PBR 90/130	PBR 60/90	PBR 40/60	RPB-45/190	RPB-90/30	IPBIV	IPBV	PB 70/30	PB 90/10
The depth of penetration of the needle of 0.1 mm, not less:	-	252	100	41	28	14	91-130	61-90	40-60	160-220	25-35	25-40	20-40	21-40	5-20
Ring and ball melting point, °C, not lower	27	34	44	55	65	81	43	47	51	40-50	80-95	75-85	90-100	70-80	90-105
Elongation, sm, no less:	28	36	78	115	77	5,5	65	55	45	-	-	3	2	3	1
Brittleness temperature, °C, not higher	-	-21,5	-18,2	-11,7	-9,5	-0,8	-17	-15	-12	-	-10	-	-	-	-
Flash Point, °C, not lower	-	240	240	240	240	250	230	230	230	240-	240	250	210	240	240
Penetration index	-	-0,26	-0,27	-0,18	-0,28	0,93	От -1,0 до +1,0			-	-	-	-	-	-
Changes in ring and ball melting point after heating, °C, not more	-	44,6	47,3	57,5	68,9	81,6	5	5	5	-	-	-	-	-	-
The mass change after heating, % wt.	0,2	1,1	0,9	1,3	0,6	1,2	-	-	-	0,8	0,5	0,5	0,5	0,5	0,5

Table 5. Physico-chemical properties of the oxidized activated goudron in accordance with SSS22245-90 “Viscous bitumen for roads”, SSS9548 “Petroleum bitumen for roofing”, SSS9812 “Insulation petroleum bitumen”, SSS6617 “Petroleum bitumen for construction”

Indices	Original goudron	Oxidation time, h							SSS 22245-90			SSS 9548-74			SSS 9812-74		SSS 6617-76			
		1	2	3	4	5	6	7	PBR 90/130	PBR 60/90	PBR 40/60	RPB-45/190	RPB-160-220	RPB-90/30	IPBIV	IPBV	PB 70/30	PB 90/10	PB 21-40	PB 5-20
The depth of needle penetration, 0,1 mm, not less:	-	377	216	131	54	59	33	28	91-130	61-90	40-60	160-220	25-35	25-40	20-40	21-40	5-20			
Ring and ball melting point, °C, not lower	27	42	45	48	63	65	88	102	43	47	51	40-50	80-95	75-85	90-100	70-80	90-105			
Elongation, sm, no less:	25	41	62	67	12,5	15	4,5	4	65	55	45	-	-	3	2	3	1			
Brittleness temperature, °C, not higher	-	-23,8	-22,1	-20,3	-2,5	0,99	32,0	51,3	-17	-15	-12	-	-10	-	-	-	-			
Flash Point, °C, notlower	240	240	250	250	250	250	250	250	230	230	230	240-	240	250	210	240	240			
Adhesion	3	1	1	1	1	1	1,5	2	-	-	-	-	-	-	-	-	-			
Penetration index	-	0,61	0,41	0,24	0,65	0,86	2,0	2,76	От -1,0 до +1,0			-	-	-	-	-	-			
Changes in ring and ball melting point after heating, °C, not more	-	-	-	-	-	-	-	-	5	5	5	-	-	-	-	-	-			
The mass change after heating, % wt.	-	0,5	0,3	0,24	0,2	0	0	0	-	-	-	0,8	0,5	0,5	0,5	0,5	0,5			

4. Summary

On the basis of the data of changes of the group chemical composition of goudron oxidation of ENPU without catalytic complex for the first six hours, the process goes on predominantly toward the accumulation of resins due to oxidation of oils, whereby only at the eighth hour and further oxidation the relative content of asphaltenes increases. The catalyst complex allows for a shorter time to reduce not only the content of PPCF due to the destruction of normal paraffins to a short circuit, but also increase the yield of asphaltenes without long-term accumulation of resins.

The catalytic complex allows to avoid long-term accumulation of resins due to the transition of the PCACF oils in the asphalt. Hydrocarbons of normal structure being contained in oils are disintegrated to shorter chains, lowering the brittleness temperature.

5. Conclusion

Active studies indicate the possibility of obtaining high-quality bitumen for a wide area of application from substandard feedstock being rich in paraffinic hydrocarbons. So, it is possible to get a road bitumen of BND90/130mark, meeting all the regulatory requirements of SSS22245-90, by the duration of oxidation of the original goudron for six hours and in the presence of a catalytic complex – for three hours. Reduction of oxidation time will significantly reduce energy consumption and reduce the cost of commercial products. Results of the analysis of the chemical composition of the group of oxidation of goudron in the dynamics indicate that in the presence of the catalytic complex there occurs a reduction of the content of paraffin-naphthenic hydrocarbons almost twice.

6. The Conflict Of Interests

The author confirms that the presented data do not contain the conflict of interests.

7. Acknowledgments

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