PRODUCTION OF PETROLEUM PITCH BY COMBINED PROCESSING SCHEME

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The rational utilization of petroleum resids and a more exhaustive processing of the resids require the development and commercialization of processes for manufacturing new types of petroleum products. One such process is the manufacture of petroleum electrode pitch as a binder and impregnating material in the manufacture of carbon end-items [1-5]. The refining industry has at its disposal considerable resources of petroleum resids (atmospheric resids, vacuum resids, cracked tars, asphalts from deasphalting operations, and heavy pyrolysis tars) that are currently worked off as boiler fuel components.

The heavy pyrolysis tars occupy a special place in this group of resids, and hence particular attention must be given to the rational processing of these stocks [6-8]. There is an increasingly urgent need to organize combined processing of heavy pyrolysis tar to obtain petroleum electrode pitches, an aromatic naphtha cut, and a high-index feedstock for carbon black production. In this article we are examining one version of a combined process in a single process unit for thermocondensation of heavy pyrolysis tar (HPT), obtaining several grades of petroleum electrode pitch and a pitch distillate.

The unit consists of two sections: a reactor section with series-connected reactors, and a mixing section. In the reactors, the heavy pyrolysis tar, preheated to 370-400°C, undergoes a thermocondensation process, yielding 2-3% gas, 55-60% pitch distillate, and 37-40% still bottoms (pitch). It has been established that the softening point of the pitch depends on the process temperature and the duration of the process, other conditions being equal. Thus, in the reactors operating in series, pitches with different softening points can be obtained simultaneously.

The electrode industry requires pitches for binders and sintering agents in three different temperature ranges: medium-temperature with 75-90°C softening point, high-temperature with 90-100°C softening point, and soft (low-temperature) with 60-65°C softening point for the impregnation of baked electrodes. The production of the different pitches in separate, free-standing units would require large expenditures of energy, since it is necessary to maintain the reactor temperatures in the 370-400°C interval for the relatively short time (15-

TABLE 1

Index	Petroleum pitch sample					
	1	2	3	4	5	6
Thermocondensation conditions						
Temperature °C	380	380	380	380	—	—
Duration, min	45	60	90	120	—	—
Yields, %						
pitch	44,01	40,22	39,02	36,92	—	—
distillate	54,61	57,99	59,01	61,04	—	—
gas	1,38	1,79	1,97	2,04	—	—
Pitch quality						
Softening point (R & B), °C	66	75	85	100	75	85
Density at 20°C, kg/m^3	1201	1206,6	1213,5	1226,1	1205,3	1220,1
Coke residue, wt.%	32,07	37,17	37,72	46,84	34,17	36,84
Elemental composition, wt.%						
carbon	92,1	92,6	93	94	92,7	93,1
hydrogen	5,8	5,4	5,3	5,1	5,4	5,2
Ash, wt.%	0,03	0,04	0,05	0,06	0,04	0,05
Group composition, wt.%						
malthenes	26,96	39,73	32,0	31,2	41,76	39,37
asphaltenes	62,17	38,96	51,6	37,6	41,71	36,76
carbenes and carboids	10,87	21,31	16,4	31,2	16,53	23,87

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60 min) that is required for the reactions of thermocondensation to proceed to the required level of HPT conversion.

In the production of electrode pitches with softening points of 100, 85, 75, and 65°C in this process unit, the energy costs can be cut almost in half by the use of a combined process technology, in accordance with a flow plan we are proposing. In this scheme, the feed is subjected to thermocondensation in series-connected reactors. From the bottom of the first reactor, a thermal tar is drawn with the desired softening point (for example, 65°C); this is used as a commercial petroleum product — impregnation-grade electrode pitch.

The remainder of the thermal tar from the first reactor passes into the second reactor in order to increase the degree of condensation, forming high-temperature electrode pitch with a softening point up to 100°C. The flow plan provides for compounding of the low- and high-temperature pitch-binders in the blending section to obtain two medium-temperature electrode pitches, for example with softening points of 75 and 85°C (R&B). The gaseous and liquid products from the thermocondensation are fractionated in order to obtain products with the desired quantities.

The scheme for obtaining various petroleum pitches in a combined process was tested under laboratory conditions. The feedstock was a pyrolysis tar having the following characteristics:

Density, kg/m^3	1039
Molecular weight	242
Carbon residue, wt.%	11.5
Elemental composition, %:	
carbon	92.2
hydrogen	7.2
sulfur	0.3
Ash, wt. %	0.01
Group composition, %:	
carbenes and carboids	0.2
asphaltenes	5.3
malthenes	94.5
Hydrocarbon group composition, wt.%:	
paraffins + naphthenes	0.4
aromatics	63.1
light	1.6
medium	4.9
heavy	56.6
resins	22.5
asphaltenes	14
Temperature, °C:	
flash point	100
autogenous ignition temperature	405
solid point	−25

The process conditions are shown in Table 1, along with the characteristics of the pitches obtained by thermocondensation (samples 1-4) and compounding (samples 5 and 6). Then the quality characteristics of samples 2 and 3, obtained by thermocondensation of the tar at 380°C, are compared with those of samples 5 and 6, which were obtained by compounding samples 1 and 4 ad 180°C, and it can be noted that samples 5 and 6 are very nearly equivalent in quality to samples 2 and 3, even though the production of samples 5 and 6 was considerably more economical in terms of consumption of material and energy resources.

The liquid fractions (pitch distillate) obtained in the process of thermocondensation of the pyrolysis tar were separated into a naphtha cut distilling below 200°C and a cut distilling above 200°C. The characterictics of the IBP-200°C cut were as follows: density at 20°C 898.7 kg/m^3, iodine number 61.2 g I_2/100 g, molecular weight 120, sulfur content 0.04% by weight, autogenous ignition temperature 403°C. The IBP-200°C cut had the following hydrocarbon composition (in % by weight): total nonaromatics 3.4; benzene 2.4; toluene 12.1; ethylbenzene and p-xylene 11.9; m-xylene 5.6; o-xylene 3.1; isopropylbenzene 1,4; styrene and indan 5.7; n-propylbenzene 0.5; methylethylbenzenes 8.3; mesitylene 0.8; pseudocumene 1.8; α-methylstyrene 1.5; dicyclopentadiene 0.4; β-methylstyrene, p- and m-diisopropylbenzene, indan, and unidentified monocyclic aromatics 34.3; naphthalenes 6.6; secbutylbenzene 0.5.

TABLE 2

Index	Specification TU 38103414-78 for feedstock for carbon black manufacture	Experimental sample
Density at 20°C, kg/m^3	1030	1050
Carbon residue, wt.%	12	0,31
Correlation index	120	122
IBP, °C	160	170
Water content, wt.%	0,5	0,15
Elemental composition, %		
carbon	—	91,4
hydrogen	—	7,2
sulfur	—	0,02
Hydrocarbon group composition, wt.%		
paraffins + naphthenes	—	None
aromatics	—	93,6
light	—	None
medium	—	9,2
heavy	—	84,4
resins	—	6,4
Temperature, °C		
flash point	—	87
autogenous ignition temperature	—	409

The characteristics of the 200°C-EP cut are shown in Table 2.

It will be noted that the naphtha cut is a highly aromatic, low-sulfur product with a relatively high density and a high content of unsaturated hydrocarbons; after appropriate upgrading treatment, it can be used as a component of commercial gasolines. The 200°C-EP cut is a high-index feedstock for carbon black manufacture.

Thus, on the basis of theoretical developments and laboratory studies, considerable promise and feasibility have been demonstrated for the production of various petroleum electrode pitches and pitch distillates in schemes for the exhaustive processing of crude oil, using combined process technology.

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