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Yu.Ya. Khlibyshyn, I.Ya. Pochapska, O.B. Grynyshyn, Z.Ya. Gnativ

THE STUDY OF THE FABRICATION OF BITUMEN FROM ACID TARS AND OIL RESIDUES

Lviv Polytechnic National University, Lviv, Ukraine

This work reveled the effects of the ratio of acid tar coupled with straight-run petroleum tars, the temperature of the process, the specific delivery rate of acid tar to the reactor, the rate of temperature elevation in the reactor the final heating temperature of the bitumen mass in the reactor and the stirring intensity of the reaction mixture in the reactor on the quality and properties of the bitumen prepared from the acid tar. The experimental findings confirmed that sulfur compounds, particularly sulfonic acids, are reduced to elemental sulfur. However, an intermediate product (i.e. hydrogen sulfide) was found only in small quantity. It was determined that the maintenance of a certain delivery temperature of reagents and a speed of their movement allows avoiding vigorous vapor evolution and excessive growth of the reaction volume, especially due to foaming. It has been shown that the initial temperature in the reactor has a little effect on the main quality factors of bitumen (such as the softening point, ductility, penetration, solubility in benzene, and the content of water-soluble compounds, acids and alkalis in bitumen); however, it significantly influences the process flow.

Keywords: acid tar, asphalt, bitumen, ductility, penetration.

Introduction

A steady increase in the consumption of goods of different application is followed by a corresponding increase in quantity of waste. This, in turn, critically brought out dangerous pollution of the biosphere by chemical and petrochemical industries. Chemical industry, including the production of oils, is one of the main sources of ecotoxicants that come into the environment [1].

Area contamination around petroleum-refining plants is observed due to the adsorption of air emissions and filtration of ecotoxicants from water bodies polluted with wastewater, and as a result of accumulation and storage of industrial waste [2–5]. Accordingly, a large environmental hazard is posed by ponds containing acid tars (ATs), formed in the process of treatment of oil fractions with sulfuric acid.

In 2014, statistical data showed that the total quantity of ATs in gathering ponds on the territory of the former USSR accounted for around 1.343 million tons, with more than 180 thousand tons of ATs generated per year.

The acid tars belong to the waste of hazard class II. Currently, the absence of commonly used procedures for their comprehensive treatment is due to some difficulties in destroying acid sludge lagoons. The acid tars are wastes from oil refining and petrochemical industries that are bulk and troublesome for disposal. They are formed during the purification of special oils such as condenser, transformer, hydraulic, medical, perfumery oil, etc., as well as in the production of flotation reagents and additives, and in sulfonation of individual hydrocarbons and petroleum fractions. Also, ATs are generated while alkylating isobutene with olefins to fabricate a high-octane blending agent of gasoline through the treatment of normal paraffins with oleum from aromatic compounds. The treatment results in an emulsion in which upper layer is acid oil and the lower one is acid sludge. The latter contains products of side reactions, an excess of sulfuric acid and a small amount of oil being adsorbed on various solid particles.

Refining oil distillates with H_2SO_4 by further alkali removal is the oldest method that has been used from the dawn of the oil industry. The application of the said reagents is implemented by numerous variants of treatment characterized by the quality of distillates, process temperature, concentration, amount of H_2SO_4, etc.

In the post-soviet area, the process of refining various petroleum fractions (oil, kerosene and gas oil) and production of commercial petroleum products by using H_2SO_4 has been carried out for over 200 years.

Acid tars represent an environmental hazard in that their chemical composition does not actually allow direct consumption. The result is that acid tars are dumped in gathering ponds, which creates a significant environmental hazard without proper utilization. Thus, environmental pollution occurs, leading to the acidification of soil and water bodies, and, consequently, to the destruction of flora and fauna. A natural continuous oxidation-reduction process causes the release of a large amount of sulfur dioxide which, in turn, contaminates the air basin. The acid tar lagoons are located on vast areas and contain thousands of tons of wastes with the total mass in Ukraine and abroad reaching millions of tons. Thus, not less than 150 thousand m^3 of acid tars are found only on the territory of Lviv region [6].

The treatment of holdover storage of acid tars in order to minimize their adverse effect on the environment is quite a difficult and vital task requiring the development of innovative procedures and equipment.

At present, the treatment with sulfuric acid is replaced by more advanced and efficient processes, such as extraction and hydrogenation; even so, the issue of accumulated acid tar treatment is very acute and requires an environmentally sound way of their disposal [7,8].

Modern technologies of ATs disposal according to the influence on wastes are as follows:

– pyrolysis under the influence of high temperatures (800–1200^{0}C) producing H_2SO_4, heat, high-sulfur coke, and activated carbon [8,9];

– low temperature decomposition within the temperature range of 150–350^{0}C followed by bitumen generation;

– water or steam hydrolysis producing dilute H_2SO_4 and fuel components;

– neutralization by various agents with the receipt of fuel, surfactants, or for waste disposal [1,2].

Obviously, this classification is purely conditional as to achieve desired results combined methods need to be applied.

In the countries of the European Union, ATs treatment technologies are aimed at generation of solid fuel from it in lump or granulated form. In many countries, main developments in this filed are designed to use ATs utilization products as road construction materials.

However, the main reported technologies of disposal are related to the fresh acid tar being obtained from manufacturing. Acid tar that has been dumped in storage in lagoons for decades differs from fresh acid tar in its properties [6,10] and, generally, is not subject to the utilization by the above-mentioned methods. This research examines one of the directions of qualified treatment of acid tar that has been kept in lagoons for a long time.

The purpose of the study was to identify the influence of various parameters on the treatment of acid tar that has been dumped in lagoons for a long time by turning it into petroleum-based bitumen.

To achieve a target goal, the following tasks were solved:

– to determine the influence on the qualitative characteristics of bitumen and smoothness of the process, that is, the ratio of acid tar to straight-run tar taken into the process; temperature of the process; specific feed rate of acid tar to the reactor; rate of temperature rise in the reactor; final heating temperature of the bituminous mass in the reactor and the intensity at which the reaction mixture is mixed in the reactor;

– to establish optimal conditions for acid tar treatment with conversion to petroleum-based bitumen.

Experimental

The research was carried out using acid tar, which has been dumped for a long time in lagoons of Lviv Research and Development Petroleum-Refining Plant [6,10], its characteristics are shown in Table 1. Also, the subjects of the research were tars extracted from Western Ukrainian paraffin-base oils by atmospheric vacuum distillation and sampled at PJSC "NPK-Galychyna" (Drohobych, Ukraine) and gas condensate residue from Eastern Ukrainian deposits, sampled at Shebelynsk Department of Gas Condensate and Petroleum Processing of PJSC "Ukrgazvydobuvannya" of National Joint-Stock Company "Naftogaz of Ukraine"; its characteristics are presented in Table 2.

The bituminous mass is generated from a mixture of acid and straight-run tars when they are simultaneously heated. At the same time, oxidation occurs with sulfuric acid as the organic mass at elevated temperatures appears to be a reducing medium for sulfuric acid. The resulting sulfuric anhydride oxidizes an organic matter, turning it into bituminous mass. The quality and yield of bitumen and the smoothness of the process can be affected by such factors as the ratio of acid to straight-run tars taken in the process, the amount and concentration of sulfuric acid in acid tar, the temperature in the reactor when acid tar is supplied,

Table 1

Acid tar group chemical composition and its physical and chemical parameters

Parameter	Parameter value
Content of oils, wt.%, including:	20.0
paraffin naphthenic hydrocarbons	7.4
monocyclic aromatic hydrocarbons	2.9
bicyclic aromatic hydrocarbons	5.7
policyclic aromatic hydrocarbons	4.0
Resin content, wt.%	7.4
Sulfonic acid content, wt.%	50.8
Content of impurities, wt.%	11.6
Water content, wt.%	10.2
Viscosity by viscometer with the hole of 5 mm at 100^0C, cSt	96.2
Acid number, mg KOH/g	8.9
Total sulfur content, wt.%	1.34

Table 2

Acid tar physical parameter and group chemical composition

Parameter	Paraffin tar	Distillation residue of gas condensate
Softening point,(ring-and-ball method), ^{0}C	42	<10
Ductility at 25^0C, cm	13	–
Penetration at 25^0C, 0.1 mm	245	>300
Group composition, wt.%:		
carbenes and carbides	–	0.09
asphaltenes	19.60	6.39
resins	24.38	20.00
oils	56.02	73.10
paraffins	5.42	6.10

the specific feed rate of acid tar to the reactor, the temperature in the reactor, rate of temperature elevation in the reactor, the final heating temperature of the bituminous mass in the reactor, and the intensity at which the reaction mixture is mixed.

Oxidized bitumens were obtained by using a laboratory installation comprising a reactor block, a cooling and recovery unit of volatile products.

The following main parameters of the properties of obtained bitumens were ductility, penetration, softening point and solubility in an organic solvent (benzene). The samples of resulting bitumens were analyzed by determining their ductility at 25^0C (according to Ukrainian regulatory documents GOST 11505-75), penetration at 25^0C (according to GOST 11501-78) and the softening point by a coefficient of gas recovery (according to GOST 11506-73), solubility in an organic solvent (according to GOST 20739–75), and the content of water-soluble compounds (according to GOST 11510-65).

Results and discussion

In the first place, we studied the effect of the ratio of acid tar to straight-run tar on the process of bitumen generation, other conditions being constant (the temperature at which acid tar is supplied of 150^0C, the specific feed rate of tar of 3 g/min·kg, the rate of temperature rise of 3^0C/min, and the final temperature of 330^0C).

The results indicated that with increasing the content of acid tar in the mixture, the softening point rises, while the ductility and penetration decreases (Figs. 1 and 2). The solubility of the resulting bitumen in benzene is more than 99% and is moderately altered in the range under investigation. It should be noted that the solubility in benzene decreases with increasing the content of acid tar in the mixture for both petroleum residues, this leads to the disturbances of homogeneity of the resulting bitumen. There are no water-soluble acids and alkalis in obtained bitumen. The content of water-soluble compounds is less than 0.2%. The yield of gaseous products grows with an increase in the acid tar mixture, and the intensity of emission is the highest in the range of 290–330^0C.

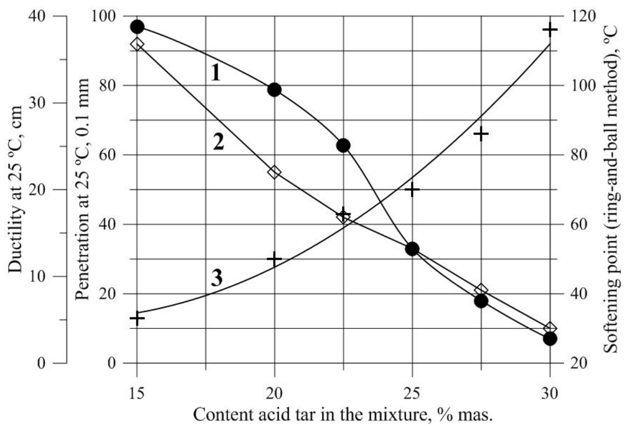

Fig. 1. The influence of the ratio of acid tar to paraffin tar on the characteristics of the bitumen: 1 – ductility, 2 – penetration, 3 – temperature point

Based on the results of these findings, it can be asserted that changing the ratio of acid tar to straight-run tar in the mixture affects the quality of bitumen in a wide range.

The next stage of the research was to determine the influence of the final heating temperature on the characteristics of the resulting bitumen at its constant acid tar content of 25% in the mixture, the specific feed rate of acid tar being 3 g/min·kg and the temperature in the reactor at which it is supplied being 160⁰C. The rate of temperature rise was 3⁰C/min. The results are summarized in Tables 3 and 4.

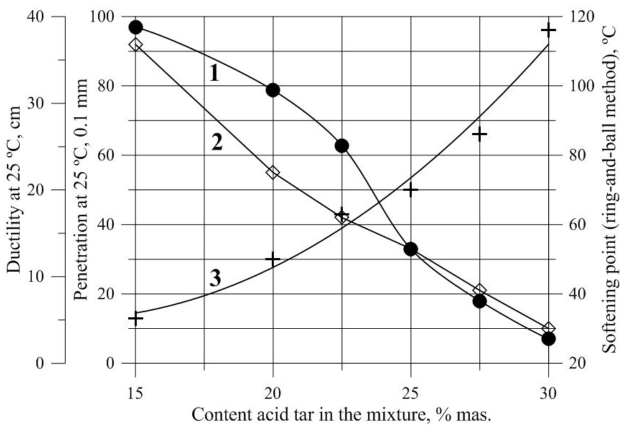

Fig. 2. The effect of the ratio of acid tar to gas condensate residue on the characteristics of the bitumen: 1 – ductility, 2 – penetration, 3 – temperature point

Table 3

The influence of final heating temperature of acid and paraffin tars on the characteristics of the resulting bitumen

Quality of bitumen	Final process temperature, ⁰C				
	250	270	300	320	350
Softening point (ring-and-ball method), ⁰C	90	93	95	92	77
Ductility at 25⁰C, cm	2.8	2.7	2.8	2.4	4.0
Penetration at 25⁰C, 0.1 mm	12	10	13	10	14
Benzene solubility, %	99.4	99.5	99.7	99.5	99.7
Content of water-soluble compounds, %	0.06	0.10	0.15	0.14	0.20

Table 4

The influence of final heating temperature of acid tar and gas condensate residue on the characteristics of the resulting bitumen

Quality of bitumens	Final process temperature, ⁰C				
	250	270	300	320	350
Softening point (ring-and-ball method), ⁰C	90	89	91	93	90
Ductility at 25⁰C, cm	2.9	3.0	2,5	3.0	2.8
Penetration at 25⁰C, 0.1 mm	15	12	11	13	12
Benzene solubility, %	99.3	99.6	99.1	99.4	99.3
Content of water-soluble compounds, %	0.14	0.11	0.08	0.09	0.10

Further, we determined the influence of the temperature in the reactor before acid tar is fed on the quality of the resulting bitumen. Also, we investigated the course of the process under the following constant conditions: the amount of acid tar of 25%, the specific feed rate of acid tar of 3 g/min·kg, the rate of temperature rise of 3⁰C/min, and the final heating temperature of 330⁰C. The research results are summarized in Tables 5 and 6.

Table 5

The influence of final heating temperature of paraffin tar during supply of acid tar on the characteristics of the resulting bitumen

Quality of bitumen	Temperature, ⁰C			
	100	130	160	190
Softening point (ring-and-ball method), ⁰C	93	92	92	95
Ductility at 25⁰C, cm	2.8	2.7	2.7	3.0
Penetration at 25⁰C, 0.1 mm	12	14	13	16
Benzene solubility, %	99.4	99.5	99.6	99.3
Content of water-soluble compounds, %	0.11	0.13	0.07	0.08

Table 6

The influence of final heating temperature of gas condensate residue during supply of acid tar on the characteristics of the resulting bitumen

Quality of bitumen	Temperature, ⁰C			
	100	130	160	190
Softening point (ring-and-ball method), ⁰C	91	90	93	95
Ductility at 25⁰C, cm	3.8	3.7	4.0	3.6
Penetration at 25⁰C, 0.1 mm	15	12	11	13
Benzene solubility, %	99.4	99.5	99.6	99.3
Content of water-soluble compounds, %	0.10	0.14	0.09	0.12

The study revealed that the initial temperature in the reactor has little effect on the main qualitative characteristics of bitumen, including the softening point, ductility, penetration, solubility in benzene, and the content of water-soluble compounds, acids and alkalis. And yet, the initial temperature in the reactor affects the course of the production process. As the temperature in the reactor rises above 160⁰C, increased foam generation together with a marked increase in the reaction mass is observed. So when acid tar is fed to straight-run tar that is heated above 100⁰C, the reaction of sulfuric acid with the most reactive components of tar initiates. The products of this reaction are water and sulfur dioxide that evaporate producing bituminous foam. The reaction mass volume is increased by 2–3 times in comparison with the total volume of acid and straight-run tars during the process with the initial temperature in the reactor of 100–180^{0}C. At higher initial temperatures in the reactor, the generation of gaseous products is even higher, which makes the process much more difficult and can cause the release of the reaction mass from the reactor. The acid tar feed to the reactor at a temperature of above 200^{0}C serves to obtain the bitumen in which the homogeneity is disturbed and available consolidating products are in the form of small grains.

Another important issue of the study was to identify the intensity of the process. The feed rate of acid tar to the reactor will determine the intensity of the process. Therefore, it is important to investigate the influence of this factor. The experimental conditions were as follows: the amount of acid tar of 25%, the temperature in the reactor of 160^{0}C, the rate of temperature rise of 3^{0}C/min, and the final heating temperature of 320^{0}C. Acid tar was registered at the feed rate of 1.5; 2; 3; and 6 g/min·kg. The obtained results showed that the specific feed rate of acid tar has no decisive impact on the quality of the resulting bitumen. The samples obtained in this way exhibited the softening point of 91–95^{0}C, ductility of 3.2–4.0 cm and benzene solubility of 99.4–99.6 (wt.)%. An increase in the specific feed rate of acid tar caused the process intensification, an increase in gas release and the foam formation. There was a significant increase in the reaction mass and its release from the reactor at the maximum speed of 6 g/min·kg.

An important factor affecting the process is the heating rate of the reaction mass or the rate of temperature rise. Under the same constant conditions, the rate of temperature rise ranging from 1 to 5.5^{0}C/min which slightly influences the quality of the bitumen produced and the process smoothness. With an increase in the heating rate, the reaction rate and the process intensity raise that leads to intense evaporation and growth of the reaction volume.

Based on the results of our findings, we can suggest the following:

– with an increase in the final temperature from 250 to 350^{0}C, the softening point and ductility are most likely to change whilst other parameters are slightly altered (as was shown by the data given in Tables 3 and 4). The softening point of the resulting bitumen decreases as the final temperature of the process raises from 250 to 350^{0}C, particularly at the final temperature of 350^{0}C.

– the ductility of the resulting bitumen do not tend to increase much with increasing final temperature. This is obviously due to the partial degradation of hydrocarbons and an increase in the amount of volatile fractions that liquefy bitumens. The decomposition is found to be the highest at 350^{0}C.

– when the final temperature of the process is changed from 250 to 350^{0}C, the bitumen solubility in benzene and the presence of water-soluble compounds do not tend to change much. The analyses of our results showed that water-soluble acids and alkalis in bitumens, which were produced under these conditions, are absent.

– at the test temperatures of 300^{0}C or less, the gas evolution does not end upon reaching the final test temperature. When the final heating temperature of the bituminous mass is above 300^{0}C, the decomposition of residual sulfur compounds in the latter part occurs at a high rate, and gaseous products are completely removed. From the comparison of the facts mentioned, it becomes clear that the final heating temperature affects the process of gas evolution, which is the conversion of sulfuric acid into sulfonic acids, which, in fact, was confirmed by laboratory analysis. This is consistent with the data reported in previous works [11–13]. Nevertheless, it should be observed that a sulfur coat appears on the walls of the refrigerator at the heating temperature of above 270^{0}C, its quantity is quite insignificant. This indicates that the sulfur compounds, particularly sulfonic acids, are reduced to elemental sulfur. The amount of an intermediate product (hydrogen sulfide) is found to be negligibly small.

– supplying acid tar to the reactor at the temperature of above 200^{0}C produces bitumen which contains consolidating products in the form of small grains as a result of disturbed homogeneity. This is due to formation of asphaltenes that are more densified and less soluble at higher temperatures. Consequently, consolidating products have not enough time to be completely dissolved in the bituminous mass. When such bitumen is held at the temperatures of 300 to 320^{0}C and thoroughly mixed, these consolidations are completely dissolved, causing bitumen to meet the requirements. Such conclusions can be considered reasonably practical because they allow technological aspects of the process to be examined in a well justified manner.

According to the results of the study, the process of preparation of bitumen from a mixture of acid and straight-run tars can be performed when they are mixed at the temperature of the mixture which should be lower than 100^{0}C. It should be also noted that the next mixture heating is to be performed at the rate of temperature rise within 1.5–2^{0}C/min, then vapor liberation and foam generation are found to be less intense, and the reaction volume is increased only by 2–3 times. However, in this case, the process takes slightly longer than while gradually supplying acid tar to straight-run tar heated above 100^{0}C. Failure to consider the said limitations in detail in terms of the study gives rise to a potentially interesting direction for further researches. In particular, they can be targeted at detecting and identifying the best process conditions by consideration of the feed rate of acid tar and rate of mixing.

However, the straight and acid tars are substances of high viscosity, and, therefore, the intensity of mass transfer will significantly affect the intensity and smoothness of the process. So then, mixing is an obligatory condition to conduct the process. Mixing intensity that underwent examination in the range of 50 to 250 rpm showed no such effect on the quality of the fabricated bitumens at equal initial conditions. The results suggest the following: if not mixed a low-quality heterogeneous bituminous mass is produced; and asphaltenes that are formed due to high molecular weight and high adhesion are precipitated on the walls of the reactor. As a result, with exposure to high temperature, asphaltenes are carbonized being turned into a low-soluble product that impedes the heating of the entire reaction mass. On the other hand, the mixing process not only enables to avoid precipitation of asphaltenes but also reduces the foam formation and the volume of the reaction mass.

Conclusions

1. The conducted studies are concerned with the influence of the ratio of acid tar to straight-run tar taken in the process, the amount and concentration of sulfuric acid contained in acid tar; the process temperature; the specific feed rate of acid tar to the reactor; the rate of temperature rise in the reactor; the final heating temperature of the bituminous mass in the reactor, and the mixing intensity of the reaction mixture in the reactor on the course of the bitumen production process.

2. The technological features of using acid tar in the bitumen production have been examined and the optimal conditions of the process have been established as follows: the acid tar content is 20 – 35% in the mixture, final heating temperature of the bituminous mass is 300–320^{0}C, the specific feed rate of acid tar in the mixture amounts is 2.5–6.0 g/min·kg, and the rate of temperature rise in the reactor is 2–5^{0}C/min. The first two factors have a significant effect on the quality of bitumens, while others affect the smoothness of the process.

3. When providing these optimal parameters, it is possible to significantly reduce the bitumen production cost, find a partial solution to the problem of disposal of acid tars that have been accumulated over the recent decades.

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ДОСЛІДЖЕННЯ ПРОЦЕСУ ОДЕРЖАННЯ БІТУМУ З КИСЛИХ ГУДРОНІВ І НАФТОВИХ ЗАЛИШКІВ

Ю.Я. Хлібишин, І.Я. Почапська, О.Б. Гринишин, З.Я. Гнатів

Встановлено вплив співвідношення взятих в процес кислого і прямогонного гудронів, температури проведення процесу, питомої швидкості подачі кислого гудрону в реактор, швидкості підйому температури в реакторі, кінцевої температури нагрівання бітумної маси в реакторі та інтенсивності перемішування реакційної суміші в реакторі на якість та властивості бітуму, одержаного з кислого гудрону. Визначено оптимальні умови для проведення процесу (вміст в суміші кислого гудрону, кінцеву температуру нагрівання бітумної маси, питому швидкість подачі кислого гудрону в суміш, швидкість підвищення температури в реакторі). Експериментальними дослідженнями підтверджено, що сполуки сірки, особливо сульфокислоти, відновлюються до елементарної сірки. Зокрема встановлено, що завдяки підтримуванню певної температури подачі реагентів та швидкості їх переміщування можна уникнути інтенсивного виділення пари та надмірного зростання реакційного об'єму, особливо за рахунок піноутворення. Показано, що початкова температура в реакторі мало впливає на основні якісні показники бітуму, такі як; температура розм'якшення, тягучість, проникливість, розчинність в бензолі, вміст водорозчинних сполук, кислот і лугів в бітумі, однак суттєво впливає на перебіг процесу.

Ключові слова: кислий гудрон, бітум, тягучість, проникність, розчинність.

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Khlibyshyn Yu.Ya., Pochapska I.Ya., Grynyshyn O.B., Gnativ Z.Ya.

Lviv Polytechnic National University, Lviv, Ukraine

This work reveled the effects of the ratio of acid tar coupled with straight-run petroleum tars, the temperature of the process, the specific delivery rate of acid tar to the reactor, the rate of temperature elevation in the reactor the final heating temperature of the bitumen mass in the reactor and the stirring intensity of the reaction mixture in the reactor on the quality and properties of the bitumen prepared from the acid tar. The experimental findings confirmed that sulfur compounds, particularly sulfonic acids, are reduced to elemental sulfur. However, an intermediate product (i.e. hydrogen sulfide) was found only in small quantity. It was determined that the maintenance of a certain delivery temperature of reagents and a speed of their movement allows avoiding vigorous vapor evolution and excessive growth of the reaction volume, especially due to foaming. It has been shown that the initial temperature in the reactor has a little effect on the main quality factors of bitumen (such as the softening point, ductility, penetration, solubility in benzene, and the content of water-soluble compounds, acids and alkalis in bitumen); however, it significantly influences the process flow.

Keywords: acid tar; asphalt; bitumen; ductility; penetration.

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