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GAS CONDENSATE RESIDUAL USAGE FOR OXIDATED BITUMEN PRODUCTION

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Abstract. The oxidation process of the paraffin gas condensate residual has been studied to obtain road bitumen. The investigation results concerning the residual joint oxidation with extract of oil selective treatment and low-paraffin tars are presented. It has been determined that bitumen obtained from the residual of paraffin gas condensate treatment does not meet the requirements setting for road bitumen. It is recommended to use the residuals for the production of building or covering bitumen.

Keywords: tar, gas condensate, bitumen, extract, oxidation.

1. Introduction

Petroleum bitumen is widely used for the production of road, waterproof and other coverings. The problem of bitumen quality is of great importance in Ukraine because the domestically produced bitumen does not satisfy the world standards, namely it has low adhesion and plasticity. The reason is the low quality of the raw material for bitumen production. The majority of Ukrainian oils contain a lot of paraffin hydrocarbons and a small amount of resins. Therefore the residuals of their treatment – tars – are bad raw material for bitumen production.

It is known that bitumen may be produced from the raw material of definite composition [1-3]. Moreover, tars from naphthenic-aromatic oils may be used for the production of bitumen of various types and tars from highly paraffinic oils – for the production of only some building types [4]. The particular investigations show that paraffins in the composition of the raw material are undesirable components for bitumen production and highly paraffinic oils are unusable for this purpose at all [5].

A lot of publications present the results concerning the production of high-quality bitumen from the residuals of Ukrainian highly paraffinic oils using different modifiers. A whole series of investigations was carried out at the Department of Oil and Gas Refining of Lviv Polytechnic National University. The oxidated petroleum bitumens produced at the Ukrainian refineries were modified by different petroleum resins (PR) using joint oxidation of tar and PR as well as oxidated bitumen and PR compounding [6]. The result was the increase of adhesion properties in 1.2-1.3 times [7, 8].

Since Ukraine refers to the countries with short oil supply, the investigations of bitumen production on the basis of alternative raw material, namely the residuals of gas condensate treatment, are of great importance.

The aim of the present work is to study the production of commercial road bitumen based on the residuals remained after the treatment of gas condensate from the East-Ukrainian deposits.

2. Experimental

The petroleum bitumen oxidation was carried out at the laboratory plant consisting of the reactor block, system of air supply, cooling unit and recovery of volatile oxidation products.

The bitumen compounding was carried out at the laboratory plant consisting of metal vessel with heating and stirrer. The process was carried out at 403–423 K for 1 h.

The initial raw material is the vacuum distillation residual of gas condensate (Tar-1) produced at Shebelynka gas-processing plant (Shebelynka, Ukraine). Its characteristic is given in Table 1. Tar-1 is characterized by the high content of oil fractions and paraffin hydrocarbons that determines its bad quality as a raw material for bitumen production.

To produce compounded bitumen we used bitumen obtained *via* oxidation of gas condensate residual from Shebelynka gas-processing plant. Its characteristic is also given in Table 1. The investigated bitumen is close by its properties to the commercial bitumens BNB-70/30 and BNK-90/40, though some characteristics do not meet the performance requirements.

Table 1

Characteristics of the raw material

Index	Tar-1	Bitumen
Group composition, mas %:		
Carbenes and carboids	0.09	1.35
Asphaltenes	6.39	22.95
Resins	20.00	20.04
Oils,	73.52	55.66
including paraffins	6.10	6.02
Softening point, K	< 283	354
Penetration, 0.1 mm	–	79
Ductility, cm	–	3

For the joint oxidation with Tar-1 we used a tar (Tar-2) recovered from Russian export oils mixture, the tar (Tar-3) recovered from oils mixture Urals-2 and an extract of oil selective treatment. All samples were obtained from JSC “Ukrtatnafta” (Kremenchuk, Ukraine). The characteristics of used tars are given in Table 2.

Table 2

Characteristics of tars

Index	Tar-2	Tar-3
Conditional viscosity, s	23.2	24.3
Flash point, K	525	519
Softening point (ring & ball method), K	303	308
Density d_4^{20}, g/cm^3	0.991	0.978

The ductility, penetration and softening point of the oxidated bitumens were determined using the standard procedures [9].

3. Results and Discussion

One of the known methods for the production of commercial bitumen is a compounding of oxidated bitumen with the initial material (tar) in various ratios. To prepare bitumen *via* compounding we used the tar obtained after gas condensate treatment and oxidated bitumen (see Table 1). The experimental results show (Table 3) that commercial bitumen is not produced *via* compounding. Namely, any bitumen with the softening point of 312–324 K (the value of commercial road bitumen) does not meet the requirements concerning penetration and ductility.

To establish the principal possibility of commercial bitumen production *via* oxidation method using the residuals of gas condensate treatment as a raw material we studied the effect of process main parameters: temperature, air consumption and oxidation time. Taking into account that 523 K is the optimum temperature for the production of road bitumen, the oxidation takes place just at the mentioned temperature. The air consumption varies within the range traditional for the production of road bitumen. The results are represented in Table 4.

At the air consumption of 174 m^3/h per 1 ton of the raw material it is impossible to obtain the commercial road bitumen: at the lowest softening temperature (314 K) the bitumen ductility is only 14 cm, though even the most oxidated road bitumen BND-40/60 with the softening point of 324 K has the ductility of 45 cm.

Table 3

Characteristics of the compounded bitumen

Tar-1 content in mixture, mas %	Bitumen content in mixture, mas %	Softening point, K	Penetration at 298 K, 0.1 mm	Ductility at 298 K, cm
30	70	323	> 300	5
35	65	320	> 300	7
40	60	315	> 300	–
45	55	308	> 300	–

Table 4

Characteristics of the oxidated bitumen

Process parameters		Bitumen yield, mas %	Bitumen characteristics		
Oxidation time, h	Air consump-tion, m^3/h·ton		Softening point, K	Penetration at 298 K, 0.1 mm	Ductility at 298 K, cm
3	174	97.1	308	–	–
4	174	96.5	309	–	–
7	174	94.7	314	266	14
12	174	91.1	358	52	2
7	239	92.9	344	87	4

Note: oxidation temperature is 523 K

The increase of air consumption and the simultaneous decrease of the process time increase the bitumen plasticity. The increase of softening point/ductility ratio indicates this fact. On the other hand, such increase is insignificant; therefore we may ascertain that pure tar obtained from gas condensate is unfit for the production of the commercial road bitumen neither *via* oxidation, not *via* combination of oxidation and compounding.

Hence, the following step of our investigations was to establish the possibility of bitumen production *via* joint oxidation of tar obtained from gas condensate and different additives.

The additives to the initial Tar-1were chosen in accordance with the following criteria:

- they should be cheaper than bitumen and commensurate by cost with the initial tar (Tar-1);
- the paraffin content should be as small as possible;
- they should be highly resinous and highly sulphuric.

Taking into account all mentioned requirements we used the extract of selective treatment of oil distillates by furfural; tar from atmospheric-vacuum distillation (Tar-2) and tar from the deasphalting plant (Tar-3). We received all additives from JSC "Ukrtatnafta" (Kremenchuk, Ukraine). The investigation results concerning the joint oxidation of Tar-1 and the additives are represented in Table 5.

The introduction of extract does not significantly change the bitumen quality (softening temperature is not practically changed) but the yield of oxidated bitumen decreases.

The addition of Tar-2 sharply increases the oxidation intensity because the softening point of obtained bitumen essentially increases (the increment of softening point is 20 K, see Tables 4 and 5). Moreover, the addition of Tar-2 increases bitumen plasticity and strength. Without the additive the bitumen ductility is 14 cm at the softening point of 314 K and its penetration is 266·0.1 mm. At the same time using Tar-2 in amount of 30 mas % the ductility increases to 30 cm at even higher softening point (320 K) and the penetration is relatively low (113·0.1 mm).

The addition of Tar-3 has the similar effect: the ductility increases and the penetration decreases. However the oxidation time is greater using Tar-3 compared with that using Tar-2. Therefore for the further investigations we used Tar-2 as the additive.

In spite of the positive effect of Tar-2 addition the obtained bitumen does not meet all demands for the commercial road bitumen. To establish the possibility of commercial road bitumen production from Tar-1 + Tar-2 mixture and to study the effect of process parameters (oxidation time, oxidant consumption, amount of Tar-2) we calculated the mathematical model on the basis of complete three-factor experiment. The dependencies of bitumen main characteristics on the process factors (X_1 – Tar-2 amount in the mixture; X_2 – oxidation time; X_3 – oxidant consumption) were obtained.

- for the softening point:

$$T_{soft} = 57.25 + 1.5\cdot X_1 + 13\cdot X_2 + 4.75\cdot X_3 - 0.25\cdot X_1X_2 - 0.5\cdot X_1X_3 + 2.875\cdot X_2X_3 \quad (1)$$

- for the ductility:

$$D = 17.25 + 1.5\cdot X_1 - 12\cdot X_2 - 3\cdot X_3 - 0.25\cdot X_1X_2 + 2.25\cdot X_1X_3 + 2.25\cdot X_2X_3 \quad (2)$$

- for the penetration:

$$P = 17.25 - 21.25\cdot X_1 - 63\cdot X_2 - 30.5\cdot X_3 + 12.5\cdot X_1X_2 + 10\cdot X_1X_3 + 15.125\cdot X_2X_3 \quad (3)$$

The most essential effect has the process time (the values of X_2 are the greatest by module) and the addition of Tar-2 has the slightest effect (coefficients near X_1 are the least).

To establish the possibility of commercial road bitumen production from Tar-1 + Tar-2 mixture we calculated the response functions at different values of process parameters on the basis of Eqs. (1-3). The optimum conditions are: the amount of Tar-2 in the raw material 45 mas %, oxidation time – 3h and air consumption – 271.5 m^3/h·ton. The characteristic of bitumen obtained under optimum conditions is represented in Table 6.

Table 5

Joint oxidation of Tar-1 and different additives (modifiers)

Modifier type and its amount	Oxidation conditions		Bitumen yield, mas %	Bitumen characteristics		
	Time, h	Air consumption, m^3/h·ton		Softening point, K	Penetration at 298 K, 0.1 mm	Ductility at 298 K, cm
Extract (20 mas %)	6	174	92.3	311	–	–
Tar-2 (20 mas %)	4	174	93.7	313	272	37
Tar-2 (20 mas %)	7	174	94.6	334	87	5
Tar-2 (30 mas %)	4	239	93.3	320	113	30
Tar-3 (20 mas %)	4	174	94.3	311	268	40
Tar-3 (30 mas %)	4	239	96.0	317	142	29

Note: oxidation temperature is 523 K

Table 6

Characteristic of bitumen obtained *via* joint oxidation of Tar-1 and Tar-2 under optimum conditions

Index	Value	Standard for bitumen BND-130/200
Penetration at 298 K, 0.1 mm	185	131–200
Softening point (ring & ball method), K	312	312–318
Ductility at 298 K, cm	35	not less than 70
Brittle temperature, K	236	not less than 256
Penetration index	-0.84	(-2)–(+1)

One can see from Table that the properties of obtained bitumen approximate to the demands for the commercial road bitumen but the ductility is insufficient. Thus we may assert that it is impossible to produce the commercial road bitumen *via* joint oxidation of gas condensate residuals and tars.

4. Conclusions

The experimental results show the impossibility of commercial road bitumen production on the basis of gas condensate residuals or its mixture with tars. The main imperfection of bitumen obtained *via* joint oxidation of gas condensate residuals and tars is the low ductility, that is unacceptable for the commercial road bitumen. We recommend to use gas condensate residuals for the production of other types of bitumen materials, namely for building and roofing asphalt, bitumen mastic, emulsions, *etc*.

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ВИКОРИСТАННЯ ЗАЛИШКУ ПЕРЕРОБКИ ГАЗОВОГО КОНДЕНСАТУ ДЛЯ ОДЕРЖАННЯ ОКИСНЕНИХ БІТУМІВ

Анотація. *Вивчено процес окиснення залишку від переробки парафінистого газового конденсату з метою одержання дорожніх бітумів. Наведено результати досліджень сумісного окиснення цього залишку з екстрактом селективного очищення олив і гудронами малопарафінистих нафт. Встановлено, що бітуми, одержані з використанням як сировини залишку від переробки парафінистого газового конденсату не відповідають вимогам, що ставляться до дорожніх нафтових бітумів. Рекомендовано використовувати ці залишки для одержання будівельних або покрівельних бітумів.*

Ключові слова: *гудрон, газовий конденсат, бітум, екстракт, окиснення.*