

*Olena Tertyshna¹, Kateryna Royenko¹, Vitalina Martynenko¹, Victoria Smesova¹,
Al'ona Gyrenko¹ and Petro Topilnytskyi²*

THE UTILIZATION OF ASPHALT-RESIN-PARAFFIN DEPOSITS AS A COMPONENT OF RAW MATERIAL FOR VISBREAKING

¹ Ukrainian State University of Chemical Technology; 8, Gagarina Ave., 49005 Dnipropetrovsk

² Lviv Polytechnic National University; 12, S. Bandery St., 79013 Lviv, Ukraine; T_olena2000@bigmir.net

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Abstract. The paper contains the results of experimental study of visbreaking process with the use of organic part of asphalt-resin-paraffin deposits (ARPD) as a raw material component. We studied the influence of ARPD amount as the additive to tar on the output fuel fractions and their qualitative parameters. The proposals on modernization of the industrial visbreaking scheme with blended raw material were made. The analysis of economic performance of the modernized process was carried out.

Keywords: visbreaking, deposits, mixed raw material, utilization, technological scheme.

1. Introduction

During the storage and transportation of oil and petroleum products in tanks, especially of a large volume, the accumulation of asphalt-resin-paraffin deposits (ARPD) occurs. ARPD amount sometimes forms a deposit layer on a tank bottom up to 10 % of its volume during several months [1, 2].

ARPD differ in a composition and they are complex systems that include oil, water, inorganic compounds and mechanical impurities which ratio varies widely.

High-molecular hydrocarbons of the paraffin series, which are a part of ARPD, have high pour point, form high-viscosity deposits under normal conditions, sometimes turning into the solid state. Polycyclic aromatic structures, containing sulfur, oxygen, nitrogen, and various trace elements, are a part of the composition of resins and asphaltenes.

Sometimes oil refineries disregard the utilization methods of ARPD, using the simplest means of deposits burning or burial at landfills. It leads to the harmful impact on the environment. Therefore the actual problem for the oil industry is using the deposits as a raw material

that will increase the depth of oil processing and reduce the negative impact of the waste on the environment.

There are several methods of the processing of solid deposits and residues which are formed during storing oil in tanks at the fields and refineries [1-9].

The thermal method consists in burning of oil deposits and usage of heat and gases. Deposits separation by means of chemical methods with the subsequent use of the obtained fractions is based on the use of solvents, demulsifying agents and surfactants. Mechanical methods include filtration, sedimentation or separation. Hydrocarbon components are the nutrition substrate for the used microorganisms in biological methods of ARPD utilization [3-5].

Utilization of oil deposits is possible when they are used as raw materials for the production of oxidized and compounded bitumen for the construction of roads and buildings, but it has a seasonal demand which does not completely solve the problem of ARPD utilization by this way [3].

It is possible to process deposits by thermo-destructive methods. There are two approaches to the process of thermodestruction of heavy hydrocarbons: deep decomposition with a maximum output of gas and distillate fractions, and with minimal output of cracking residue. Eventually, they are coking processes which increase the depth of oil refining to the maximum.

The visbreaking process promotes the depth of oil refining. It consists in low decomposition of heavy fractions to obtain fuel oil with lower viscosity without using distillate fractions for the thinning of fuel oils. Visbreaking is widespread in European countries and is the most developed and the least expensive one among the known methods of thermal processing of oil residues [6-9].

The gas obtained in visbreaking plants has the high content of methane and ethane, and moderate content of unsaturated hydrocarbons (25–30 wt %) And it is usually used as fuel for the oil refinery needs after hydrogen sulfide removal.

Light gasoline fractions after refining from sulfur compounds can be added to finished gasoline or to gasoline, which is sent to processes of hydrofining and reforming.

Visbreaking vacuum gas-oil is used as a motor fuel. Residue of visbreaking is used as a boiler fuel or its component. The viscosity of the resulting boiler fuel reduces by 6-10 times relative to the raw material and at the same time the temperature of pour-point decreases by 6–10 K [7, 8].

Each of these methods of thermal destruction of deposits has its advantages and disadvantages in the technological design of the process. Therefore, the decision to use a particular technology is taken on the basis of the plant type, as well as the production capacity of distillate products.

The aim of this study is to develop the basis of the visbreaking effective technology including asphalt-resin-paraffin deposits in raw materials. To achieve this goal the

following problems are solved: i) investigation of the visbreaking process of straight tar and tar mixtured with an organic part of ARPD in a flow reactor; ii) determination of the optimal amount of deposits in the visbreaking raw materials to get the maximum output of the fuel fractions with simultaneous production of the residual which meets requirements of the boiler fuel; iii) development of the technological scheme and economic justification of the modernized reaction block of the visbreaking industrial plant with the capacity of 500 tons per year.

The implementation of this technology will enable to receive additional quantities of gas-oil and gasoline fractions that can be used as the raw material for motor fuel or as a raw material of catalytic cracking, and the residue as the raw material for catalytic cracking or fuel oil.

The objects of research are tar and bottom deposits in a tank of oil storage with physical and chemical characteristics given in Table 1 [9].

Table 1

Physical and chemical characteristics of the visbreaking raw materials

Parameter	Tar sample	ARPD
Density at 293 K, kg/m ³	997	940
Molecular weight	790	670
Sulfur content, wt %	2.4	1.3
Coke ability, wt %	17.3	-
Pour point, K	304	301
Kinematic viscosity, mm ² /s		
at 353 K	518	960
at 373 K	245	316
Organic part, wt %	100	95.8
Hydrocarbon type content, wt %:		
paraffins	10.2	27.1
aromatics	53.3	33.18
resins	28.4	11.1
asphaltenes	6.1	16.5

2. Experimental

The laboratory-scale plant (Fig. 1) was used for the investigation of the effect of ARPD organic part addition to the tar on light products output and residue quality in the visbreaking process.

The visbreaking process was carried out at the temperature of 713 K and the volume rate of material feed of 3.0 h⁻¹. The product was distilled at atmospheric pressure to obtain petrol (overpoint – 453 K) and gas-oil fraction (453–623 K) and the residue with the beginning of boiling point above 623 K.

ARPD samples were diluted at a ratio of 1:3 with oil solvent C155/200 (standard of Ukraine), heated to the temperature of 323–328 K and filtered. The organic part of ARPD contained in the filtrate was separated from the petroleum solvent by simple distillation. The tar with the

temperature of 343–373 K and organic part of ARPD in a certain proportion were mixed in the raw material block. The temperature of the blended material in the reactor block was kept in the range of 423–453 K with the use of electric heating.

The mixture of the tar with ARPD organic part was sent to the heating block by means of a dosing pump. ARPD-tar mixture was heated in the furnace to the process temperature (703–723 K) and sent to the reactor block where visbreaking process proceeded. The temperature in the reactor was maintained within 703–723 K with the use of an additional electric heating, the pressure was no more than 0.3 MPa. Sampling of light vapor fractions which was produced in the process was carried out through a straight condenser. The resulting condensate was collected in series-connected separators and the gas fraction was directed through the gas outlet to the gas meter.

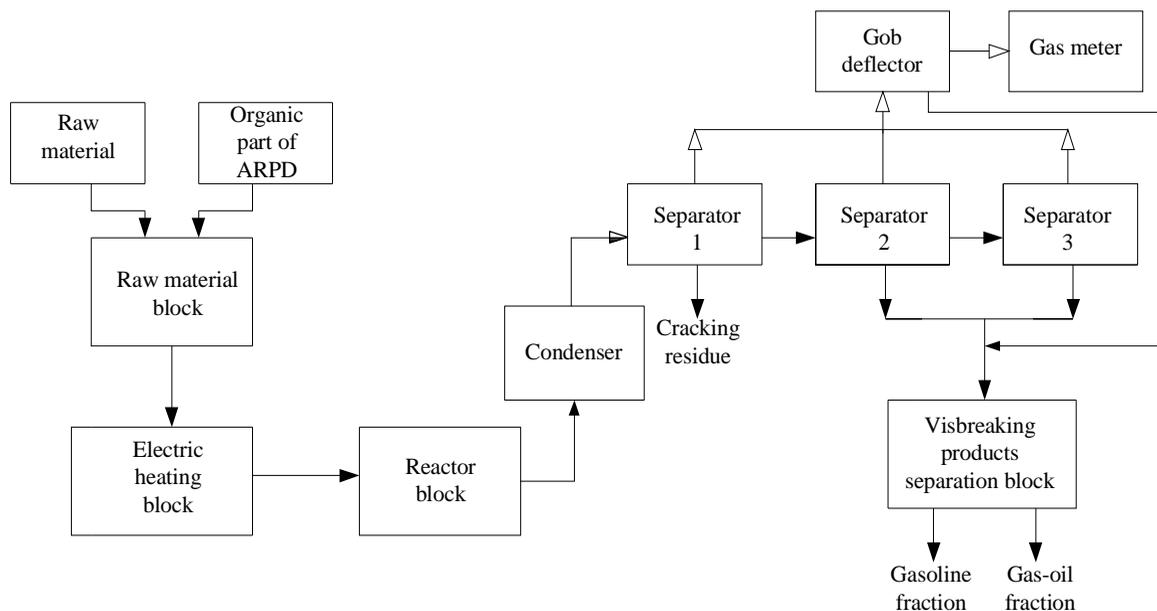


Fig. 1. Block diagram of the laboratory-scale plant of visbreaking process with the use of ARPD organic part

In all experiments the amount of gasoline and gas-oil, gas and distillation residue was measured, and the material balance was calculated.

The physical and chemical properties of oil products were estimated: determination of kinematic viscosity, hydrocarbon composition of heavy oil residues (determination was performed in an oil refinery laboratory), coking, sulfur, density, pour point, fractional composition, molecular weight, refractive index.

The study was conducted by adding 10, 20, 30 and 40 wt % ARPD to the tar. The fractions yield was measured and kinematic viscosity of the raw material and visbreaking residue was determined. After each experiment the amount of coke in the reactor was controlled.

ARPD influence on the quality indicators of visbreaking raw material was estimated by the change of the disperse characteristics of the mixture, kinematic viscosity, pour point, density depending on the content, the yield of light distillates, coking degree and qualitative indicators of the residue.

Heavy oil disperse systems, which include the mixture that is the subject of research, are complex colloid-disperse systems, which properties depend on many factors. Asphaltenes, which part increases in raw material mixture, tend to aggregation in the bulk of dispersion medium and adsorption on surfaces. The development of the aggregation process is accompanied by the loss of kinematic stability of the system. There is a need to identify the maximum concentration of ARPD, which excess can provoke the loss of aggregative stability of disperse systems.

The change in dispersion characteristics of the raw mixture was evaluated by an average diameter of the dispersed phase, which was determined from the optical density [12]. Optical density of oil in toluene-hexane mixture (the ratio of 30:70) was measured with a photocolimeter KFK-3 at the wavelength of $\lambda_1 = 530$ and $\lambda_2 = 680$ nm. When diluting the particles sizes of the dispersed phase change, therefore the character of their change depending on the material composition is examined. From the obtained values of optical density the wave coefficient b and the particles surface area S were calculated:

$$b = \frac{\lg D_{\lambda 1} - \lg D_{\lambda 2}}{I_2 - I_1} \quad (1)$$

$$S = 8.08 \cdot 10^3 \cdot b \quad (2)$$

where $D_{\lambda 1}$ and $D_{\lambda 2}$ are optical densities at wavelength λ_1 i λ_2 , respectively.

The average surface diameter of particles was calculated as:

$$d_p = 6000 / (\rho \cdot S) \quad (3)$$

where ρ is density of the oil solution, kg/m^3 .

3. Results and Discussion

Generalized results of the study of the influence of ARPD content on the qualitative characteristics of the raw material mixture are shown in Fig. 2.

In the whole range of ARPD content in tar from 0 to 40 % the decrease of density and pour point is observed

which corresponds to the properties of the original components. The influence of ARPD content on the dynamic of change of the dispersed particles size, viscosity and pour point becomes apparent at the 20 % threshold crossing. When the part of ARPD is more than 20 %, intensive aggregation of particles, lowering of the pour point and viscosity increase are observed. This is due to the growing influence of asphaltenes on the aggregative stability of colloid-disperse system.

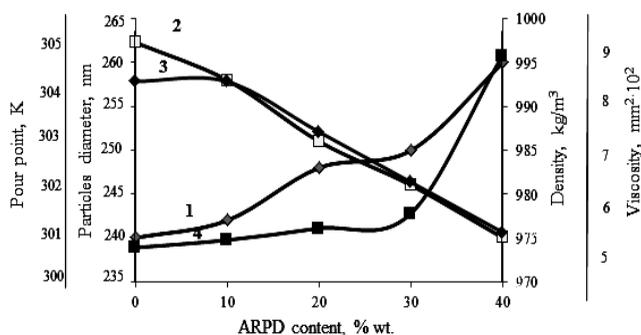


Fig. 2. Dependence of the characteristics of raw material mixture on ARPD content: particles diameter, nm (1); density, kg/m³ (2); pour point, K (3) and viscosity, mm²/s at 353 K (4)

The influence of ARPD on viscosity and the amount of visbreaking products are summarized in Table 2 and Fig. 3.

When adding 10 wt % of ARPD there was observed slightly increased yield of distillate fractions, insignificant coking, and insignificant change of viscosity of the cracking residue compared to the residue after tar visbreaking. The increase of the deposits amount in raw material to 20 % is accompanied by an increased output of gasoline and gas-oil fractions, low change of viscosity of visbreaking residue which meets normative requirements.

There was observed the significant increase of coking, viscosity growth of the feedstock and a signi-

ficant increase in viscosity of visbreaking residue when adding 30 and 40 % of ARPD.

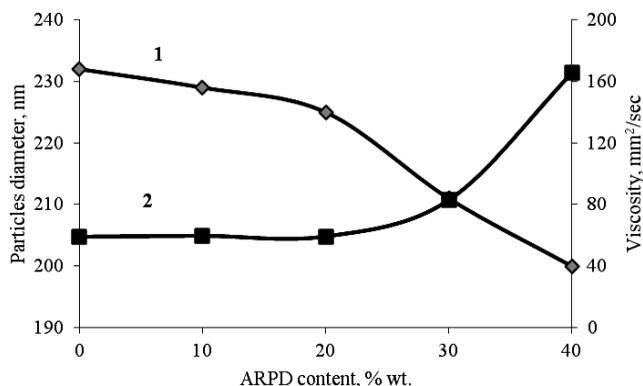


Fig. 3. Dependence of the characteristics of cracking residue on ARPD content: particles diameter, nm (1) and viscosity of visbreaking residue at 353 K, mm²/s (2)

These results are explained by the changes in the composition of the initial mixture of hydrocarbon raw materials. Addition of ARPD increases the relative content of asphaltenes and paraffins, decreases the amount of resins and aromatic compounds (Table 2). Asphaltenes can be converted relatively poorly during visbreaking, while resins are converted into lighter hydrocarbons which have characteristics of distillates. The higher asphaltenes content in raw material and the less resin content in it, the less reduction in viscosity of the visbreaking residue is. The increase in viscosity of the visbreaking residue is due to the formation of consolidation products. At the same time, the feature of aromatic hydrocarbons is their tendency to reactions of consolidation with the formation of condensed aromatic hydrocarbons. Products of consolidation are the source material for the formation of resin-asphalt and coke-like substances. Raw material with high content of aromatic hydrocarbons is the least desirable for the processing with the aim to obtain light products – it requires a strict regime of the process and has a significant tendency to coking.

Table 2

The results of laboratory investigation of visbreaking process

Material/parameter	Mixture number				
	1	2	3	4	5
	Mixture composition, wt %				
Tar	100	90	80	70	60
ARPD	0	10	20	30	40
	Products yield				
Hydrocarbon gas	2.3	2.9	3.7	4.1	4.3
Gasoline fraction (overpoint – 453 K)	3.0	3.8	4.7	5.0	5.2
Gas-oil fraction (453–623 K)	6.7	8.4	10.7	11.6	15.1
Visbreaking residual > 623 K	86.8	84.2	80.9	79.0	74.4
Coking (visually)	negligible	negligible	negligible	considerable	substantial

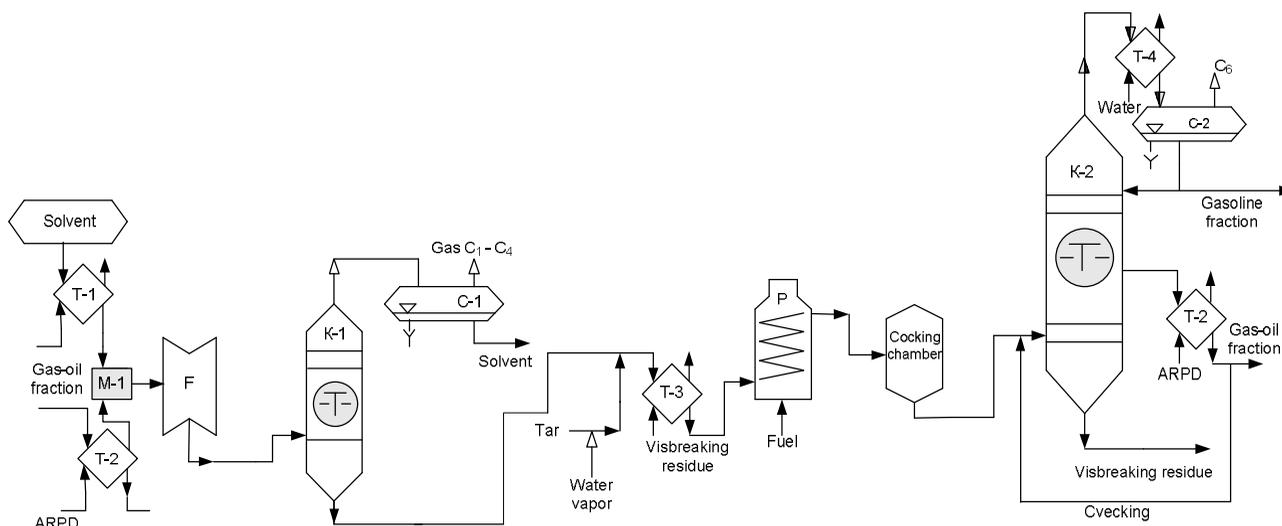


Fig. 4. Joint scheme of tar visbreaking process with the addition of organic part of ARPD: T-1, 2, 3, 4, 5, 6 – heat exchangers; F – vacuum filtration unit; C-1, 2 – separators; K-1, 2 – rectification columns; P – furnace, M – mixer

Table 3

Comparison of economic indicators of visbreaking process of pure tar and tar with the addition of ARPD organic part

Raw material	Composition, %	Quantity, ths. tons	Price, UAH/ton	Cost, ths. UAH
Taken: tar	100	500	8000	4000000
Received:				
gas	2.3	11.5	3000	34500
gasoline fraction	3.0	15.0	10000	150000
gasoil fraction	6.7	33.5	10000	335000
residue	86.8	434.0	9000	3906000
Total	98.8	–	–	4425500
Income	–	–	–	425000
Taken:				
tar	83.3	500	8000	4000000
ARPD	16.7	100	3000	300000
Altogether	100.0	600	11000	4300000
Received:				
gas	3.7	22.2	3000	66600
gasoline fraction	4.7	28.2	10000	282000
gasoil fraction	10.7	64.2	10000	642000
residue	80.9	485.4	9000	4368600
Total	–	–	–	5359200
Income	–	–	–	1059200

It was experimentally established that ARPD addition to raw materials of visbreaking up to 20 wt % does not significantly increase the relative content of asphaltenes and aromatic compounds, does not influence aggregative stability of raw material and does not significantly affect the qualitative and quantitative characteristics of the final products of the process.

As a result of laboratory simulation of the visbreaking process with a remote reactor when ARPD is

added to the raw material the industrial visbreaking process scheme is proposed. For that the block of pretreatment of heavy oil deposits was included in the existing technological scheme. Solvent is heated in the heat exchanger T-1, it moves to the mixer M-1 where ARPD is added after heating in the heat exchanger T-2 by gasoil. After the mixer the homogenized mixture is filtered and goes to the column K-1, where the solvent is distilled off the top outlet, and ARPD goes from the

bottom. Modernized scheme of thermal destruction of blended raw material is shown in Fig. 4.

Hot tar (363 K) from the preliminary oil distillation plant is mixed with water vapor and pretreated ARPD, then it passes the tube space of the heat exchanger T-3 and is fed to the coil pipe of the furnace P where it is heated to the temperature of 703–723 K. The use of water vapor as a turbolator prevents coagulation and consolidation of the main cocking components – asphaltenes. After the furnace the raw material is subjected to visbreaking in the cocking-chamber under the pressure of 4.2 MPa. The product mixture is sent to the fractionating column K-2. Before the column inlet the mixture is cooled by means of cold gas-oil, supplied to the line. Gas-gasoline mixture gets out of the column top and it is cooled in the heat exchanger T-4 to the temperature of 318 K with cold water. In the separator C-2 the gas-product mixture is separated into fat gas and gasoline fraction. A part of gasoline returns into the column for irrigation. The outlet for gas-oil fraction is in the middle part of the column. Then gas-oil is cooled in the water heat exchanger T-2, the part of it returns as a recirculate to the inlet of raw material into the column. The visbreaking residue is taken from the bottom of the column.

To confirm the practicability of the proposed method of ARPD utilization [13, 14], a comparative analysis of production economic indicators was carried out for the processing of straight tar and with the addition of ARPD organic part with the production rate of 500 tons per year. The results of laboratory experiments were taken as the basis of calculations (Table 2) [15]. Calculation of the main efficiency indexes of pure tar processing and the project with the addition of ARPD organic part is summarized in Table 3.

Table data analysis shows that the income from the processing of tar in the mixture with 20 % ARPD is 1059200 thousand UAH, and the income from the processing of pure tar is 425000 thousand UAH, which is 2.5 times less. Even considering the cost of visbreaking modernization, the usage of ARPD in the tar processing is the extremely cost-effective solution that allows to get more components of fuels from wastes.

4. Conclusions

1. The main principles of the process of tar visbreaking with the addition of asphalt-resin-paraffin deposits, which are partly waste products, were developed.

2. A laboratory-scale plant for the study of the processes of thermal decomposition of heavy oil residues was made.

3. Optimal conditions of visbreaking of blended raw materials, with fuel fractions and boiler fuel as the product, were determined.

4. A basic technological scheme of industrial plant of tar visbreaking with the addition of 20 wt % asphalt-resin-paraffin deposits was proposed.

5. The economic performance of the modernized scheme in industry was estimated for the blended raw material visbreaking plant of 500 ton per year. The calculations results prove the efficiency of ARPD utilization since an additional amount of light oil and boiler fuel are obtained.

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ВИКОРИСТАННЯ АСФАЛЬТОСМОЛОПАРАФІНОВИХ ВІДКЛАДІВ ЯК КОМПОНЕНТА СИРОВИНИ ВІСБРЕКІНГУ

Анотація. Приведено результати експериментальних досліджень вісбрекінгу з використанням органічної частини асфальтосмолопарафінових відкладів (АСПВ) як сировинного компонента. Вивчено вплив кількості добавки АСПВ до гудрону на вихід паливних фракцій та їх якісні показники. Крайні результати одержано при додаванні до сировинної суміші 20 % мас. АСПВ. За результатами лабораторного моделювання розроблено пропозиції щодо модернізації промислової технологічної схеми вісбрекінгу з використанням сумішевої сировини. Проведено аналіз економічних показників модернізованого процесу.

Ключові слова: вісбрекінг, відклади, сумішева сировина, утилізація, технологічна схема.