THEORETICAL ASPECTS OF CHEMMOTOLOGY, CHEMICAL TECHNOLOGY AND ENGINEERING

1.1 THE PROBLEMS OF FORMATION OF ASPHALT-RESIN-PARAFFIN DEPOSITS. PREVENTION AND UTILIZATION

Olena Tertyshna, Kostiantyn Zamikula, Oleh Tertyshnyi

Oil dispersed systems (ODS) contain asphaltenes, resins and paraffins which can promote the formation of asphalt-resin-paraffin deposits (ARPD) on the surfaces of process equipment.

The rate of deposits formation is influenced by the oil composition, namely, the ratio of paraffins, resins and asphaltenes, and by the hydrodynamic and temperature conditions of its transportation, storage and processing [1]. Asphaltenes, peptized and stabilized by resins, are characterized by high melting points (~300 ^{o}C) and are partly in the solid state in oil. They do not form a joint crystals or solid solutions with hydrocarbons, and serve only as centers of aggregation and crystallization. Resins in oil form true solutions and are located in the dispersion medium. Part of the resin, the pour point of which is close to the pour point of hydrocarbons, crystallizes forming mixed crystals or solid solutions. The other part forms the solvate shell around the solid particles.

Asphaltenes behave as coagulants, resins – like peptizers, preventing the merging of crystals and the formation of spatial grid [1].

ARPD formation and growth are promoted by the temperature gradient which occurs in the near-wall layer of pipeline and heat exchangers as a result of raw material cooling.

Typically, deposits are removed without prior analysis of the reasons of their formation and accumulation in various units of industrial equipment [2]. The creation of a well-founded kinetic model of ARPD formation and growth will allow to develop ways of deposition minimization, and in the future it will allow to prevent their formation.

The kinetics of deposits formation from oil sample, which was taken from the storage tank at the refinery, was investigated. Oil characteristics of the content of potentially solid components are presented in Table 1.

ARPD formation was studied using a method of «coldfinger test».

A glass of oil (200 ml) was placed in a thermostatic bath, where with stirring at a speed of 120 Rev/min it was heated to the temperature of 30, 40 and 50 ^{o}C. The copper tube («coldfinger») with the surface of 744.45 mm^2 was cooled with running water to a temperature of 10 ^{o}C. Preliminarily weighed and degreased tube was placed in the center of the glass with oil so that it was at the height of 3 cm from the bottom. The tube was removed from the oil after 5 min and weighed. To remove stuck deposit hot water was ran through the tube, and then ARPD was collected. Small intervals of exposure (5 min) were adopted to minimize the influence of thermal resistance of the deposit layer.

Table 1

Oil characteristics

Characteristic	Value
1	*2*
Asphaltenes (A)	0,1
Paraffins (P)	1,0
Resins (R)	15,9

Table 1 continue

1	2
Ratio P/(A+R)	0,06
Ratio R/(P+A)	14,45
Density, $\cdot 10^{-3}$, kg/m^3	843,4
Viscosity, Pa·sec	1,096·
Pour point, ^{0}C	-18

Processing of experimental data was performed using logarithmic (1) and exponential (2) kinetic models, which were chosen to describe the kinetics of ARPD formation from the condensate [3].

$$\frac{dm}{d\tau} = k_{1\log} \cdot k_{2\log}^{-m},$$ (1)

$$\frac{dm}{d\tau} = k_{1\exp} - k_{2\exp} \cdot m,$$ (2)

where m – deposit mass; $k_{1\log}, k_{1\exp}, k_{2\log}, k_{2\exp}$ – rate constants; τ – deposition time.

The constants $k_{1\log}, k_{1\exp}$ correspond to the deposit formation on the tube at the initial moment of time. The values of the constants $k_{2\log}, k_{2\exp}$ were selected on the principle of best approximation of experimental data using the built-in genfit function for nonlinear regression of the general form in Mathcad.

The average particle size of the sample solution was determined by the photoelectrocolorimetric method on the KFK-3 colorimeter at two wavelengths of light 530 and 680 nm.

We assumed that the particles of the dispersed phase were spherical and calculated their average diameter d_n (nm) by the formula:

$$d_n = 6000/(\rho \cdot S),$$ (3)

where ρ is the density of the dispersed phase particles, $\rho = 1,2$ g/cm^3 [4]; S is the specific interphase surface, m^2/g, which was calculated by the equation:

$$S = 8.08 \cdot 10^3 \cdot \frac{\lg D_{\lambda 1} - \lg D_{\lambda 2}}{\lambda_1 - \lambda_2},$$ (4)

where $D_{\lambda 1}$ and $D_{\lambda 2}$ are the optical densities at wavelengths λ_1 and λ_2.

Formation and sedimentation of AS were accelerated by centrifugation of the petroleum solution in toluene (solvent) with *n*-hexane (precipitant) for 12 minutes. The rotational velocity of the centrifuge was 4000 rpm. The stability factor was determined, which is the ratio of the concentrations of components (or characteristics) of the petroleum dispersion system after centrifugation in two layers, separated from each other at a certain distance in the direction of the deposition forces [4].

The stability factor was calculated by the formula:

$$F = \frac{D_1}{D_2},$$ (5)

where D_1, D_2 are the optical densities of the upper and lower layers, respectively, at a wavelength of 680 nm.

The mechanism of the PPVO action was estimated from the results of the IR spectral analysis of samples of the pure petroleum and the petroleum with additives on the spectrometer Spectrum BX II in the range of 400–4000 cm^{-1}. The spectral coefficients were determined by the ratio of the characteristic absorption bands [4].

Dynamics of the deposit formation from the oil sample depending on the temperature difference between the oil and the tube surface is presented in Table 2.

Table 2

Mass of the deposit on the tube surface

Temperature gradient, ^{0}C	Duration of test, min					
	5	10	15	20	25	30
	Mass of the deposit, mg					
20	1,45	2,8	4,1	5,15	5,86	6,1
30	1,87	3,53	4,93	6,13	7,1	7,4
40	2,73	5,27	7,53	9,53	10,15	10,25

The results of the experiment showed that at the initial stage (15–20 min) the main mass of the deposit forms on the tube and it is about 83–93 % of all deposit mass. After twenty minutes of experiment, the rate of deposit accumulation reduced markedly. One of the reasons of slow deposit accumulation is exhaustion of the oil bulk relatively potentially solid components.

The results of the calculation of the rate constants for both equations at three values of temperature gradient are presented in Table 3.

Table 3

The constants of kinetic models of ARPD deposition from oil

ΔT, ^{o}C	$\dfrac{dm}{d\tau} = k_{1\log} \cdot k_{2\log}{}^{-m}$		$\dfrac{dm}{d\tau} = k_{1\exp} - k_{2\exp} \cdot m$		T^*, ^{o}C
	$k_{1\log}$	k_{2log}	$k_{1\exp}$	k_{2exp}	
20	0,379	1,181	0,356	0,039	-0,93
30	0,477	1,159	0,440	0,045	-0,70
40	0,806	1,138	0,720	0,053	-0,56

Here T^* is the dimensionless temperature parameter corresponding to the driving force of the sedimentation process:

$$T^* = \frac{T_c - T_w}{T_{oil}} \tag{6}$$

where T_c, T_w, T_{oil} are the pour points of oil, of the tube surface and of the oil in the glass, respectively (^{o}C).

If taking into account that in the selected experimental conditions T_c, T_w are constant, the parameter T^* only depends on the temperature of oil heating.

From Table 3 it is seen that the values of the constants k_1 are close for both models, while the constants k_2 differ considerably. Such comparison allows to make clear the mechanism of deposition directly on the surface at initial time points and in the process of their accumulation. At small values of the constant k_1 the rate of instantaneous deposition from oil is rather low, for which the value of $R/(A+P)$, i.e. the ratio of peptizer (resin) to the amount of potentially solid crystallizable components ($P+A$), is sufficiently large.

Using the found values of constants the direct problem of modeling the kinetics of ARPD formation in accordance with equations (1) and (2) was solved. The comparison of calculated and experimental values of the deposit mass is presented in Fig.1.
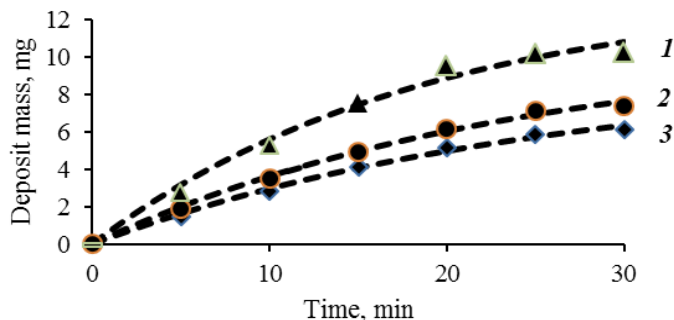

Fig. 1. Dynamics of ARPD accumulation from oil at the temperature difference
between the oil and the surface of the tube, ΔT, °C:
1 – 40; *2* – 30; *3* – 20. Points correspond to experimental data,
dashed lines are the calculated curves according to the equations (1), (2)

The analysis of Fig. 1 shows that both the logarithmic and the exponential models give almost full coincidence with experimental data. Model verification was performed by the least-squares method (Table 4).

Table 4

The results of the calculation of deviations of experimental and calculated values
of the deposits accumulation rate

	Logarithmic model			Exponential model		
ΔT, °C	20	30	40	20	30	40
Sum of squared deviations	0,238	0,204	1,622	0,163	0,122	1,066

Comparison of deviations shows that when using the exponential model the discrepancy between the experimental and calculated data is minimal. Therefore, to describe the kinetics of the process of the deposits formation the exponential equation is more accurate.

The dependence of the rate constants $k_1 = f(T^*)$ and $k_2 = f(1/T^*)$ for both models are linear and described by the equations given in Table 5.

Table 5

The relation of the rate constants with temperature parameter T^*

Logarithmic model	Exponential model
$k_{1\log} = 0{,}893T^* + 0{,}130$	$k_{1\exp} = 1{,}02T^* + 0{,}388$
$k_{2\log} = 1{,}294/T^* - 0{,}261$	

Substitution of the values of the constants from Table 5 in the equation (2) for the exponential model as more accurate, allows to obtain the kinetic equation relating the rate of the deposits growth with temperature factor T^*:

$$\frac{dm}{d\tau} = 1{,}02T^* + 0{,}388 - 1{,}294/T^* - 0{,}261 \cdot m \tag{7}$$

8

To assess the influence of the layer thickness of the deposit formation on the deposition rate, the dynamics of single (20 min) formation of the deposit were compared with cumulative (with intermediate unloading every 5 minutes) formation (Fig. 2).
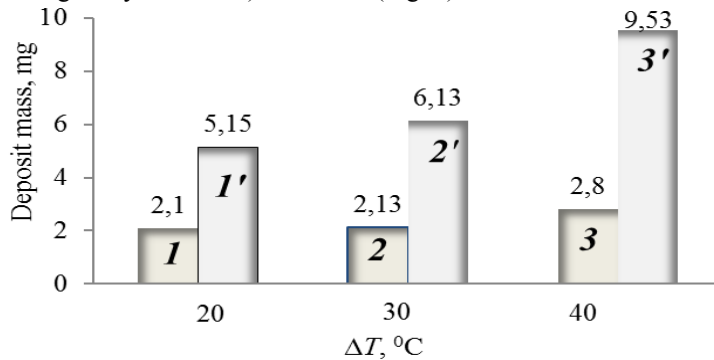

Fig. 2. The mass of the deposit formed at single (*1*, *2*, *3*) and cumulative (*1'*, *2'*, *3'*) formation of the deposit (20 min) from oil depending on the temperature gradient of oil and the tube ΔT

It is seen that the mass of the deposit obtained during continuous deposition is 2.5–3 times less than during its regular removal. This is due to the changes in temperature of the process. It is natural that the growth of ARPD layer on the surface of the tube prevents heat transfer between the cooled surface and the tube, distorting the true temperature gradient set in the experiment. The results of the model thermal calculations performed in accordance with the methods [2] are given in table 6.

Table 6

The temperature regime of ARPD deposition, depending on the hydrodynamics
and the layer thickness of the deposit at the temperature of the tube 10 $^{\circ}$C

Oil temperature, ^{0}C	Heat-transfer coefficient, W/m^2·K		Deposit layer thickness, м	Heat resistance of the deposit δ/λ, m^2·K/W	Heat-transfer coefficient K_T,W/m^2·K	Actual difference between oil and the tube, $^{\circ}$C
	from the wall side, α_1	from oil, α_2				
1	*2*	*3*	*4*	*5*	*6*	*7*
Turbulent regime						
30	500	300	-	-	187	12
			0,001	0,005	97	6,1
			0,002	0,01	65	4,1
40	500	300	-	-	187	18
			0,001	0,005	97	9
			0,002	0,01	65	6,3
50	500	300	-	-	187	25
			0,001	0,005	97	12,6
			0,002	0,01	65	8,5

Table 6 continue

Laminar regime + natural convection						
1	*2*	*3*	*4*	*5*	*6*	*7*
30	10	60	-	-	8,6	2,7
			0,001	0,005	8,2	2,6
			0,002	0,01	7,9	2,5
40	10	60	-	-	8,6	4,2
			0,001	0,005	8,2	4,0
			0,002	0,01	7,9	3,8
50	10	60	-	-	8,6	5,6
			0,001	0,005	8,2	5,3
			0,002	0,01	7,9	5,1

Data shown in Table 6 indicate that in the turbulent regime the increase in the thickness of the deposit on the surface of the tube to 1 mm cuts the actual temperature difference by half, and when the layer thickness is 2 mm – by three. Under conditions of laminar flow and natural convection the temperature difference is only 2.5–5.6 degrees. It is obvious that the temperature rise in the surface layer of the deposit slows down the process of formation of ARPD solid particles and their accumulation. The conditions corresponding to the turbulent regime under actual conditions can be observed when operating heat transfer equipment. Natural convection occurs when transporting oil products through pipelines and during storage in tanks and containers.

The next stage of the study was the search for effective and inexpensive ways to combat the formation of ARPD and the directions for their processing.

The product of processing of vegetable oils (PPVO) have been used as asphaltene precipitation inhibitorfrom ODS [5, 6].

PPVO is a by-product of the production of biodiesel fuelcomponents [5,6]. The additive was synthesized in the laboratory according to the chemical modification technique by glycerolysis of rapeseed and castor oil with composition (% by weight): rapeseed – 75–80 % and castor – the rest: $CH_3–(CH_2)_5–^{12}CH(OH)–CH_2–CH=CH–(CH_2)_7–O–CH_2–CH(OH)–CH_2–O–C(O)R',R''$, where R, R', R'' are $C_{17}H_{33}$; $C_{17}H_{31}$; $C_{17}H_{29}$ radicals of any combination. Industrial additives were commercial inhibitors Pachem P-501; Pachem-P-505; Pachem PS-603/X [7].

PPVO was added to the petroleum at the concentrations of 0.07, 0.09 and 0.1 % v/v. Industrial additives were dosed in quantities according to the manufacturer's recommendations for their use: Pachem P-501– 0,07 % v/v, Pachem-P-505–0,07 % v/v, Pachem PS-603 / X – 0,1 % v/v.

The results of the additives influence on the petroleum stability were estimated by changing the average diameter of particles of the dispersed phase with the use of KFK-3 photocolorimeter at the wavelengths of 680 nm by measuring the optical density of the petroleum-toluene mixture (in the ratio of 1:1) with PPVO.

The effectiveness of the additive action on the aggregative stability of the petroleum is presented in Fig. 3,4.

Sediment formation was observed only in the case of the pure petroleum. Determination of the average diameter of the disperse particles in the upper and lower layers of the petroleum samples after centrifugation (Fig. 3) showed that the additives prevent or significantly decrease coagulation. In the pure petroleum under the action of centrifugal force the average particle size of the disperse phase is more than 225 nm. When using the additives, the difference in diameters in the upper and lower layers is insignificant and the lowest value is achieved when using 0.09 % v/v PPVO (sample 3). The average size of the disperse particles in the lower layer correlates with the stability factor – from 0.344 for the pure petroleum to 0.692 with PPVO (sample 3).

The effectiveness of the PPVO additive corresponds to the effectiveness of known proven industrial additives.

Blank column – lower layer of the centrifugate; shaded column – upper layer of the centrifugate.
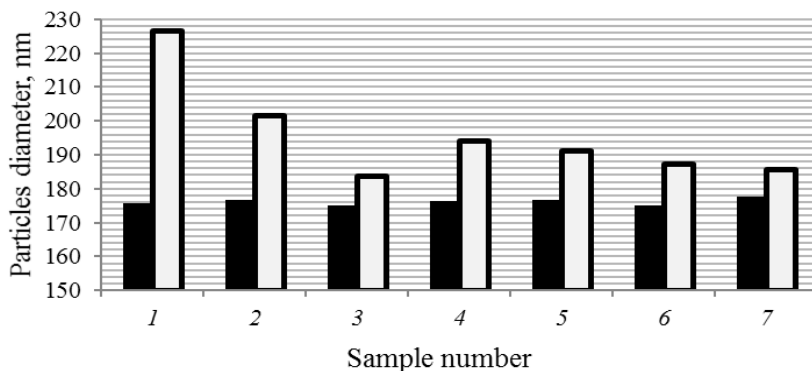

Fig. 3. The value of the disperse particles diameter in the upper and lower layers of the centrifugate of the petroleum solution samples, nm:
1 – pure petroleum; petroleum with the additive: *2* – 0.07 % PPVO; *3* – 0.09 % PPVO; *4* – 0.12 % PPVO; *5* – 0.07 % Pachem P-505; *6* – 0,07 % Pachem P-501; *7* – 0,1 % Pachem PS-603/X
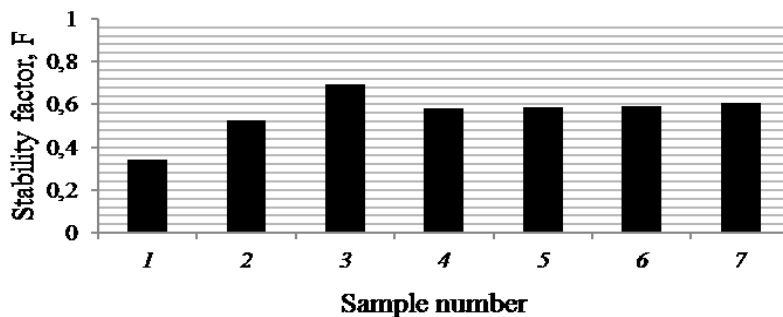

Fig. 4. The value of the stability factor of the petroleum samples:
1 – pure petroleum; petroleum with the additive: *2* – 0.07 % PPVO; *3* – 0.09 % PPVO; *4* – 0.12 % PPVO; *5* – 0.07 % Pachem P-505; *6* – 0,07 % Pachem P-501; *7* – 0,1 % Pachem PS-603/X

IR spectral analysis of the petroleum sample (Fig. 5) showed the presence of paraffin structures of normal and iso-structure, the presence of long paraffin chains (absorption bands are 1462, 1377, 727 cm^{-1}). The presence of aromatic structures (absorption bands are 1605, 1032, 810, 873 cm^{-1}) is noted. The absorption bands of 742, 810, 873, 1032 cm^{-1} indicate the presence of condensed bi-, tri-, and polycyclic aromatic structures in the petroleum. Carbonyl group C–O is absent, petroleum is not oxidized. Sulfoxide group (SO) is present in the absorption band of 1030 cm^{-1}. A strong peak is observed in the region of 2850–2950 cm^{-1}, which indicates the presence of aliphatic CH bonds.
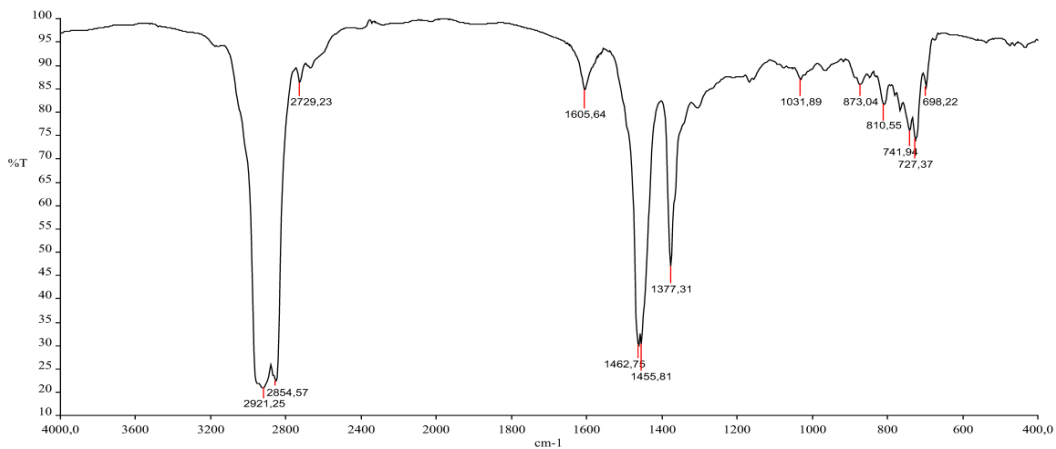
Fig. 5. IR spectra of the pure petroleum

In the IR spectrum of the PPVO (Fig. 6) the peak at about 1750 cm^{-1} are related to valence vibrations of carbonyl groups of aliphatic carboxylic acid esters. The vibrations of the C–O–O at the region of 1300–1000 cm^{-1} confirm the presence of esters. The peak at 3474 cm^{-1} is related to glyceride OH groups.
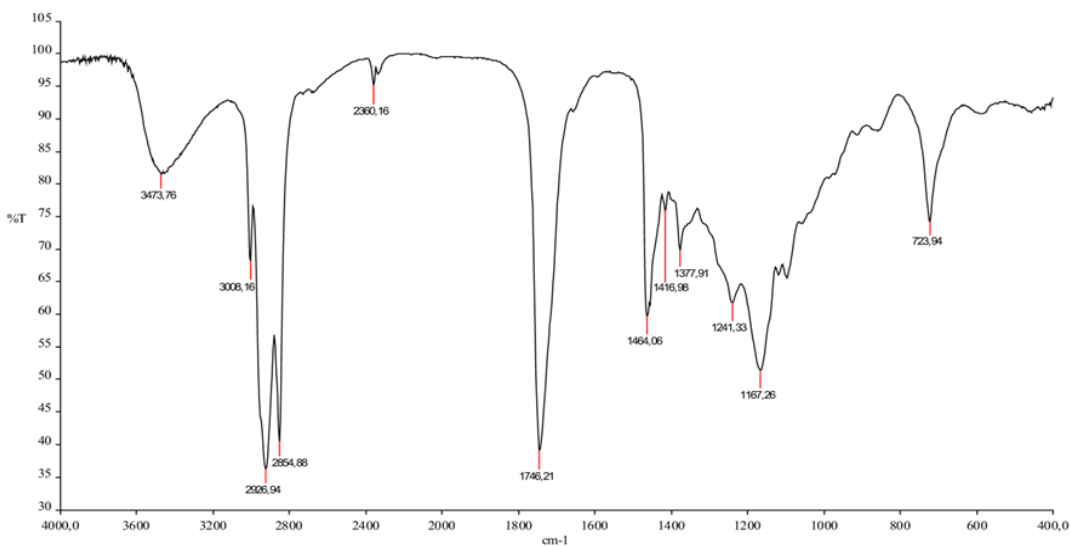

Fig. 6. IR spectra of PPVO

In the petroleum sample with PPVO additive the presence of any new chemical compounds was not found. It is clear from infrared spectrum (Fig 7) that this sample is just the mixture of the above mentioned substances.
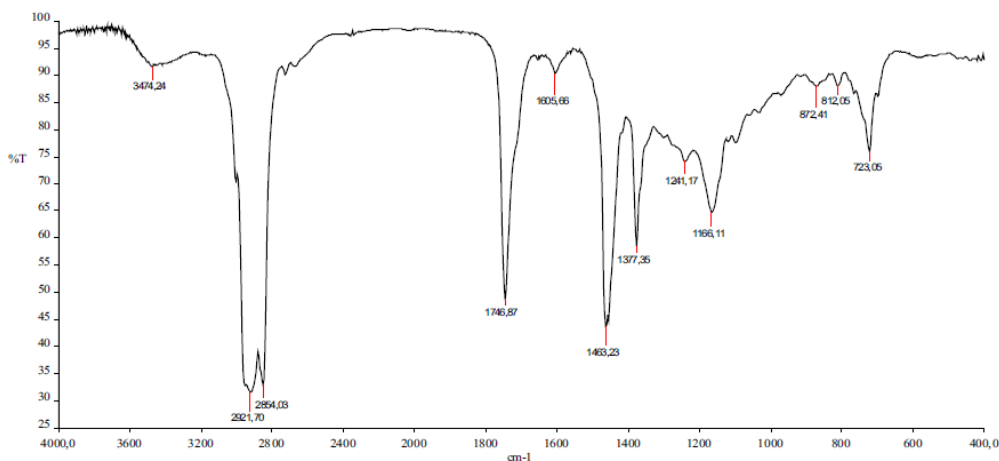
Fig. 7. IR spectra ofthe petroleum with 0.09 % PPVO.

With IR spectral analysis it was established that industrial additives Pachem-P -505 and Pachem-P-501 contain aromatic and alkyl groups, carboxylic acid esters, and also free carboxylic acids. Pachem-PS-603X differs in the increased content of aromatic and alkyl groups, and absence of carboxylic acids. As in the case of PPVO when adding these industrial agents any chemical interaction was not registered.

Apparently the active substances of the additives are surface-active agent. And they are glycerides of fatty acids.

In attempt to estimate quantitatively the influence of additives components on the stabilizing action we used the method of quantitative analyses of hydrocarbonic fragment in petroleum based on IR spectroscopy [8]. The method is considered as most informative for petroleum systems and uses the following absorption bands as characteristic: 727 cm^{-1} (alkane structures with $(CH_2)_x$, $X \geq 4$), 1377 cm^{-1} (branched alkane structures), 1605 cm^{-1} (aromatic structures). It should be noted that fragments concentration in different samples found as the surface under the peaks in the IR spectra cannot be compared owing to the different layer thickness of the samples. Petroleum samples can be compared for the following coefficients: branching coefficient C_b is the ratio of optical density 1377 cm^{-1} (D_{1377}) to optical density 727 cm^{-1} (D_{727}); aliphatic coefficient C_{al} is the ratio of D_{1377} and D_{727} sum to D_{1605}; aromaticity coefficient C_{ar} is the ratio of D_{1605} to D_{727}.

The results for the studied samples with the additives are presented in Table 7.

Table 7

Results of the quantitative analysis of IR spectra of the samples

Petroleum sample	C_b	C_{ar}	C_{al}	F
Pure petroleum	2,06	0,59	5,20	0,35
Petroleum + 0.07 % Pachem P-505	2,49	0,56	6,17	0,59
Petroleum + 0.07 % Pachem P-501	1,86	0,57	5,00	0,59
Petroleum + 0.1 % Pachem PS-603X	2,22	0,65	4,96	0,6
Petroleum + 0.07 % PPVO	1,94	0,57	6,17	0,52
Petroleum + 0.09 % PPVO	2,61	0,53	6,44	0,7

Taking into account nanometer size of the dispersed phase it is clear that IR spectra show only the composition of the dispersion medium because of the infrared radiation diffraction on the nanoparticles.

There are not clear correlation between stability factor and one of the coefficients, but the best value of stability factor F corresponds to the increase of aliphaticy and branching and the decrease of aromaticity coefficients for the Petroleum + PPVO systems. As C_{ar} changes insignificantly, C_{al} and C_b increase by a different value, we inferred that amount of soluble aromatic compound and aliphatic $(CH_2)_x$ groups in the dispersion medium grows in an almost equal degree, whereas amount of branched alkane structures rises in a greater degree.

We can assume that PPVO additive acts as a surfactant displacing natural petroleum surfactants from the particles surface into the dispersion medium and the mechanism of action of Pachem additives differs.

One of the directions of utilization of oil deposits is proposed to add them to the raw materials of the process of visbreaking – tar, the physico-chemical characteristics of which are given in Table 8 [9].

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.

Table 8

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
Cokeability, % wt.	17,3	-
Pour point, K	304	301
Kinematic viscosity, mm^2/sec		
at 353 K	518	960
at 373 K	245	316
Organic part, % мас.	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

The laboratory-scale plant (Fig. 8) was used for the investigation of the effect of ARPD samples were diluted at a ratio of 1:3 with oil solvent C155/200 (GOST 3134–78), heated to the temperature of 323–328 K and filtered. The organic part of ARPD containing in the filtrate was separated from 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.
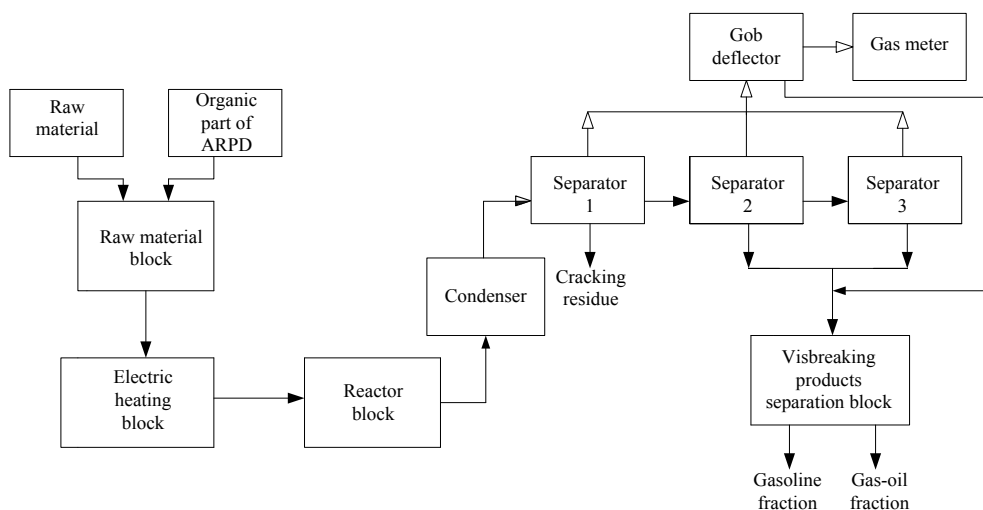
Fig. 8. Block diagram of the laboratory-scale plant of visbreaking process with the use of ARPD organic part

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 (430–450 $^{\circ}$C) and sent to the reactor block where visbreaking process proceeded. The temperature in the reactor was maintained within 430–450 $^{\circ}$C with the use of an additional electric heating, 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.

In all experiments the amount of gasoline and gasoil, 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), cocking, sulfur, density, pour point, fractional composition, molecular weight, refractive index.

Generalized results of the study of the influence of ARPD content on the qualitative characteristics of the raw material mixture are shown in Fig. 9.

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 residue.

The change in the dispersion characteristics of the raw material mixture was estimated on the average diameter of the particles of the dispersed phase, the method of determination of which is described above.

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.
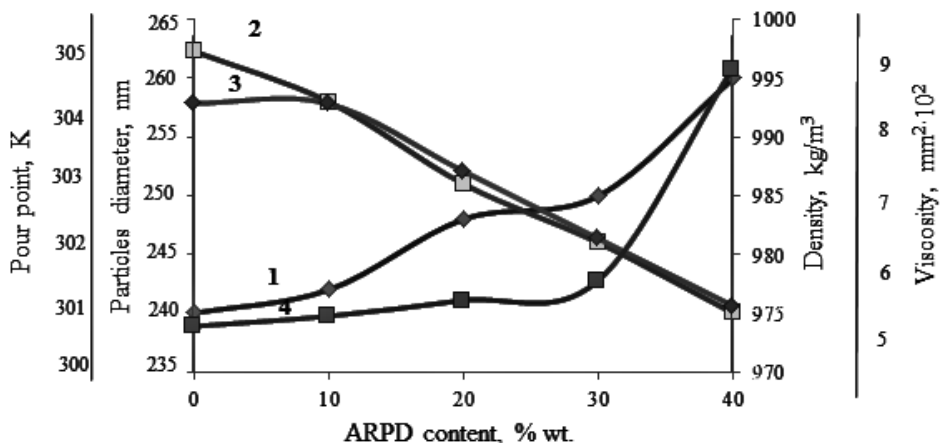
Fig. 9. Dependence of the characteristics of raw material mixture on ARPD content:
1 – particles diameter, nm; *2* – density, kg/m^3; *3* – pour point, K; *4* – viscosity, mm^2/sec at 353 K.

The influence of ARPD on viscosity and the amount of visbreaking products are summarized in Table 9 and Fig. 10.

Table 9

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 (over point – 453 K)	3,0	3,8	4,7	5,0	5,2
Gasoil 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

When adding 10 % wt. of ARPD there was observed slightly increased yield of distillate fractions, insignificant cocking, 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 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 cocking, viscosity growth of the feedstock and a significant increase in viscosity of visbreaking residue when adding 30 and 40 % of ARPD.

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 7). Asphaltenes can be conversed 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.

16

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 consolidationare 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 cocking.
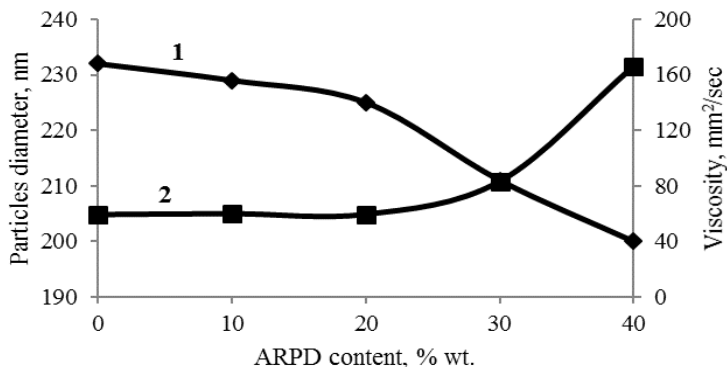

Fig. 10. Dependence of the characteristics of cracking residue on ARPD content:
1 – particles diameter, nm; *2* – viscosity of visbreaking residue at 353 K, mm^2/sec

It was experimentally establish that ARPD addition to raw materials of visbreaking up to 20 % by weight 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 raw material the industrial visbreaking process scheme was 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 solvent is distilled off the top outlet, and ARPDgoes from the bottom. Modernized scheme of thermal destruction of blended raw material is shown in Fig. 11.

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 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 recirculat to the inlet of raw material into the column. The visbreaking residue is taken from the bottom of the column.
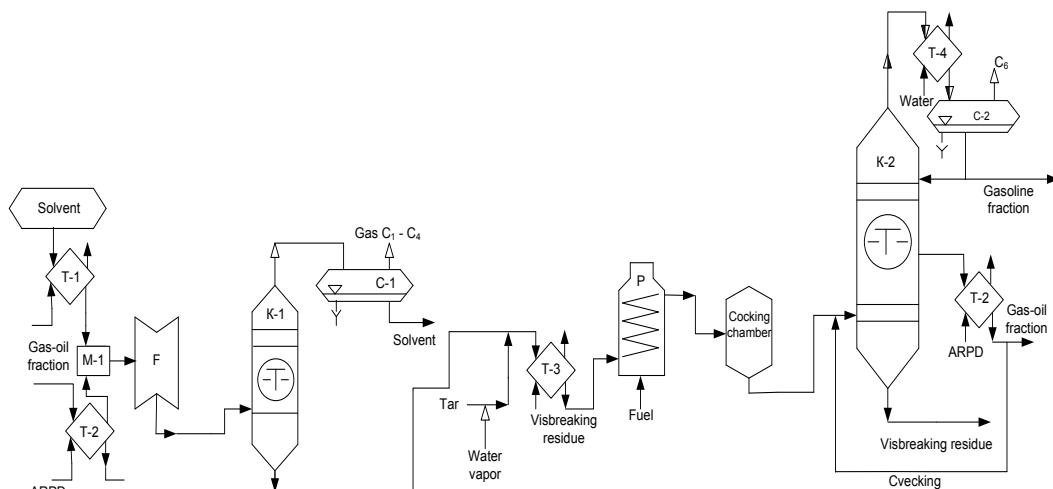
Fig. 11. Joint scheme of tar visbreaking process with addition of organic part of ARPD.
T-1, 2, 3, 4, 5, 6 – heat exchangers; F – vacuum filtration unit; C-1, 2 – separators;
K-1, 2 – rectification columns; P – furnace, M – mixer

The rate of the deposits formation on metal surfaces when the values of the temperature gradient are 20–45 $^{\circ}$C with the greatest certainty is described by the exponential kinetic equation, the numerical parameters of which depend on the ratio of the temperatures of oil, the tube and oil pour point.

It is shown that when the deposit layer thickness is 1 mm the temperature gradient decreases, causing reduction of the rate of deposit accumulation by 2,5–3 times compared with the clean tube.

The ability of an additive PPVO made from oils of vegetable origin to the increase of the petroleum stability factor from 0.34 to 0.692 has been demonstrated.

The optimal concentration of PPVO was 0.09 % v/v.

The stabilizing action mechanism of the additive, which consists in the adsorption of theadditive's polar parts on the paraffin surface with the simultaneous formation of nonpolar alkyl chains, which are guided in the dispersion medium and thus create repulsion forces between the aggregates, is established.

Analysis of IR spectra of experimental samples showed that the use of plant additives and industrial additives and their effects are not accompanied by chemical interaction with the oil dispersed medium.

It was developed the basis of the process of tar visbreaking with asphalt-resin-paraffin deposits, which are partly waste product, into the fuel fractions.

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

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

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

РЕФЕРАТ

Олена Тертишна, Костянтин Замікула, Олег Тертишний
Український державний хіміко-технологічний університет, t_elena2000@bigmir.net

ПРОБЛЕМИ ФОРМУВАННЯ АСФАЛЬТО-СМОЛО-ПАРАФІНОВИХ ВІДКЛАДЕНЬ. ЗАПОБІГАННЯ ТА УТИЛІЗАЦІЯ

Утворення і накопичення асфальто-смоло-парафінових відкладень (АСПВ) призводить до зменшення пропускної здатності трубопроводів, скорочує корисну ємність резервуарів, знижує ефективність роботи теплообмінної апаратури.

Актуальним завданням є вивчення процесу утворення АСПВ для подальшої розробки методів зниження їх кількості та шляхів переробки органічної частини АСПВ.

Об'єкт дослідження – нафта, присадки різних типів, гудрон та відклади донного накопичення резервуару зберігання нафти.

Мета роботи – встановлення кінетичних параметрів процесу формування АСПВ залежно від температури середовища і її хімічного складу, вивчення впливу присадок на дисперсні характеристики нафти, розробка ефективної технології вісбрекінгу із залученням до сировини АСПВ.

Ключові слова: асфальто-смоло-парафінові відклади, кінетика, присадка, вісбрекінг, утилізація.

РЕФЕРАТ

Елена Тертышная, Константин Замикула, Олег Тертышный
Украинский государственный химико-технологический университет, t_elena2000@bigmir.net

ПРОБЛЕМЫ ФОРМИРОВАНИЯ АСФАЛЬТО-СМОЛО-ПАРАФИНОВЫХ ОТЛОЖЕНИЙ. ПРЕДОТВРАЩЕНИЕ И УТИЛИЗАЦИЯ

Образование и накопление асфальто-смоло-парафиновых отложений (АСПО) приводит к уменьшению пропускной способности трубопроводов, сокращает полезную емкость резервуаров, снижает эффективность работы теплообменной аппаратуры.

Актуальной задачей является изучение процесса образования АСПО для дальнейшей разработки методов снижения их количества и путей переработки органической части АСПО.

Объекты исследования – нефть, присадки различных типов, гудрон и отложения донного накопления резервуара хранения нефти.

Цель работы – установление кинетических параметров процесса формирования АСПО в зависимости от температуры среды и ее химического состава, изучение влияния присадок на дисперсные характеристики нефти, разработка эффективной технологии висбрекинга с привлечением к сырью АСПО.

Ключевые слова: асфальто-смоло-парафиновые отложения, кинетика, присадка, висбрекинг, утилизация.

ABSTRACT

Olena Tertyshna, Kostiantyn Zamikula, Oleh Tertyshnyi
Ukrainian State University of Chemical Technology, t_elena2000@bigmir.net

THE PROBLEMS OF FORMATION OF ASPHALT-RESIN-PARAFFIN DEPOSITS. PREVENTION AND UTILIZATION

The formation and accumulation of asphalt-resin-paraffin deposits (ARPD) leads to pipelines capacity's reduction, reduces the useful capacity of tanks, reduces the heat exchange equipment efficiency.

The actual task is to study the process of ARPD formation for further development of methods for reducing their quantity and ways of processing the organic part of ARPD.

The objects of the study are oil, additives of various types, tar and bottom accumulation deposits of the oil storage tank.

The purpose of this work is to determine the kinetic parameters of the ARPD formation process depending on the medium temperature and its chemical composition, to study the additives effect on oil's disperse characteristics, to develop effective visbreaking technology using ARPD as a part of raw material.

Key words: asphalt-resin-paraffin deposits, kinetics, additive, visbreaking, utilization.

REFERENCES

1. *Tumanyan B.P*. Scientific and applied aspects of the theory of oil disperse systems / B.P. Tumanyan. – M .: Technika, 2000. – 333 p.

2. *Bansal R*. Dynamic simulation for optimising pigging frequency for dewaxing / R. Bansal, B. Ravishankar, S. Sharma, K. Afzal // SPE Oil and Gas India Conference and Exhibition. – March 2012. – P.28–30.

3. *Botne K. K*. Modelling wax deposition with deposition–release models / K. K. Botne. – NTU, Norwegian University of Science and Technology, Trondheim, December 2011. – 33 p.

4. *Gilyazetdinov L. P*. et al. The effect of soot vibration milling on the rheological and optical properties of printing inks. Dep. in VINITI number 1460–76 dep. 17.

5. *Kirichenko V. I*. Chemical and technological aspects of complex processing of technical vegetable oils new environmentally friendly products / V.I. Kirichenko // Questions of chemistry and chemical technology. – 2008. – № 1. – P. 141–144.

6. *Kirichenko V.I.* Composition materials from technical oils: nanotechnology effective effect / V.I. Kirichenko // Problems of Tribology. – 2012. – № 2. – P. 67–73.

7. Paraffin Inhibitor: Pachem–P–505 // PaChemTechSp. z o.o. ul. Ossowskiego 39 09–410 [Electronic reference]. – Access mode: Płockwww.pachemtech.eu.

8. *Sunyaev Z.I.* Oil dispersion systems / Z.I. Syunyaev, R.Z. Safiyev, R.Z. Syunyaev – M.: Khimiya, 1990. – 226 p.

9. The utilization of asphalt–resin–paraffin deposits as a component of raw material for visbreaking / [Olena Tertyshna, Kateryna Roienko, Vitalina Martynenko et al.]. // Chemistry and Chemical Technology. – 2016. – Vol. 10. – No. 3. – P. 361–366.

1.2 THE BIOMASS USE TO OBTAIN HIGH-PURITY CARBONACEOUS MATERIALS

Lina Kieush[1], Serhii Fedorov[1], Andrii Koveria[2], Artem Sybyr[1]

Among the renewable sources, biomass is a promising resource since it is abundant and is the neutral nature of carbon. The term of "biomass" embraces the biodegradable component of products, wastes and residues from agricultural sources (including vegetable substances and animal substances), forestry and the products of related industries, including fish and aquaculture, as well as biodegrading fractions of wastes, including industrial and municipal wastes of biological origin [1].

The biomass resource can be considered as an organic substance, in which the energy of sunlight is stored in chemical bonds. When the bonds between the elements adjacent to carbon, namely, hydrogen and oxygen molecules are broken, for instance, via combustion, these substances release their stored chemical energy. With regard to the European Biomass Association, AEBIOM (currently Europe Bioenergy[1]), bioenergy will show stable growth rates by 2020 (Fig. 1). According to the forecasts, the consumption of biomass for heating will increase to 90 ktoe. It is expected that receiving heat for heating will remain the leading issue on bioenergy market. Moreover, the usage of biomass will grow to about 20 ktoe in the industry of electricity generation and 29 ktoe for biofuels for transport.

The main goal of Bioenergy Europe is to develop a sustainable bioenergy market based on fair business conditions. Bioenergy Europe is a non-profit international organisation founded in Brussels in 1990, which brings together about 40 associations and 90 companies, as well as academic and research institutes from all over Europe. Bioenergy Europe is the main organisation, which also includes the European Pellet Council (EPC), the European Industry of Pellet Suppliers (EIPS) and the International Biomass Torrefaction Council (IBTC).