УДК 547.912.66

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КІНЕТИКА УТВОРЕННЯ АСФАЛЬТСМОЛОПАРАФІНОВИХ ВІДКЛАДІВ З НАФТИ

Дослідження кінетики формування асфальтосмолопарафінових відкладів (АСПВ) методом "холодного стрижня" показало, що як для парафіністої, так і для малопарафіністої нафти швидкість росту відкладень описується експоненціальним рівнянням, константи якого лінійно залежать від температурного фактора – співвідношення градієнта температур між нафтою і стрижнем і температурою застигання нафти. Розрахунковим шляхом встановлено вплив товщини шару АСПВ і режиму руху нафти на швидкість утворення АСПВ на холодній стінці.

Ключові слова: асфальтосмолопарафінові відклади, метод "холодного стрижня", кінетична модель, константи швидкості

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KINETICS OF FORMATION ASPHALT-RESIN-PARAFFIN DEPOSITS FROM OIL

Kinetics of the asphalt-resin-paraffin deposits formation was studied by the "coldfinger test" method. It was shown, that the rate of the deposits growth from both paraffin and non-paraffin oils is described by the exponential equation. Kinetic constants of these equations are linearly depending on the temperature factor, which is the ratio of temperature gradient between oil and the tube "coldfinger" to the oil pour point. The influence of deposit thickness and regime of oil movement on the rate of deposits growth was calculated.

Key words: asphalt-resin-paraffin deposits, "coldfinger test" method, kinetic model, rate constants.

Problem statement. 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 formation and accumulation of paraffins leads to a pipeline throughput reduction, reduces an actual reservoir capacity, brings down an efficiency of heat exchangers.

Analysis of recent researches and publications. 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^{0}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 [2].

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 [3]. 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 aim of the work was to determine quantitative kinetic parameters of the process of ARPD formation depending on the temperature of the medium and its chemical composition.

Presentation of basic material and discussion of results. 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.

Table 1

Oil characteristics

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

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 ^{0}C. The copper tube (“coldfinger”) with the surface of 744.45 mm^2 was cooled with running water to a temperature of 10 ^{0}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.

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.

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 of Heimdal field (Norway) [4].

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

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

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 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, ^{0}C	$\frac{dm}{d\tau} = k_{1\log} \cdot k_{2\log}^{-m}$		$\frac{dm}{d\tau} = k_{1\exp} - k_{2\exp} \cdot m$		T*,^{0}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:

$$T^* = \frac{T_c - T_w}{T_{oil}}, \qquad (3)$$

where Tc, Tw, Toil are the pour points of oil, of the tube surface and of the oil in the glass, respectively (^{0}C).

If taking into account that in the selected experimental conditions T_c, и 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 peptizator (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.

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 (Tabl 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*) и k_2=f(1/T*) for both models are linear and described by the equations given in Table 5.

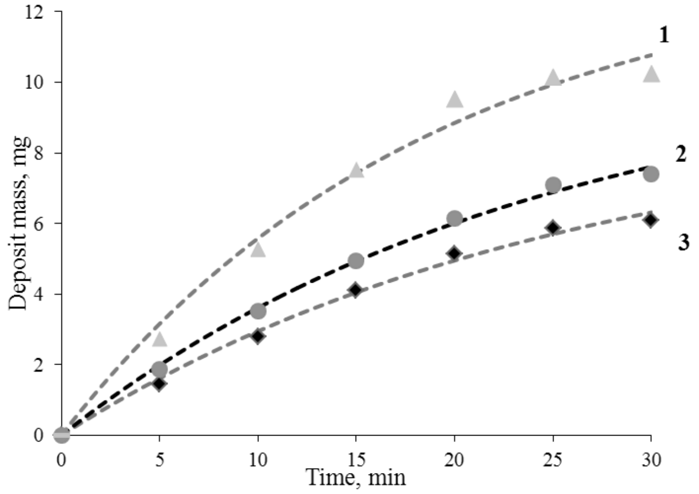

Fig. 1. Dynamics of ARPD accumulation from oil at the temperature difference between the oil and the surface of the tube, DT, °C: 1– 40; 2 – 30; 3 – 20. Points correspond to experimental data, dashed lines are the calculated curves according to the equations (1), (2).

Table 5

The relation of the rate constants with temperature parameter T*

Logarithmic model	Exponential model
k_{1log}=0,893T*+0,130	k_{1exp}=1,02T*+0,388
k_{2log}=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*:

$$\frac{dm}{d\tau} = 1{,}02T^* + 0{,}388 - 1{,}294 / T^* - 0{,}261 \cdot m\,. \tag{4}$$

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).

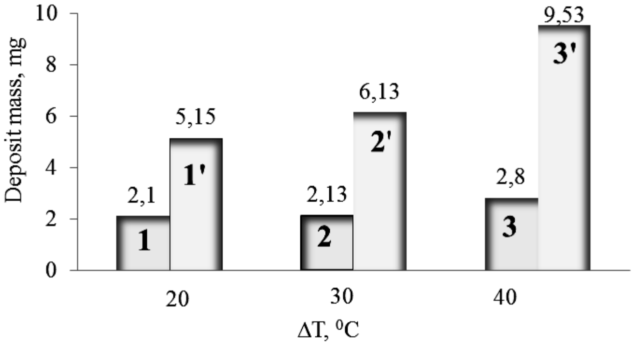

Fig. 2. The mass of the deposit formed at single (1, 2, 3) and cumulative (1', 2', 3') formation of the deposit (20 min) from oil depending on the temperature gradient of oil and the tube ΔT

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 [6, 7] 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 ^{0}C

Oil temperature, ^{0}C	Heat-transfer coefficient, W/m^2·К		Deposit layer thickness, м	Heat resistance of the deposit δ/λ, m^2·К/W	Heat-transfer coefficient К$_T$, W/m^2·К	Actual difference between oil and the tube, ^{0}C
	from the wall side, α_1	from oil, α_2				
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
Laminar regime + natural convection						
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.

Conclusions. The rate of the deposits formation on metal surfaces when the values of the temperature gradient are 20–45 ^{0}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.

1. Tumanyan B. P. Nauchnyie i prikladnyie aspektyi teorii neftyanyih dispersnyih sistem / B. P. Tumanyan. – M.: Tehnika, 2000. – 333 s. 2. Tronov V. P. Mehanizm obrazovaniya smolo-parafinovyih otlozheniy i borba s nimi / V. P. Tronov. – M.: Nedra, 1969. – 192 s. 3. Ovchar E. V. Ingibirovanie asflto-smolo-parafinovyih otlozheniy v neftyah: avtoref. dis. kand. him.nauk 02.00.13/ Ovchar Elena Vyacheslavovna, Rossiyskiy universitet nefti i gaza im. I. M. Gubkina. M. – 161 s. 4. Botne K. K. Modelling wax deposition with deposition-release models. NTU, Norwegian University of Science and Technology, Trondheim, December 2011. – 33 p. 5. Mohamadshahi N., Nazar A. R. S. Experimental evaluation of the inhibitors per-formance on the kinetics of asphaltene flocculation // Journal of Dispersion Science and Technology. – 2013. – Vol. 34. – P. 590–595. 6. Perri Dzh. Spravochnik inzhenera-himika. – T. 1. Per. s angl. – M.: Himiya, 1968. – 508 s. 7. Kasatkin A. G. Osnovnyie protsessyi i apparatyi himicheskoy tehnologii. – M.: Himiya, 1973. – 754 s.