Journal of Engineering Physics and Thermophysics, Vol. 77, No. 5, 2004

CHANGE IN THE RHEOLOGICAL PROPERTIES OF HIGH-PARAFFIN PETROLEUMS UNDER THE ACTION OF VIBROJET MAGNETIC ACTIVATION

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UDC 662.276.7

The influence of the method of vibrojet magnetic activation on the rheological properties of high-paraffin petroleums has been investigated. The maximum decrease in the rheological characteristics of the petroleums was obtained in 20-min vibrojet treatment. It has been noted that the maximum effect of vibroaction is observed for petroleums with a higher-than-average content of paraffins. The role of the magnetic component contributing to the decrease in the congelation point and the amount of the basic sediment in the petroleums under study has been shown.

At present there is a worldwide tendency toward increasing the fraction of viscous and high-congealing petroleums in the total volume of petroleum recovered. The rheological and hydrodynamic characteristics of such petroleums are significantly deteriorated with decrease in the temperature in the process of recovery, transportation, and storage, which results in the asphalt-resin-paraffin deposits (ARPDs) on the walls of technological equipment and, as a consequence, in considerable disruptions of technological processes. A distinctive feature of a petroleum disperse system is its tendency toward changing the degree of dispersion under the influence of external factors (temperature, pressure, chemical additions, and physical fields), since the structures formed in petroleum show thermodynamic instability under thermal and dynamic actions [1, 2].

It has been established that, varying the intensity of external mechanical actions, one can control the properties of structured systems of high-viscosity and high-paraffin petroleums in a wide range. The results of investigations of the surface phenomena and rheology of petroleum enable one to judge the change in the structural parameters of a petroleum system and the depth of the transformations in it [3].

One of the most efficient mechanical actions is vibration accelerating different processes. It increases mass and heat exchange, decreases mechanical resistance, accelerates chemical reactions, and enables one to attain very low values of the effective (structural) viscosity. Vibration technologies are widely used in the petroleum and chemical industries; their use enables one to attain the limiting level of destruction of the crystalline structure of paraffin hydrocarbons in a short time interval and to maintain this level over the period of time required for mass-exchange processes [4].

The method of vibrojet magnetic activation (VJMA) [5, 6] has found increasing use recently in the petroleum and petroleum refining industries in the preparation of high-viscosity petroleums for transportation, cleaning of bottom settings from tanks, and in the preparation of drilling muds, cement slurries, polymeric compositions, and water-oil emulsions. In the process of vibrojet treatment, petroleum or petroleum products are pumped through the air gap of an electromagnet and are simultaneously subjected to the action of an electromagnetic field, vibration, shear stresses, and periodic decompression. Vibrojet treatment destroys the colloidal petroleum structure existing in the petroleum disperse system, which leads to a significant change in the rheological properties of the petroleum.

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1062-0125/04/7705-1034

TABLE 1. Physicochemical Properties of Petroleums and Petroleum Products

Petroleum under study	ρ_{20}, kg/m^3	T_{con}, ^oC	Weight fraction in the petroleum, %, of		
			asphaltenes	resins	paraffins
Ostanino petroleum	867	–6.8	2.1	6.7	10.3
Tabagan petroleum	871	–1.5	2.3	8.8	13.2
Urman petroleum	872	–4.2	6.1	11.2	8.2

With account taken of the fact that VJMA has a complex action on the petroleum disperse system, it seems of interest to study the distinctive features of the rheological behavior of petroleums after vibrojet treatment in greater detail.

Experimental. We selected petroleums of three oil fields of the Tomsk Region — Ostanino, Tabagan, and Urman petroleums — as the objects of investigation. The petroleums are highly paraffinic (content of paraffins higher that 6%) and are characterized by a low density and a high congelation point (Table 1). The high viscosity-temperature characteristics of these petroleums are responsible for the problems arising in recovery, transportation, and storage under the conditions of low temperatures.

The petroleum samples under study were treated on a laboratory analog of a VSP-0.25 immersion jet vibrator of the GEOFIT Scientific-Production Company (Tomsk) at a commercial frequency of 50 Hz with vibroaccelerations to 100 g; the power consumption of the vibrator was 30 W [7].

The limiting strength of the magnetic field in the air gap of the VSP-0.25 is

$$H = WI/\delta_{min} = 1000 \cdot 2/1 \cdot 10^{-3} = 2 \cdot 10^6 \text{ A/m} .$$

In the course of the experiment, a sample of volume 250 ml was treated for 5–60 min. The rheological characteristics of petroleum before vibrojet treatment and after it were determined with a Reotest 2.1 rotational viscosimeter and capillary viscosimeters for 20 h. We calculated the values of the dynamic viscosity (η) for rates of shear of 3 to 80 sec^{-1} and the kinematic viscosity (ν) (in the experiments, the values of ν correspond to the values of η for rates of shear of 3–9 sec^{-1}). The wall effect of slip occurring between the walls of coaxial cylindrical meters of the S1 type was disregarded. The congelation point was determined according to the All-Union State Standard 20287-91. Sedimentation was evaluated quantitatively on a unit developed based on the "cold rod" method [8]. The influence of vibrojet treatment on the rheological properties of highly paraffinic petroleums was studied on the basis of three parallel experiments in comparison to the behavior of these petroleums under analogous conditions without treatment. The disagreements between successive measurements and arithmetic mean values do not exceed 4.3% for the dynamic viscosity and 2.1% for the kinematic viscosity, 2.5% for the congelation point of the petroleum, and 4.6% in determination of the amount of ARPDs.

Results and Discussion. The rheological dependences $\eta = f(\gamma)$ at 20^{o}C for the highly paraffinic petroleums under study are given in Fig. 1. The rate of shear impressively influences the fluidity of the petroleums, and they possess the properties of non-Newtonian fluids for rates of shear to 100 sec^{-1}. Physical action (VJMA in our case) on the structured petroleum system whose dispersed phase is presented by both the molecular crystals of petroleum paraffins and the associates of resin-asphaltene substances leads to the transformation of crystallization structures and associative formations and, as a consequence, to a strong change in the structural-rheological properties [9, 10]. The destruction of the paraffin structure in highly paraffinic petroleums under vibration action is due to the breaking of dispersion bonds. The vibration-treated petroleum shows Newtonian properties in the process of flowing, the rheological curve is partially rectified, and a substantial decrease in the values of the limiting shear stress and the effective viscosity is observed.

We studied the manner in which vibrojet treatment influences the viscosity of petroleum. The optimum time at which the maximum effect of decrease in the dynamic viscosity was obtained is equal to 20 min for all the petroleums under study. Thus, the values of the dynamic viscosity decreased 3.5 times for Ostanino petroleum and 2.5 times for Tabagan petroleum (Fig. 1a and b). For Urman petroleum, characterized by the minimum content of paraffin, the dynamic viscosity decreased 7.5 times after 20 min of vibrojet treatment (Fig. 1c). Further increase in the time of vibrojet treatment to 40 and 60 min substantially decreases its efficiency. This is probably due to the appearance of

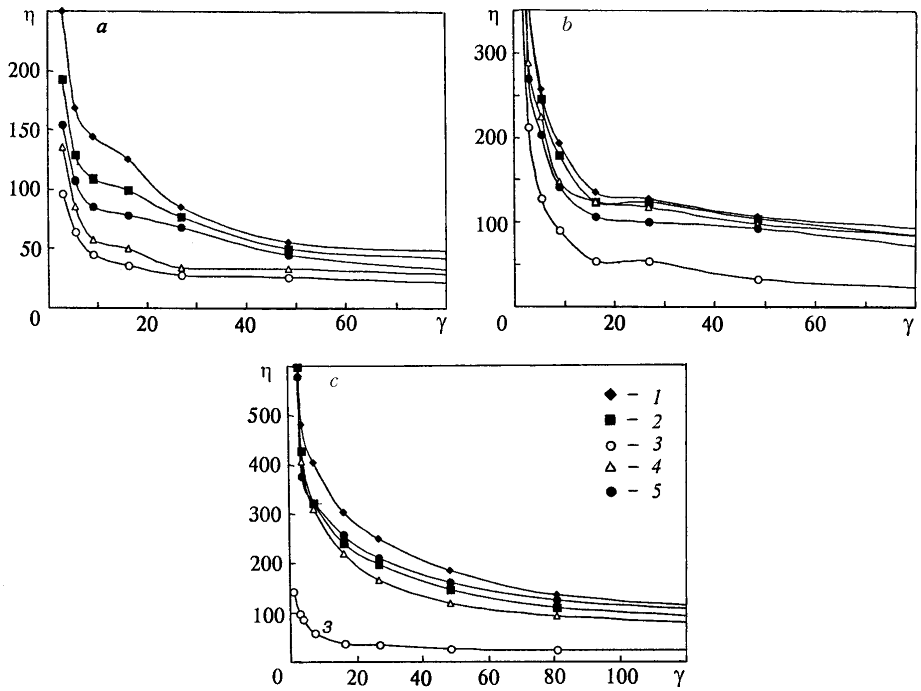

Fig. 1. Dynamic viscosity vs. rate of shear for Ostanino (a), Tabagan (b), and Urman (c) petroleums for vibrojet treatment times of: 1) 0; 2) 5; 3) 20; 4) 40; 5) 60 min. η, mPa·sec; γ, sec^{-1}.

both inertial (near) coagulation and the "effect of vibration strengthening of the structure", which is characterized by a sharp increase in the effective viscosity [11].

If we proceed from the colloidal-disperse structure of highly paraffinic petroleums, the relation of the components of the dispersed place (paraffins, resins, and asphaltenes) and the dispersion medium consisting of liquid-phase components (oils and low hydrocarbons) plays an important role in vibrojet treatment. In the initial period of vibrojet treatment, we have the destruction of the crystalline structure of paraffin and its transfer from the dispersed phase to the dispersion medium. The dissolution of paraffin is accompanied by a decrease in the petroleum viscosity. A 20-min vibrojet treatment corresponds to the optimum relation of the dispersed phase and the dispersion medium, i.e., to the minimum viscosity. With further increase in the time of vibration treatment, the solubility of paraffin in the dispersion medium sharply drops, which leads to a substantial growth in the viscosity.

The relaxation processes occurring in highly paraffinic petroleums are based on the phenomenon of thixotropy as the characteristic feature of structured media. Since the petroleum disperse system is thermodynamically mobile, the rheological properties of highly paraffinic petroleums are restored to their initial values within a certain time after the vibrojet treatment. Therefore, the relaxation time is an important factor from the practical viewpoint. The process of relaxation of the rheological processes was considered with the example of the time variation of the kinematic viscosity of the petroleums under study after a 20-min vibrojet treatment (Fig. 2). It was established that the relaxation time depends on the content of paraffins in the petroleum: for Tabagan petroleum with the largest amount of paraffins, we observe the restoration of the initial values of the dynamic viscosity after 8 h (curves 2 and 2^*). In the case of Ostanino petroleum the initial values are restored after 8 to 15 h (curves 1 and 1^*) and it takes a longer period of time — about 20 h — to completely restore the rheological parameters of Urman petroleum (curves 3 and 3^*).

Of particular importance in the case of vibration actions are resins and asphaltenes. They are natural surfactants and their presence in the petroleum disperse system leads to a significant reduction in the force of coagulation cohesion. Resin-asphaltene substances prevent the formation of a three-dimensional structural network, and the paraffin crystals remain in the mobile state in intermicellar form [12]. Noteworthy is the similarity between the rheological behavior of vibration-treated highly paraffinic petroleums and the rheological behavior of structured disperse systems in combined use of vibration action and surfactants. In this case resins and asphaltenes act as surfactants and perform the

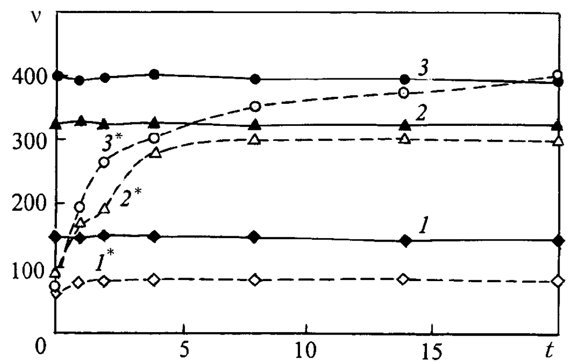

Fig. 2. Variation in the kinematic viscosity with time for Ostanino (1), Tabagan (2), and Urman (3) petroleums before and after (*) 20-min vibrojet treatment. ν, $mm^2 \cdot sec$; *t*, h.

function of a structural-mechanical barrier on the particle surface; they prevent the coagulation of the particles of the dispersed phase, increasing the depth and rate of structural destruction [11].

According to the literature data [13], vibration action leads to a substantial change in the petroleum viscosity but does not influence, in practice, the process of sedimentation and the congelation point. Magnetic treatment decreases the congelation point and the amount of the basic sediment formed in paraffinic petroleums [9, 14–16]. This is usually related to the influence of the magnetic field on resin-asphaltene substances which possess paramagnetic properties and are the most reactive part of petroleum [17]. Therefore, it is of great interest to consider the problem of influence of the VJMA method combining vibration and magnetic actions on the amount of ARPDs and the congelation point of highly paraffinic petroleums (Table 2).

It was established that the amount of the ARPD formed largely depends on the content of paraffins in the petroleums. Thus, the maximum amount of the basic sediment (14.4 g) was formed from Tabagan petroleum (wt. fraction of paraffins 13.2%). However, in addition to paraffins, the efficiency of vibrojet treatment is substantially influenced by the content of resin-asphaltene substances: we noted a decrease in the amount of the basic sediment after vibrojet treatment for 5 and 20 min only in the case of Ostanino and Tabagan petroleums (resin-asphaltene substances/paraffins = 0.86 and 0.84 rel. units respectively). A substantial increase in the amount of ARPDs (of 2.5 times after 5 min of vibrojet treatment) is observed in vibrojet treatment of Urman petroleum (RASs/paraffins = 2.1 rel. units). This is attributable to the fact that this petroleum is characterized by a high content of asphaltenes possessing significant paramagnetic and adhesive properties [18]. Further increase in the time of vibrojet treatment to 40–60 min leads to an increase in the mass of the sediment formed in Ostanino and Tabagan petroleums but in the case of Urman petroleum, conversely, the amount of the ARPD gradually decreases.

An increase in the vibration-treatment time from 5 to 60 min leads to a gradual decrease in the congelation point T_{con}: from 2.4°C after 5 min of vibrojet treatment to 13°C after 60 min of vibrojet treatment for Ostanino petroleum and from 2.8 to 8.7°C for Tabagan petroleum. The maximum decrease in the congelation point is noted for Urman petroleum — from 10°C after 5 min of vibrojet treatment to 17.1°C after 60 min of vibrojet treatment.

Thus, the efficiency of the VJMA method largely depends on both the selection of the optimum parameters of vibrojet treatment for which the maximum improvement in the rheological properties — decrease in the viscosity, the congelation point, and the amount of the basic sediment formed — of highly paraffinic petroleums is attained and the distinctive features of the group composition of petroleums — the content of paraffins, resins, and asphaltenes.

CONCLUSIONS

1. The complex action of the VJMA method combining vibration and magnetic components produces the deepest and most varied change in the rheological characteristics of highly paraffinic petroleums. The vibration component decreases 2 to 7 times the dynamic viscosity of highly paraffinic petroleums; a substantial decrease in the amount of the basic sediment and a reduction in the congelation point are observed.

TABLE 2. Influence of the Time of Vibrojet Treatment on the Amount of Asphalt-Resin-Paraffin Deposits and the Congelation Point of Petroleums

Vibrojet-treatment time, min	Amount of ARPDs, g/100 g of petroleum	T_{con}, °C
	Ostanino petroleum	
0	8.0	–6.8
5	6.2	–9.2
20	6.5	–13.8
40	8.3	–17.5
60	9.7	–19.8
	Tabagan petroleum	
0	14.4	–1.5
5		–4.3
20	9.5	–5.0
40	12.2	–5.8
60	18.2	–10.2
	24.7	
	Urman petroleum	
0	9.0	–4.2
5	22.8	–14.2
20	17.8	–15.1
40	16.2	–16.2
60	14.5	–21.3

2. Highly paraffinic petroleums characterized by a higher-than-average content of crystalline paraffin are highly structured colloidal-disperse systems composed of reactive natural surfactants — resins and asphaltenes. The complex composition of the petroleums as the object of investigation and the use of the complex method of action make it impossible to clearly formulate a unified approach to the description of the mechanism of action of vibrojet treatment on petroleums. But the laboratory investigations carried out can be used for prediction of the behavior of petroleums with a certain content of paraffins and resin-asphaltene substances in recovery, transportation, and storage.

NOTATION

g, free fall acceleration, m/sec^2; H, limiting strength of the magnetic field, A/m; I, electromagnet-coil current, A; T_{con}, congelation point of petroleum, °C; t, time, h; W, number of turns in the electromagnet coil; γ, rate of shear, sec^{-1}; δ_{min}, minimum gap of the electromagnet, m; ρ_{20}, density of petroleum at 20°C, kg/m^3; η, dynamic viscosity, mPa·sec; ν, kinematic viscosity, mm^2/sec. Subscripts: con, congelation; min, minimum.

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