

STRUCTURING FEATURES OF NON-NEWTONIAN OILS

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ABSTRACT

The rheology problems of non-Newtonian oil, accompanied by the physical phenomena of formation and destruction of coagulation structures and aggregates, significantly affecting the flow are considered and analyzed. Also are considered issues of hydrodynamic interaction of particles leading to the formation of disordered structures, which significantly change the rheological properties of non-Newtonian oil. It has been noted that the formation of coagulation structures depends on energy dissipation, viscosity, stress or shear rate, and the size of the particles forming the structure. With increasing asphalt-resin content in the oil, the probability of particle collision increases, increasing the rate of formation of various disordered structures up to a framework that nullifies the rate of oil flow. Non-Newtonian oils are characterized by a fairly high content of asphalt-resinous substances and paraffinic compounds that are prone to coagulation structures and aggregates. This factor significantly affects the rheological properties of the oil, primarily its effective viscosity and diffusion, making its transport and storage difficult.

Keywords: rheology, non-Newtonian oil, coagulation structures, models, asphalt-resinous substances, kinetics, technology.

Introduction

The world has huge reserves of heavy oils that show non-Newtonian properties, and their use is limited by a lack of efficient extraction, transport, and refining technologies.

Non-Newtonian oils are characterized by a fairly high content of asphalt-resinous substances and paraffinic compounds that are prone to coagulation structures and aggregates. This factor significantly affects the rheological properties of the oil, primarily its effective viscosity and diffusion, making its transport and storage difficult. At the same time, there are many methods of improving the rheological properties of oils required in the production, transportation, and refining of the latter. They are associated with improving temperature conditions, as well as creating efficient technologies using various chemical reagents that reduce the surface tension and viscosity of rheological fluids and many other factors that enable intensification of the extraction, transport, and refining processes. The flow of highly viscous fluids and dispersed systems with a high content of dispersed particles is characterized by certain complexities, mainly related to the non-linearity of the disordered structure and the properties of the carrier phase. Accordingly, the rheology of such systems, at present, can be classified as:

- the rheology of highly viscous systems (oils, greases, gels, oils, heavy refinery

fractions, etc.) which do not obey Newtonian fluid flow laws [1-4] $\tau = -\eta \partial U / \partial x$

- the rheology of dispersed systems (oil suspensions and emulsions) is characterized by the formation and collapse of coagulation structures due to the hydrodynamic interaction of different particles, whereby the rheological flow properties depend on particle content and properties as well as on shear stress and elasticity limit [5-7]
- a special class of problems related to the rheology of non-Newtonian oils or oil

Dispersion systems containing, in addition to solid-phase particles, liquid water droplets and gas bubbles, asphaltenes, resins, and, at low temperatures, paraffin particles dissolved in oil [8-10]. The presence of this spectrum of particles of various varieties and nature leads to the formation of highly complex coagulation structures, subsequently transforming into aggregates, clusters of aggregates, up to the formation of a viscoelastic framework [6, 11-13].

Formation of disordered coagulation structures and aggregates in oils

The flow of oil disperse systems is accompanied by various physical phenomena of hydrodynamic interaction, and collision, resulting in the formation of coagulation structures and aggregates, in which energy dissipation plays an important role. Hydrodynamic interaction of particles among themselves is observed at their high concentrations when the distance between the particles allows them to collide:

$l \approx 80a^3 \sqrt{\rho_d / C_m}$ The probability of a particle collision is determined by many factors: the number of particles themselves per unit volume, their shape and properties, the properties of the medium, the flow velocity, and temperature, on which important parameters such as diffusion coefficient and viscosity depend. In viscous fluid flow, the dissipative function is determined as

$$\varphi_D = 2\eta_C \left(\frac{\partial V_x}{\partial x} \right) + 2\eta_C \left(\frac{\partial V_y}{\partial y} \right)^2 + \eta_C \left(\frac{\partial V_x}{\partial y} + \frac{\partial V_y}{\partial x} \right)^2 \quad (1)$$

The energy dissipated in the volume of the liquid is expressed by the formula

$$-\frac{dE}{dt} = \int \frac{\eta_C}{2} \left(\frac{\partial V_1}{\partial x_1} + \frac{\partial V_k}{\partial x_i} \right)^2 dv \quad (2)$$

Energy dissipation per unit mass of flow is defined as follows

$$\varepsilon_R = -\frac{dE}{dt dm} = \frac{\eta_C}{2} \left(\frac{\partial V_1}{\partial x_r} + \frac{\partial V_k}{\partial x_i} \right)^2 \quad (3)$$

where

$$d_m = \rho_c dv$$

For non-Newtonian oils, expression (Eq. (3)) will be written as

$$\varepsilon_R = -\frac{dE}{dt dm} = k_0 \left(\frac{\partial V_1}{\partial x_r} + \frac{\partial V_k}{\partial x_i} \right)^{n+1} \quad (4)$$

where $k_0 = \frac{n_c}{2} \left(\frac{\partial V}{\partial y} \right)^{n-1}$ - consistency coefficient. In the one-dimensional case for

viscoplastic oil flow, by applying expression (Eq. (4)), we have

$$\varepsilon_R = k_0 \dot{\gamma}^{n+1} \quad (5)$$

Coagulation structures are formed by *intermolecular* bonds between the particles, moreover, if liquid interlayers remain between the particles, then the thickness of these interlayers significantly affects the strength of the coagulation structure. Aggregate-unstable oil systems are characterized by the inconstancy of the medium due to continuous structuring and changes in the physical properties of the particles, i.e., changes in volume and size of asphaltene particles caused by their interaction, collision, coagulation, and crushing at a certain concentration in an enclosed volume [14].

Connection between the Structure and Viscosity of Oil Dispersal Systems

The connection between the structure and viscosity of oil dispersal systems as well as the features of their non-Newtonian flow is explained by a change in structure resulting from the emergence and collapse of aggregates from asphaltene particles in the presence of resins. Oil-structured systems containing high molecular paraffin crystals, resins, and asphaltene particles at very low laminar flow velocities or in the absence of flow form a chain or in the extreme case a continuous grid (frame) between itself and the structure of the porous medium. shows the formation of a framework of asphaltene particles contained in oil [5, 9].

In [15] it is noted that real oil disperse systems are classified by activation energies into two structural groups differing by the nature of intermolecular interaction of particles in an oil disperse medium. These groups are distinguished from each other by their asphaltene and resin content and, they can be classified into immobile with low asphaltene content, and, interacting with high asphaltene content. **Figure 2** illustrates the characteristic changes in activation energies for the two groups.

A large amount of asphalt-resin substances in the oil reduces the activation energy and creates more favorable conditions for the formation of coagulation structures. The change in mass of non-deformable nano aggregates is defined as

$$\frac{dm}{dt} = (m_\infty - m)\omega \quad (6)$$
$$t = 0, m = m_0$$

where ω is the frequency of particle collision.

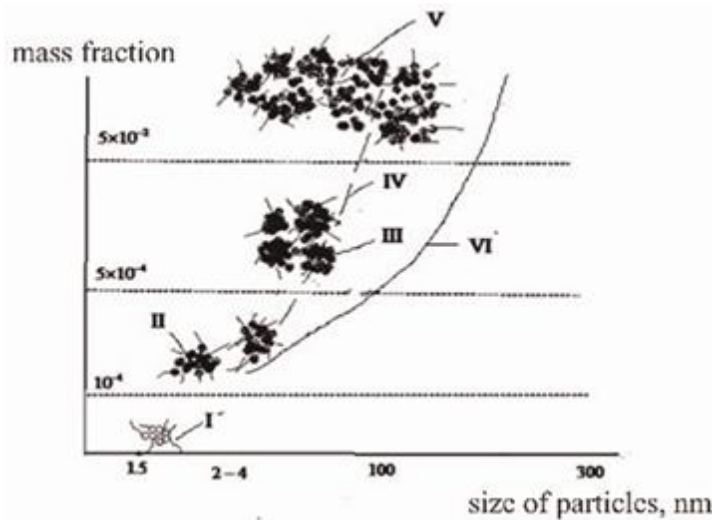


Figure 1.

Asphaltene particle aggregation in oils: I- single molecules and particles; II- nanoaggregates; III- clusters of nanoaggregates; IV- unstable suspension; V- viscoelastic framework; VI- stable emulsion with toluene.

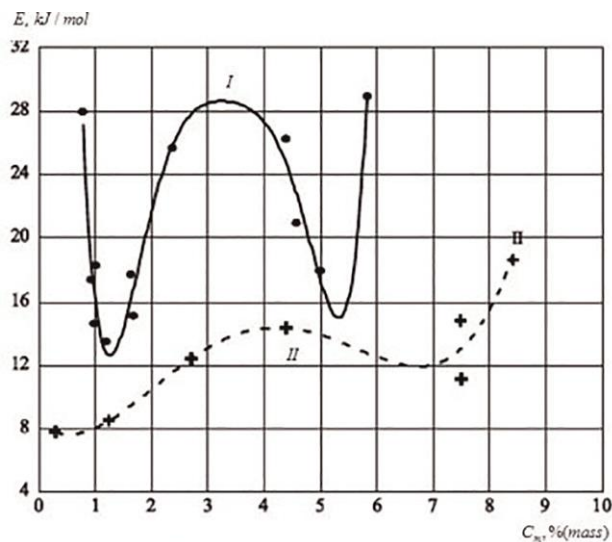


Figure 2.

Dependence of activation energy on asphaltene content for the stationary group (I) and the interacting group (II).

The solution to this equation will be represented as

If assume $m = m_{\infty} - (m_0 - m_{\infty}) \exp(-\omega t)$ (7) that $m_{\infty} > m_0$, we will get

$$m = m_{\infty} [1 - \exp(-\omega t)] \quad (8)$$

where m_{∞} is the limiting steady mass of the aggregate, m_0 - is the initial mass of the aggregate.

Assuming the spherical shape of nano aggregates and imagine that, the size of the $m = \frac{\pi}{6} \alpha^3 \rho$ nano-aggregates, will be defined in the following form, considering (Eq. (7)),

$$a_g = a_{g\infty} \left[1 - \exp \left(-C_0 \phi_0 \left(\frac{\varepsilon_R}{\nu_c} \right)^{1/2} t \right) \right]^{1/3} \quad (9)$$

For laminar flow, the formation of aggregates is expressed by an equation of the form.

$$\alpha_g = \alpha_{g\infty} [1 - \exp(-8\pi DN_0 \alpha_0 t)] \quad (10)$$

According to **Figure 3**, the size of the nano-aggregates fluctuates in range and the maximum size of the framework is limited by the presence of pore or tube walls. The frequency of collisions between asphaltenes increases as the rises of volume fraction of asphaltene particles. The relaxation time for turbulent flow is defined by the expression $\tau_R = (\nu_c / \varepsilon_R)^{1/2}$ and for laminar flow $\tau_R = 3\nu_c / (8kTN_0)$, which leads to a rapid reaching of the final aggregate size. With increasing oil viscosity, for both laminar and turbulent flows, the collision frequency of asphaltene particles decreases, which inhibits the rate of nanoaggregate formation.

Maxwell's rheological equation for a viscoelastic fluid in substantive derivatives is written as [3]

$$\lambda \left(\frac{\sigma\tau}{\sigma t} + U \frac{\sigma\tau}{\sigma y} \right) + \tau = \eta_c \dot{\gamma} \quad (11)$$

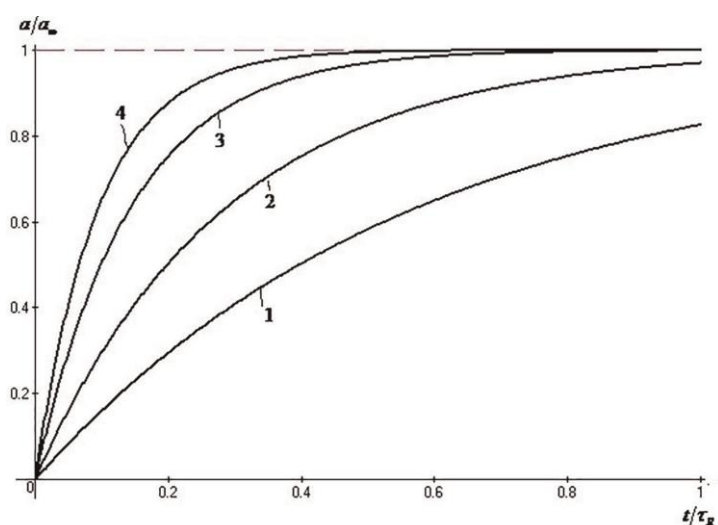


Figure 3.

Variation of nano-aggregate size over time depending on the content of asphaltene particles in

the oil: 1 — $\varphi = 0.05$; 2 — 0,1; 3 — 0.2; 4 — 0.3...

A special form of equation (Eq. (11)), is given in the following form

$$\lambda \left(\frac{\partial \tau}{\partial t} + U \frac{\partial \tau}{\partial y} \right) + \tau = 0 \quad (12)$$

The solution of Eq. (12) can be represented as

$$\tau = C_1 f(y - Ut) \exp(-\tau/\lambda) \quad (13)$$

Substituting this solution into (Eq. (13)) we obtain the identity. Here $\lambda = \eta_c / G$ - is the relaxation time by Maxwell, U - is the rate of displacement of the deformation front, $f(y - Ut)$ - is the function defining the deformation displacement front in the framework, y - is the coordinate, G - is the modulus of shear elasticity, $\dot{\gamma} = d\gamma / dt$ - is the rate of shift, τ_0 - is the ultimate shift stress or the yield stress.

Moreover, if $\tau \leq \tau_0$, then $\dot{\gamma} = 0$. The complete solution of equation (Eq. (13)) will be

$$\tau = C_1 f(y - Ut) \exp(-\tau/\lambda) \tau_0 \quad (14)$$

Otherwise, the equation can be represented in logarithmic form

$$\ln \tau = \ln \tau_0 - t/\lambda + \ln (C_1 f(y - Ut)), \tau_0 = \eta_c \dot{\gamma} \quad (15)$$

The value t/λ in equation (Eq. (15)) characterizes the deformation of the viscoelastic framework in time and depends on the velocity or pressure gradient. In approximation, this dependence can be presented as the Weissenberg number.

$$t/\lambda = t \dot{\gamma} / We f \left[\left(\text{grad} P / (\text{grad} P)_0 \right)^n \right], (\text{where } We = \lambda \dot{\gamma})$$

As can be seen from above mentioned, the reduction in asphalt-resin content while dissolving them in aromatic hydrocarbons inhibits the formation of various disordered structures.

Results

The problems of the rheology of non-Newtonian oil, accompanied by physical phenomena of formation and destruction of coagulation structures and aggregates, significantly affecting the flow have been considered and analyzed. The issues of hydrodynamic interaction of particles lead to the formation of disordered structures that significantly change the rheological properties of

non-Newtonian oil.

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Nomenclature:

τ - shear stress, τ_0 - yield strength, U - the average flow velocity, η - dynamic viscosity, α - particle diameter, ρ_c, ρ_d - are density of the medium and particles, C - concentration, η_c, η_d - dynamic viscosity of the medium, D_T - coefficient of turbulent diffusion of a liquid, m - mass of substance, ε_R - specific energy dissipation per unit mass, R - radius of the particle, t - time, T - temperature, λ - the scale of turbulent pulsations, ν_c, ν_d - kinematic viscosity of the medium and particles, τ_p - relaxation time, ω - frequency of turbulent coalescence. v_1 - is the pulsating velocity of the turbulent flow, v_k - is the rate of gravitational sedimentation of particles,

C_m – concentration, E – flow’s energy, x and y – coordinates, n – is an indicator of the degree of non-Newtonian fluids, n_c – is agitator velocity, $\dot{\gamma}$ – ratio of dynamic viscosity of particles to the viscosity of the medium, $a_g, a_{g\infty}$ – current and maximum size of aggregate, C_0 – initial concentration, φ_0 – is the volume fraction of particles in, N_0 – initial number of droplets per unit volume, a_0 – initial size of the particles, τ_R – is relaxation time, k – permeability coefficient, C_1 – is drag coefficient of particle, P – pressure, ρ_c, ρ_d – are density of the medium and particles.

ОСОБЕННОСТИ СТРУКТУРЫ НЕНЬЮТОНОВСКИХ НЕФТЕЙ

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АБСТРАКТ

Рассмотрены и проанализированы проблемы реологии неньютоновской нефти, сопровождающиеся физическими явлениями образования и разрушения коагуляционных структур и агрегатов, существенно влияющими на течение. Также рассмотрены вопросы гидродинамического взаимодействия частиц, приводящие к образованию неупорядоченных структур, существенно изменяющих реологические свойства неньютоновской нефти. Отмечено, что образование коагуляционных структур зависит от диссипации энергии, вязкости, напряжения или скорости сдвига, а также размера частиц, образующих структуру. С увеличением содержания асфальтосмол в нефти увеличивается вероятность столкновения частиц, увеличивая скорость образования различных неупорядоченных структур вплоть до каркаса, сводящего на нет скорость течения нефти. Неньютоновские нефти характеризуются достаточно высоким содержанием асфальтосмолистых веществ и парафиновых соединений, склонных к коагуляции структур и агрегатов. Этот фактор существенно влияет на реологические свойства нефти, в первую очередь на ее эффективную вязкость и диффузию, затрудняя ее транспортировку и хранение.

Ключевые слова: реология, неньютоновская нефть, коагуляционные структуры, модели, асфальтосмолистые вещества, кинетика, технология

QEYRİ NYUTON NEFTİNİN QURULUŞUNUN XÜSUSİYYƏTLƏRİ

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XÜLASƏ

Axına əhəmiyyətli dərəcədə təsir edən koaqulyasiya quruluşlarının və aqreqatların əmələ gəlməsi və parçalanma kimi fiziki hadisələri ilə müşayiət olunan qeyri-nyuton neftlərin reologiyasının problemləri nəzərdən keçirilir və təhlil edilir. Qeyri-nyuton neftinin reoloji xassələrini əhəmiyyətli dərəcədə dəyişən nizamsız quruluşların əmələ gəlməsinə səbəb olan hissəciklərin hidrodinamik

qarşılıqlı təsiri məsələlərinə də baxılır. Qeyd edilir ki, koaqulyasiya quruluşların formalaşması enerjinin yayılmasından, özlülükdən, gərginlikdən və ya sürüşmə sürətindən, həmçinin quruluşu əmələ gətirən hissəciklərin ölçüsündən asılıdır. Neftdə asfalten qatranlarının miqdarının artması ilə hissəciklərin toqquşma ehtimalı artır, müxtəlif nizamsız quruluşların əmələ gəlmə sürətini karkasa qədər artırır ki, bu da neft axınının sürətini sifirə endirir. Qeyri-Nyuton neftinin konstruksiyaların və aqreqatların koaqulyasiya meyilli olan asfalt-qatranlı maddələrin və parafin birləşmələrinin kifayət qədər yüksək tərkibi ilə xarakterizə olunur. Bu amil neftin reoloji xassələrinə, ilk növbədə onun effektiv özlülüyünə və diffuziyasına əhəmiyyətli dərəcədə təsir edir, onun daşınmasını və saxlanmasını çətinləşdirir.

Açar sözlər: reologiya, qeyri-nyuton nefti, koaqulyasiya quruluşlar, modellər, asfalt-qatran maddələri, kinetika, texnologiya

