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THE INFLUENCE OF AN ADDITIVE OF VEGETABLE ORIGIN ON THE AGGREGATIVE STABILITY OF PETROLEUM

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Abstract

The results of a study of the influence of vegetable origin additives on the aggregative stability of petroleum disperse systems, which is dependent on asphaltenes, are set out. The inhibitory action of the additives, synthesized in laboratory conditions from rapeseed and castor oil processing products, was compared with industrial additives. The average diameter of dispersed phase particles and the stability factor of the system were determined. The precipitation process was accelerated by centrifugation. Comparison of the average diameter of the particles in the upper and lower layers of the centrifugate showed a significant decrease in their difference when using vegetable origin additives. The best result was obtained with 0.09% additives. The effectiveness of their action corresponds to the results of tested industrial additives. The analysis of IR spectra and spectral coefficients allowed us to interpret changes in the functional groups of petroleum which occur in the presence of synthesized vegetable origin additives as well as industrial additives.

Keywords:

Petroleum;
Vegetable oil;
Additive;
Inhibitor;
Stability;
IR spectrum.

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Introduction

The purpose of the work was to study the influence of additives of various origins on the dispersion characteristics and the asphaltene/resin aggregative stability of petroleum by using optical methods. Petroleum is a disperse system inclined to instability under certain conditions [1]. The aggregative stability of petroleum dispersed systems is the ability of the system to maintain an even distribution of the disperse phase particles in the volume of the system for a certain time. And it is important in transportation, processing, storage and application of petroleum systems.

The disperse particles in petroleum consist of a core, which is formed from molecules of asphaltenes with a high C:H ratio, and solvated shells of resinous substances and polycyclic aromatic compounds [2]. The dispersion medium is liquid hydrocarbons including paraffins. Such systems are thermodynamically unstable and tend to separation (into layers) owing to coagulation of the disperse particles and further sedimentation. It occurs slowly even under normal conditions and intensifies when conditions for coagulation are favourable. Sediments are called heavy oil deposits or asphaltene sediments (hereinafter referred to as

«AS») and contain resinous substances and paraffin wax besides asphaltenes.

Dispersants (nonpolymeric surfactants) and inhibitors (polymer (resin) surfactants) are used to improve the stability of petroleum [3]. Inhibitors increase the stability of dispersed system and dispersants decrease the particle size. Polymeric surfactant inhibitors can act as dispersant. Conventionally, the following synthetic surfactants are used: polyisobutylene succinimides, alkylphenols, ethoxylated nonylphenols, alkylbenzenesulfonic acids, fatty acids and amines, polyether, and various commercial mixtures [4-6].

Vegetable oils have been used as asphaltene precipitation inhibitors [7, 8]. They are economically acceptable and environmentally friendly.

We suggest addition of inexpensive and nontoxic by-products of the production of biodiesel fuel components for the stabilization of petroleum disperse systems. The additive was synthesized from the product of processing of vegetable oils (hereinafter «PPVO») and first used for the improvement of oil tribological properties [9-11].

The subjects of the study were pure petroleum and the petroleum with additives of various types: PPVO and industrial wax inhibitors.

PPVO was synthesized in the laboratory according to a chemical modification technique by glycerolysis of rapeseed and castor oil with composition (% by

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Characteristic	Value
Density, kg/m ³	843
Viscosity, mm ² /sec (cSt)	8.4830
Pour point, °C	-8
Asphaltenes (A), % w/w	1.0
Paraffins (P), % w/w	8.16
Resins (R), % w/w	7.2

weight): rapeseed - 75-80% and castor – the rest: CH₃-(CH₂)₅₋₁₂CH(OH)-CH₂-CH=CH-(CH₂)₇-O-CH₂-CH(OH)-CH₂-O-C(O)R',R'', where R, R', R'' are C₁₇H₃₃; C₁₇H₃₁; C₁₇H₂₉ groups in any combination. Industrial additives were commercial inhibitors Pachem P-501; Pachem-P-505; Pachem PS-603/X [12].

The main characteristics of the petroleum are given in table 1.

Research technique

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 influence of the additives on the petroleum stability was estimated by measuring the change in the average diameter of particles of the dispersed phase using a KFK-3 photocolimeter at the wavelength of 680 nm by measuring the optical density of a 1:1 mixture of petroleum and toluene with PPVO.

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

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

where ρ is the density of the dispersed phase particles, $\rho = 1.2$ g/cm³ [13]; S is the specific interphase surface, m²/g, which was calculated by the equation:

$$S = 8.08 \cdot 10^3 \cdot \frac{\lg D_{\lambda_1} - \lg D_{\lambda_2}}{\lambda_1 - \lambda_2}$$

where D_{λ_1} and D_{λ_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 into two layers, separated from each other at a certain distance in the direction of the deposition forces [14]. They are called upper and lower layer below indicating the sampling zone but not the deposit presence.

The stability factor was calculated by the formula:

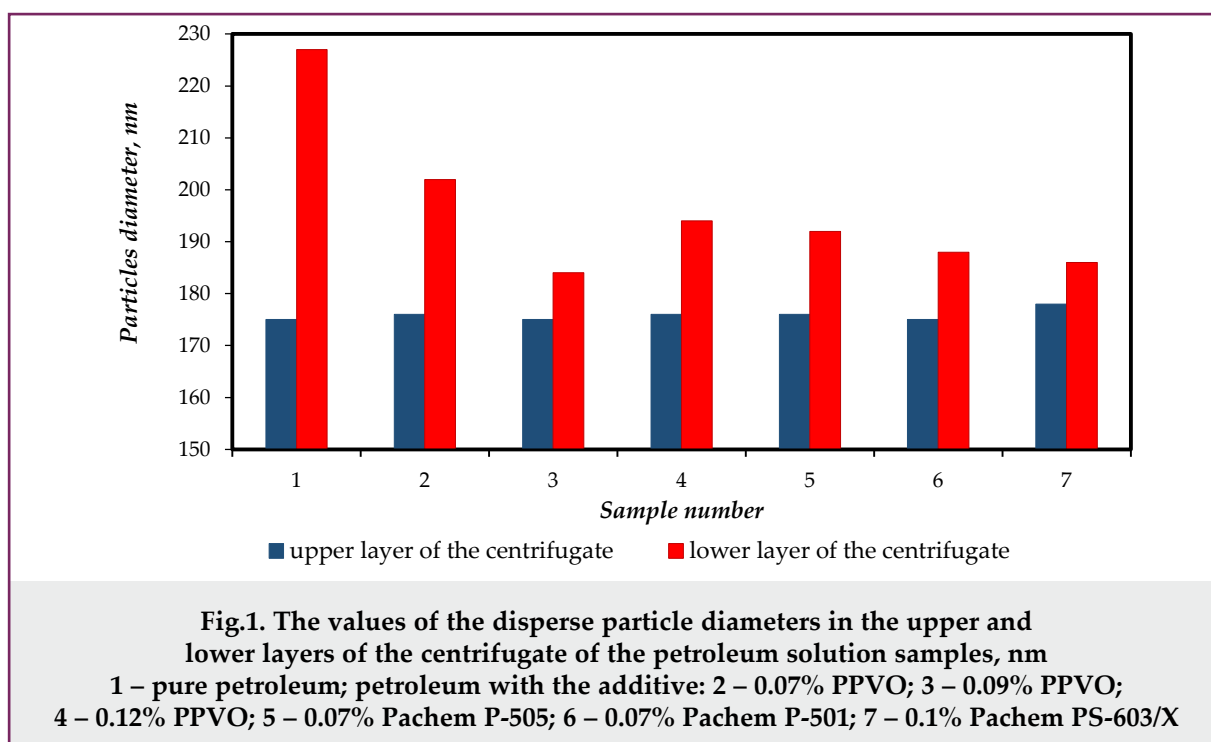
$$F = D_1/D_2$$

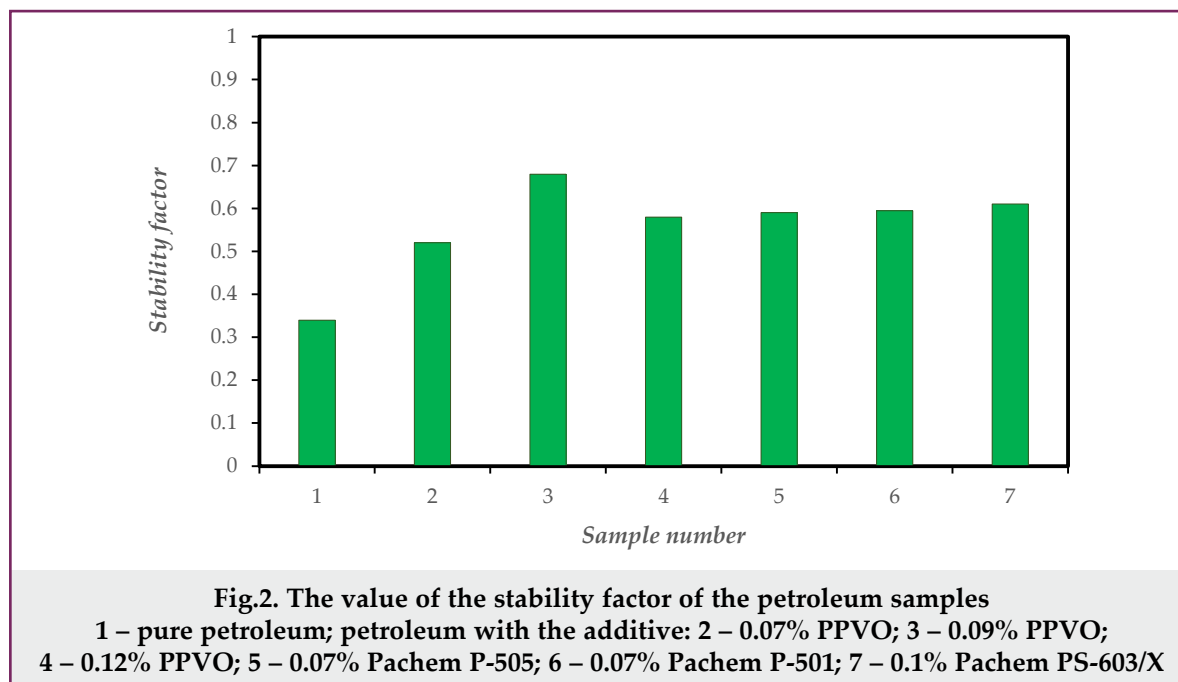
where D_1 , D_2 are the optical densities of the upper and lower layers, respectively, at a wavelength of 680 nm.

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 [15].

Results and discussion

The effectiveness of the additive action on the aggregative stability of the petroleum is presented in figures 1, 2.





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.1) 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 was more than 225 nm. When using the additives, the difference in diameters in the upper and lower layers was insignificant and the lowest value was 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.

IR spectral analysis of the petroleum sample (fig.3a) showed the presence of paraffin structures of normal and iso-structure, the presence of long paraffin chains (with absorption bands at 1462, 1377, 727 cm^{-1}). The presence of aromatic structures (absorption bands at 1605, 1032, 810, 873 cm^{-1}) was noted. The absorption bands at 742, 810, 873, 1032 cm^{-1} indicate the presence of condensed bi-, tri-, and polycyclic aromatic structures in the petroleum. Carbonyl groups C-O were absent, indicating that the petroleum was not oxidized. Sulfoxide groups (SO) were present as shown by the absorption band at 1030 cm^{-1} . A strong peak was observed in the region of 2850-2950 cm^{-1} , which indicates the presence of aliphatic CH bonds.

In the IR spectrum of the PPVO (fig. 3b) the peak at about 1750 cm^{-1} is related to valence vibrations of carbonyl groups of aliphatic carboxylic acid esters. The vibrations of the C-O-C groups in the region of 1300 – 1000 cm^{-1} confirm the presence of esters. The peak at 3474 cm^{-1} is related to glyceride OH groups.

In the petroleum sample with PPVO additive no

new chemical compounds were found. It is clear from infrared spectrum (fig.3c) that this sample is just the mixture of the above mentioned substances.

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 no chemical interaction was registered.

Apparently the active substances of the additives are surface-active agents and they are glycerides of fatty acids.

In attempt to quantitatively estimate the influence of components of the additives on the stabilizing action, we used a method of quantitative analyses of hydrocarbon fragments in petroleum based on IR spectroscopy [16]. The method is considered as most informative for petroleum systems and uses the following absorption bands as characteristic: 727 cm^{-1} (alkane structures with $(\text{CH}_2)_x$, $X \geq 4$), 1377 cm^{-1} (branched alkane structures), 1605 cm^{-1} (aromatic structures). It should be noted that concentration of components 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 Cal is the ratio of D_{1377} and D_{727} sum to D_{1605} ; aromaticity coefficient Car is the ratio of D_{1605} to D_{727} .

The results for the studied samples with the additives are presented in table 2.

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 diffraction of infrared radiation by

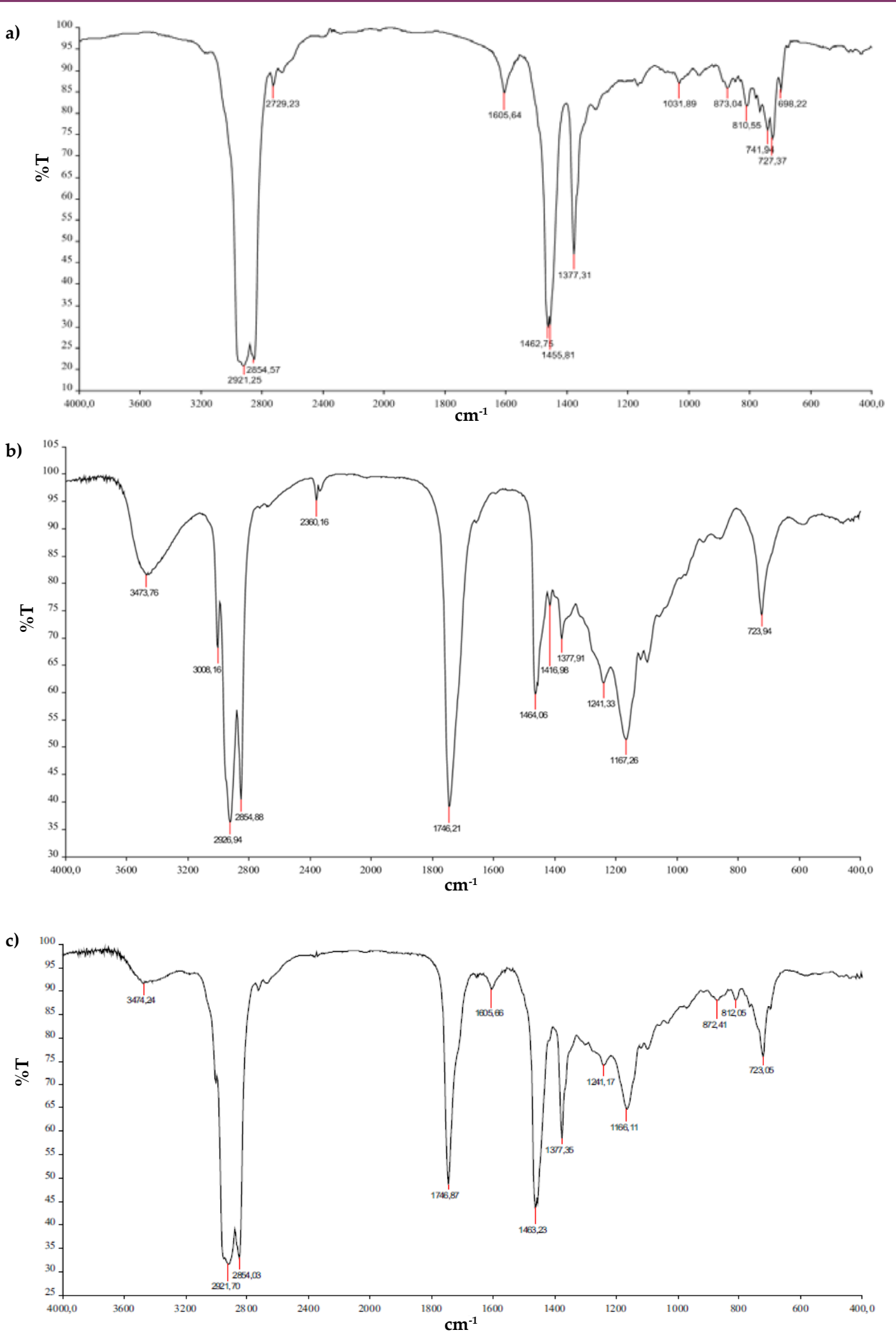


Fig.3. IR spectra: a) the pure petroleum; b) PPVO; c) the petroleum with 0.09% PPVO

Results of the quantitative analysis of IR spectra of the samples				Table 1
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

the nanoparticles.

There are no clear correlations between stability factor and any of the coefficients, but the best value of stability factor F corresponds to the increase of aliphaticity 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.

Conclusions

1. 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.
2. The optimal concentration of PPVO was 0.09% v/v.
3. The effectiveness of the synthesized product corresponds to the level of action of the industrial additives.
4. No chemical interaction between the additives and the petroleum dispersion was detected.
5. PPVO acts as a surfactant, apparently displacing natural petroleum surfactants from the asphaltene particles surface into the dispersion medium.

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Влияние добавки растительного происхождения на агрегативную стабильность нефти

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Реферат

Изложены результаты исследования влияния добавок растительного происхождения на агрегативную стабильность нефтяных дисперсных систем, обусловленную влиянием асфальтенов. Ингибирующее действие добавок, синтезированных в лабораторных условиях из продуктов переработки рапса и касторового масла, сравнивали с промышленными присадками. Определены средний диаметр частиц дисперсной фазы и коэффициент устойчивости системы. Процесс осаждения ускоряли центрифугированием. Сравнение значений среднего диаметра частиц в верхнем и нижнем слоях центрифугата показало существенное уменьшение их разницы при введении растительных присадок. Лучший результат получен при использовании 0.09% растительных присадок. Эффективность их действия соответствует результатам апробированных промышленных присадок. Анализ ИК-спектров и спектральных коэффициентов позволил интерпретировать изменения функциональных групп нефти при добавлении синтезированных присадок растительного происхождения и присадок промышленного производства.

Ключевые слова: нефть; растительное масло; присадка; ингибитор; стабильность; ИК-спектр.

Neftin aqreqat sabitliyinə bitki mənşəli əlavənin təsiri

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Xülasə

Məqalədə neft dispers sistemlərinin asfaltenlərdən asılı olan aqreqat sabitliyinə bitki mənşəli əlavələrin təsirinin tədqiqatının nəticələri verilmişdir. Raps və gənəgərçək yağının emalından alınan məhsulların laboratoriya şəraitində sintezləşdirilmiş əlavələrinin ingibirləşdirici təsiri sənaye aşqarları ilə müqayisə edilmişdir. Dispers fazanın hissəciklərinin orta diametri və sistemin dayanıqlılıq əmsalı müəyyən edilmişdir. Çökmə prosesi sentrifuqa vasitəsilə sürətləndirilmişdir. Sentrifuqanın yuxarı və aşağı qatlarında hissəciklərin orta diametrinin qiymətlərinin müqayisəsi bitki aşqarların tətbiqi vaxtı onların fərqlinin əhəmiyyətli dərəcədə azalmasını göstərmişdir. Ən yaxşı nəticə bitki aşqarların 0.09% istifadəsi zamanı alınmışdır. Onların təsir effektivliyi təsdiqlənmiş sənaye aşqarlarının nəticələrinə uyğun olmuşdur. İQ-spektrlərin və spektral əmsalların analizi bitki mənşəli sintezləşdirilmiş aşqarların və sənaye aşqarlarının əlavə edilməsi vaxtı neftin funksional qruplarının dəyişikliklərini interpretasiya etməyə imkan vermişdir.

Açar sözlər: neft; bitki yağı; aşqar; inhibitor, sabitlik; İQ-spektr.