Chapter 2
Effect of Polymer Additives on the Rheological Properties of Heavy High-Viscosity Oil

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Nomenclature

PPG	polypropylene glycol
PEG	polyethylene glycol
GC	gas condensate
GPD	Gas Processing Department

2.1 Introduction

Nowadays the reserves of light oil with low viscosity are exhausted. Therefore, there is an urgent necessity to introduce into operation the fields of heavy reserves, such as high-viscosity oils and natural bitumen. Oil fields of this type are usually characterized by a high concentration of metals and sulfur compounds, high values of density, viscosity, and high content of asphaltic bitumen. The distinctive features of this type of oils are the high enough content of metals and sulfuric compounds, high density, viscosity, and coking ability, as well as a significant amount of asphaltene and resinous compounds. Due to the mentioned features, these oils are tough to be dehydrated. Moreover, these oils can cause corrosion of equipment, which would lead to an emergency shutdown of the refinery (Polishchuk and Yashchenko 2005; Farmanzade et al. 2016; Zinov'yev et al. 2013a, b; Roschin et al. 2015; Bratychak and Gunka 2017; Topilnytskyy et al. 2014; Romanchuk and Topilnytskyy 2010; Gajek et al. 2012; Topilnytskyy et al. 2019).

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Rheological properties are essential parameters of oil field products. The study of rheological properties allows to justify and integrate the new technology, which could increase the efficiency of oil recovery during the operation of certain facilities. The peculiarity of the rheological properties of heavy oils in contrast to most oils is the dependence of dynamic oil viscosity on applied shear stress, as well as flow rate. Considering that oil is a non-Newtonian fluid, its colloidal state (disperse phase +disperse medium), intermolecular interactions occurred in it, and formation of the oil structure is significant (Farmanzade et al. 2016; Zinov'yev et al. 2013a, b). There are some peculiarities of non-Newtonian fluids. Their viscosity decreases under the influence of the velocity gradient V $dV/dx = G$, where G is the shear rate. In the range of high values of G (as a rule, at room temperature $G > 10^2\ s^{-1}$ for oil), when the viscosity very weakly depends on the shear rate, it is assumed that the colloidal solution becomes a Newtonian fluid.

Experts argue that such countries as Canada, Russia, and Venezuela have the largest reserves of heavy oils. The USA, China, Mexico, Brazil, and Iran have sizable reserves, and Ukraine has approximately 2% of the world's reserves. However, the extraction of such oils in Ukraine is insufficient and complicated. That is why there are almost no publications on their exploration (Polishchuk and Yashchenko 2005). One of the largest oil and gas fields in Ukraine (Yablunivske field) is situated in the Dnieper-Donets basin (Poltava region). Considering that this field is successfully being developed, it may serve as an additional source for the production of oil, gas, and gas condensate.

The capacity and economic efficiency of the pipeline depend on the oil properties. Viscosity is a main restriction of the required pumping speed. The decrease in oil viscosity reduces the hydraulic resistance of the pipeline and energy consumption for pumping. In the regions with low ambient temperatures, the oil viscosity reaches such values that the energy consumption for pumping substantially increases the cost of produced oil. In some cases, the pumping becomes impossible. To increase the efficiency of viscous and high-viscosity oil transportation, they are subjected to pretreatment. There are many ways to reduce oil viscosity, including polymer additives (Topilnytskyy et al. 2014; Romanchuk and Topilnytskyy 2010; Grinishin et al. 2013; Syunyayev et al. 1990; Bashkirtseva and Sladovskaya 2014; Pyshyev et al. 2016, 2017; Demchuk et al. 2018; Al-Ameri et al. 2013; Kasatkin 1961).

Chemical reagents used to reduce the oil viscosity provide the conditions that prevent the formation of collective colloidal structures, reduce gravity between colloidal particles, and preserve the colloidal component in the form of single particles.

The reagents are selected depending on the oil composition in such a way. They will not have an adverse effect on oil processing. Typical concentrations of reagents are usually from tens to hundreds of grams per 1 ton of oil.

The introduced synthetic polymer products can change oil viscosity and shear stress. Usually, esters, alcohols, and various polymers are used.

The Aim of the Research: to determine the rheological properties of resin-rich heavy oil with the introduction of polymeric additives, to reduce the oil viscosity, and to find ways of heavy oil processing.

2.2 Research Methods

To study the rheological properties, we used the high-viscosity oil of Yablunivske field from two wells:

Sample 1 – oil with a density of 977 kg/m^3 at 20 °C from well 88.
Sample 2 – oil with a density of 972 kg/m^3 at 20 °C from well 337.

To increase the oil recovery of wells and improve the transportation of oil due to the reduction of oil viscosity, we studied the effect of temperature, share rate, and addition of polymer additives on the rheological properties of the oil. For this purpose, we used Rheomat-30 viscometer produced by Contraves AG (Switzerland). The viscometer is equipped with a rotary-type adapter and coaxial cylinders. The rate gradient varied from 0 to 452 s^{-1} (a measuring system CM409.484 consisting of a cylinder d = 25 mm and chambers d = 23.8 mm with a total volume of 40 cm^3); the temperature varied from 20 °C to 70 °C. The Rheomat 30 Contraves is a rotary viscometer used to determine the viscosity of materials within a wide range. Its open concentric system allows measurements by immersion. The measuring cone and the tube are rigidly connected; the measuring unit is driven by a DC motor.

The UH-8 thermostat with a unique flow cell produced by MLW company (Germany) was used to maintain the experimental temperature. Heat carrier was demineralized water.

The method is based on determining the dynamic viscosity within the range of $0.1–4 \cdot 10^5$ Pa·s. The essence is to record the moment of resistance to rotation of the inner cone filled with the test material at different gradients of the strain rate, followed by the calculating shear stress and dynamic (effective) viscosity.

Dynamic (effective) viscosity was calculated according to the formula viscosity (η):

$$\eta = \eta_{\text{rep}} \cdot \alpha, \qquad (\text{Pa} \cdot \text{s})$$

where η_{rep} is a viscosity, with a value of viscosity corresponding to the switch position at the definite shear stress, Pa·s, and α is the indication on the device scale, %.

Shear stress (τ) was calculated from the ratio:

$$\tau = \eta \cdot D_{\text{rep}}, \qquad (\text{Pa})$$

where D_{rep} is a value of shear rate corresponding to the switch position at the definite shear stress, s^{-1}.

Polyethylene glycol (PEG, molecular weight 400, density $d_{20} = 1130$ kg/m^3), polypropylene glycol (PPG, molecular weight 400, density $d_{20} = 1010$ kg/m^3), and demulsifier of PM brand (the content of ethylene and propylene oxides copolymer is 70%, density 1000 kg/m^3) were added separately in the amount of 3% per sample to improve the rheological properties. Before adding, the oil was heated to 50 °C.

The dynamic viscosity and shear stress of samples from both wells were investigated at 20 °C, 30 °C, and 40 °C. After the addition of polymer additives the measurements were carried out again.

The possibility of obtaining residual bitumen from a mixture of oils from well 88 and well 337 of the Yablunivske field was examined.

2.3 Results and Discussion

The most critical physical and chemical properties of oils are presented in Table 2.1. Degassing oil of the Yablunivske field belongs to heavy, high-viscosity, high-sulfur oils. It is abnormally viscous. The values of coking ability and pour point are high; therefore, the content of asphaltenes and resins in the oil is also high. It means that difficulties will occur when transporting oil, especially during the cold season. Additional efforts regarding the reduction of pour points will be necessary. The quantity of chloride salts and water in the samples is also great. The reason is the absence of desalination and dehydration stages before oil processing. The kinematic viscosity at 50 °C is relatively high. The following technological parameters are determined and calculated according to the viscosity: oil fluidity in the reservoir during oil production, the type of invading fluent, the filtration rate in the reservoir, the conditions of transportation through the pipeline, the pump capacity, etc.

The rheological curves in the τ-η-D coordinates (Figs. 2.1, 2.2, 2.3, 2.4, 2.5 and 2.6) were plotted using the obtained results.

The addition of polymer additives significantly affects the rheological properties of oils. The figures show the experimental results obtained at four values of shear rate: 4.52, 21.0, 97.3, and 452 s^{-1}. The most significant effect is observed at a shear rate of 452 s^{-1}. The shear stress of sample 1 at 20 °C, 30 °C, and 40 °C are 1338.40, 564.03, and 261.94 Pa, respectively. When polypropylene glycol is added,

Table 2.1 Physicochemical properties of oil

Property	Sample 1	Sample 2
Density at 20 °C, kg/m^3	977	972
Kinematic viscosity at 50 °C, mm^2/s	326	386
Coking ability, %	9.8	7.3
Pour point, °C	14	8
Content of water, %	4.9	5.6
Content of chlorides, mg/dm^3	2900	6280
Content of sulfurous resins, vol. %	16.9	14.8

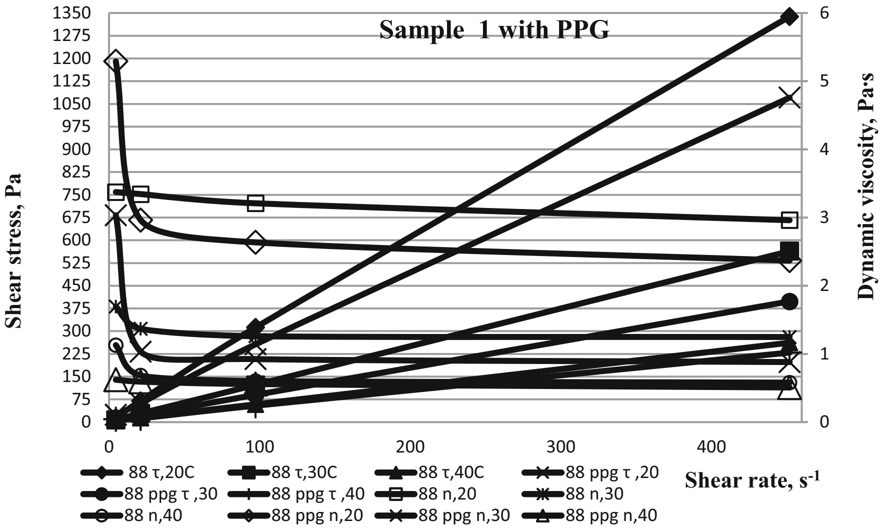

Fig. 2.1 Rheological properties of sample 1 with PPG at temperatures of 20 °C, 30 °C, and 40 °C

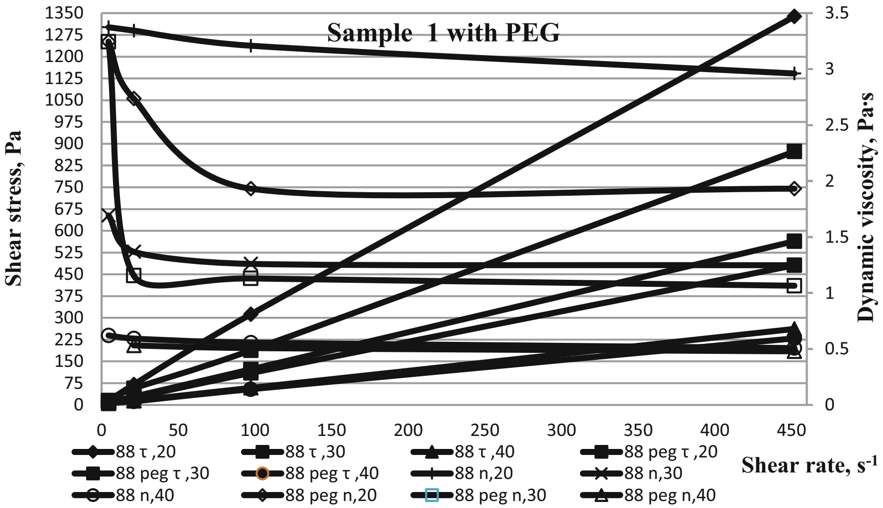

Fig. 2.2 Rheological properties of sample 1 with PEG at temperatures of 20 °C, 30 °C, and 40 °C

the shear stress is 1070.7, 398.33, and 229.44 PA, respectively. The addition of polyethylene glycol reduces the shear stress to 873.13, 481.18, and 2176.69 Pa, respectively. Moreover, the addition of the PM demulsifier to sample 1 reduces the shear stress to 924.11 Pa at 20 °C and 200.76 and 97.19 Pa at higher temperatures, respectively.

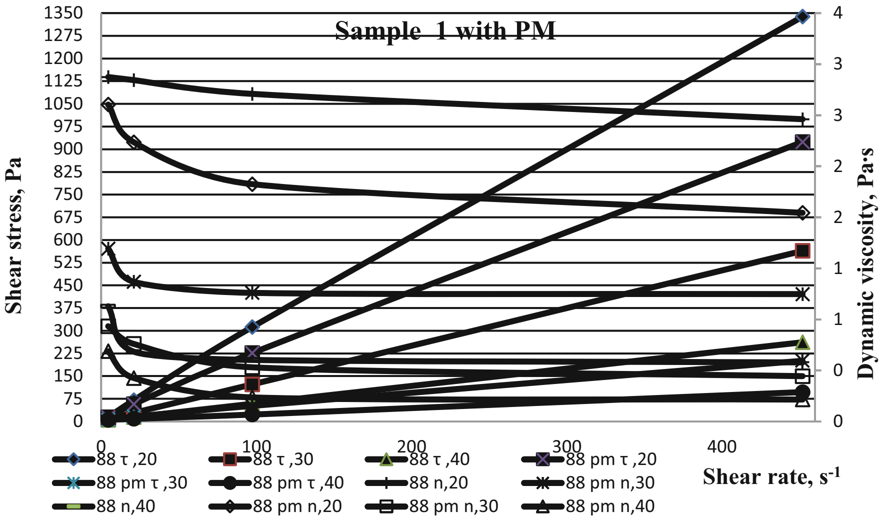

Fig. 2.3 Rheological properties of sample 1 with PM at temperatures of 20 °C, 30 °C, and 40 °C

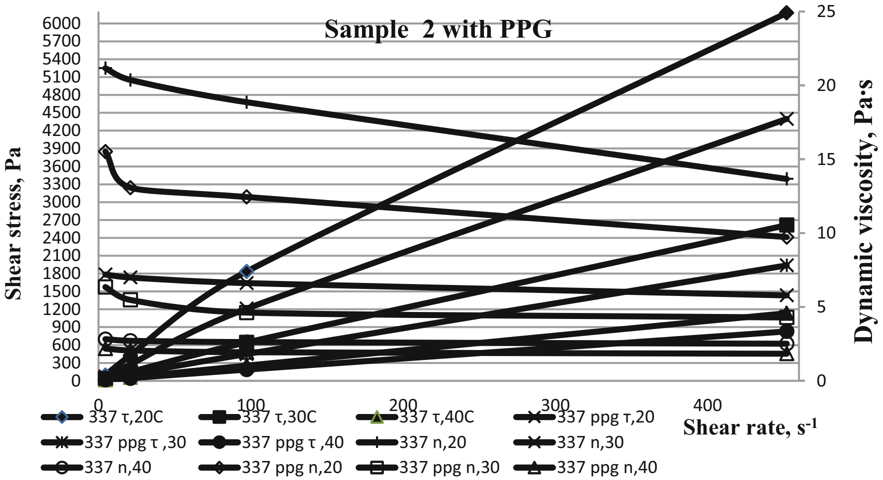

Fig. 2.4 Rheological properties of sample 2 with PPG at temperatures of 20 °C, 30 °C, and 40 °C

The addition of polymer additives to sample 2 also significantly affects the shear stress. Thus, at the shear rate of 452 s^{-1} the values of shear stress are 6177, 2613, and 1134 Pa at temperatures of 20 °C, 30 °C, and 40 °C, respectively. For this sample, the addition of polypropylene glycol shows slightly better results. The shear stress at the above-mentioned temperatures decreases to 4397.5, 1937.45, and 828.52 Pa, respectively. The addition of polyethylene glycol and PM demulsifiers also reduces the shear stress.

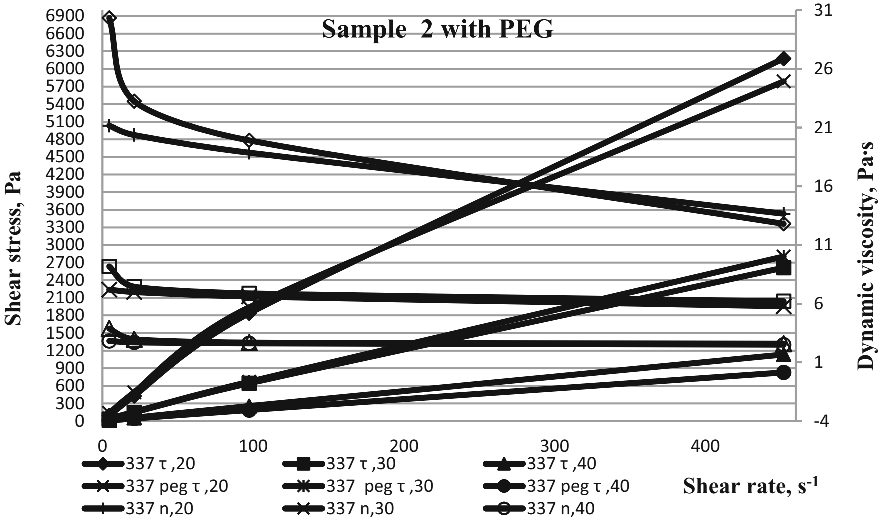

Fig. 2.5 Rheological properties of sample 2 with PEG at temperatures of 20 °C, 30 °C, and 40 °C

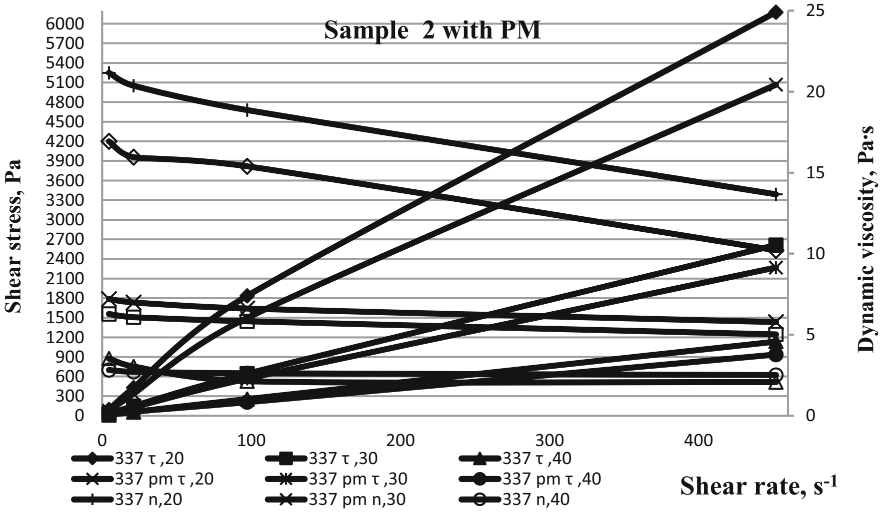

Fig. 2.6 Rheological properties of sample 2 with PM at temperatures of 20 °C, 30 °C, and 40 °C

The addition of polymer additives to high-viscosity oils also has a significant effect on reducing the dynamic viscosity. Thus, the dynamic viscosity of sample 1 at the temperatures of 20 °C, 30 °C, and 40 °C is 2.961, 1.248, and 0.579 Pa·s, respectively. When adding PPG, PEG, and PM demulsifier, the value decreases by 20–35% at a shear rate of 452 s^{-1}. For sample 2, the dynamic viscosity is 13.666, 5.781, and 2.51 Pa·s, respectively. When PPG and PEG are added, the dynamic viscosity decreases insignificantly, but a PM demulsifier reduces this value by 25%.

Even though polymer compounds reduce the viscosity of heavy oil, such viscosity is not enough to smoothly pump oil through the pipeline. One of the possible solutions is to add gas condensate (GC) to the oil. Gas condensates from Shebelinsky, Yablunivsky, and Yarivsky Gas Processing Departments (GPD) were used for research in 30% relative to oil. The characteristics and solubility of oils in them are shown in Table 2.2.

Based on an analysis of the properties of oils in the GC, it was found that in the Yablunivsky and Shebelinsky GC oils dissolved poorly and the mixture was not homogeneous. This GC differs in fractional composition from the Yarivsky GC and obviously contains alkane hydrocarbons in their compositions, which do not dissolve asphalt-resinous substances well. Yarivsky gas condensate differs significantly from others, namely, by the end boiling point. It indicates the presence of aromatic hydrocarbons providing the dissolution of asphalt-resin compounds. Therefore, 30% of Yarivsky GC was used to reduce the viscosity. The viscosity of oils from well 88 and 337 is shown in Table 2.3.

Table 2.2 Fractional distillation of GC from different GPD and oil solubility in them

% of distillation	Distillation temperature of GC from different GPD, °C		
	Yablunivsky	Shebelinsky	Yarivsky
Initial boiling point	45	65	56
10%	49	69	80
20%	51	61	92
30%	54	70	102
40%	57	71	111
50%	60	71,5	122
60%	66	73	139
70%	74	74	160
80%	81	77	210
90%	93	81	320
End boiling point	120 (99%)	93 (98.5%)	350 (92%)
Density, kg/m3	696	732	758
Refraction index, n20D	1.4015	1.4150	1.4353
Oil solubility in condensates			
Sample 1	The mixture of oil and condensate is inhomogeneous. During storage the bottom sediment is formed. The density of the mixture along the height of the cylinder is inhomogeneous		The mixture of oil and condensate is homogeneous
Sample 2			

Table 2.3 Change in oil viscosity with the addition of Yarivsky gas condensate in the amount of 30%

Sample	Kinematic viscosity at 50 °C, mm^2/s	
	Without GC	With GC
Sample 1	326	56.5
Sample 2	386	69.6

Thus, the addition of gas condensate from Yarivsky GPD reduced the viscosity of oils by more than five times.

The next step of investigations was to establish the technological possibility of obtaining residual bitumen using a mixture of oils from wells 88 and 337 of the Yablunivske field. To do this, a mixture of these oils (1:1) was prepared. The mixture was dehydrated at temperature of 50 °C with the addition of a demulsifier PM-1441 type A manufactured by JSC Barva. The mixture was distilled using an Engler apparatus to obtain fractions of sufficient quantity for analysis.

Distillation of the oil mixture

Initial boiling point	51 °C
Up to 120 °C	30% (solvent) was distilled
From 120 °C to 200 °C	10% was distilled
From 200 °C to 340 °C	30% was distilled
Residue	0%

Analysis of the distillation data showed that the content of heavy gasoline fractions relative to the oils mixture is 14%, diesel fractions 43%, and the residue 43%. The obtained residue (after 330–350°C) was examined for compliance with the requirements for standard paving bitumen BD 60/90 (Table 2.4).

Table 2.4 Analysis of the residue after 330–350 °C for compliance with the paving bitumen BD 60/90 according to SOU 45.2–00018112-069: 2011

Index	Experiment 1	Experiment 2	Experiment 3	The standard for BD 60/90
Initial boiling point, °C	51	51	51	–
Distilled up to 120 °C, %	29	30	30	–
Distilled from 120 °C to 200 °C, %	11	10	9,5	–
Distilled from 200 °C to 330 °C, %	26	–	–	–
Distilled from 200 °C to 340 °C, %	–	29	–	–
Distilled from 120 °C to 350 °C, %	–	–	31	–
Residue, %	34	31	29,5	–
The softening temperature of the residue, °C	41	49	68	44–52
Penetration at 25 °C of the residue, 0.1 mm	100	65	20	61–90
Ductility of the residue, cm	110	105	60	100

2.4 Conclusions

We studied two oil samples from different wells of Yablunivske field and investigated their main properties.

Based on obtained results, the following procedure for the preparation and processing of oil mixture from Yablunivske field is recommended:

1. The addition of polymer additives PEG, PPG, copolymers of ethylene oxide, and propylene to high-viscosity oils significantly reduces the viscosity and shear stress and will help to reduce energy consumption in oil production and transportation.
2. To reduce the oil viscosity and production of oil, it is necessary to introduce a diluent into the reservoir; the diluent is gas condensate from Yarivsky GPD in 20–30%.
3. The residue after distillation will be a high-quality residual bitumen. The grade of bitumen will be determined by the temperature regime of the atmospheric column. The production of paving bitumen BD 130/200 is possible after fraction distillation up to 330 °C; deeper distillation will result in the production of bitumen BD 90/130 or BD 60/90. The determination of all indices will be carried out in the course of further researches.

References

Al-Ameri M, Grynyshyn O, Khlibyshyn Y (2013) Modification of residual bitumen from orhovytska oil by butonal polymeric latexes. Chem Chem Technol 7(3):323–326

Bashkirtseva NYU, Sladovskaya AYU (2014) Osobennosti primeneniya PAV v protsessakh transportirovki vysokovyazkikh neftey. Vestnik tekhnologicheskogo universiteta 17(14): 449–451

Bratychak MM, Gunka VM (2017) Khimiya nafty i gazu. Lvivska polytekhnika, Lviv

Demchuk Y, Sidun I, Gunka V, Pyshyev S, Solodkyy S (2018) Effect of phenol-cresol-formaldehyde resin on adhesive and physico-mechanical properties of road bitumen. Chem Chem Technol 12(4):456–461. https://doi.org/10.23939/chcht12.04.456

Farmanzade AR, Karpunin NA, Khromykh LN, Yevsenkova AA, Al′-Gobi G (2016) Issledovaniye reologicheskikh svoystv vysokovyazkoy nefti Pecherskogo mestorozhdeniya. Int Res J 3(45): 116–119. https://doi.org/10.18454/IRJ.2227-6017

Gajek A, Zakroczymski T, Topilnytsky P, Romanchuk V (2012) Protective properties and spectral analysis of nitrogen- and oxygen-containing corrosion inhibitors for oil equipment. Chem Chem Technol 6(2):209–219. https://doi.org/10.23939/chcht06.02.209

Grinishin OB, Al′-Ameri MSA, Khlibishin YY (2013) Kharakteristika i napravleniya pererabotki tyazholykh vysokosernistykh neftey. Vostochno-yevropeyskiy zhurnal peredovykh tekhnologiy 5(6):27–31

Kasatkin AG (1961) Osnovnyye protsessy i apparaty khimicheskoy tekhnologii. Goskhimizdat, Moskva

Polishchuk YM, Yashchenko IG (2005) Vysokovyazkiye nefti: analiz prostranstvennykh i vremennykh izmeneniy fiziko-khimicheskikh svoystv. Electron Sci J Oil Gas Business 1:1–31

Pyshyev S, Gunka V, Grytsenko Y, Bratychak M (2016) Polymer modified bitumen: Review. Chem Chem Technol 10(4s):631–636. https://doi.org/10.23939/chcht10.04si.631

Pyshyev S, Gunka V, Grytsenko Y, Shved M, Kochubei V (2017) Oil and gas processing products to obtain polymers modified bitumen. Int J Pavement Res Technol Open 10(4):289–296. https://doi.org/10.1016/j.ijprt.2017.05.001

Romanchuk V, Topilnytskyy P (2010) Investigation of reagents with different chemical compositions for protection of oil primary refining equipment. Chem Chem Technol 4(3):231–236. https://doi.org/10.23939/chcht04.03.231

Roschin PV, Zinoviev AM, Struchkov IA, Kalinin ES, Dziwornu CK (2015) Solvent selection based on the study of the rheological properties of oil. Int Res J 6–1(37):120–122

Syunyayev ZI, Safiyeva RZ, Syunyayev RZ (1990) Neftyanyye dispersnyye sistemy. Chimiya, Moskva

Topilnytskyy P, Romanchuk V, Boichenko S, Golych Y (2014) Physico-chemical properties and efficiency of demulsifiers based on block copolymers of ethylene and propylene oxides. Chem Chem Technol 8(2):211–218. https://doi.org/10.23939/chcht08.02.211

Topilnytskyy P, Paiuk S, Stebelska H, Romanchuk V, Yarmola T (2019) Technological features of high-sulfur heavy crude oils processing. Chem Chem Technol 13(4):503–509. https://doi.org/10.23939/chcht13.04.503

Zinov'yev AM, Ol'khovskaya VA, Kovalev AA (2013a) Obosnovaniye analiticheskoy modeli psevdoustanovivshegosya pritok nelineyno vyazkoplastichnoy nefti k vertikal'noy skvazhine. J Central Committee Rosnedra 2013(2):40–45

Zinov'yev AM, Ol'khovskaya VA, Maksimkin NM (2013b) Proyektirovaniye sistem razrabotki mestorozhdeniy vysokovyazkoy nefti s vnedreniyem modeli nen'yutonovskikh techeniya i rezul'tatov issledovaniya skvazhin na pritok. Petroleum Business J 2013(1):5–14