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Selectivity in Improvement of Rheological Properties of Crude Oil

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Abstract: Recently the steady tendency to increase in volumes of transportation, oil was outlined. Thus, developments new or optimization of the applied technologies of transportation of oil taking into account their rheological properties and operational characteristics of pipelines are necessary for the solution of a task of increase in volume of pumping of oil. Because of relevance of a problem, results of the pilot studies mixed crude oil by physical and chemical methods are of great interest. The researches conducted by us showed what when mixing crude oil should be considered a factor of interference of structures crude oil for the purpose of assessment inadmissible and optimum separate components of concentration. However many from used in the present a number of shortcomings, narrow have time of additives the spectrum of action, their insufficient solubility in the crude oils and oil products. Therefore development of new additives is relevant and has scientific and practical values.

Keywords: Physical and Chemical, Incompatibility, Compounding, Viscosity, SNPX-2005

1. Introduction

In recent years a considerable part of oil production is provided with inclusion in process of development of fields with heavy, high-viscosity crude oil. Production and transportation of similar to crude oil are complicated because of high viscosity and temperature of hardening, abnormal rheological behavior. The feature of these rheological properties of crude oil is shown in inconstancy of their dynamic viscosity depending on tension of shift and speed of the movement of liquid. At transport high-paraffinic the intensive parafinization of pipelines, decrease in their capacity occurs crude oil that considerably complicates operation and leads to growth of labor and material inputs. High-paraffinic oil at low temperatures show sharply expressed non-Newtonian (viscoplastic, viscoelastic, thixotropic) properties without which it is impossible to organize rational operation of wells, collecting, preparation and transport of crude oil. At a stop of process of transfer in oil paraffin structures which durability depends on the maintenance of paraffin fractions, time of rest of oil, conditions of formation of paraffin structures and other factors are formed. Renewal of process of transfer demands sometimes creation of such starting pressure which in size considerably exceed operating pressures of pipelines, fittings and the equipment.

At production and transportation of oil questions of the asphalt pitch of paraffin deposits (APPD) continue to remain relevant in spite of the fact that many various ways of their prevention and removal are already developed. Practice showed that the asphalt pitch of paraffin deposits of deposits remains the most perspective way of prevention a chemical method of impact on oil with use of additives (additives) of different function – depressor (reducing oil hardening temperature), inhibiting (APPD preventing emergence), etc. In oil industry use very large amount of additives, but the greatest distribution was gained by high-molecular polymeric connections of various types. It should be noted that the available additives –regulators of rheological properties of oil are not deprived of shortcomings. In some cases they show weak efficiency or have no regulating effect at all. Therefore a relevant scientific and applied task is development of new polymeric compositions for regulation of viscous and temperature properties crude oil. Sharing of several ways of impact on oil disperse systems, for example, application of various options of electric, electromagnetic, magnetic, vibration or acoustic fields is perspective. At the same time the effects corresponding to increase or, on the contrary, decrease in orderliness of supramolecular structure of substances are rather easily reached. Fight against APPD provides holding actions for two directions – to prevention of loss of deposits and their removal. An important ecological and economic task – collecting, transportation, preparation, processing and utilization of APPD and oil slimes. Further progress in area of transport and preparation problem is connected by crude oil with achievements in the field of chemistry of oil and development of new approaches to impact on oil disperse systems.

In the past Oil refinery (OR) were under construction for distillation of usual light crude oil. The current economy, changes in the price of crude oil and change of demand for distillates force OR to reduce the cost of the raw materials used by them for distillation. As a rule, it is reached by mixture of expensive light oil with heavy (non-standard) oil of poor quality, or purchase of ready mixes. Low-quality oil include heavy crude oil from the known fields and also the accidental oil supplied to the market by dealers from around the world. These grades of oil of more poor quality can be got at low price. Their mixture with expensive oil is inevitable in production of the oil mixtures having optimum properties for processing at the minimum expenses. OR around the world were under construction from such engineering positions and of such materials which allowed to carry out distillation of strictly certain types of oil. These plants were constructed on the basis of the certain types of crude oil available in their regions, the cost of certain types of oil in the market and primary demand for light distillates for production of gasoline. Distillation of crude oil, is generally directed to production of components of gasoline, such as light and average distillate. Quite recently, and especially in the USA and in Europe, demand for fuel was displaced from gasoline on diesel fuel. It means that while in the past generally easy grades of crude oil were overtaken, today OR have to be capable to overtake heavier grades. The margin of processing went down for many plants which could not adapt to change of a situation. Technological restrictions forced many OR to buy expensive light crude which is not allowing to produce specifically those distillates which are in the greatest demand in the market. For many plants of loss were too big. Many of them were closed or switched from distillation to mixture.

2. Materials and Methods

Today mixture of crude oil is made or on mixing installations, or OR which buy different types of the budgetary crude oil. Additional costs of oil refining with a high rate of TAN are in limits of 1.15-1073 $/barrel, but economy makes 43.54-62.7$/barrel. They improve its chemical and physical properties with receiving at the minimum expenses of synthetic oil which can be processed on the equipment of OR and allows to receive valuable distillates [1, 2]. Qualitative parameters determine the market value of each type of oil. The most important characteristics of quality are density, the total acid number (TAN) and content of sulfur. Specific weight of API varies from light crude (high API, small density) to heavy oil (low API, high density). Sulfur is present at crude oil in the form of hydrogen sulfide and polysulfides. These sulfur-containing molecules partially decay at distillation while hydrogen sulfide is emitted. Sulfur and other sour components which are contained in crude oil such as naphthenic acids, have high corrosion activity and are responsible for acidity of oil. These characteristics generally determine the price paid for different types of crude oil. Crude oil with a high rate of TAN is characterized by smaller quantity of easy components, high density and viscosity, low temperature of hardening, high content of nitrogen, high content of dense asphalt, high content of salts and heavy metals, and a low exit of light oil distillates. Oil office for it in the desalinating installation is much more difficult, than for usual oil. These properties also cause poor quality of the products received their such crude oil and their high corrosion activity. As a rule, crude oil with a high rate of TAN call "accidental crude oil". Its price is about 80% of the cost of usual crude oil. Additional costs of oil refining with a high rate of TAN are in limits of 1.15-10.73$/barrel, but economy makes 43.54-62.7$/barrel in comparison with processing of usual oil. Thus, use of such oil is very attractive in any possible way to processors. In the past most OR were projected and under construction of materials, according to crude oil, available to them, and ease of its purchase.

It limits variability of many oil refineries in purchase of other types of oil, with other qualities [3, 4]. Many of these plants which are under construction for distillation of light crude with the low content of sulfur are limited concerning processing of heavy types of fuel. Important differences in their physical and chemical properties do distillation of heavy oil more difficult, in comparison with distillation of light crude. Heavy oil is sour and has bigger corrosion activity, than light crude. Higher viscosity, tendency to formation of rainfall and various streams complicate maintenance of stable supply of raw materials which is necessary for a stable exit of products, quality and reliability. Differences in boiling temperatures for light and heavy crude crude demand use of various operating temperatures, such as temperature of preliminary heating, various temperatures of distillation, the top shoulder strap and so on. Heavy types of fuel are rich with asphaltenes and metals and also other pollutants which worsen quality of work of the desalinating installation.

For achievement of favorable economic results when processing crude oil it is often necessary to mix two or more different types of crude oil before carrying out various processes of processing. However there are specific problems connected with mixing of different types of crude oil. The first main problem is incompatible with each other that leads to contamination, sometimes even to an equipment stop (pipelines, tanks, heat exchangers, furnaces, rectifying columns, etc.). Other main problem connected with mixing crude oil and other hydrocarbons, is generation of emulsions of oil and water in a system.

Shows results of the conducted researches that one of the reasons which causes not miscibility various crude oil is presence of organic solid matter in the form of the besieged asphaltenes in mix crude oil. It is known that asphaltenes are soluble in aromatic connections, such as toluene, but insoluble in compounds of paraffin, such as n-pentane. The main problem connected with presence of asphaltenes at different types of crude oil is what asphaltenes often drops out in a deposit of solution during mixing of different types of crude oil remain still unresolved. So far there is a need for creation of practical and economic favorable means and ways of determination of ability to mixing differently sortable crude oil.

3. Results and Discussions

Follows, will note that resources and efforts to development of new methods and technologies for a solution of the problem of mixing of crude oil allowed to achieve only partial success in creation of practical and economic (rational) ways of mixing.

Researches of the last years drew a conclusion that nonlinear deviations of properties of mix differently sortable crude oil from the existing models of ideal mixes most likely are caused by structural transformations of oil nanophases [5]. At concentration of asphaltenes in mix crude oil to the corresponding borders of nanophases perhaps emergence of undesirable manifestations of incompatibility. Thus, the existing recommendation about technologies of mixing should add with the criteria taking into account interference as a part of separate components allowing to make necessary assessment of "unacceptable" and also "optimum" concentration of asphaltenes and other high-molecular chemical compounds in oil mixtures [6]. Various models of the considered processes existing now do not allow to predict changes of indicators of quality of examinees of oil mixtures with a sufficient accuracy, necessary for engineering calculations yet.

The analysis of composition of high-viscosity oils shows that though their density is close, rheological and physical and chemical properties considerably differ from each other. Looking at physical and chemical characteristics of the high density and bituminous oils extracted on oil fields in Azerbaijan, Russia and the USA, apparently, that they completely differ from each other (Table 1).

Table 1. *Properties of some high-viscosity oils of Azerbaijan, Russian Federation and Canada.*

Results	Mordov-Karmal	Ashalcin	Suqu-shlin	Atabaska	Murad-khanlı
Density, kg/m^3	952–970	960–965	980	1014	878
Viscosity, mPa·s	2500–3000 (7–9ºC)	6000–17000 (7–9ºC)	$2 \cdot 10^6$ (7–9ºC)	$(1–5) \cdot 10^6$ (5–6ºC)	2100-2400 (7–9°C)
Group comp. %- mass.					
Asphaltenes	4,78–7,6	6,4–8,7	14	16,1	4,8
Resin	18,3–23,3	20,1–38	33	39	12,7
Oils	4	53–73	54	21	3,6
Quantity of paraffin, %- mass.	1,12	Min. 0,5	–	–	9,6
Element composition, %- mass.					
C	83,2	80,8–81,9	82,7	83,1	84,1
H	11,0	10,5–11,2	10,2	10,1	11,8
S	4,7	3,2–4,6	4,7	4,8	3,5
N	0,3	0,4–0,5	0,4	0,4	0,2
O	0,8	3,3–3,6	2,0	1,1	0,4

The results show that it would not be right to classify oils from concentration in terms of density, viscosity, and sulfur in terms of the chemical composition of the oil, which should be studied in a wider range [7].

Recently, the most effective outcome for improving the rheological properties of oils has been achieved by the addition of chemical reagents [8]. The most widely spread of these are high-molecular compounds of different types: copolymers of vinyl acetate copolymers, copolymers of ether, which are formed by unsaturated acids (acrylic or methacryl), oxygenous fragments of functional substituent quinine compounds (polyoxyethyl and complex ether groups) and others. For example, these chemical reagents can be used to regulate the rheological properties of oil and cause unavoidable adverse events in the production. Thus, such reagents have little or no effect on the improvement of the rheological properties of high-density, resin-asphaltenic oils [9]. Therefore, the production and use of new type reagents is still needed to regulate the rheological properties of oil.

Such approvals are the subject of theoretical discussion, and have not been justified in production. R-140, GY-3, DANOX-501, DNN-2005, CCP, AR-174 are used to regulate the rheological properties of oil extraction and storage in several countries. The most effective reagents for these oils from the CIS countries are the chemical reagents of the RK. The composition of this reagent is mainly made up of solvents (native oils and oils) and compositions (a mixture of synthetic depressor additives mixture with native oils). This reagent is considered to be economically ineffective due to unwanted conditions in oil mixing when used in oil transportation.

3.1. Results

The effect of the SNPX-2005 additive on the improvement of the realogue of oil from the resin, asphaltenes, was of great interest [10-12]. For this, the kinematic viscosity of

Muradkhanli and Sangacal crude oils was checked in the reduced ratio of SNPX-2005 additive. The results of the inspection showed that the added value added to the oil, the price of the cinematic extract of oil, was considerably greater than the price it had received before it was added. Given that oil has a high viscosity, it has been investigated dynamically with their Ratase style.

To measure influence of oil samples on dynamics of their viscosity, SNPX-2005 was added to Muradkhanli and Sangacal crude oils of 0.8 kg / t. Measurements were measured in 5, 10, 20°C temperatures and at change of the coping stages (1-12, 0.333; 0.6; 1; 1.8; 3; 5.4; 9; 16.2; 27; 48.6; 81; 145.8 seconds^{-1} are compatible to a gradient). The sum of SNPX-2005 which is let out in oils was reduced up to 1.0 kg / t, and new measurements in 5°C were executed. Dynamics of dynamic viscosity at various stages, reflecting Muradkhanli and Sangacal crude oils in 20, 10 and 5°C and addition of a dose of SNPX-2005 0.8, 1.0 kg / t is reflected in the figures 1-12.

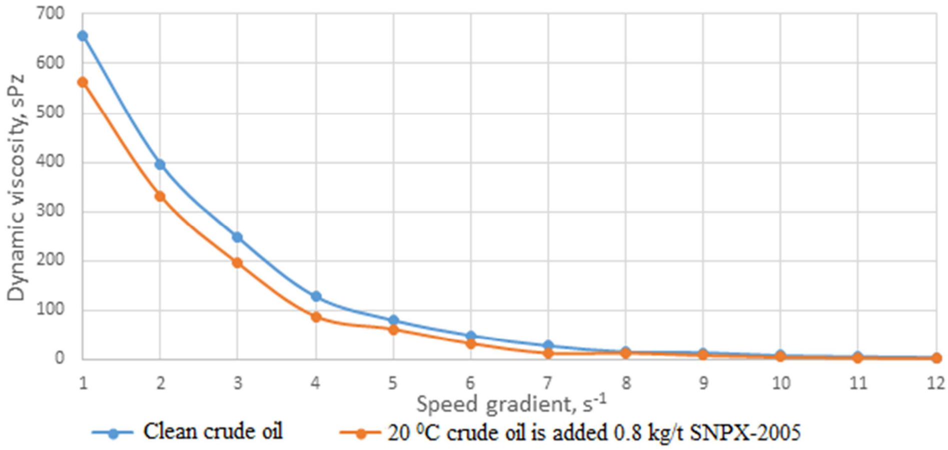

Figure 1. *20°C Muradkhanli crude oil is added 0.8 kg/t SNPX-2005.*

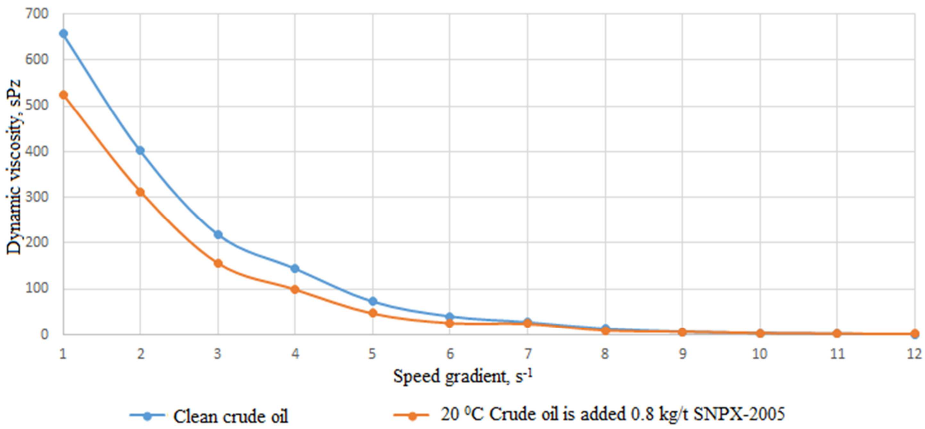

Figure 2. *20°C Sangacal crude oil is added 0.8 kg/t SNPX-2005.*

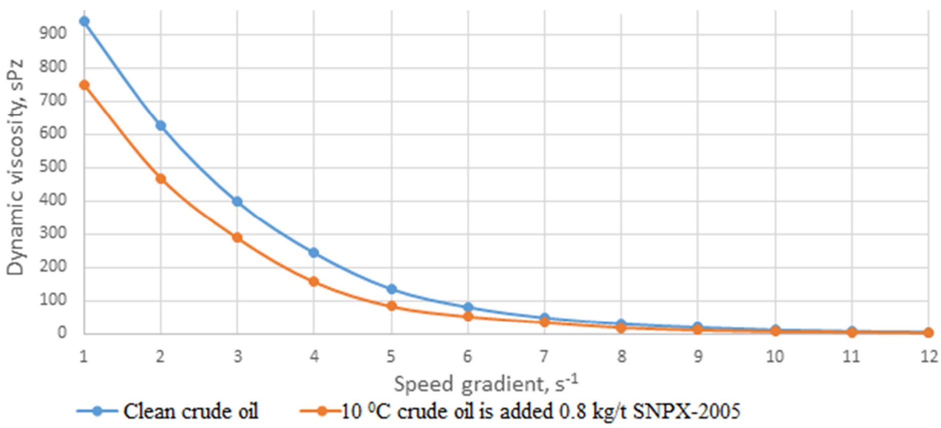

Figure 3. *10°C Muradkhanli crude oil is added 0.8 kg/t SNPX-2005.*

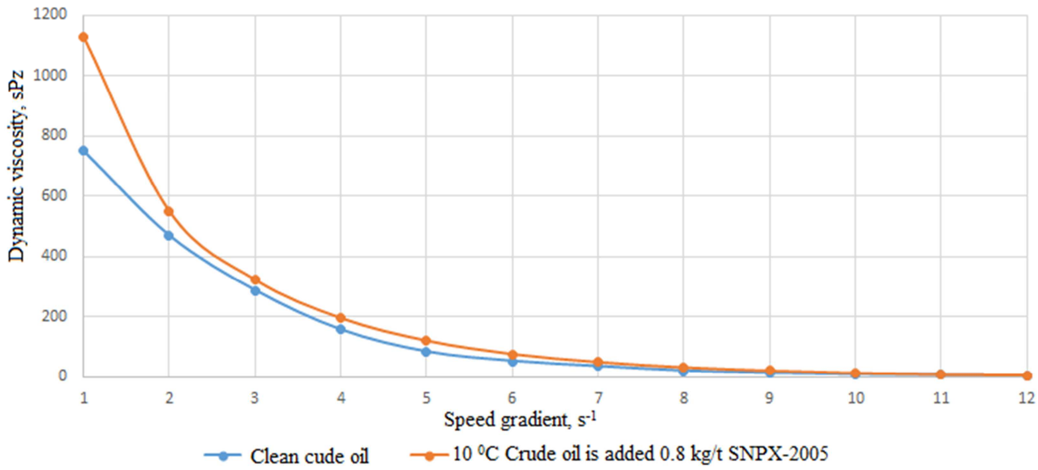

Figure 4. *10°C Sangacal Crude oil is added 0.8 kg/t SNPX-2005.*

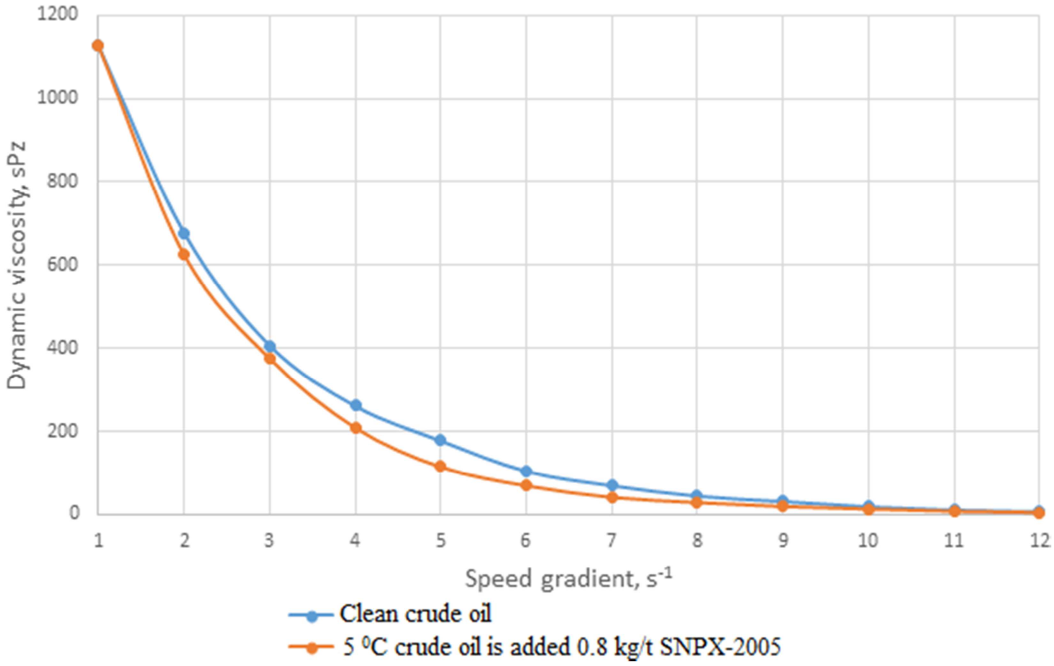

Figure 5. *5°C Muradkhanli crude oil is added 0.8 kg/t SNPX-2005.*

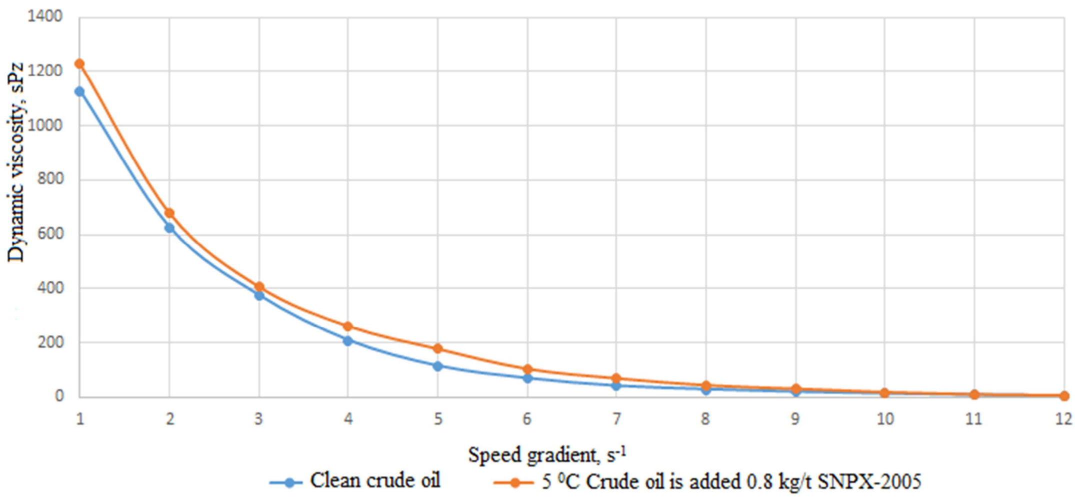

Figure 6. *5°C Sangacal crude oil is added 0.8 kg/t SNPX-2005.*

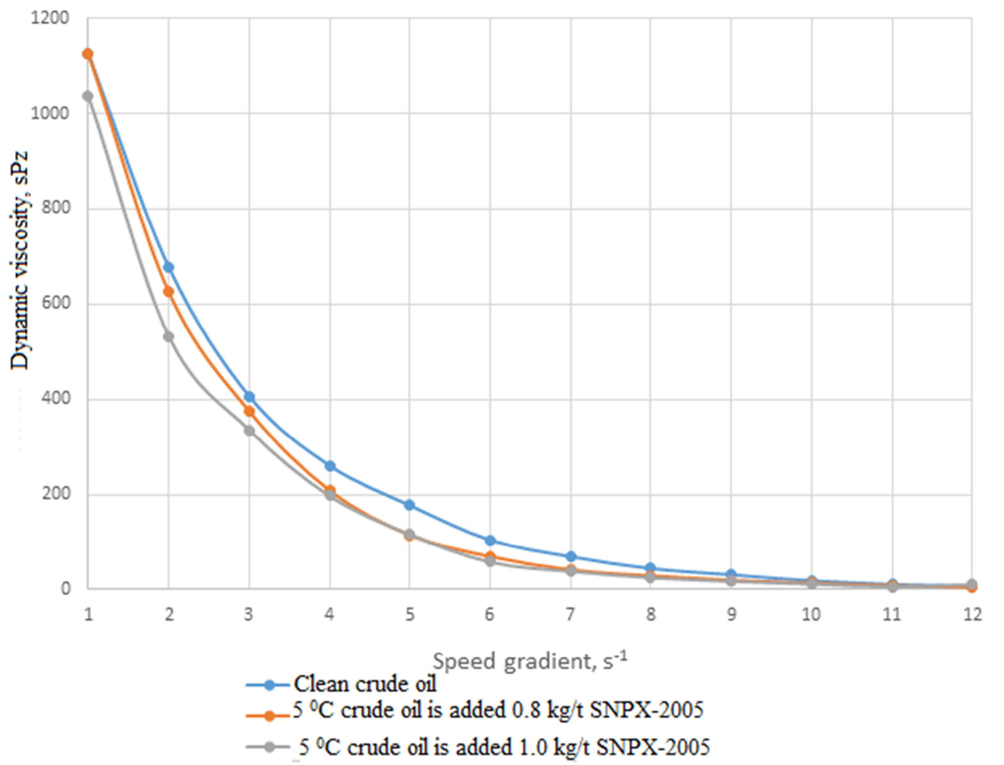

Figure 7. *5°C Muradkhanli crude oil is added 0.8, 1.0 kg/t SNPX-2005.*

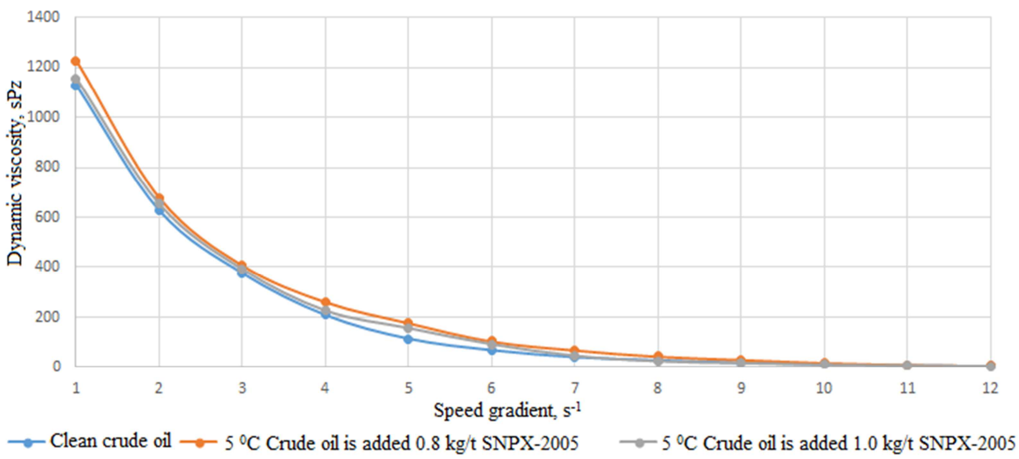

Figure 8. *5°C Sangacal crude oil is added 0.8, 1.0 kg/t SNPX-2005.*

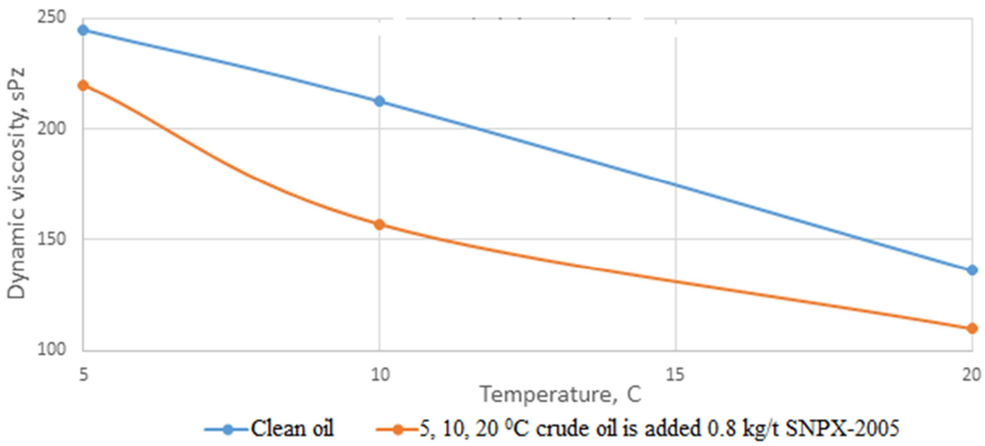

Figure 9. *5, 10, 20°C Muradkhanli crude oil is added 0.8 kg/t SNPX-2005.*

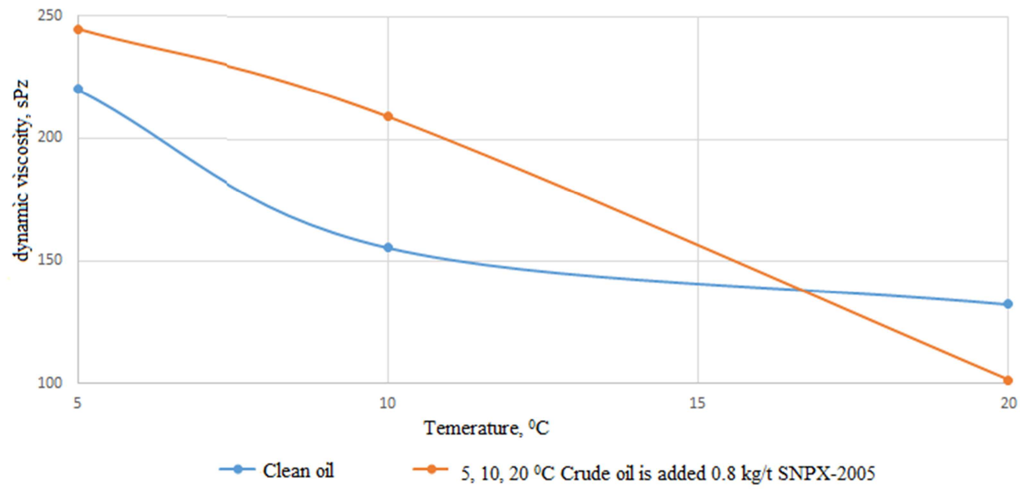

Figure 10. *5, 10, 20°C Sangacal crude oil is added 0.8 kg/t SNPX-2005.*

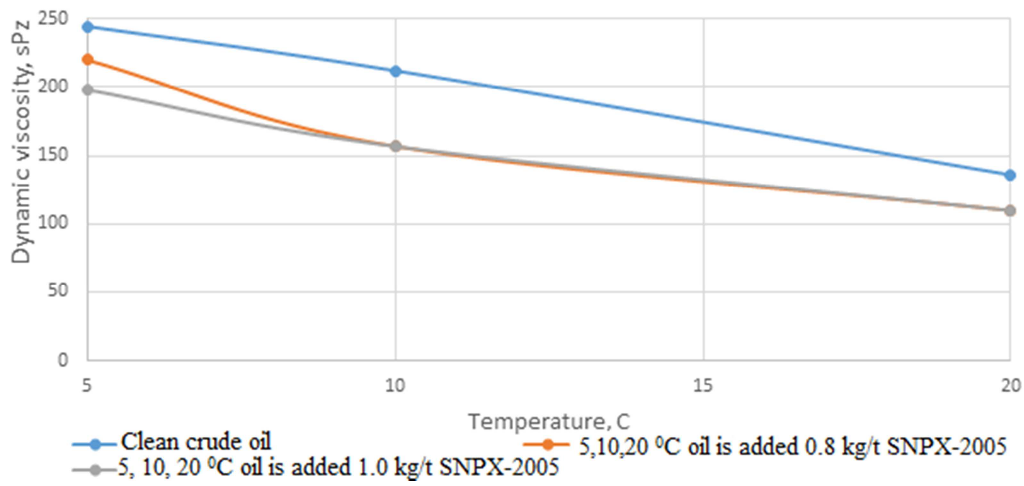

Figure 11. *5, 10, 20°C Muradkhanli crude oil is added 0.8 and 1.0 kg/t SNPX-2005.*

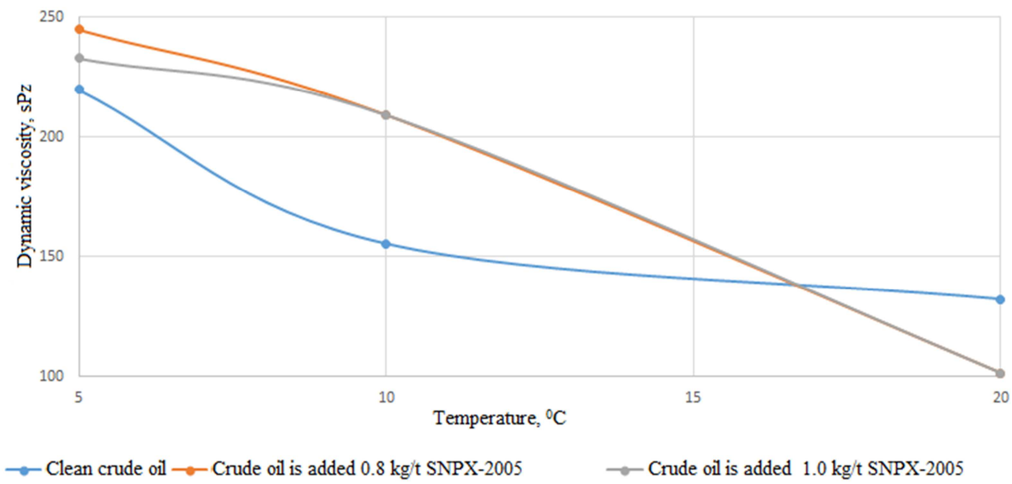

Figure 12. *5, 10, 20°C Sangacal crude oil is added 0.8 and 1.0 kg/t SNPX-2005.*

Our analysis shows that the SNPX-2005 has a different ability to affect the realm of Muradkhanli and Sangacal crude oils. Muradkhanli and Sangacal crude oils has a different effect on the mixed oils generated by mixing in different proportions. As can be seen from the photographs, the additive of 0.8 kg / t has a mean decline of 20°C at 19.3 %, 10°C at 26.1 % and 5°C for 10.1%. This shows that at low temperatures, the effect of the additive on the stream decreases at all speeds, increasing the content of the additive to 5°C by increasing the amount of additive to 1.0 kg / t.

3.2. Results Analysis

Along with physical and chemical properties of mix, the software has to be focused also on the possible profit got from mixture. It demands that the software also included: Cost various crude oil and their mixes, price of final distillates and other products of oil processing. Separate tanks, load into the mixing tank where they mix up before obtaining homogeneous structure. Contents of tanks mechanically mix up. It is necessary to select tests for definition whether mix is uniform and whether it meets its predetermined specification. In case of not compliance mix correction has to be made. All procedure of mixture in tanks is very labor-consuming and expensive. Unlike mixture in the tank, line mixture is carried out by simultaneous giving of different types of crude oil in the tank of final mix by means of the static line mixing device. Effectively and unmistakably to operate mixture process, line analyzers are necessary. The set ratio of streams at various gives to nefty mix of the required quality. Line mixture allows to adjust in line quality of mix by change of a ratio of the given raw materials. Mix is produced instantly, and there is no need to mix it in mixture tanks. Effectively and unmistakably to operate mixture process, line analyzers that instantly are necessary to measure mix parameters at the exit and to provide to operators of mixture necessary information on qualitative parameters of the received mix. It allows to adjust mix in real time on a stream in mixture process, providing mix with predetermined properties. It excludes the adjusting repeated mixture in volume the whole tank and also reduces an exit of unnecessary sub-standard products. The volumes of final distillates demanded by the market long and expensive laboratory analyses are necessary for check of real physical properties of mix. If these properties are not reached, repeated mixture is required. Effective mixture demands line monitoring of properties of mix throughout all production cycle the Chemical composition from each oil different. Despite the fact that whether oil is clean, or it is mix crude oil, for maintenance of stable quality of products line correction has to be carried out continuously. It demands sampling in real time and checks of physical properties of mix throughout all production cycle. Among all analyzers available in the market, line analyzers of the nuclear magnetic resonance (NMR) are the most suitable for this purpose.

4. Conclusion

Given that, in reality, most solid bodies and liquids, especially oil and petroleum products, behave like galoid systems, rheological physico-chemical science helps explain the causes of changes and changes in mechanical effects in dispersed systems and high molecular compounds.

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