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A new simulation model to polymer-oil interaction

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Abstract:
Background:
The extraction of crude oil is carried out on sites mostly inaccessible to the construction of a refinery. This fact is due to the inaccessibility of the oil fields (the location of the extraction wells is on hard-to-reach lands) and especially the extracted quantities, which usually do not ensure a frequency desired by the beneficiary (usually the crude oil deposits are subject to a natural decline process). That is precisely why the extracted crude oil is transported to the refineries through various delivery systems (pipelines, railways or cars). But pipeline transport is the cheapest way to transport them to their processing centers (which are located in industrial areas and usually more than 50 km from the oil fields). In Romania, the different conditions for the formation of crude oil, as well as the quantity and quality of their crude oil, differ from one oil field to another. That is precisely why the transport is mostly carried out in a mixture or in the form of water-in-oil emulsions. This mode of transport leads to the loss of the quality of the crude oils and the modification of their processing conditions, depending on the mixtures made and not on the individual properties of the crude oils.
Materials and Methods:
In order to study the influence of additives on the rheological characteristics of crude oils, two additives were created that were dosed in a mixture with crude oils and the evolution of the freezing curve of these mixtures was determined depending on the amount of additive added as well as their distillation curves depending on distillation temperature.
Results : the freezing temperature decreases from (30 to 14)°C, by 16°C, using additive depressant 1, and decreases by 12°C (30 to 18)°C using additive depressant 2, and their action is not lost over time (check was made after 48 hours). As the dose of addition increases, the efficiency increases, from the point of view of the intended goal (lowering the freezing point), but not from the economic point of view.
Also, a small variation in the quality of the obtained petroleum products was found, the additives used not affecting the distillation of the added crude oils.
Key Word: polymer, oil additives, effects of additives,

I. Introduction

Romania is a crude oil producing country that can extract about 3,500,000 tons of gasoline, crude oil and condensate. All these primary commodities are processed in the PETROBRAZI refinery. It has a current capacity of 4,300,000 tons and has the possibility of expansion to 5,000,000 tons.

But the multitude of crude oils extracted (their type and quality), led to the need to develop a classification of them. The need to additize crude oils is an absolutely normal requirement, as it ensures optimal and safe transport. Also, oil companies has the possibility to ensure a selected transport of these crude oils.

Worldwide, there are many classifications of crude oils that take into account the presence or absence of metallic, non-metallic or radioactive components, the distillation curve and the quantities of finished products obtained.

The classifications made took into account:

- the chemical composition of the crude oil;
- their properties (crude oils) or some fractions extracted from it;
- the content in different commercial fractions,
- the possibilities of processing crude oils.

The first classification analyzed is according to chemical composition.

Thus the class of hydrocarbons, the amount of paraffin in the oil and the bitumen content in the fractions distilled between 250°C and 300°C were determined. (Table 1).

Analyzing the density of crude oils (which, in the case of crude oils of the same nature and origin, can also indicate the content of light fractions) and the correlation of two or more physical properties (based on characterization factors, viscosity index, ratio of molecular mass and density) leads to obtaining a classification based on hydrocarbon classes. These take into account the physical properties of crude oils and petroleum fractions.

Table 1. Classification of crude oils according to chemical composition, %

Crude oil classes	**Fraction structures 250-330°C**			**Contents fraction**	
	Paraffine	**Naphtenic**	**Aromatic**	**Parafine**	**Asphalt**
paraffinic	46-61	22-32	12-23	1,5-10	0-6
paraffinic-naphthenic	42-45	38-39	16-20	1,0-6	0-6
naphthenic	15-26	61-76	8-15	urme	0-6
paraffinic-naphthenic-aromatic	27-35	36-47	26-33	0.5-1	0-10
flavored	0-8	57-78	20-25	0,0-0,5	0-20

Table 2. Oil clasification based to the fraction

Class	**Density of oil**		**Oil caracteristic based to fraction**		**Simbol**
	I	**II**	**I**	**II**	
1 2 3	<0,825	<0,875 0,876-0,943 >0,944	Paraffinic	Paraffinic Intermediate Naphthenic	PP PI PN
4 5 6	0,826-0,860	<0,875 0,876-0,943 >0,944	Intermediate	Paraffinic Intermediate Naphthenic	IP II IN
7 8 9	>0,861	<0,875 0,876-0,943 >0,944	Naftenic	Paraffinic Intermediate Naphthenic	NP NI NN

The classification is a function of the density measured at 15 ^{0} C, and this type of classification has the disadvantage that the presence of some naphthenic or aromatic structures can lead to a change in density.

At the same time, sulfur and oxygen compounds in non-paraffinic crude oils can change the density of the analyzed crude oil.

In the transportation of crude oil at the present time, three classes of crude oil are present [1]:

- asphaltic or non-paraffinic - type A;
- semi-paraffin - type B;
- paraffinic - type C.

The analysis of Romanian crude oils led to their classification, depending on the content of white products obtained after distillation and which is the newest classification [T.Chiş-2012], crude oils being divided into:

- A1 - (24.3%) Heavy crude oil, without paraffin, < 60% "white products"
- A2 - (16.5%) Heavy crude oil, without paraffin, > 60% "white products"
- B - (8.4%) Semi-paraffin oil
- C1 - (17.9%) Paraffinic crude oil, < 65% "white products"
- C2 - (30.9%) Paraffinic crude oil, > 65% "white products"
- Condensate (2.0%).

The pumpability of crude oil through pipelines must be ensured so that the freezing temperature is a maximum of 7 degrees below the ground temperature and the viscosity is a maximum of 100 cSt.

That is precisely why, analyzing the quality of the extracted crude oil and the conditions for pumping it through the pipeline, it was found that:

a. Type C (paraffinic) crude oils have a high freezing point. They also have a large amount of white goods,

b. Type A (asphalt) crude oils have a high viscosity. At the same time, they also have a large amount of heavy products obtained after refining.

Therefore, for the transportation of crude oils, it is necessary to create mixtures of crude oils as follows:

a. By diluting with low viscosity products to reduce the viscosity of A-type crudes,

b. By diluting with products that have a low freezing point, which will reduce the freezing point of C-type crudes.

Usually the diluents are other types of crude oil or finished products not normally found in oil fields.

Also, in order not to affect the quality of the crude oil and therefore of the refining products (since the dilution of light crude oil with heavy products results in non-compliant diesel or gasoline), petroleum additives are used, which are chemical substances that are mixed with the crude oil basis, achieves the improvement of their properties [2].

These additives are usually polymers (or other chemical agents), which modify the precipitation of paraffin crystals from the solution.

The mechanisms for changing the solution are the following:

• The additive can come out of the solution at a temperature higher than the stabilization temperature of the paraffin solution and has no effect on it;

• The additive can come out of the solution at an equilibrium temperature of the paraffin solution and co-crystallize with the paraffin, offering the possibility of improving viscosity and freezing;

• The additive can leave the solution at a lower temperature than the equilibrium temperature of the paraffin solution. In this case it absorbs the paraffin crystals.

II. Material And Methods

The main additives used to improve the rheological properties of petroleum products are macromolecular additives.

These are usually the only class of compounds used in practically all petroleum products starting with crude oil itself [3,4].

An explanation of this wide use can be the fact that, under the generic name of macromolecular additives, products of great diversity are brought together (both in terms of molecular mass and especially of chemical structure).

These molecular additives can perform, in addition to the specific functions of a macromolecule, other very varied functions, such as:

- change in viscosity,
- modification of the pour point,
- increasing the quality of crude oils, covering the vast majority of classes of known additives [5].

Taking the molecular mass as a criterion, oil additives can be divided into two large groups [6]:

- actual macromolecular additives. They have molecular masses between 10^4 and 10^6 and a main function of improving the rheological properties of petroleum products. Secondary these additives can also be paraffin crystal modifiers or dispersants;
- additives with a relatively low molecular weight, between 10^3 and 10. They are rather classified as oligomers, without significant effects on the rheological properties.

Additives with relatively low molecular weight are modifiers of the crystalline structure of paraffins or can be used as antioxidants.

In many cases, the macromolecular chain is used only as an oleophilic residue, carrying a functional group with a specific effect.

Depressant additives, with the exception of those based on alkyl naphthalene or alkyl phenols, are, for the most part, macromolecular compounds.

Among them, a first category is represented by copolymers with long alkyl chains of acrylic, methacrylic, fumaric, maleic, vinyl esters, etc. [5].

These additives can be made both in versions with high molecular masses, especially for oils, and in versions with low molecular masses, especially for crude oils.

A second category, of more recent date, is represented by the copolymers of ethylene with vinyl acetate, produced exclusively at low molecular masses of 2000-10000 and containing different percentages of vinyl acetate depending on the destination.

The depressant additives were initially used in the case of paraffinic oils, obtaining drops of the freezing point of 20-30°C, which at first sight would allow a reduction in the degree of dewaxing with special economic effects.

A second group of oil products that consume a lot of depressant additives is diesel fuel.

In general, the additives mentioned above, possibly with some structural modifications, allow obtaining winter diesels with freezing temperatures of -25 at -30°C.

As with oils, characterizing low temperature behavior based on freezing temperature alone has proven to be insufficient; thus, products with low freezing temperatures, led to the blocking of filters installed in the fuel tanks of motor vehicles with paraffin crystals.

In these conditions, the filterability limit temperature method was introduced to characterize these products, which determines the blocking temperature with paraffin crystals of a standard filter.

The introduction of this method led to the need to lower the freezing temperature of non-additive diesel fuels to values between -7°C and -12°C.

In these conditions, the use of suitable depressants allows both a decrease in the freezing point by 15 to 20° and a decrease in the filterability temperature by 7 to 15°C.

Research on the mechanism of action of depressant additives has been carried out in the vast majority on polymers with long alkyl chains. In all cases, an obvious proportionality was found between the freezing temperature of the product subjected to additive and the length of the alkyl chain of the depressant additive.

The proposed mechanism of action is based on the adsorption of the additive on the surface of the paraffin crystals, leading to an alteration of their shape and size and preventing their agglomeration into macrocrystalline aggregates [7].

It is appreciated that for the process to be effective it is necessary for the additive to crystallize itself immediately after its adsorption on the surface of the crystals.

III. Result

One method of improving pumpability is the use of various additives (to lower the freezing point and/or viscosity).

These additions can be polymers or other chemical agents, which modify the precipitation of paraffin crystals from the solution, through one of the following mechanisms:

• the modifier comes out of the solution at a temperature slightly higher than the equilibrium temperature of the paraffin solution;

• the modifier leaves the solution at an equilibrium temperature of the paraffin solution and co-crystallizes with the paraffin;

• the modifier comes out of the solution at a temperature slightly lower than the equilibrium temperature of the paraffin solution and is absorbed on the paraffin crystals.

The modifier present in the solution, acting through one of the above mechanisms, tends to maintain the paraffin molecules as separate entities, by reducing the cohesive forces between the crystals and the adhesion forces between the paraffin crystals and other surfaces.

The vast majority of modifiers proposed as depressants for crude oils are macromolecular compounds. Among them, two groups stand out:

1. ethylene - vinyl acetate copolymers, with relatively low average molecular masses of 1000-10000, having the general structure:
2. copolymers of unsaturated esters with long alkyl chains.

There are also some depressants that limit paraffin deposits, and others that slightly reduce the crystallization temperature.

Depressant additives are used in the transportation of crude oils to lower their freezing points so that they can be transported through pipelines.

A large number of additives have been produced for this purpose, most of which are low molecular weight copolymers such as copolymers of maleic, acrylic and methacrylic esters. Most of these depressants have a disadvantage, that is, they have a narrow operating range (40-60°C) and the additive does not prevent the deposition of paraffin crystals on the pipe walls.

Three patented additives were created in Romania through patents RO 67487, RO 113057, RO 116550.

In patent RO 67487, a depressant additive was created for paraffinic crude oils with a freezing temperature of around +20 °C. This additive is obtained by copolymerizing vinyl acetate with fumaric diesters containing 20-22 carbon atoms in the alkyl chain.

Also, patent RO 113057 uses copolymers of vinyl acetate with fumaric diesters with 20-22 carbon atoms in the alkyl chain, the additive obtained being useful in the transport of crude oils with a freezing point of +16 to +20 °C.

It is found that although the addition of crude oils ensures a corresponding reduction of the freezing point, over time paraffin deposits appear on the walls of the conduits, which requires frequent stops to remove them. The formation of these deposits is due to the fact that the respective additives do not ensure a dispersion of the paraffin crystals in the crude oil mass, which leads to their deposition over time.

The technical problem proposed in patent RO 116550 is the development of an antidepressant additive composition that also exhibits a dispersing action on paraffin deposits on the walls of pipelines that transport crude oil.

The process of obtaining the additive consists in subjecting to a terpolymerization with vinyl acetate, at a temperature of 80-100 °C, for 14-16 hours, in the presence of benzoyl peroxide, a mixture consisting of a fumaric diester, containing in percentage molar 4-6% C_{18} fumarate, 45-55% C_{20} fumarate, 35-30% C_{22} fumarate, 15-7% C_{24} fumarate, 1-2% C_{26} fumarate and a fumaric monoester of the same number of carbon atoms, in the alkyl chain.

So this additive consists of a toluene solution containing 45-55 % terpolymer resulting from the terpolymerization of 60-70 mol % vinyl acetate with 35-25 mol % fumaric diester with C_{18}-C_{26} alkyl chains and 5 mol % fumaric monoster with the same number of carbon atoms in the alkyl chain, the remaining 55-45% being toluene.

The additive is obtained as follows:

- in a reactor equipped with a stirrer, thermometer, heating jacket, Dean-Stark elbow and refrigerant, dose 300 grams of fatty alcohol (0.90 mol) with a content of 6% fraction C_{26}, 58 grams of fumaric acid (0, 5 mol) and 240 grams of toluene,

- the reaction mixture is heated with stirring to a temperature of 60-70 °C, temperature gradually, temperature at which 2 ml of oleum sulfuric acid is added. The temperature is then raised gradually, depending on the reflux, up to 120-130 °C. the esterification reaction is finished after 5-6 hours, when the amount of water collected is 14.5-15.5 ml. Afterwards, the product is cooled to 60-70 °C, being neutralized with 30 grams of solid Na_2CO_3 for 2-3 hours, then left to settle for 30-60 minutes.

The final reaction product is a reddish brown fluid with a toluene content of 40 % saponification figure 120-130 mg KOH/g and 10 mol % fumaric monoester.

It can also be obtained like this:

- in a reactor equipped with a stirrer, thermometer, heating jacket, Dean-Stark elbow and refrigerant, dose 320 grams of fatty alcohol (0.90 mol) with a content of 12% alcohol fraction C_{18}, 14% alcohol fraction C_{20}, 73% alcohol fraction C22 and 1% alcohol fraction C24, 58 grams of fumaric acid (0.5 mol) and 250 grams of toluene,

- the reaction mixture is heated with stirring to a temperature of 60-70 °C, temperature gradually, temperature at which 2 ml of oleum sulfuric acid is added. The temperature is then raised gradually, depending on the reflux, up to 120-130 °C. the esterification reaction is finished after 5-6 hours, when the amount of water collected is 14.5-15.5 ml.

- The toluene solution 40% by weight of this mixture consisting of 90% mixed fumaric diester and KOH/g and the acidity index 2-3 mg KOH/g after neutralization,

- It undergoes thermopolymerization with 65 g of vinyl acetate, 400 g of mixed fumaric diester and monoester mixture. The reaction takes place in a reactor, benzoyl peroxide in a total amount of 5 g being added fractionally in three parts at intervals of 5-6 h.

- After the terpolymerization period at 99-102 °C for 16-14 h, the product is cooled to 60-70 °C and diluted with 145 g for a concentration of 50% by weight of toluene, mixing for 30- 40 minutes.

To study the influence of additives on the rheological characteristics of crude oils, two additives were created.

The additive made in the Ovidius University laboratory consists of:

- 75 ml o,m,p-xylene with C_8H_{10} content 96%, Fe 0.00001 g, HCl 0.0004 acidity, resistance to evaporation 0.001%, water 0.02, density 0.865
- 15 ml of liquid vinyl acetate $C_4H_6O_2$, density 0.93, boiling point 73°C,
- 10 ml of formic acid, for the elimination of biological poultices,

The second additive consists of:

- 75 ml of probe condensate, density 0.72,
- 15 ml of liquid vinyl acetate $C_4H_6O_2$, density 0.93, boiling point 73°C,
- 510 ml of formic acid, for the elimination of biological poultices,

Each additive was boiled at 80 °C degrees for 1 hour and then cooled.

The additive was used in mixture with crude oils.

The equations for the behavior of the distillation curve as a function of the distillation temperature are (y is the quantity distilled % and x is the read temperature ^{0} C:

Crude oil

$y = -3E^{-10}x^4 + 3E^{-05}x^3 - 0.0163x^2 + 3.1969x - 179.74$

$R^2 = 1$

Crude oil+ Additive 1

$y = 1E^{-07}x^4 - 5E^{-05}x^3 + 0.0042x^2 + 0.9622x - 90.583$

$R^2 = 1$

Crude oil + Additive 2

$y = 3E^{-07}x^4 - 0.0002x^3 + 0.0482x^2 - 4.3478x + 142.75$

$R^2 = 1$

The freezing temperature decreases from (30-14)°C, by 16°C, using additive depressant 1, and decreases by 12°C (30-18)°C using additive depressant 2;

Their action is not lost in time (check was done after 48 hours).

IV. Discussion

Usually the diluents are other types of crude oil or finished products not normally found in oil fields.

Also, in order not to affect the quality of the crude oil and therefore of the refining products (because for the dilution of light crude oil with heavy products, a non-compliant diesel or gasoline is obtained), petroleum additives are used, which are chemical substances that are mixed with the crude oil base, improves their properties.

These additives are usually polymers (or other chemical agents), which modify the precipitation of paraffin crystals from the solution.

The mechanisms for changing the solution are the following:

• The additive can come out of the solution at a temperature higher than the stabilization temperature of the paraffin solution and has no effect on it;

• The additive can come out of the solution at an equilibrium temperature of the paraffin solution and co-crystallize with the paraffin, offering the possibility of improving viscosity and freezing;

• The additive can come out of the solution at a lower temperature than the equilibrium temperature of the paraffin solution. In this case it absorbs the paraffin crystals.

V. Conclusion

To study the influence of additives on the rheological characteristics of crude oils, two additives were created.

Mixed with crude oil the freezing temperature decreases from (30-14)°C, by 16°C, using additive depressant 1, and decreases by 12°C (30-18)°C using additive depressant 2;

Their action is not lost in time (check was done after 48 hours) and the best depressant (efficiency: 85.71%) that lowered the freezing point from (+30 to +5°C) is depressant 1, at a dose of 1200 ppm and t = 40°C.

As the dose of addition increases, the efficiency increases, from the point of view of the intended goal (lowering the freezing point), but not from the economic point of view.

References

[1]. Anderson A, Al-Mohaimeed AM, Elshikh MS, et al. (2021) Exergy and Energy Analysis of α-Fe_2O_3-Doped Al_2O_3 Nanocatalyst-Based biodiesel blends—Performance and emission characteristics. J Energy Resour Technol 143. https://doi.org/10.1115/1.4050488 doi: 10.1115/1.405048,

[2]. Chis T.-Optimisation of Roumanian Oil Blend, SGEM Conference, Varna, 2012,pp,314-320, SGEM Conference Proceedings, ISSN 1314-2704,

[3]. Chis, T., Radulescu, R., Stoianovici, D., Vlădescu, R. (2023). A new model of oil pipeline (oleduct) risk assessment. International Journal of Safety and Security Engineering, vol. 13, no. 1, pp. 175-185. https://doi.org/10.18280/ijsse.130120.

[4]. Ershov M.A., Savelenko V.D., Makhova U.A., et al., New insights on introducing modern multifunctional additives into motor gasoline. Sci Total Environ 2021, 152034. https://doi.org/10.1016/j.scitotenv.2021.152034 doi: 10.1016/j.scitotenv.2021.152034

[5]. Yilmaz İ, Taştan M, Investigation of hydrogen addition to methanol-gasoline blends in an SI engine. Int J Hydrogen Energy, 2018 43: 20252-20261. https://doi.org/10.1016/j.ijhydene.2018.07.088 oi: 10.1016/j.ijhydene.2018.07.088

[6]. Fahim, M. A., Al-Sahhaf, T. A., & Elkilani, A. Fundamentals of petroleum refining, 2009, Elsevier.

[7]. Ghanbari M, Mozafari-Vanani L, Dehghani-Soufi M, et al. (2021) Effect of alumina nanoparticles as additive with diesel-biodiesel blends on performance and emission characteristic of a six-cylinder diesel engine using response surface methodology (RSM). Energy Convers Manage: X 11: 100091. https://doi.org/10.1016/j.ecmx.2021.100091 doi: 10.1016/j.ecmx.2021.100091

[8]. Guzmán-Osorio FJ., Domínguez-Rodríguez VI., Adams RH., Lobato-García CE., Guerrero-Peña A., Barajas-Hernández JR., Classification of petroleum origin and integrity by FTIR, Egyptian Journal of Petroleum, Volume 30, Issue 2, 2021, Pages 63-67, ISSN 1110-0621, https://doi.org/10.1016/j.ejpe.2021.03.003,