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**STUDY OF HEAT TREATMENT AND COOLING RATE  
OF OIL MIXTURES TRANSPORTED  
BY “KUMKOL-KARAKOIN-BARSENGIR-ATASU” PIPELINE**

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**Abstract.** *Transportation of Kazakhstan waxy crude oil mixtures through long distance pipelines, such as «Kumkol-Karakoin-Barsengir-Atasu» entails various difficulties due to its composition. One of the most effective way to improve rheology is using heat treatment. The objective of this work is to investigate the effect of heat treatment on the rheology of oil mixtures and wax deposition tendenc in addition, to studying the influence of cooling rate and kinetics of wax crystallisation in accordance to the JMAK (Johnson-Mehl-Avrami-Kolmogorov) theory. The results indicate that increasing the value of heat treatment leads to improvment of rheological parameters of oil mixtures and a decrease in wax deposition but no change to the shape of crystals.*

**Keywords:** *rheology, paraffin, wax deposition, JMAK theory*

## 1. Introduction

The waxy crude oils of the eastern part of Kazakhstan create many problems during their transportation through long distance pipelines, such as «Kumkol-Karakoin-Barsengir-Atasu» pipeline due to their physico-chemical characteristics. At lower temperature, wax can crystallize and precipitate on the surfaces of pipe walls. Because the temperature at the walls is less than the temperature at the center of the flow line, it leads to a temperature gradient and concentration gradient causing molecular diffusion of the paraffin crystals towards the wall [1]. Over time, build-up of the solid deposit will reduce the internal diameter and eventually will block the line [2]. According to Burger et al. the deposition of wax occurs as a result of lateral transport by diffusion, shear dispersion and Brownian motion [3]. A number of factors that can affect the rate of paraffin deposition are as follows: temperature of the crude, temperature of the pipeline wall, flow rate, residence time, wax concentration, pipe roughness and others. Wax deposition causes an increase in the pressure drop at high flow rates, which can result in higher pumping costs and reduced throughput. Therefore, there are different methods for removal and prevention of wax formation such as mechanical methods like scraping and pigging, thermal methods like hot-oiling, chemical inhibition methods and also more

sophisticated methods such as ultra-sonic removal, electro-magnetic treatment and microbial inhibition [4-8]. Due to differences in physico-chemical characteristics of every crude oil, there is no single technique available for all crude types [9].

Thermal methods are comparatively straight forward and effective in all kind of crude oils that deposit predominantly paraffin wax [10]. Hot oiling is one of the most commonly used and oldest methods for transportation of highly waxy oils. The main objective of any thermal method is to maintain fluid temperature well above the Wax Appearance Temperature (WAT). The effectiveness of thermal methods directly depends upon heat transferred to oil. In the heating process, extra heat energy is supplied to the system to melt the deposited paraffin waxes and to maintain sufficient temperature in the system to halt further precipitation. In order to improve the efficiency of different treatments, theoretical analyses and several thermodynamic models were designed for simulation and prediction of paraffin precipitation in crude oils [11-13].

Therefore, it is crucial to study and analyze conditions and parameters that can improve rheological behaviour of crude oils and oil mixtures.

## **2. Materials and methods**

### **2.1. Materials**

Oil mixtures transported by «Kumkol-Karakoin-Barsengir-Atasu» pipeline were prepared by mixing of: Kumkol (64 %), Akshabulak (32 %), Ariskoe (4 %) crude oils and labelled as Kumkol mixture 1. Kumkol mixture 2 was prepared by adding Konys (6 %) crude oil to Kumkol mixture 1.

### **2.2. Methods**

Pour point was measured according to ASTM D 5853 with the help of «S.D.M.-530» (Germany) equipment. Wax appearance temperature and morphology of oil mixtures were measured by Linkam Hotstage equipment that consists of a polarized microscope (Holland) with combined video camera VC 301. Mechanical impurities were determined in accordance with GOST 6370-83 standard. Paraffins asphaltenes and resins content was calculated according to GOST 11851-85. Analyses of paraffins in oil mixtures were made using a PerkinElmer AutoSistemXL (USA) gas chromatograph. Effective viscosity and shear stress were measured on a Brookfield rheometer «EuroPhysics Rheo 2000» (UK) combined with a thermostatic “cylinder-cylinder” measuring system MS-CC45 and measuring element MB-CC 48. Such parameters as temperature, shear rate and measurement frequency were controlled by RHEO 2000 (2.6) software. Inhibition of wax precipitation was investigated using cold finger equipment that modeled the process of wax precipitation in the pipeline [14]. The amount of wax de-

posits was measured with and without heat treatment and then the paraffin inhibition efficiency (PIE) was calculated according to the following Eq. 1 [15]:

$$PIE = \frac{W_f - W_t}{W_f} \times 100 \quad (1)$$

where  $W_f$  is the reference amount of paraffin deposition without treatment (g), and  $W_t$  is the amount of paraffin deposition with heat treatment (g). The degree of crystallinity ( $\delta_r$ ) is measured by the relative wax deposition, obtained from cold finger method using Eq. 2:

$$\delta_r = \frac{\delta_t - \delta_0}{\delta_0} \quad (2)$$

where  $\delta_t$  is the total deposition at time  $t$  (min),  $\delta_0$  is the weight of maximum depositions obtained from the deposition curves when equilibrium has been achieved (g). The JMAK phase transition equation named after the individuals who derived it (Johnson-Mehl-Avrami-Kolmogorov) [16-20] is used to describe crystallization kinetics in oil mixtures by the Eq. 3:

$$1 - X = e^{-Kt^n} \quad (3)$$

where  $X$  is the volume fraction of crystalline material and  $K$  is the growth rate,  $n$  is the Avrami exponent, which characterises the structure of the crystal and also the nature of nucleation.

Replacing  $X$  by  $\delta_r$  from Eq. 2 and taking log twice in Eq. 3 it can be written as:

$$\log[-\ln(1 - \delta_r)] = \log K + n \log(t) \quad (4)$$

By plotting the left side in Eq. 4 versus  $\log(t)$ , the slope of the straight line  $n$  and the intersection  $K$  can be obtained. The Avrami coefficient is helpful in order to understand the mechanism of phase transformation dependent on both nucleation and growth mechanisms.

### 3. Results and discussion

#### 3.1. Physical characteristics of Kumkol oil mixtures

The physical characteristics of Kumkol oil mixtures is given in Table 1. Oil mixtures are waxy crude oil with low asphaltene contents. Kumkol oil mixture 2 is heavier and the wax content is as high as 13.1% which had a strong effect on the pour point and rheological behavior of the oil mixture.

Table 1. Physical characteristics of oil mixtures

No	Oil sample	Density, kg/m <sup>3</sup>	Asphaltene, (wt.%)	n-Paraffins, (wt.%)	Resins, (wt.%)	Mechanical impurities, (wt.%)
1	Kumkol oil mixture 1	816,6	0,32	17,8	5,60	>0.05
2	Kumkol oil mixture 2	818,4	0,33	18,9	5,78	>0.05

The chain size analysis obtained by gas chromatography for the Kumkol oil mixtures is shown in Fig. 1. It presented a nearly normal distribution, with chain sizes from 17 to 50 carbon atoms. The highest mass percent was found for a chain with 21 carbon atoms, corresponding to 9.11 % for Kumkol oil mixture 2. High contents of 8 % and 7 %, were also found for C32 and C25.

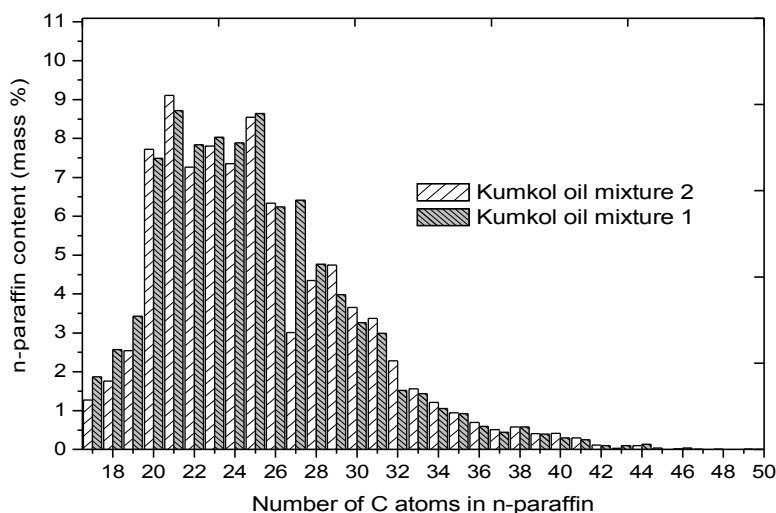


Fig. 1. Chain size distribution of the Kumkol oil mixtures

### 3.2. Wax Appearance Temperature (WAT)

A microscope equipped with polarization filters and hotstage equipment was used to measure the WAT of the 2 oil systems. The sample was placed between glass plates in Linkam Hotstage equipment and heated to 85 °C. The initial temperature was dependent on the WAT of the oil. The effects of cooling rate on WAT are shown in Fig. 2.

The graph shows the wax appearance behavior of the 2 oil mixtures. The curves show that increasing the cooling rate has a significant effect on the WAT.

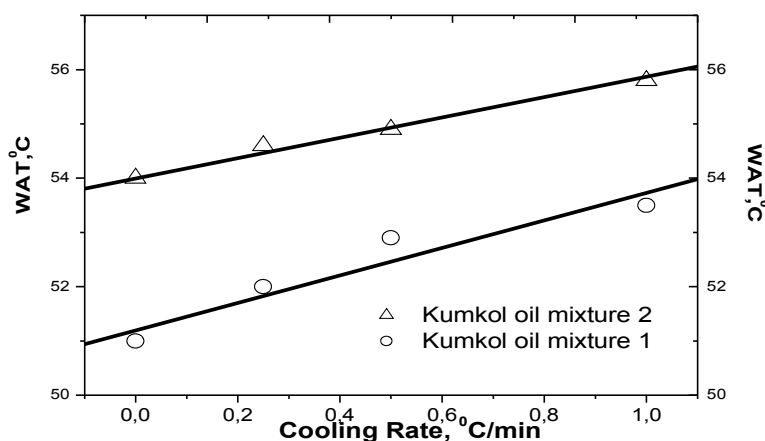


Fig. 2. Effect of cooling rate on WAT for Kumkol oil mixtures.

### 3.2. Rheological behavior of the Kumkol oil mixtures

The rheological behavior of the Kumkol oil mixtures are summarized in Fig. 2 and 3. It may be observed that the effective viscosity and shear stress decrease with increase in temperature. For Kumkol oil mixture 1 shear stress changes from 65 to 1.2 Pa on increasing heat treatment from 50 °C up to 65 °C. The same tendency is seen for Kumkol oil mixture 2. The effective viscosity of the oil mixture treated to 65 °C decreases by a factor of 30 times compared to treating only to 50 °C. Tables 2 and 3 show the changes of rheological parameters of oil mixtures versus temperature. For all oil mixtures, decreasing the temperature leads to increases in their viscosities. Kumkol oil mixture 1 and 2 treated to 50 °C shows non-Newtonian characteristics and high values of pour point. Such rheological behavior may be explained in terms of a nucleation process. At high temperatures (60-65 °C) mostly all wax is dissolved in solution and decreasing the temperature firstly leads to formation of centers of crystallization (nucleus) and secondly to their growth. In these conditions the oil behaves like a typical homogeneous isotropic liquid with Newtonian character even under low temperatures (Table 2, HT to 60 and 65 °C). At 50 °C and below, wax nuclei are already formed and decreasing the temperature leads to intensive growth of wax crystals forming a solid phase in the crude, which sharply increases the viscosity [21, 22].

Table 2. Dependence of rheological parameters on rate of heat treatment for Kumkol oil mixtures

Sample	t, °C	Kumkol oil mixture 1			Kumkol oil mixture 2		
		t, Pa (D = 5 c <sup>-1</sup> )	h, Pa·s (D = 5 c <sup>-1</sup> )	PPT, °C	t, Pa (D = 5 c <sup>-1</sup> )	h, Pa·s (D = 5 c <sup>-1</sup> )	PPT, °C
HT to 50 °C	15	0,641	0,127	+15	0,238	0,047	+15
	10	2,649	0,525		0,979	0,194	
	5	9,092	1,800		4,695	0,930	
	0	22,38	4,424		23,92	4,738	
	-5	31,71	6,267		46,88	9,283	
HT to 55 °C	15	0,005	0,011	+9	0,005	0,011	+12
	10	0,257	0,042		0,257	0,042	
	5	0,352	0,070		0,352	0,070	
	0	1,900	0,376		1,900	0,376	
	-5	6,172	1,222		7,260	1,438	
HT to 60 °C	15	0,055	0,011	+6	0,050	0,010	+9
	10	0,080	0,016		0,070	0,014	
	5	0,346	0,069		0,396	0,078	
	0	0,753	0,149		1,871	0,370	
	-5	3,954	0,783		4,784	0,947	
HT to 65 °C	15	0,045	0,009	+6	0,045	0,009	+6
	10	0,065	0,013		0,065	0,013	
	5	0,220	0,036		0,352	0,070	
	0	0,425	0,084		0,720	0,142	
	-5	2,411	0,477		2,653	0,525	

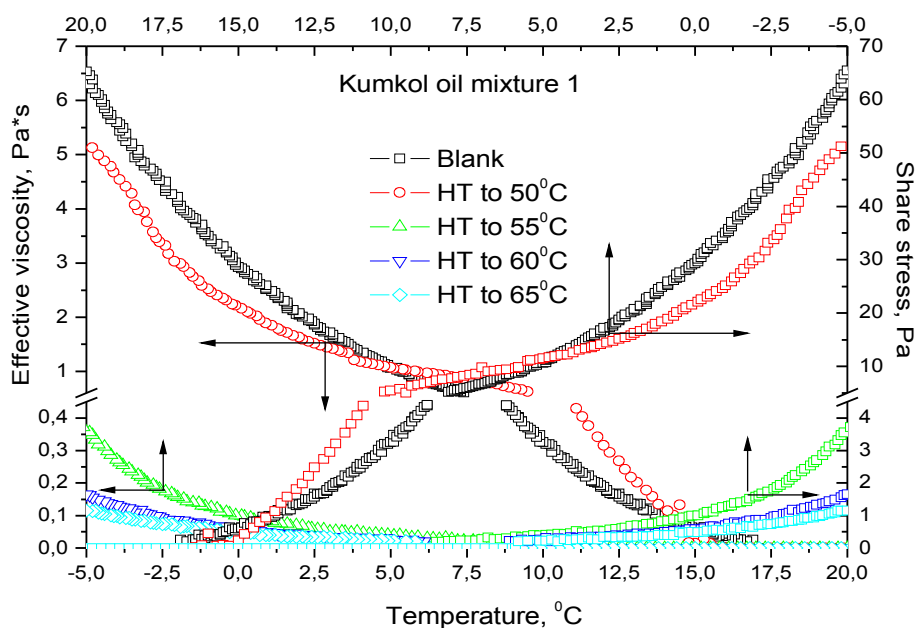


Fig. 3. Temperature dependence of effective viscosity and shear stress of heat treated Kumkol oil mixture 1

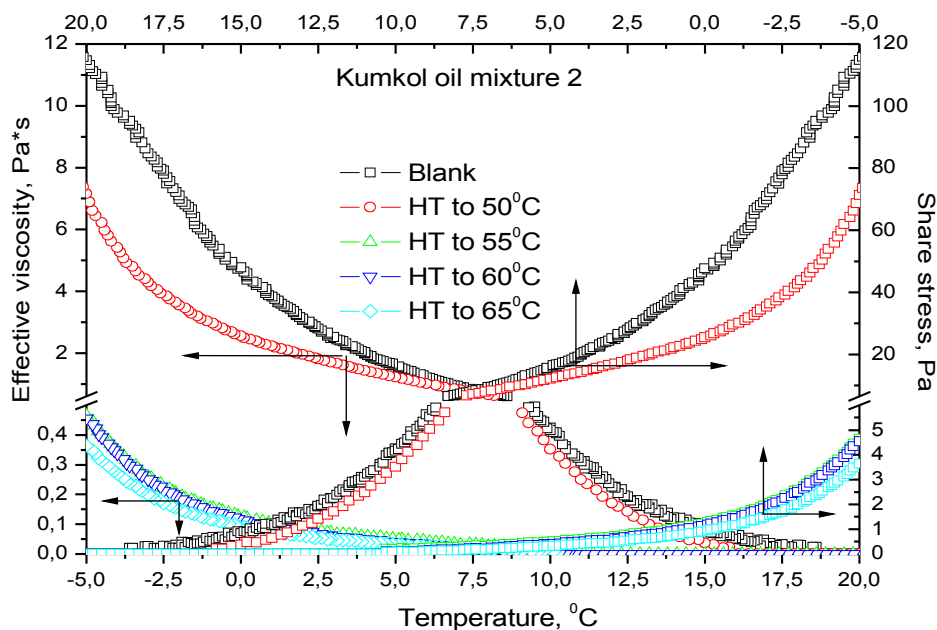


Fig. 4. Temperature dependence of effective viscosity and shear stress of heat treated Kumkol oil mixture 2

### 3.3. Optical Microscopy

Fig. 5 shows views using an optical microscope of the oil mixtures at 20 °C with different rates of heat treatment. It will be observed that the solid wax particles (the dark areas) form a homogeneous mass, evenly distributed throughout the whole sample. With increasing of temperature of treatment, the waxes have a smaller size and are more dispersed. Therefore, heat treated oils mixtures beginning from 55 °C show better rheological behavior and pour point reduction.

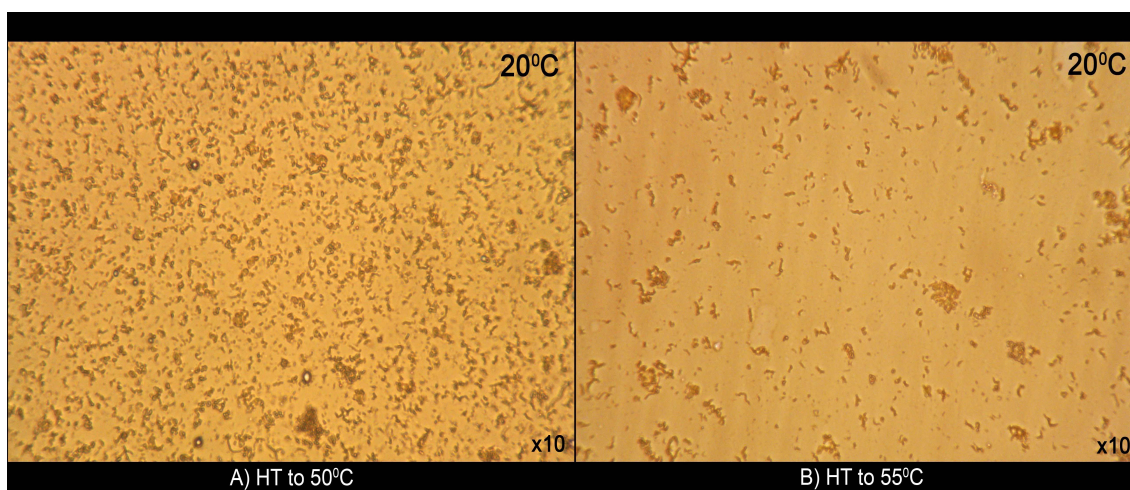


Fig. 5. Optical microscopy of the oil mixture Kumkol 2 at 50 °C(A) and 55 °C(B)

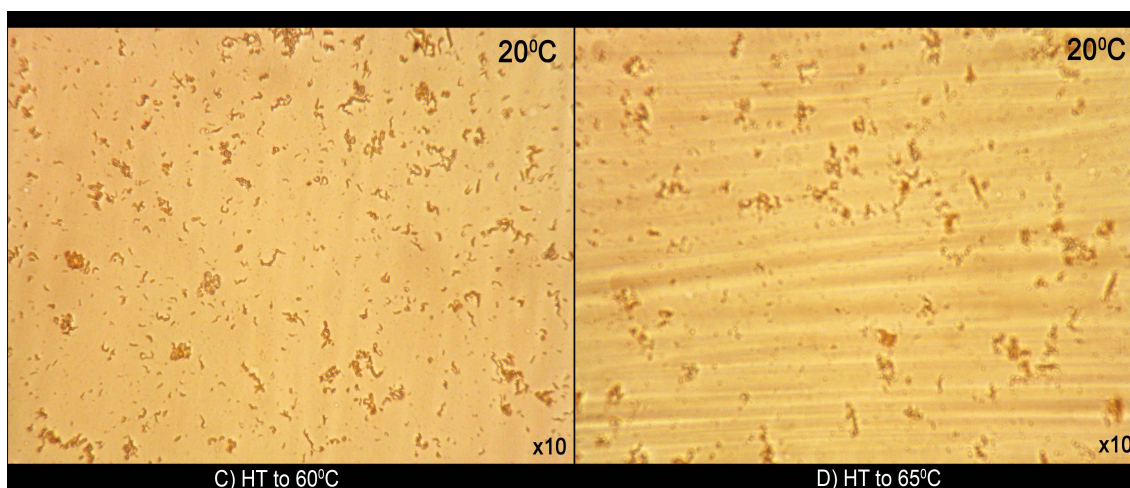


Fig. 6. Optical microscopy of the oil mixture Kumkol 2 at 60 °C(C) and 65 °C(D)

### 3.4. Wax deposition and Avrami exponent

The results obtained on deposition of wax from Kumkol oil mixtures with different degrees of heat treatment are presented in Table 3. Without any treatment, crude oil mixtures precipitate more than 7 gm of wax deposit. The wax deposition is reduced to 3,7 gm for Kumkol oil mixture 1 when increasing the value of heat treatment. Heat treatment below 60 °C displays higher efficiencies, reducing the wax deposition more than 45 % in contrast to the crude samples.

Table 2. Amount of wax deposition in the cold finger for different values of HT

Sample	Mass of waxes, g								
	Blank	HT 50 °C	PEI (%)	HT 55 °C	PEI (%)	HT 60 °C	PEI (%)	HT 65 °C	PEI (%)
Kumkol oil mixture 1	7,1	3,9	45,0	3,8	46,5	3,7	47,8	3,7	47,8
Kumkol oil mixture 2	7,7	4,4	42,8	4,3	44,1	4,2	45,4	4,2	45,4

By analyzing the growth phase curves using the JMAK theory, some crystallization/deposition kinetics can be extracted by plotting  $\log[-\ln(1-\delta_r)]$  versus  $\log(t)$  in Fig. 5. The values of crystallization kinetics is shown in Table 3. The growth rate ( $K$ ) generally increases with decreasing heat treatment. This is expected, as the higher the amount of wax nuclei (Fig. 5) the more wax crystals deposit in the first minutes of the

experiment and as a consequence the higher the crystallization rate. The Avrami exponent decreases with increase of the wax concentration in solution.

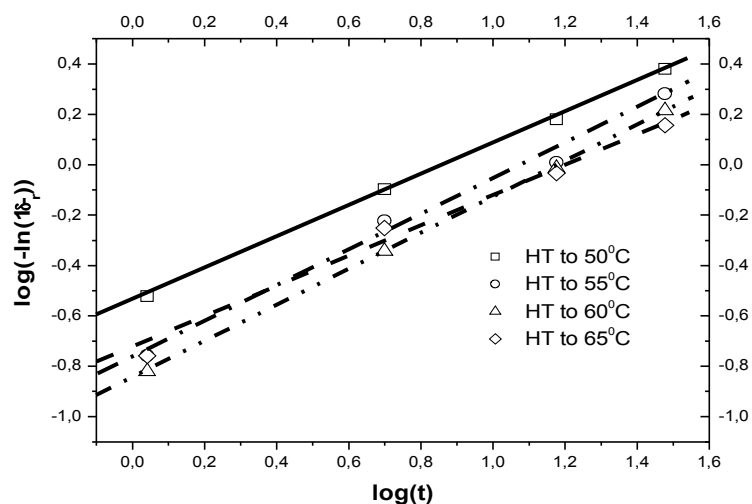


Fig. 5. Avrami plot for different values of heat treatment of Kumkol oil mixture 1.

According to the JMAK theory if the values of  $n$  are equal to 1 or below, the wax crystals will be of rod-like shape and growth is characterized as one-dimensional [21]. Therefore for both oil mixtures and values of heat treatment the crystals have rod-like or needle-like shape. Electron microscope pictures (Fig. 5 and 6) show that the shapes of the crystals are matched well with the kinetic evaluations.

Table 3. Avrami parameters for oil mixtures

Sample		Avrami parameters				
		Blank	HT 50 °C	HT 55 °C	HT 60 °C	HT 65 °C
Kumkol oil mixture 1	$n$	1.04	0.70	0.40	0.42	0.47
	$K$ (min <sup>-1</sup> )	0,37	0,25	0.16	0.14	0.12
Kumkol oil mixture 2	$n$	1.12	0,86	0.51	0.48	0.44
	$K$ (min <sup>-1</sup> )	0.41	0.29	0.19	0.17	0.14

This method is not as precise as direct measurements, but can give information about nucleation in advanced stages of crystallization, in cases simulating real conditions (temperature gradient and constant movement of oil).

## Conclusions

The study shows that the level of heat treatment has a great impact on the rheological behavior of oil mixtures. Considering the fact that sometimes due to technological scheme it is impossible to treat oil above WAT, the study of conditions that allows optimization of the process of transportation becomes a primary task. Heat treatment beginning from 55 °C reduces the viscosity of crude oil mixtures and helps to obtain preferable rheological parameters. From the Avrami analysis, it is found that the increase of temperature of heat treatment reduces the Avrami exponent, and also decreases the growth rate, suggesting that the crystallization mechanism is one-dimensional growth, with instantaneous nucleation predominating for both oil mixtures and for all values of heat treatment.

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