To the assessment of thermal stability of biopolymer systems

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Abstract

To diagnose thermal stability based on rotational viscometry data, an integral index for assessing the rheological properties of drilling fluids has been proposed. It is independent of their rheological model under thermobaric conditions of the well. According to the laboratory research of xanthan gum-based biopolymer systems, the possibility of assessing thermal stability in regard to the dependence of the integral index on temperature has been shown. The accuracy of thermal stability assessment has been confirmed by laboratory studies of the Biocar-TF biopolymer system at temperatures up to 170 ℃.

Keywords: biopolymer system, integral index, rheological properties, thermal stability.

The economic feasibility of constructing deep wells is largely related to ensuring the stability of borehole and high quality of productive formations opening. One of the promising directions for achieving this goal is the use of biopolymer flushing systems, which have recently been widely used while drilling oil and gas wells in Ukrainian fields and have proven their effectiveness in difficult mining and geological conditions [1, 2].

The success of using biopolymer systems is determined by the compliance of their rheological and filtration properties with the geothermal conditions of the well. Low thermal stability of polysaccharides that make up the base of such drilling fluids limits their use at great depths. This problem can be partially solved by increasing the mineralization of biopolymer systems with monovalent salts [1, 3–5]. The use of biopolymer systems beyond the thermal stability limits of the components requires methods ensuring accurate control of the permissible limit of their use.

We know that the rheological properties of biopolymer systems are most sensitive to changes in external factors [5, 6]. The thermal stability of biopolymer systems can be assessed with high accuracy using the results of HPHT rheometry. The criterion of thermal stability of xanthan gum-based biopolymer systems is T_m – the temperature at which the orderly structure of the polymer begins to break down, which is determined by the characteristic point of the curve on the viscosity graph or shear stress dependence on temperature at any shear rate [5–8]. When T_m is reached, the spatial structure of polymer molecules undergoes conformational changes – the molecules move from an ordered state to a less ordered one (Fig. 1). Such changes lead to a sharp decrease in the rheological parameters of the flushing system and increase the rate of thermal destruction [7, 9].

It is believed that T_m for xanthan gum-based biopolymer systems does not depend on the shear rate and to determine it, one curve from the entire set of curves obtained at different rotation speeds of the HPHT viscometer rotor is sufficient [5]. However, at different speeds, there are significant differences in the changes of the shear stress depending on the temperature. Accordingly, the assessment of thermal stability performed using one of the curves does not give an objective result. Quite often this phenomenon is observed in highly mineralized or heavy-weighted biopolymer systems. Figure 2 shows the curves of the shear stress dependence on temperature for the highly mineralized Biocar-TF biopolymer system [4, 10] with a density of 1370 kg/m^3 (well 11, Olefirivka block, Semerenky field), obtained at different rotation speeds of the HTHP OFITE 1100 viscometer rotor. For the given set of curves, their characteristic points at high and low speeds are significantly different. Accordingly, the error in the T_m according to this method [6] can be about 10 ℃.

In order to improve the accuracy of the T_m estimation, the entire range of shear rates should be considered. For this purpose, it is proposed to use an integral indicator that reflects a generalized assessment of the rheological properties of liquids in the measurement range [11]. It can be estimated from the

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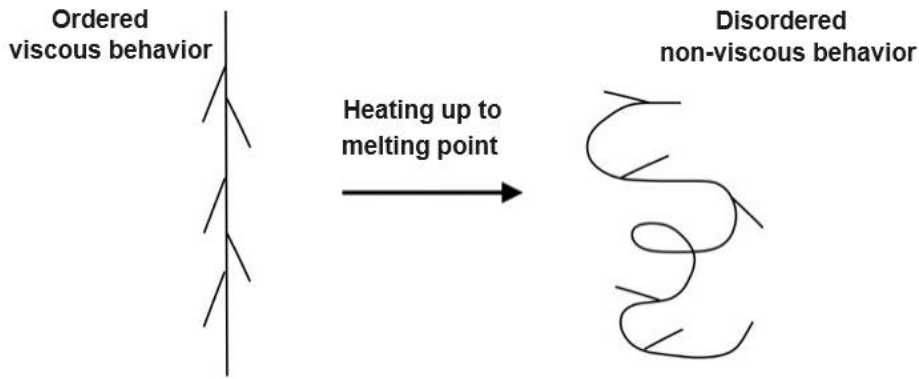*   Corresponding author:
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Figure 1 – Conformational changes in the xanthan gum molecule after heating to melting point temperature

rheological curve $\tau(a, \omega)$ over the entire range of the temperatures studied.

$$\varepsilon = \int_0^{\omega_{max}} \tau(a, \omega) d\omega,$$

where a is a vector of rheological properties; ω is angular rotation speed of the viscometer cylinder; ω_{max} is the maximum value of the angular velocity of the cylinder rotation for rheological properties estimation.

Figure 3 shows the limit of thermal stability based on the integral index ε for the Biocar-TF biopolymer system given above (well 11, Olefirivka block, Semerenky field). The rheological properties were measured with HTHP viscometer OFITE 1100. The obtained data were processed using methods [12, 13] and the Rheometry software package [14]. A single generalized curve has been constructed for the most adequate rheological models at each point of the temperature range of 30–170 °C and has allowed for a more accurate assessment of the thermal stability of the Biocar-TF biopolymer system, which is $T_m = 145$ °C.

The legality of using the T_m indicator as a criterion of thermal stability of biopolymer systems based on xanthan gum, the high accuracy and, accordingly, the technological expediency of using the proposed method are confirmed by the dependence curves for the integral indicator ε on the temperature in the heating – cooling mode (Fig. 4). The obtained results indicate that heating the xanthan gum solution to a temperature that is 5 °C lower than T_m does not lead to a change in the shape of the curve of the integral index ε upon further cooling. However, heating to a temperature that is 5 °C higher than the value of T_m leads to a change in the rheological properties of the xanthan gum solution and further deviation of the integral index ε curve. Such a decrease in the rheological parameters of the solution is a consequence of the polymer destruction of xanthan gum, which occurs even when the limit of its thermal stability is relatively slightly exceeded.

To check the reliability of $T_m = 145$ °C, calculated from the integral index ε, a series of laboratory studies has been conducted to determine the limit of heat resistance of the biopolymer system during its long-term heating. This method of analysis makes it possible to estimate the thermal stability of biopolymer systems with high accuracy, but requires a large number of laboratory studies.
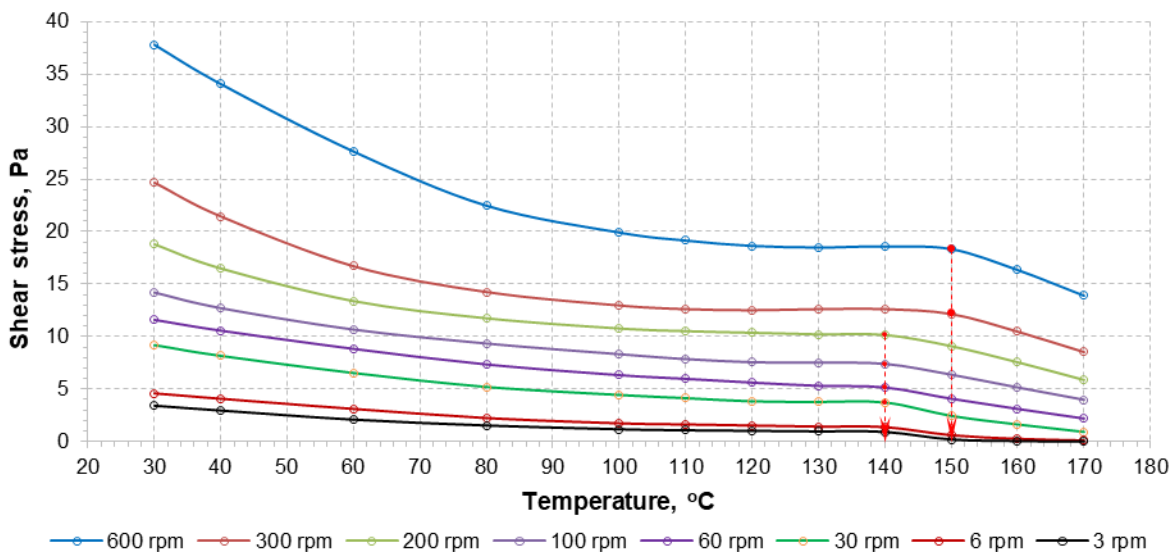

Figure 2 – Dependence of the shear stress of the Biocar-TF biopolymer system on the temperature for different rotation speeds of the viscometer rotor
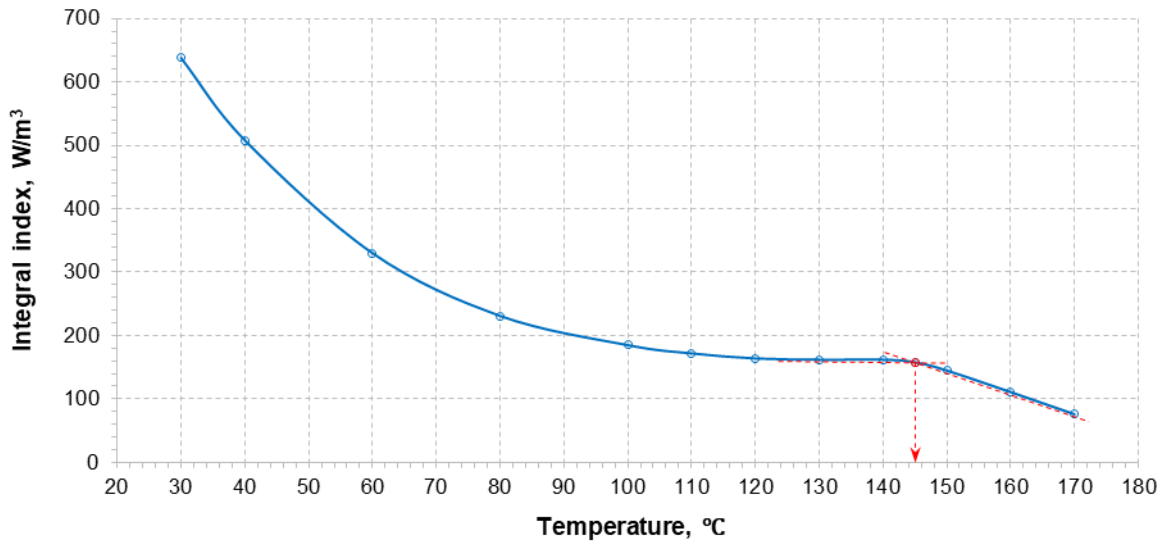
Figure 3 – Dependence of the integral index ε of the Biocar-TF biopolymer system on temperature
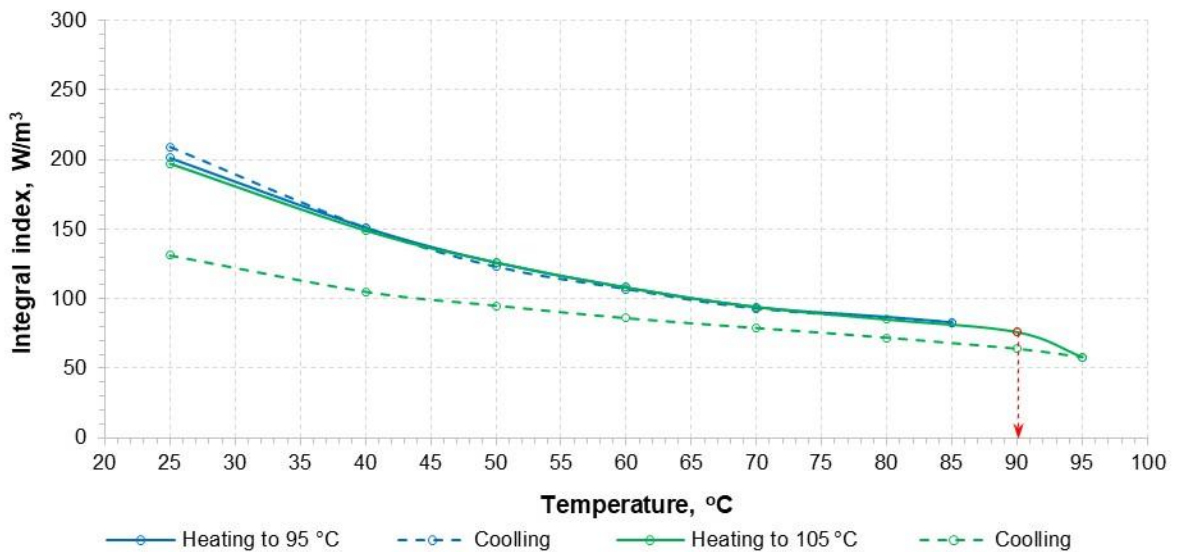

Figure 4 – Change of the integral index ε in the "heating – cooling" mode
for an aqueous solution of xanthan gum with a concentration of 0.5 %

For this purpose, samples of the Biocar-TF biopolymer system from well 11, Olefirivka block, Semerenky field were subjected to successive repeated heating at temperatures that were clearly higher or lower than the calculated value of T_m – a pre-established thermal stability limit. From the results presented in Table 1 it is clear that after 24 hours of heating at a temperature of 140 °C, the technological properties of the biopolymer system remained almost unchanged. However, heating at a temperature of 150 °C led to its complete destruction, irreversible deterioration of technological properties, delamination, and the presence of sludge and darkening of the filtrate (Fig. 5). Such processes are a clear sign of polymer destruction, which is a consequence of the excess of a thermal resistance limit. Consequently, the pre-established value of $T_m = 145$ °C for the integral index ε provides fairly accurate results and can be used as a criterion for the thermal stability of biopolymer systems.

Recently, biopolymers different from xanthan gum in origin and molecular structure have been used by various industries [15, 16]. According to [15, 17], such substances exhibit a high thickening ability and may have a different rheological behavior. Data on the attempts to develop biopolymer systems based on them [15, 16, 18] is available. Thus, the method used to determine the ultimate thermal stability for such systems may differ.

The results shown in Figure 6 indicate significant differences in the rheological behavior of different types of biopolymers. Among all the agents studied, the melting point T_m is correctly expressed only for xanthan and welan gums. According to its value, the limit of thermal stability for xanthan gum is 90 °C, for welan gum – 138 °C in a fresh-water medium. At the same time, welan gum is characterized by a tendency to increase rheological parameters with an increase in the temperature. This ability is associated with the

**Table 1 – Results of long-term heating of the Biocar-TF biopolymer system**

Test	Funnel Viscosity (100/200), s	Fluid Loss, cm³/30 min		$Gel_{10\,s/10\,min}$, Pa	Bingham model		Herschel–Bulkley model			Mud Cake Friction Coefficient	pH index
		API $\Delta p = 0.7$ MPa	$HTHP$ under $T = 145$ °C and $\Delta p = 3.5$ MPa		Yield Point, Pa	Plastic Viscosity, Pa·s	Yield Stress, Pa	Consistency Index, Pa·s^n	Flow Index		
Biopolymer system	12	2.7	10.6	3.8/5.3	10.1	0.023	3.41	0.24	0.70	0.17	9.25
Heating at 140 °C											
Biopolymer system after 8 hours	12	2.4	10.5	3.8/5.3	10.5	0.023	3.32	0.26	0.68	0.16	9.23
Biopolymer system after 16 hours	12	2.5	10.5	3.8/5.3	9.6	0.022	3.42	0.26	0.69	0.16	9.22
Biopolymer system after 24 hours	11	2.5	10.8	3.8/4.8	10.1	0.022	3.31	0.27	0.67	0.15	9.18
Heating at 150 °C											
Biopolymer system after 8 hours	9	3.2	19.5	2.9/3.8	6.2	0.018	2.87	0.13	0.73	0.19	8.35
Biopolymer system after 16 hours	6	4.1	26.2	2.4/2.9	6.2	0.017	2.59	0.09	0.78	0.25	8.01
Biopolymer system after 24 hours	4	6.5	44.5	1.4/1.4	4.3	0.017	1.27	0.10	0.77	0.31	7.13

macromolecular structure and is unique and not inherent in other biopolymer agents.

Guar, locust bean and konjac gums are characterized by a sharp decrease in viscosity when critical temperature is reached. With such a change in rheological properties, the characteristic point of the curve is absent, which excludes the possibility of determining the limit of thermal resistance using the above method.

Figure 7 shows the dependence curves of the integral index ε on temperature in the heating – cooling mode for a guar gum solution. The results obtained indicate that complete restoration of the rheological properties of the drilling fluid occurs in almost the entire temperature range of the studies, including high temperatures corresponding to the minimum residual values of the integral index ε. Irreversible changes in the polymer structure of guar gum occur only upon reaching a certain critical temperature, at which the viscosity of the polymer solution decreases to the level of solvent viscosity. At this stage, irreversible thermal destruction of the polymer units begins, which manifests itself in a decrease in rheological properties with further cooling of the system. Accordingly, such a critical temperature can be taken as the limit of thermal stability for polymers with a temperature rarefaction character close to linear. According to this method, the thermal resistance limit of guar gum is 130 °C, and it is 110 °C for the locust bean and konjac gums.
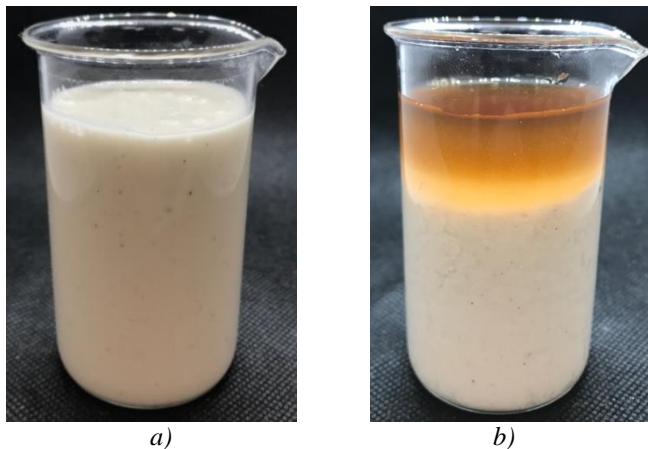
a) at a temperature of 140 °C; b) at a temperature of 150 °C

Figure 5 – Biocar-TF biopolymer system from well 11 of the Olefirivka block of the Semerenky field after 24 hours of heating
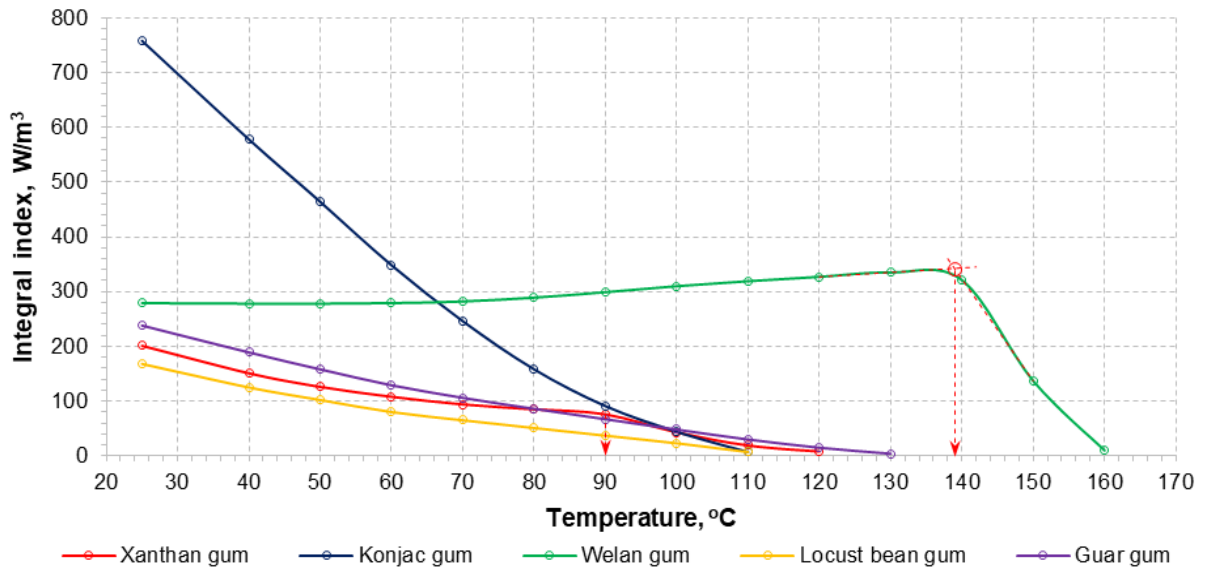
Figure 6 – Dependence curves of the integral index ε on temperature in a fresh-water medium for solutions of various biopolymers with a concentration of 0.5 %
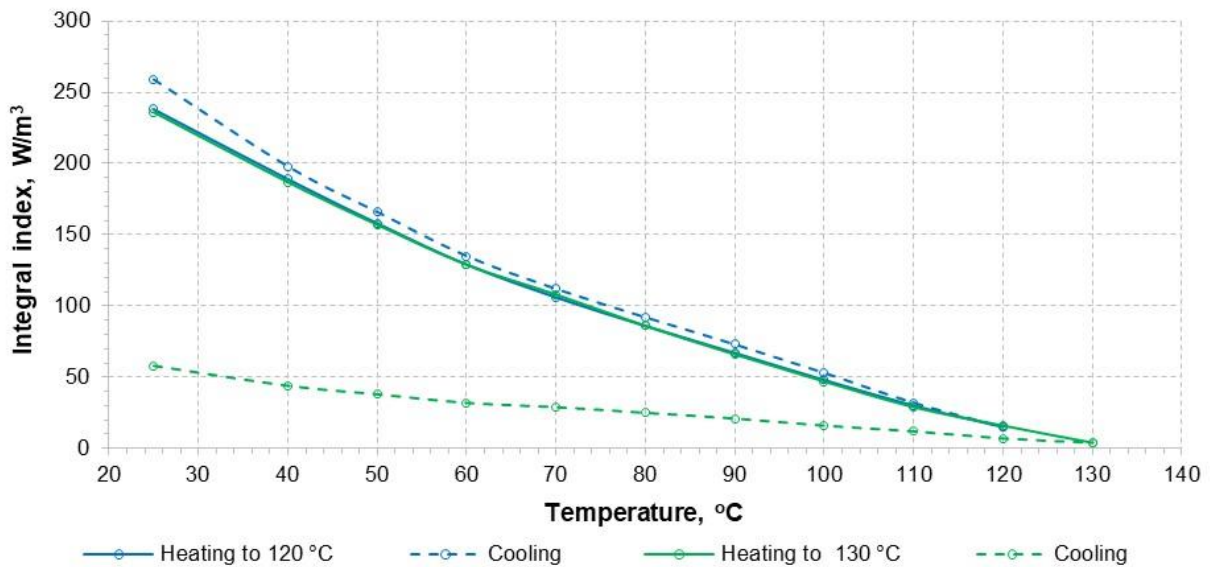

Figure 7 – Dependence curves of the integral index ε on temperature in the heating – cooling mode for a guar gum solution with a concentration of 0.5 %

Most often, a comparison of the viscous properties of drilling fluids and polymer agents is carried out based on the apparent viscosity and rheological parameters of the Bingham model [3]. However, depending on the component composition, drilling fluids can be described by different rheological models [11–14]; the same applies to the rheological behavior of biopolymers. In particular, xanthan and welan gums correspond to the Herschel-Bulkley model, and konjac, guar and locust bean gums correspond to the Ostwald model. It is impossible to compare liquids according to different rheological models and reducing them to one model can lead to significant errors.

The proposed integral index ε allows objective evaluation of the rheological properties of liquids of different natures. Figure 8 shows the comparison of aqueous solutions of biopolymers with different

rheological models in terms of the integral index ε and apparent viscosity. The obtained results have significant differences, since the apparent viscosity index, determined at one speed of rotation of the viscometer rotor, does not reflect the real viscous properties of biopolymers, especially for liquids with high pseudoplasticity (in this case, it is welan and xanthan gums). The integral indicator ε covers the entire range of measurement speeds, considers all the features of their rheological behavior and can be used for a more accurate comparison of liquids based on viscosity properties.

A reliable assessment of the thermal stability of a biopolymer system ensures the objectivity of its compliance with the thermobaric conditions of the well and the existing possibilities of physical and chemical influence to control technological properties.
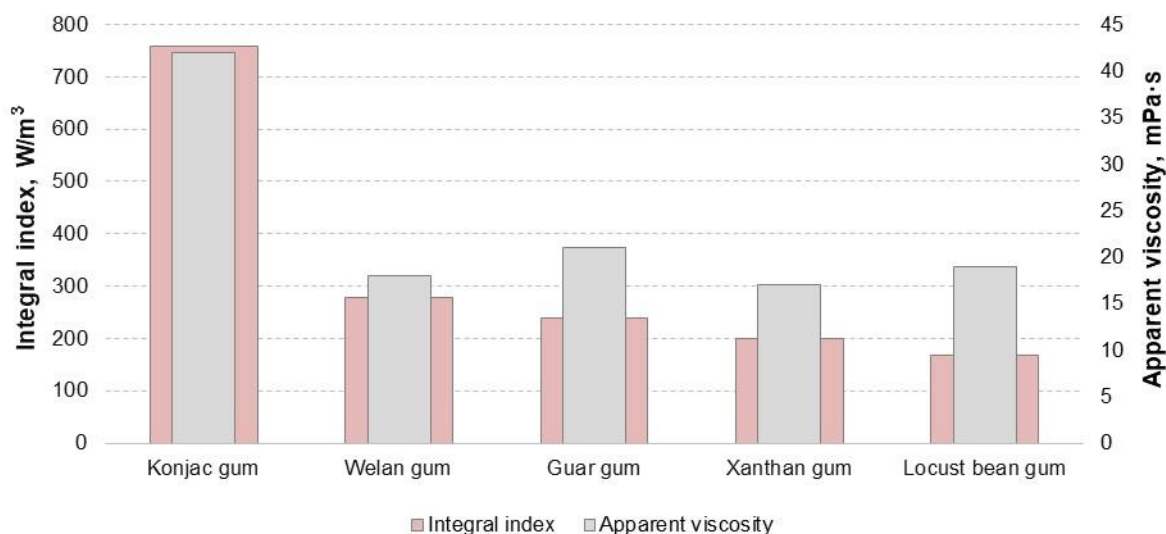
**Figure 8 – Comparison of aqueous solutions of biopolymers
with a concentration of 0.5 % in terms of integral index ε and apparent viscosity**

Conclusions

There integral indicator has been proposed for assessing the rheological properties of drilling fluids in the measured range of shear rates, independent of their rheological model under thermobaric conditions of the well. The possibility of using the dependence of the integral index on temperature to diagnose the thermal stability of biopolymer systems based on xanthan gum has been substantiated.

Laboratory studies of the thermal stability of the Biocar-TF biopolymer system have confirmed the reliability of their assessment due to the integral indicator of rheological properties. This provides higher accuracy in assessing thermal resistance compared to shear stress or apparent viscosity.

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До оцінки термічної стійкості біополімерних систем

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Для діагностики термічної стійкості за даними ротаційної віскозиметрії запропоновано інтегральний показник оцінювання реологічних властивостей бурових розчинів, який не залежить від їх реологічної моделі в термобаричних умовах свердловини. За результатами лабораторних досліджень біополімерних систем на основі камеді ксантана показано можливість оцінки термічної стійкості за особливістю залежності інтегрального показника від температури. Точність оцінки термічної стійкості підтверджено лабораторними дослідженнями біополімерної системи Біокар-ТФ при температурах до 170 °C.

Ключові слова: *біополімерна система, інтегральний показник, реологічні властивості, термічна стійкість.*