

Synthesis of Carboxymethyl Starch for increasing drilling mud quality in drilling oil and gas wells

K M Minaev¹, D O Martynova², A S Zakharov¹, R R Sagitov¹, A A Ber¹ and O S Ulyanova¹

¹ Tomsk Polytechnic University, 30 Lenina prospect, 634050, Tomsk, Russia

² Tomsk State University, 36 Lenina prospect, 634050, Tomsk, Russia

E-mail: minaevkm@bk.ru, martynova1847@gmail.com

Abstract. This paper describes the impact of carboxymethyl starch preparation conditions on physicochemical properties of polysaccharide reagent, widely used as fluid loss reducing agent in drilling mud. Variation of the main parameters of carboxymethylation is researched in the experiment. The following conditions such as temperature and reaction time, amount of water, as well as ratio of NaOH to monochloroacetic acid define the characteristics of carboxymethyl starch. The degree of substitution is defined for polysaccharides, as well as the characteristics of samples have been studied by infrared spectroscopy. Rheological characteristics and fluid loss indicator have been investigated to study the impact of the reagents on drilling mud quality.

1. Introduction

Being natural polysaccharide, starch is characterized by unique characteristics, such as high biocompatibility and annual renewability of raw material resources (potato plant, corn, rye, wheat, cassava, pea, etc.) that distinguish it from cellulose derived from wood, which period of maturing is 18 – 20 years for fast growing wood. In addition, another obvious advantage of starch is the ability to control the properties of polysaccharide by chemical, physical, bacteriological, biotechnological or mixed affect.

Due to its unique characteristics as natural polymer, starch is used as a base for production of a wide range of products. Chemically modified starch is produced by large companies, such as Akzo Nobel and Avebe (Netherlands), Raisio Chemical, Grain Processing Corp. (the USA), INQUIL® (Brazil), Henkel (Germany) Aloja Starkelsen (Latvia), Rolnas (Poland), etc. All of them have produced a wide range of starch. One of the main directions of application of their chemically modified starch production is the petroleum industry [1].

Starch was the first polymer reagent used for the drilling muds. In 1939 it was added to salt muds in the western part of Texas to regulate the filtration properties. However, with the introduction of polymer reagents based on cellulose ethers, especially carboxymethylcellulose, widespread use of starch started to reduce. This was primarily due to the need to use bactericides and low thermostability of starch reagents [2].

Currently, the natural starch is not used in drilling muds. Instead of it, the following types of modified starch are applied to regulate filtration and rheological characteristics of drilling muds as carboxymethyl, hydroxyethyl, starch hydroxypropyl, and phosphates of starch as well as oxidized starch. Carboxymethyl starch (CMS) is the most commonly used starch among all modified starch reagents. Providing the required filtration properties of drilling mud in free-salined mud and saline-based mud, carboxymethyl starch can be used as a cheaper alternative of carboxymethyl cellulose. It is characterized by good water solubility, resistance to high content of salt, high durability to thermal and bacteriological affect.



Despite the fact that the carboxymethyl starch is available on an industrial scale, it is urgent to research the technology of its production with the required characteristics and its application as a component of drilling mud. For this purpose various syntheses of carboxymethyl starch are developed. The most important methods to obtain carboxymethyl starch are dry method, extrusion, aqueous method and organic solvent slurry method.

Dry method of obtaining carboxymethyl starch is the easiest one, but it requires a period of time from several hours to several days and, the given carboxymethyl starch is characterized by low degree of substitution that restricts its further application.

As for extrusion method, it is characterized, on the one hand, by some technological advantages, in particular, high productivity, energy efficiency, but, on the other hand, it contains many additives, which require additional purification. The use of water as a reaction medium may be accompanied by gelling carboxymethyl starch, which leads to low degree of substitution and difficulties in the process of its extraction from a reaction vessel, as well as increase in the time of drying [3]. carboxymethyl starch with a high degree of substitution and a low content of additives can be obtained by the suspension procedure with a mixture of water and organic solvent as a reaction medium. It is suggested to add such amount of water that is sufficient for swelling starch grains at increased temperature, but not sufficient for gelling and agglomeration of polysaccharide. Swelling starch grains promotes rapid access of substances to a reaction zone, but their destruction impedes this process [4]. Therefore, the retention of starch grains is a key factor that determines industrial importance of the procedure that simplified considerably synthesis of carboxymethyl starch [5]. In addition to this procedure, excess swelling of starch grains can also be controlled by addition of cross-linking agents prevented full destruction of starch grains due to formation of intra- and intermolecular covalent bonds between polysaccharide chains. This treatment also increases the stability of grains to pH medium and high shear pull impact [6]. The proportion of chemical bonds is generally low in relation to the total weight of starch and the number of anhydroglucose units in grains in total, therefore to increase the efficiency of the procedure, the substances containing some active groups, for example, dialdehydes are used as cross-linking agents [7, 8]. Glyoxal refers to such substances, but being widely used as a cross-linking agent for starch and cellulose in pulp and paper industry, it is not enough studied. It might be suggested to get efficient conditions of carboxymethylation for modification of starch by cross-linking agents due to alkaline solution with $\text{pH} = 7.5 - 12$ [9].

The main parameters defining the efficiency of carboxymethylation by suspension procedure are the following: a type of solvents, amount of alkali, fluid, temperature, and reaction time [10]. Therefore, the purpose of the paper is to define the optimal conditions of carboxymethyl starch obtaining.

2. Materials and methods

Carboxymethyl starch was prepared by the following stages. Firstly, 13.8 gm of starch and 5.2 ml of sodium hydrate saturated solution were added to monochloroacetic acid solution, and then, if it was necessary, cross-linking agents in a form of 40% solution were injected. The mixture was heated to the reaction temperature and stirred for 1 hour. The resulting product was filtered, purged several times by ethanol, and dried at temperature of 50°C .

In the paper the ratio of alkali to monochloroacetic acid in carboxymethylation agent, the type of starch, the volume and type of solvent, water mass fraction in solvent content, amount of glyoxal as a cross-linking agent, as well as temperature and reaction time are varied (Table 1).

Table 1. Content of reaction mixture and reaction condition of carboxymethylation

Sample	Type of starch	Ratio m(NaOH)/m (monochloroacetic acid)	Solvent	V(solvent), ml	Temperature, °C	Reaction time, min	Glyoxal percent by weight, %.	Degree of substitution
CMS-IV	potato starch	0.88	water	25	40	10	-	60
CMS-cl-VI	potato starch	0.88	isopropanol	40	30	60	5	44
CMS-VI	potato starch	0.88	isopropanol	40	30	60	-	36
CMS-VII	potato starch	0.88	butanol-2	40	30	60	-	30
CMS-8	corn starch	0.88	isopropanol	40	30	60	-	30
CMS-10	potato starch	1.75	isopropanol	40	30	60	-	23
CMS-14	potato starch	3.50	isopropanol	40	30	60	-	11
CMS-11	potato starch	0.88	isopropanol	40	45	60	-	30
CMS-cl-11	potato starch	0.88	isopropanol	40	45	60	1	31
CMS-12	potato starch	0.88	isopropanol	40	55	60	-	26
CMS-cl-12	potato starch	0.88	isopropanol	40	55	60	1	33
CMS-13	potato starch	0.88	isopropanol	40	65	60	-	33

The chemical composition of samples was studied by FTIR spectroscopy using ATR method (attenuation total reflection) by Nicolet 6700 (Thermo Scientific) in a range of 400 – 4000 cm^{-1} . The degree of substitution of carboxymethyl starch was defined by the formula

$$\gamma = 162 \cdot \omega \cdot 100 / (2300 - 80 \cdot \omega), \quad (1)$$

taking into account sodium content in the samples, obtained by atomic absorption,

where γ – the degree of substitution, showing number of OH groups, substituted by carboxymethyl in a chain of 100 anhydroglucose units;

ω – sodium mass fraction, % wt.

To evaluate viscosity fluctuation in the studied samples of carboxymethyl starch, the rotor viscometer OFITE 800 was used. The apparent viscosity (AV), mPa·s was calculated by the formula “test value of viscometer at 600 rpm”/2.

$$\frac{\text{test value of viscometer at 600 rpm}}{2} \quad (2)$$

Wall-plastering properties of drilling mud were determined by the filter press OFITE. To investigate the influence of carboxymethyl starch on drilling mud, a model system, consisting of fresh drilling mud (5% solution of modified bentonitic drilling mud powder) and saline-based mud (5% solution of modified bentonitic drilling mud powder+400 gr/dm³ NaCl) was used.

3. Results and discussion

3.1. Reaction temperature

Evaluating the influence of carboxymethylation reaction temperature of potato starch on its characteristics was carried out in the temperature range from 30⁰ to 65⁰C. It is shown that by using a cross-linking agent, the ratio of drilling mud viscosity to the temperature of carboxymethylation is characterized by 45⁰C maximum temperature, while in the case of a cross-linking agent absence, this parameter increases at higher temperature up to 55⁰C (fig.1).

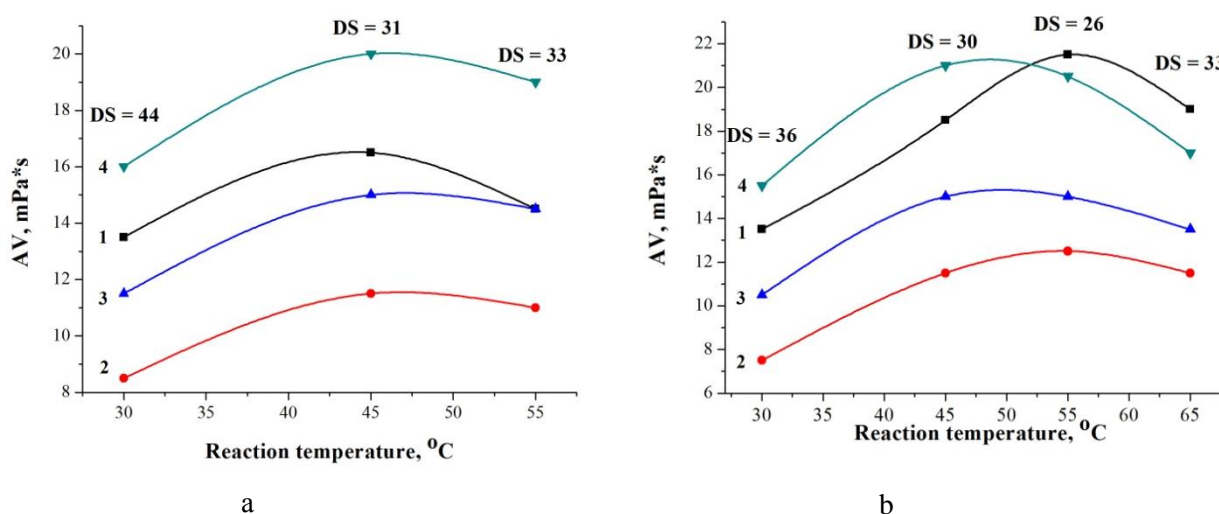


Figure 1. The dependence of drilling mud viscosity on temperature of carboxymethylation a) with a cross-linking agent; b) without a cross-linking agent. 1 – fresh drilling mud; 2 – salt mud (5% - carboxymethyl starch); 3 – salt mud (1% - carboxymethyl starch);4 – salt mud (1,5% - carboxymethyl starch).

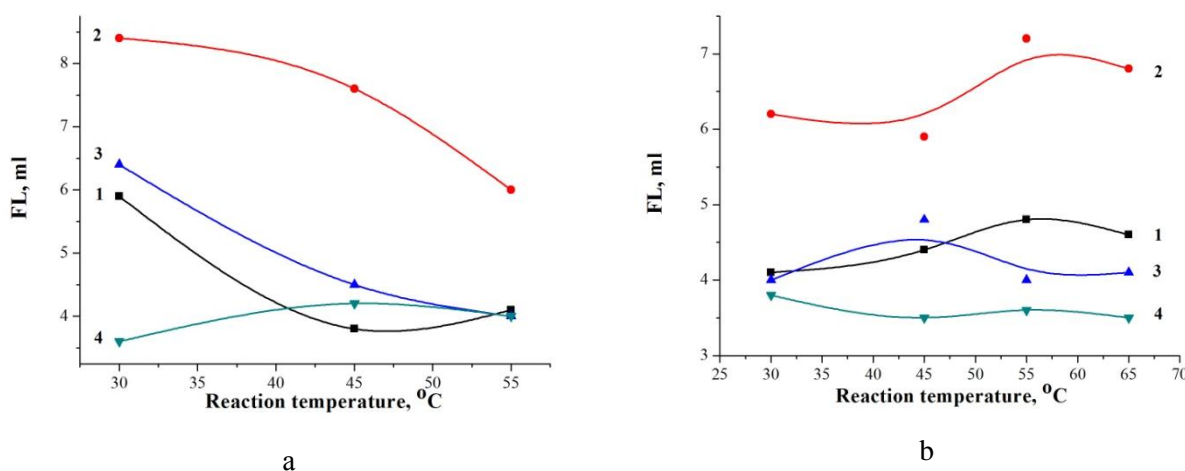


Figure 2. The dependence of reaction temperature of carboxymethylation on the fluid loss indicator a) with a cross-linking agent; b) without a cross-linking agent. 1 – fresh drilling mud; 2 – salt mud (5% - carboxymethyl starch); 3 – salt mud (1% - carboxymethyl starch);4 – salt mud (1,5% - carboxymethyl starch).

An increase in the reaction temperature of starch carboxymethylation, accompanied by the introduction of the cross-linking agent results in lowering the fluid loss indicator (fig. 2a). Despite this fact the degree of substitution is maximum at low temperature of synthesis. It is known that lowering filtration in a medium of polymer reagents is due to absorption into positively charged clay particles with solvation shell formation, and increasing viscosity of a dispersion system due to partial or complete free fluid fixation. Therefore, it can be concluded that viscosity of a dispersion system influences significantly drilling mud filtration in low carboxymethyl starch muds. However, inverse relation is observed in high carboxymethyl starch mud (fig. 2a), where the lowest fluid loss indicator corresponds to maximum degree of substitution and is a result of stronger adsorptive influence of carboxymethyl starch with clay particles due to more numbers of OH-groups in a polymer chain.

When a cross-linking agent is absent, synthesis temperature has little effect on fluid loss properties of fresh drilling mud and salt mud with synthesized samples of carboxymethyl starch (fig. 2b). The fluid loss indicator was more subjected to a change in reaction temperature for the samples with a cross-linking agent. At the same time, the samples of carboxymethyl starch without a cross-linking agent provide less fluid loss properties under the equal conditions.

3.2. Ratio $m(\text{NaOH})/m(\text{monochloroacetic acid})$

Changing the fluid loss properties of fresh drilling mud is not registered due to changing the ratio $m(\text{NaOH})/m(\text{monochloroacetic acid})$, because all obtained samples demonstrate sufficient degree of substitution to solve carboxymethyl starch and act without aggressive mineral influence (fig. 3a).

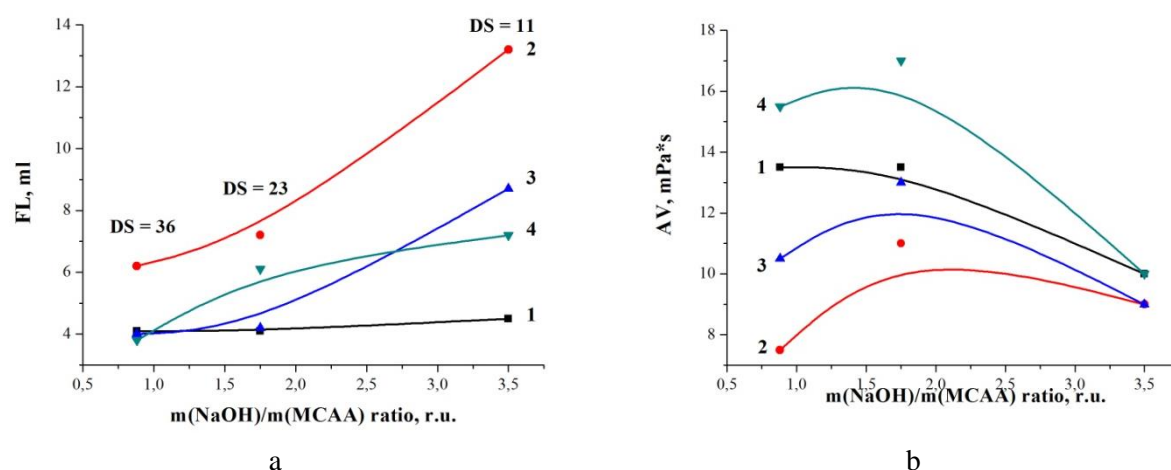


Figure 3. The dependence of ratio $m(\text{NaOH})/m(\text{monochloroacetic acid})$ on the fluid loss indicator and apparent viscosity a) with a cross-linking agent; b) without a cross-linking agent.

1 – fresh drilling mud; 2 – salt mud (5% - carboxymethyl starch); 3 – salt mud (1% - carboxymethyl starch); 4 – salt mud (1,5% - carboxymethyl starch).

When ratio $m(\text{NaOH})/m(\text{monochloroacetic acid})$ has become more, it is observed a significant decrease of degree of substitution caused an increase in the velocity of hydrolysis side reaction of *monochloroacetic acid* and, respectively, a decrease in alkylating agent used in carboxymethylation of starch. As a result, a fluid loss indicator increases sharply, but apparent viscosity decreases in salt muds with high $m(\text{NaOH})/m(\text{monochloroacetic acid})$ (fig. 3b).

3.3. Solvent

The samples obtained in water are characterized by the highest viscosity in comparison with carboxymethyl starch obtained in suspension media (fig. 4a). Such behavior can be explained by the homogeneous conditions of carboxymethylation in water due to destruction of starch kernels, that provides higher viscosity. A fluid loss indicator of the sample does not differ from samples obtained in isopropanol and butanol-2 (fig. 4b).

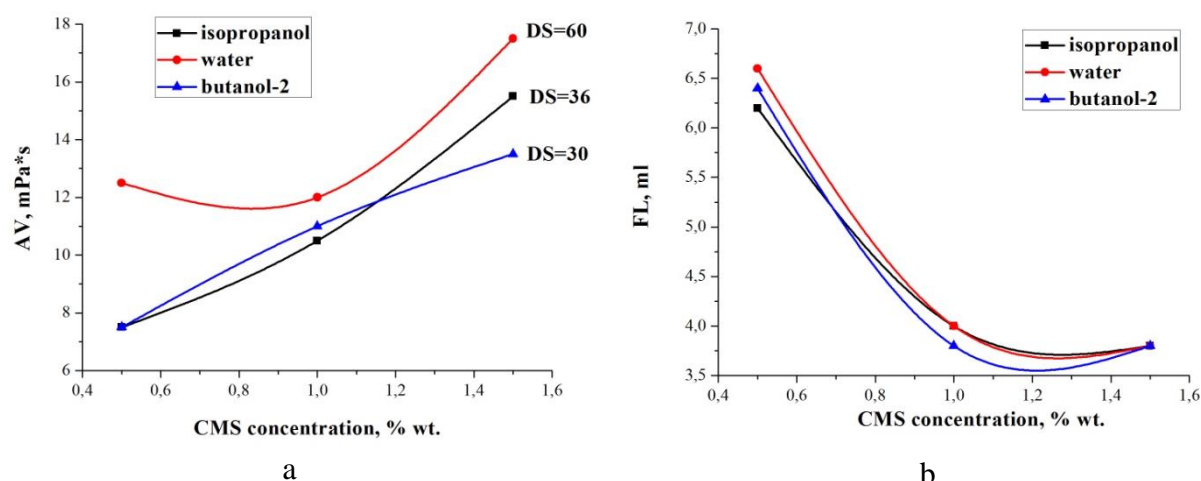


Figure 4. The impact of a solvent on viscosity (a) and a fluid loss indicator (b) of saline-based mud with different concentration of polysaccharide.

3.4. Types of starch

It is proved that viscosity and a fluid loss indicator of salt mud with carboxymethyl starch on a basis of corn is higher than potato starch (fig. 5a). It can be explained by the fact that corn starch is more resistant to chemical and physical influences and has higher molecular weight, so, that provides a higher polymerization number and a lower degree of substitution.

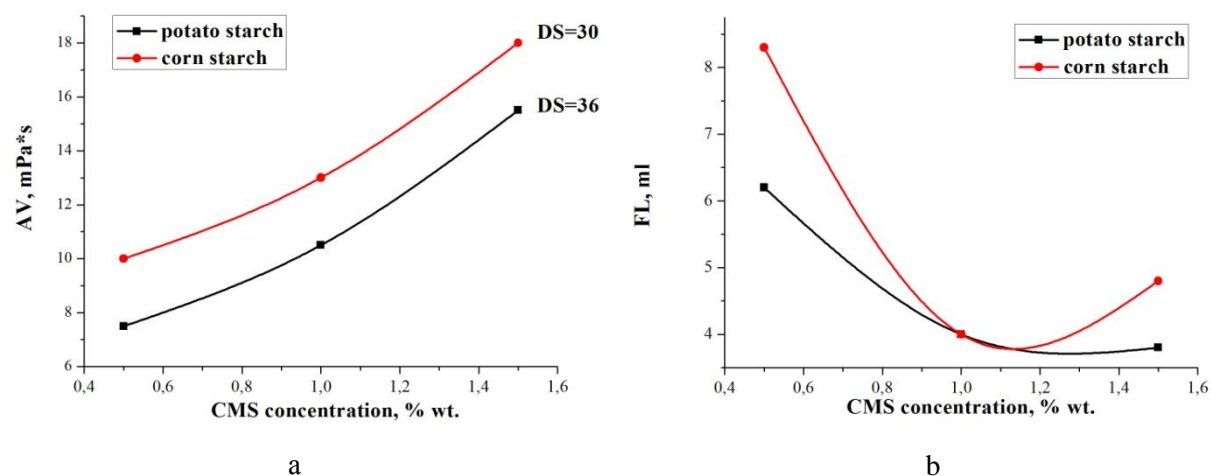


Figure 5. The impact of a type of starch on viscosity (a) and a fluid loss indicator (b) of saline-based mud with different concentration of polysaccharide.

In spite of this, a fluid loss indicator of the potato starch sample is lower as compared with corn starch, because of the determined impact of higher degree of substitution of the carboxymethyl starch.

3.5. Research of carboxymethyl starch samples by FTIR spectroscopy

A broad absorption band is observed on IR -spectra of the samples in 3400 cm^{-1} corresponding to stretching vibrations of OH -groups, as well as intra- and intermolecular hydrogen bonds [11]. An absorption band corresponds to vibrations of isolated OH-groups. Decreasing the intensity of these bands indicates reducing the fraction of OH-groups in a result of substitution by carboxymethyl in case of substitution of the native starch by carboxymethyl starch. The bands at 2930 cm^{-1} and 2878 cm^{-1} refer to stretching vibrations of C-H bonds. During starch carboxymethylation, primary and secondary OH-groups of starch are subjected to esterification, and as a result glycoside bonds are partially destroyed, it leads to decrease in molecular weight of starch. It is proved by a new peak at $1700\text{-}1750\text{ cm}^{-1}$ showing an ester group formation. the bands about 1600 cm^{-1} corresponding to carboxymethyl ether groups are registered

At spectra of the substituted samples. In 1200-1500 cm^{-1} intra deformation vibrations of $-\text{CH}_2$, $-\text{CH}$, $-\text{COH}$ groups are observed and it is sensitive with respect to a change in conformation of $-\text{CH}_2\text{OH}$ group. In particular, an absorption band at 1423 cm^{-1} shows scissoring vibrations of $-\text{CH}_2$ group. An absorption band about 1082 cm^{-1} corresponds to valence vibrations $-\text{OCH-O-CH}_2$ groups. Low-intensity bands in zone 500-700 cm^{-1} correspond to out-of-plane vibrations of OH-group of glucopyranose ring.

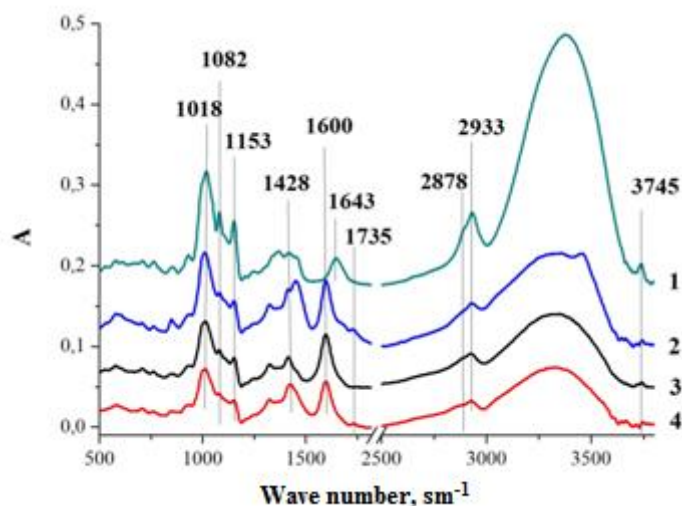


Figure 6. IR -spectra of the samples of the native potato starch (1), carboxymethyl starch in butanol-2 (2), carboxymethyl starch in isopropanol (3), carboxymethyl starch in water (4).

4. Conclusion

To sum up, during the experiment described in the paper:

1. the samples of carboxymethyl starch have been obtained by suspension procedure in organic solvents and water for drilling mud;
2. the influence of synthesis condition of carboxymethyl starch on fluid loss and rheological properties of fresh drilling mud and salt mud has been studied;
3. it is shown that the highest viscosity of drilling mud is observed for carboxymethyl starch obtained in water;
4. the change in infra-red spectra of the carboxymethyl starch samples in carboxymethylation has been evaluated.

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References

- [1] Kryazhev V N, Romanov V V, Shirokov V A 2010 *Khimija Rastitelnogo Syrja* Vol. **1** pp. 5.
- [2] Grey J R, Darly G S 1985 Composition and properties of drilling agents (flushing fluids) *Nedra M.* pp. 509.
- [3] Bhandari P N, Hanna M A 2011 *Industrial & Engineering Chemistry Research* Vol. **50** pp. 12784.
- [4] Villwock V K, BeMiller J N 2005 *Starch/Stärke* Vol. **57** pp. 281.
- [5] Spychaj T, Wilpiszewska K, Zdanowicz M 2013 *Starch/Stärke* Vol. **65** pp. 22.
- [6] Kaur L, Singh J, Singh N 2006 *Journal of the Science of Food and Agriculture* Vol. **86** pp. 1945.
- [7] Uslu M-K, Polat S Vol. **87** pp. 1994.
- [8] Minaev K, Martynova D, Knyazev A, Zaharov A, Shenderova I 2014 *IOP Conference Series: Earth and Environmental Science* 21, 012035.
- [9] Kittipongpatana N, Janta S, Kittipongpatana O 2011 *Pakistan Journal of Pharmaceutical Sciences* Vol. **24** pp. 415.
- [10] Bhattacharyya D, Singhal R S, Kulkarni P R 1995 *Carbohydrate Polymers* Vol. **21247** pp. 253.
- [11] Joshi G, Naithani S, Varshney V K, Bisht S S, Rana V, Gupta P K 2015 *Waste Management* Vol. **38** pp. 33.