

<https://helda.helsinki.fi>

Synthesis and Characterization of Carboxymethylated Cornstarch

Nurakhmetova, Zh. A.

2019

Nurakhmetova , Z A , Kurbashev , E P , Selenova , B S , Borke , T , Aseyev , V & Kudaibergenov , S 2019 , ' Synthesis and Characterization of Carboxymethylated Cornstarch ' , Izvestiâ Nacional'noj akademii nauk Respubliki Kazahstani , vol. 1 , no. 1 , pp. 6-15 . <https://doi.org/10.32014/2019.2518-1491.1>

<http://hdl.handle.net/10138/303225>

<https://doi.org/10.32014/2019.2518-1491.1>

publishedVersion

Downloaded from Helda, University of Helsinki institutional repository.

This is an electronic reprint of the original article.

This reprint may differ from the original in pagination and typographic detail.

Please cite the original version.

ISSN 2518-1491 (Online),
ISSN 2224-5286 (Print)

ҚАЗАҚСТАН РЕСПУБЛИКАСЫ
ҰЛТТЫҚ ҒЫЛЫМ АКАДЕМИЯСЫНЫҢ

Д.В.Сокольский атындағы «Жанармай,
катализ және электрохимия институты» АҚ

Х А Б А Р Л А Р Ы

ИЗВЕСТИЯ

НАЦИОНАЛЬНОЙ АКАДЕМИИ НАУК
РЕСПУБЛИКИ КАЗАХСТАН
АО «Институт топлива, катализа и
электрохимии им. Д.В. Сокольского»

NEWS

OF THE ACADEMY OF SCIENCES
OF THE REPUBLIC OF KAZAKHSTAN
JSC «D.V. Sokolsky institute of fuel, catalysis
and electrochemistry»

SERIES
CHEMISTRY AND TECHNOLOGY

1 (433)

JANUARY – FEBRUARY 2019

PUBLISHED SINCE JANUARY 1947

PUBLISHED 6 TIMES A YEAR

ALMATY, NAS RK

NAS RK is pleased to announce that News of NAS RK. Series of chemistry and technologies scientific journal has been accepted for indexing in the Emerging Sources Citation Index, a new edition of Web of Science. Content in this index is under consideration by Clarivate Analytics to be accepted in the Science Citation Index Expanded, the Social Sciences Citation Index, and the Arts & Humanities Citation Index. The quality and depth of content Web of Science offers to researchers, authors, publishers, and institutions sets it apart from other research databases. The inclusion of News of NAS RK. Series of chemistry and technologies in the Emerging Sources Citation Index demonstrates our dedication to providing the most relevant and influential content of chemical sciences to our community.

Қазақстан Республикасы Ұлттық ғылым академиясы "ҚР ҰҒА Хабарлары. Химия және технология сериясы" ғылыми журналының Web of Science-тің жаңаланған нұсқасы Emerging Sources Citation Index-те индекстелуге қабылданғанын хабарлайды. Бұл индекстелу барысында Clarivate Analytics компаниясы журналды одан әрі the Science Citation Index Expanded, the Social Sciences Citation Index және the Arts & Humanities Citation Index-ке қабылдау мәселесін қарастыруда. Web of Science зерттеушілер, авторлар, баспашылар мен мекемелерге контент тереңдігі мен сапасын ұсынады. ҚР ҰҒА Хабарлары. Химия және технология сериясы Emerging Sources Citation Index-ке енуі біздің қоғамдастық үшін ең өзекті және беделді химиялық ғылымдар бойынша контентке адалдығымызды білдіреді.

НАН РК сообщает, что научный журнал «Известия НАН РК. Серия химии и технологий» был принят для индексирования в Emerging Sources Citation Index, обновленной версии Web of Science. Содержание в этом индексировании находится в стадии рассмотрения компанией Clarivate Analytics для дальнейшего принятия журнала в the Science Citation Index Expanded, the Social Sciences Citation Index и the Arts & Humanities Citation Index. Web of Science предлагает качество и глубину контента для исследователей, авторов, издателей и учреждений. Включение Известия НАН РК в Emerging Sources Citation Index демонстрирует нашу приверженность к наиболее актуальному и влиятельному контенту по химическим наукам для нашего сообщества.

Б а с р е д а к т о р ы
х.ғ.д., проф., ҚР ҰҒА академигі **М.Ж. Жұрынов**

Р е д а к ц и я а л қ а с ы:

Ағабеков В.Е. проф., академик (Белорус)
Волков С.В. проф., академик (Украина)
Воротынцев М.А. проф., академик (Ресей)
Газалиев А.М. проф., академик (Қазақстан)
Ергожин Е.Е. проф., академик (Қазақстан)
Жармағамбетова А.К. проф. (Қазақстан), бас ред. орынбасары
Жоробекова Ш.Ж. проф., академик (Қырғыстан)
Иткулова Ш.С. проф. (Қазақстан)
Мантасян А.А. проф., академик (Армения)
Пралиев К.Д. проф., академик (Қазақстан)
Баешов А.Б. проф., академик (Қазақстан)
Бүркітбаев М.М. проф., академик (Қазақстан)
Джусипбеков У.Ж. проф. корр.-мүшесі (Қазақстан)
Молдахметов М.З. проф., академик (Қазақстан)
Мансуров З.А. проф. (Қазақстан)
Наурызбаев М.К. проф. (Қазақстан)
Рудик В. проф., академик (Молдова)
Рахимов К.Д. проф. академик (Қазақстан)
Стрельцов Е. проф. (Белорус)
Тәшімов Л.Т. проф., академик (Қазақстан)
Тодераш И. проф., академик (Молдова)
Халиков Д.Х. проф., академик (Тәжікстан)
Фарзалиев В. проф., академик (Әзірбайжан)

«ҚР ҰҒА Хабарлары. Химия және технология сериясы».

ISSN 2518-1491 (Online),

ISSN 2224-5286 (Print)

Меншіктенуші: «Қазақстан Республикасының Ұлттық ғылым академиясы» Республикалық қоғамдық бірлестігі (Алматы қ.)

Қазақстан республикасының Мәдениет пен ақпарат министрлігінің Ақпарат және мұрағат комитетінде 30.04.2010 ж. берілген №1089-Ж мерзімдік басылым тіркеуіне қойылу туралы куәлік

Мерзімділігі: жылына 6 рет.

Тиражы: 300 дана.

Редакцияның мекенжайы: 050010, Алматы қ., Шевченко көш., 28, 219 бөл., 220, тел.: 272-13-19, 272-13-18,
<http://chemistry-technology.kz/index.php/en/arithiv>

© Қазақстан Республикасының Ұлттық ғылым академиясы, 2019

Типографияның мекенжайы: «Аруна» ЖК, Алматы қ., Муратбаева көш., 75.

Главный редактор
д.х.н., проф., академик НАН РК **М. Ж. Журинов**

Редакционная коллегия:

Агабеков В.Е. проф., академик (Беларусь)
Волков С.В. проф., академик (Украина)
Воротынцев М.А. проф., академик (Россия)
Газалиев А.М. проф., академик (Казахстан)
Ергожин Е.Е. проф., академик (Казахстан)
Жармагамбетова А.К. проф. (Казахстан), зам. гл. ред.
Жоробекова Ш.Ж. проф., академик (Кыргызстан)
Иткулова Ш.С. проф. (Казахстан)
Манташян А.А. проф., академик (Армения)
Пралиев К.Д. проф., академик (Казахстан)
Баешов А.Б. проф., академик (Казахстан)
Буркитбаев М.М. проф., академик (Казахстан)
Джусипбеков У.Ж. проф. чл.-корр. (Казахстан)
Мулдахметов М.З. проф., академик (Казахстан)
Мансуров З.А. проф. (Казахстан)
Наурызбаев М.К. проф. (Казахстан)
Рудик В. проф., академик (Молдова)
Рахимов К.Д. проф. академик (Казахстан)
Стрельцов Е. проф. (Беларусь)
Ташимов Л.Т. проф., академик (Казахстан)
Тодераш И. проф., академик (Молдова)
Халиков Д.Х. проф., академик (Гаджикистан)
Фарзалиев В. проф., академик (Азербайджан)

«Известия НАН РК. Серия химии и технологии».

ISSN 2518-1491 (Online),

ISSN 2224-5286 (Print)

Собственник: Республиканское общественное объединение «Национальная академия наук Республики Казахстан» (г. Алматы)

Свидетельство о постановке на учет периодического печатного издания в Комитете информации и архивов Министерства культуры и информации Республики Казахстан №10893-Ж, выданное 30.04.2010 г.

Периодичность: 6 раз в год

Тираж: 300 экземпляров

Адрес редакции: 050010, г. Алматы, ул. Шевченко, 28, ком. 219, 220, тел. 272-13-19, 272-13-18,
<http://chemistry-technology.kz/index.php/en/arhiv>

© Национальная академия наук Республики Казахстан, 2019

Адрес редакции: 050100, г. Алматы, ул. Кунаева, 142,
Институт органического катализа и электрохимии им. Д. В. Сокольского,
каб. 310, тел. 291-62-80, факс 291-57-22, e-mail:orgcat@nursat.kz

Адрес типографии: ИП «Аруна», г. Алматы, ул. Муратбаева, 75

E d i t o r i n c h i e f

doctor of chemistry, professor, academician of NAS RK **M.Zh. Zhurinov**

E d i t o r i a l b o a r d :

Agabekov V.Ye. prof., academician (Belarus)
Volkov S.V. prof., academician (Ukraine)
Vorotyntsev M.A. prof., academician (Russia)
Gazaliyev A.M. prof., academician (Kazakhstan)
Yergozhin Ye.Ye. prof., academician (Kazakhstan)
Zharmagambetova A.K. prof. (Kazakhstan), deputy editor in chief
Zhorobekova Sh.Zh. prof., academician (Kyrgyzstan)
Itkulova Sh.S. prof. (Kazakhstan)
Mantashyan A.A. prof., academician (Armenia)
Praliyev K.D. prof., academician (Kazakhstan)
Bayeshov A.B. prof., academician (Kazakhstan)
Burkitbayev M.M. prof., academician (Kazakhstan)
Dzhusipbekov U.Zh. prof., corr. member (Kazakhstan)
Muldakhmetov M.Z. prof., academician (Kazakhstan)
Mansurov Z.A. prof. (Kazakhstan)
Nauryzbayev M.K. prof. (Kazakhstan)
Rudik V. prof., academician (Moldova)
Rakhimov K.D. prof., academician (Kazakhstan)
Streltsov Ye. prof. (Belarus)
Tashimov L.T. prof., academician (Kazakhstan)
Toderash I. prof., academician (Moldova)
Khalikov D.Kh. prof., academician (Tadjikistan)
Farzaliyev V. prof., academician (Azerbaijan)

News of the National Academy of Sciences of the Republic of Kazakhstan. Series of chemistry and technology.
ISSN 2518-1491 (Online),
ISSN 2224-5286 (Print)

Owner: RPA "National Academy of Sciences of the Republic of Kazakhstan" (Almaty)

The certificate of registration of a periodic printed publication in the Committee of Information and Archives of the Ministry of Culture and Information of the Republic of Kazakhstan N 10893-Ж, issued 30.04.2010

Periodicity: 6 times a year

Circulation: 300 copies

Editorial address: 28, Shevchenko str., of. 219, 220, Almaty, 050010, tel. 272-13-19, 272-13-18,

<http://chemistry-technology.kz/index.php/en/arhiv>

© National Academy of Sciences of the Republic of Kazakhstan, 2019

Editorial address: Institute of Organic Catalysis and Electrochemistry named after D. V. Sokolsky
142, Kunayev str., of. 310, Almaty, 050100, tel. 291-62-80, fax 291-57-22,
e-mail: orgcat@nursat.kz

Address of printing house: ST "Aruna", 75, Muratbayev str, Almaty

NEWS

OF THE NATIONAL ACADEMY OF SCIENCES OF THE REPUBLIC OF KAZAKHSTAN

SERIES CHEMISTRY AND TECHNOLOGY

ISSN 2224-5286

<https://doi.org/10.32014/2019.2518-1491.1>

Volume 1, Number 433 (2019), 6 – 15

UDC 541.64+678.744

**Zh.A. Nurakhmetova^{1,2}, E. P. Kurbashev³, B.S. Selenova²,
T. Borke⁴, V.O. Aseyev⁴, S.E. Kudaibergenov^{1,2}**

¹Institute of Polymer Materials and Technology, Almaty, Kazakhstan;

²Satbayev University, Almaty, Kazakhstan;

³Almaty Technological University;

⁴University of Helsinki, Helsinki, Finland

nurakhmetova86@mail.ru

SYNTHESIS AND CHARACTERIZATION OF CARBOXYMETHYLATED CORNSTARCH

Abstract. The aim of this study is preparation and characterization of carboxymethylated cornstarch (CMCS) for potential application as water based drilling fluids. The cornstarch was modified by sodium monochloroacetate. The structure of cornstarch and CMCS was established by H^1 NMR and FTIR spectroscopy. The degree of carboxymethylation of cornstarch determined by H^1 NMR spectroscopy was equal to 80%. The viscosity-average molecular weights (M_η) of pristine cornstarch and CMCS calculated from Mark-Kuhn-Houwink equation $[\eta]=K_\eta \cdot M^a$ are equal to $2.15 \cdot 10^3 \text{ g} \cdot \text{mol}^{-1}$ and $2.75 \cdot 10^5 \text{ g} \cdot \text{mol}^{-1}$ respectively. The temperature dependent viscosity of CMCS was measured in water by Ubbelohde viscometer, while the rheological properties of CMCS in dependence of polymer concentration and ionic strength of the solution were evaluated by rheoviscometer. The thermal characteristics of samples were determined by differential scanning calorimeter (DSC) and thermogravimetric (TGA) and differential thermal analyzer (DTA). The morphological properties of cornstarch and CMCS were studied by scanning electron microscopy (SEM). The structural-mechanical, filtration and filter cake forming properties of drilling fluids and fluid loss indicators of CMCS were found.

Keywords: cornstarch, modification, carboxymethylated cornstarch, degree of substitution, viscosity-average molecular weight, viscosity, rheology, drilling fluids.

Introduction

The interest in natural polysaccharides has increased considerably in recent years, as they are candidates for many commercial applications in different industrial sectors like food, textile, paper, petroleum, and pharmaceuticals [1]. Products made from starch have attracted the interest of researchers and companies due to the abundance of starch in nature, its low cost and biodegradability [2-5]. The carboxymethylation of starch in alkaline solution with sodium monochloroacetate was first carried out in 1924 [6]. Currently many papers concerning the carboxymethylation of starch were published with the aim to optimize the reaction conditions, to increase the yield of product and to increase the degree of substitution (DS) [7]. Starch is unique raw material resources due to high biocompatibility and annual renewability (potatoes (5%), corn (82%), wheat (8%), etc.) that distinguish it from cellulose derived from wood, which period of maturing is 18-20 years for fast-growing wood [2, 8-9]. Starch is a carbohydrate consisting of linear and helical amylose molecules and branched amylopectin molecules with general chemical formula $(C_6H_{10}O_5)_n$ [10-12].

Starch was the first polymer reagent used for the drilling muds in 1939 [13]. However, with the introduction of polymer reagents based on cellulose ethers widespread use of starch started to reduce. This was primarily due to the need to use bactericides and low thermostable starch reagents [2].

Currently, the natural starch is not used in drilling fluids. Instead of it, the following types of modified starch such as carboxymethyl, hydroxyethyl, as well as oxidized starch are applied to regulate the filtration and rheological characteristics of drilling muds. The chemical modification of cornstarch is performed to overcome the insolubility in water, hardly controlled viscosity after gelatinization, the turbidity of aqueous solutions [14]. Carboxymethylated starch (CMS) is the most commonly used material among the modified starch reagents. It is a starch derivative in which the –OH groups is partially substituted by ether group (-O-CH₂COOH) [15]. It is characterized by good resistance to high content of salt, high durability to thermal and bacteriological affect [16]. The CMS has a wide applicability due to water-solubility, high viscosity and stability as a fluid loss reducing agent in drilling fluid [10, 17]. The application of CMS in enhanced oil recovery is also growing [18].

The main objective of this work is to synthesize and characterize CMCS with potential application as additives in water-based drilling fluids. These materials were also evaluated regarding their thermal resistance and rheological behavior in the presence of various salts. Starch is a perspective material from practical point of view because it is non-toxic, contains easily modifiable functional groups and is ecologically friendly [19].

Experimental part

Materials

Cornstarch was purchased from LLP "Zharkent Starch-Factory". Sodium monochloroacetate (Na-MCA) ClCH₂COONa was obtained from Merck-Schuchardt (Hohenbrunn, Germany). The chemical reagents used in this investigation (NaOH, CH₃CH₂OH, NaCl, KCl, MgCl₂, CaCl₂, HCl, LiBr, d₆-DMSO, and d₁-TFA were purchased from Sigma Aldrich (Finland) and used as received.

Synthesis of carboxymethylated cornstarch (CMCS)

Modification of cornstarch was carried out in two steps [19]. Firstly, alkalization was performed by mixing of 0.4 g cornstarch, 1.2 mL ethanol and 0.28 mL aqueous 11.5 M NaOH solution at 25°C, the mixture was stirred for 20 min. In the second step, 0.28 g Na-MCA was added and the reaction mixture was heated to 58°C and stirred during 100 min. The precipitated in ethanol CMCS was filtered and dried under vacuum at 50°C.

Methods

¹H NMR of cornstarch and CMCS were recorded on a Bruker Avance III 500 spectrometer at 70°C according to procedure [20]. The viscosity-average molecular weights of the cornstarch and CMCS were determined by Mark-Kuhn-Houwink equation, $[\eta]=K_{\eta} \cdot M_{\eta}^a$, where M_{η} is the viscosity-average molecular weight and the parameters K_{η} and a are related to local stiffness of the polymer and depend on the nature of polymer, solvent and temperature. The Fourier Transform Infrared (FTIR) spectra of the starch samples were registered by FTIR spectrometer Carry 660 (Agilent, USA). The viscosity of cornstarch and CMCS solutions was measured by Ubbelohde viscometer at 25±0.1 °C. The rheological behavior of CMCS solutions was monitored with the help of Rheolab QC, Anton Paar (Austria). The thermal characteristics of samples were determined with the help of DSC 131 EVO Setaram and TGA «Labsys EVO» Setaram (France). The samples were heated from 25 to 500 °C at heating rate 10°C/min. The size and ζ-potential of CMSC was determined with the help of Dynamic Light Scattering (DLS) device Malvern Zetasizer Nano ZS90 (UK). Scanning electron micrographs were obtained with the help of SEM (Jeol JSM-6490LA, Japan). Static shear stress (SSS) measurements after 1 min and 10 min (SSS₁ and SSS₁₀) were performed by means of the instrument SNS-2 (Russian Federation). Water yield of the drilling muds (W) was determined by VM-6 instrument (Russian Federation). The thickness of the filter cake (δ) was measured by the instrument WIKA IV-2 (Russian Federation).

Results and Discussion.

Modification of cornstarch

The carboxymethylation of cornstarch proceeds by two steps:

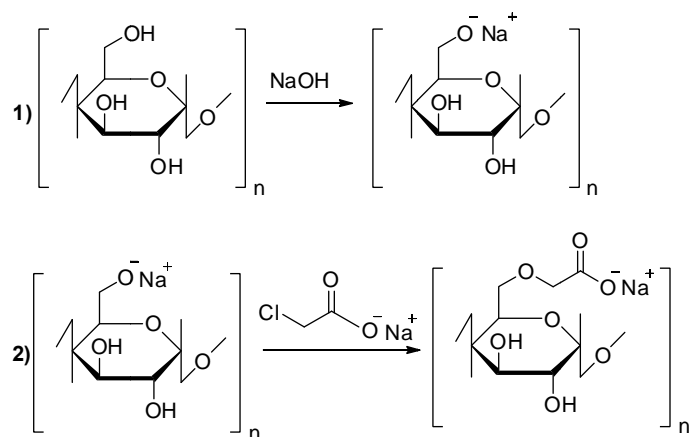
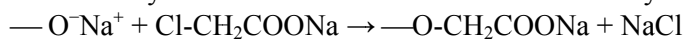


Figure 1 -Modification of corn starch with sodium monochloroacetate

In the first step (1) the OH groups are transformed to $\text{O}^- \text{Na}^+$, then on the second step (2) the Na^+ ions are eliminated by chlorine of sodium monochloroacetate by the following reaction:



As a result a fully water-soluble carboxymethylated cornstarch (CMCS) with DS = 80% was obtained.

Identification of the CMCS structure by ^1H NMR and FTIR spectroscopy

^1H NMR spectrum of CMCS registered at 70 °C is shown in Figure 2.

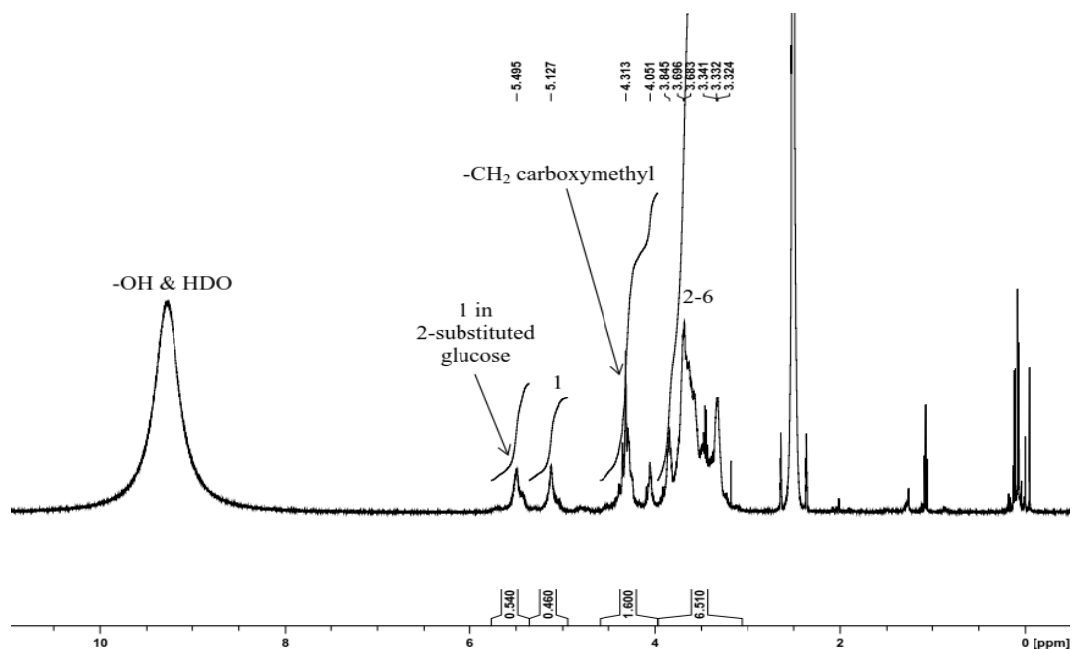


Figure 2 - ^1H NMR spectrum of CMCS in $\text{d}_6\text{-DMSO}$

The substitution degree of CMCS determined from the methylene signal of the carboxymethyl substituent (4.31 ppm) and the anomeric protons of glucose (5.13 and 5.50 ppm) was equal to 80%.

FTIR spectra of pristine and modified cornstarch are compared in Figure 3.

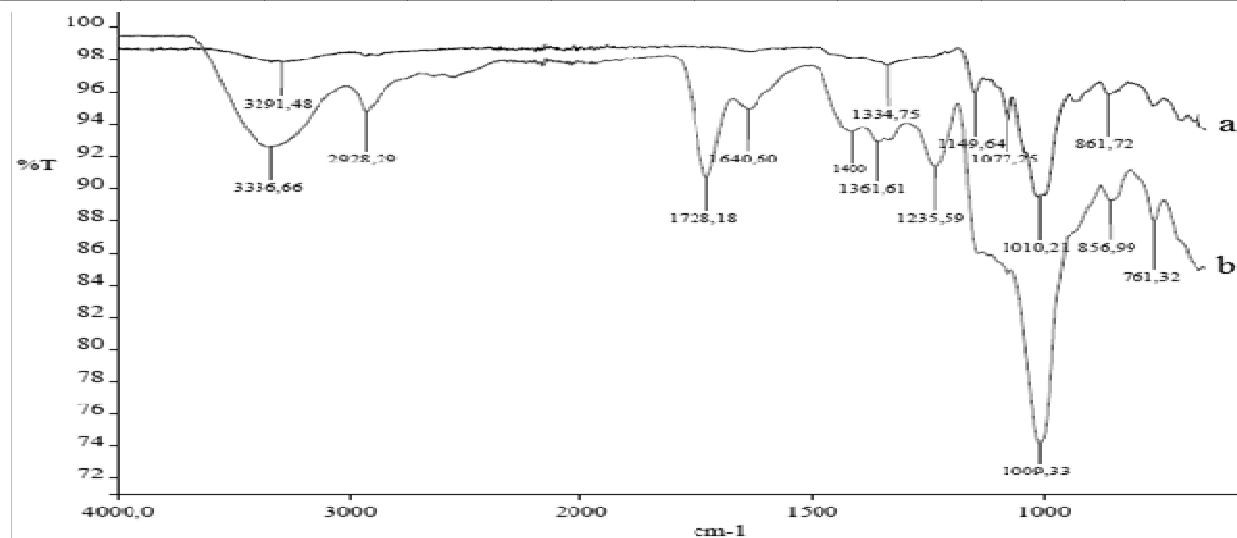


Figure 3 - FTIR spectra of cornstarch (a) and CMCS (b)

The broad bands between 3336 and 3291 cm^{-1} is assigned to OH stretching vibrations due to hydrogen bonding between the hydroxyl groups. The band around of 2928 cm^{-1} belongs to CH_2 symmetrical stretching vibrations. A new peak at 1728 cm^{-1} is specific for ester groups, the bands at 1640 and 1400 cm^{-1} are related to asymmetric and symmetric vibrations of carboxylate ions (COO^-). At 1200-1360 cm^{-1} the vibrations of CH_2 , CH, and C-OH groups are observed. An absorption band at 1009 cm^{-1} corresponds to stretching vibrations of ether groups $-\text{OCH}-\text{O}-\text{CH}_2$. Low intensive bands in the range of 860-760 cm^{-1} correspond to out-of-plane vibrations of OH-group of glucopyranose ring. Thus, both ^1H NMR and FTIR spectra of CMCS reveal that the modification by Na-MCA takes place to obtain the water-soluble derivatives of cornstarch.

Viscosity-average molecular weight (M_η) of CMCS

The viscosity-average molecular weight (M_η) of the CMCS was calculated by the Mark-Kuhn-Houwink relationship $[\eta]=K_\eta \cdot M^a$ taking into account that $K_\eta=2.0 \cdot 10^{-4}$ and $a=0.75$ for a standard starch in 0.1 M aqueous NaCl at 25°C [2].

The viscosity-average molecular weights (M_η) of cornstarch and CMCS were found to be $2.15 \cdot 10^3 \text{ g} \cdot \text{mol}^{-1}$ and $2.75 \cdot 10^5 \text{ g} \cdot \text{mol}^{-1}$ respectively. A significant increase in the M_η of the cornstarch after carboxymethylation is due to the presence of bulkier carboxymethyl groups in modified cornstarch.

Viscosity measurements

The influence of temperature on solution behavior of CMCS is shown in Figure 4.

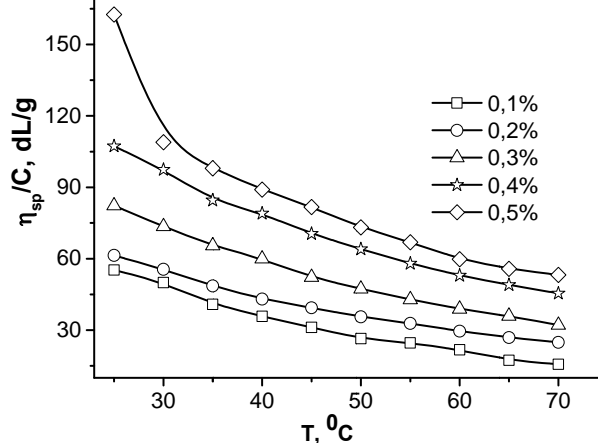
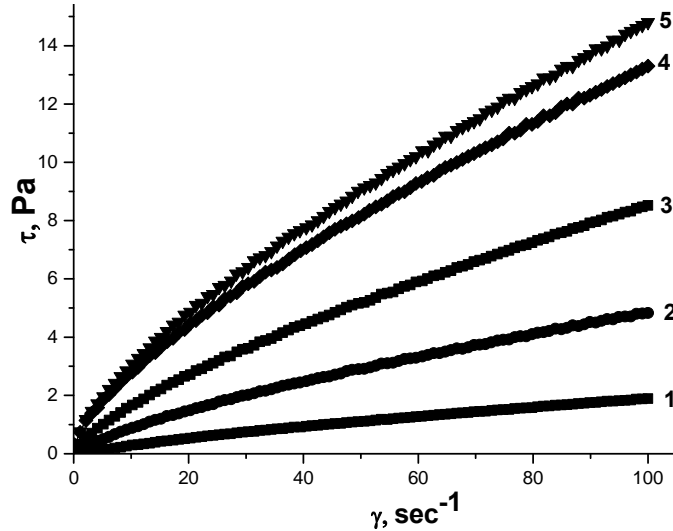


Figure 4 – Temperature dependent reduced viscosity of aqueous solutions of CMCS

The reduced viscosity of aqueous solutions of CMCS gradually decreases with increasing of the temperature. This may be connected with a gradual disaggregation of macromolecular associates due to destruction of hydrogen bonds.

Rheological characteristics of CMCS solutions

Rheological properties are considered as important parameters to evaluate the applicability of the CMCS as drilling fluids. The CMCS solutions represent the pseudo plastic liquids and are suitable for the formulation of drilling fluids.



(1) 0.25, (2) 0.5, (3) 1, (4) 2, (5) 1.5 wt.%
Figure 5 – Concentration dependent shear stress-shear rate curves of aqueous solutions of CMCS

As the polymer concentration increases the solution viscosity increases as well. However, increasing of the polymer concentration higher than 1.5 wt.% is not efficient. Therefore it is expected that the optimal concentration of CMCS for shear rate is 1.5 wt.%.

Dependences of shear stress on shear rate for CMCS solutions in the presence of NaCl, KCl, MgCl₂ and CaCl₂ are shown in Figure 6.

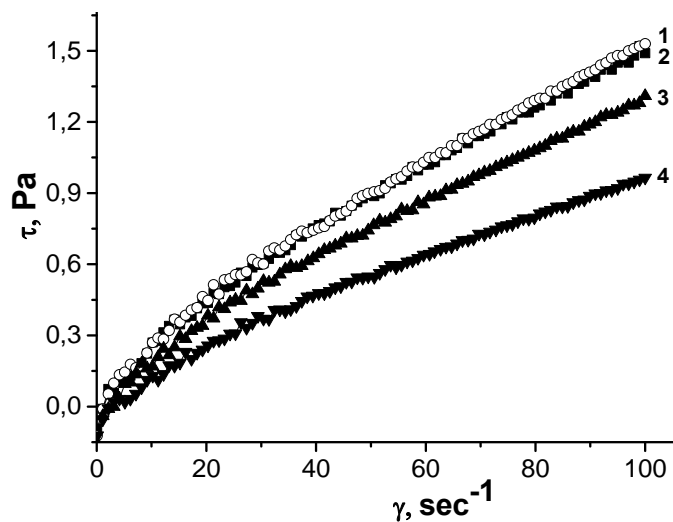


Figure 6 - The shear stress-shear rate curves of 0.5% wt.% CMCS solutions at the ionic strength of $\mu=0.01$ adjusted by NaCl (1), KCl (2), MgCl₂ (3) and CaCl₂ (4)

Aqueous solutions of CMCS behave polyelectrolyte character that is suppressed upon addition of low-molecular-weight salts. The viscosity resistant behavior of CMCS in saline water provides the stability of drilling muds in a wide range of salt concentrations.

Thermal characteristics of cornstarch and CMCS

Thermal properties of cornstarch and CMCS derived from DSC are shown in Figure 7. The appearance of exothermic peaks at 80.2 and 83.3 °C is probably due to removal of residual moisture. The broad endothermic peaks at the interval of temperature 285.85-392.77 and 251.3-326.87 °C probably reflect the crystallization of cornstarch and CMCS, respectively.

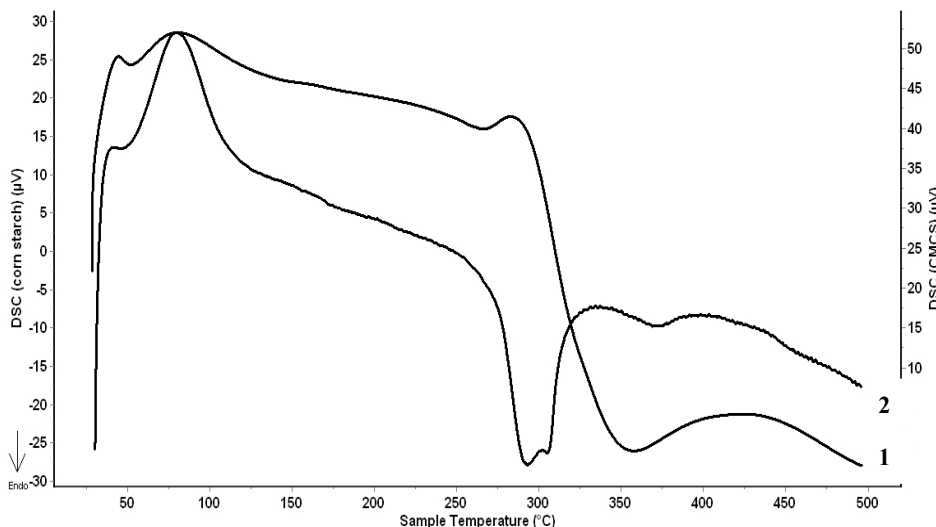


Figure 7 - DSC curves of cornstarch (1) and CMCS (2)

Mass loss percentages for cornstarch and CMCS were calculated from TGA data (Figure 8). TGA studies reveal high heat resistance for CMCS as compared to the cornstarch. CMCS loses 38.47 % of the mass, while cornstarch – 45.83

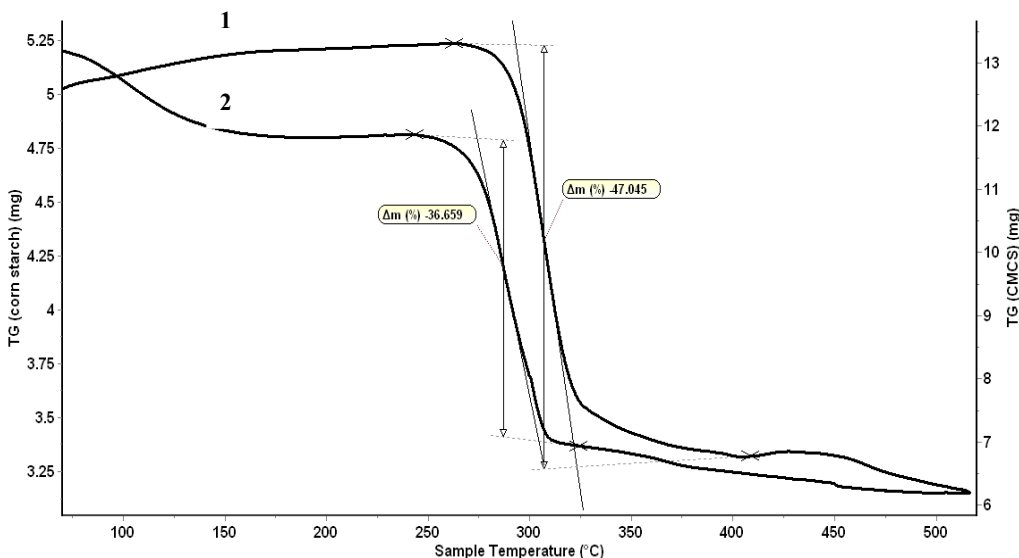


Figure 8 - TGA curves of cornstarch (1) and CMCS (2)

DLS measurements

Table 2 shows the average sizes and ζ -potentials of CMCS. The size distribution of CMCS is varied from 235 nm to 1034 nm. The negative values of the ζ -potentials of CMCS in water confirm the substitution of hydroxyl groups of cornstarch by carboxymethyl moieties.

Table 1 – The average sizes and ζ -potentials of CMCS in water

| C, wt.% | Size, nm | ζ -potential, mV |
|---------|----------|------------------------|
| 0.1 | 1034 | -85 |
| 0.2 | 633 | -60 |
| 0.3 | 235 | -56 |
| 0.4 | 487 | -50 |
| 0.5 | 552 | -53 |

Morphology of cornstarch and CMCS

The SEM images of cornstarch and the CMCS are compared in Figure 9. SEM showed the carboxymethylation to change the structure of starch granules, compared with native cornstarch. Cornstarch granules are smooth, round in shape with sizes ranging from 5 to 15 μm . After carboxymethylation the granules of cornstarch are bigger in size (400-500 μm) and the granular surface becomes rough and scaly. Probably these changes are due to modification of cornstarch affected by strong alkaline environment and heat treatment.

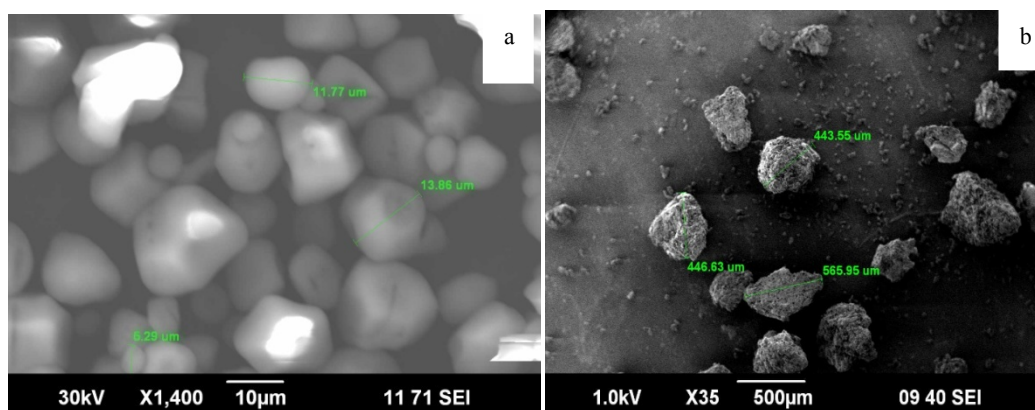


Figure 9 - SEM images of cornstarch (a) and CMCS (b)

Formulation of drilling fluids

The drilling fluids (DF) composed of gellan, xanthan, CMCS, Polyanionic cellulose (PAC), KCl and bentonite were formulated to obtain an appropriate DF with optimal solution density (ρ), relative viscosity (η_{rel}), dynamic shear stress (DSS), fluid loss indicator (W), thickness of mud cake (δ), and ratio of static shear stress (SSS_1/SSS_{10}).

Properties of drilling fluids

The structural-mechanical, filtration and filter cake forming properties of model system, consisting of 0.1% gellan, 0.2% xanthan, 0.25-0.35% CMCS at the interval of pH 9.2-10.0 are summarized in Table 2. Analysis shows that all drilling fluids based on CMCS possess good structural-mechanical and filtration characteristics. The thickness of filter cake may be increased by adding 4 wt.% of bentonite. The thixotropic characteristics of drilling fluids are improved with increasing of CMCS concentration. Moreover, the CMCS with high DS due to good water-solubility and high viscosity is more beneficial than industrial starch that is applied for formulation of drilling fluids.

Table 2 – Composition and characteristics of drilling fluids

| № | Ratio DF*, % | | | | | | pH | ρ , g/cm ³ | η_{rel} , sec | DSS, Pa | W ₃ , cm ³ | δ , mm | SSS ₁ /SSS ₁₀ , dPa |
|--------------------|--------------|------------|-------------|------------|----------|-----------|------------|----------------------------|--------------------|------------|----------------------------------|---------------|---|
| | gellan | xanthan | CMCS | PAC | KCl | bentonite | | | | | | | |
| 1 | 0.1 | 0.2 | 1** | 0.5 | 0 | 4 | 10 | 1.03 | 54 | 1.2 | 5 | 0.4 | 8/15 |
| 2 | 0.1 | 0.2 | 1** | 0.5 | 1 | 4 | 9.8 | 1.04 | 52 | 1.4 | 5 | 0.4 | 7.5/14 |
| 3 | 0.1 | 0.2 | 1** | 0.5 | 3 | 4 | 9.6 | 1.05 | 52 | 1.7 | 5 | 0.4 | 7/13 |
| 4 | 0.1 | 0.2 | 0.25 | 0.5 | 0 | 1 | 9.2 | 1.02 | 33.6 | 1.7 | 6 | 0.4 | 3.3/5.3 |
| 5 | 0.1 | 0.2 | 0.25 | 0.5 | 0 | 2 | 9.4 | 1.06 | 35.7 | 1.7 | 5.5 | 0.4 | 5/7 |
| 6 | 0.1 | 0.2 | 0.25 | 0.5 | 1 | 4 | 9.6 | 1.08 | 32.8 | 1.6 | 5 | 0.5 | 9.8/11.5 |
| 7 | 0.1 | 0.2 | 0.35 | 0.5 | 2 | 4 | 9.7 | 1.08 | 35.3 | 1.5 | 5 | 0.5 | 12.3/13.9 |
| *The rest is water | | | | | | | | | | | | | |
| ** Industrial CMCS | | | | | | | | | | | | | |

Samples No. 6 and 7 containing gellan, xanthan, CMCS and PAC in the presence of 4% bentonite exhibit the best SSS₁/SSS₁₀ characteristics that are applicable as drilling fluids [21].

Conclusion

Water-soluble CMCS were prepared by carboxymethylation of cornstarch. The introduction of carboxymethyl groups into the structure of cornstarch was detected by FTIR and ¹H NMR spectroscopy. The viscosity-average molecular weight of CMCS is much higher than unmodified cornstarch. Aqueous solutions of CMCS show a high viscosity that decreases upon increasing of temperature and salt addition. The thermal, morphological and rheological properties of CMCS have been evaluated. Water-based optimal drilling fluids composed of various polysaccharides, salt and bentonite have been formulated and suggested for application.

ӘОК 541.64+678.744

**Ж.А. Нұрахметова^{1,2}, Э.П. Құрбашев³, Б. С. Селенова²,
Т. Борке⁴, В. О. Асеев⁴, С. Е. Құдайбергенов^{1,2}**

¹Полимерлік материалдар және технологиялар институты, Алматы, Қазақстан;

²Сәтбаев университеті, Алматы, Қазақстан;

³Алматы технологиялық университеті;

⁴Хельсинки университеті, Хельсинки, Финляндия

КАРБОКСИМЕТИЛДЕНГЕН ЖҮГЕРІ КРАХМАЛЫН СИНТЕЗДЕУ ЖӘНЕ СИПАТТАУ

Аннотация. Бұл жұмыстың мақсаты карбоксиметилденген жүгері крахмалын (КМЖК) алу, сипаттау және бұл үлгілерді су негізіндегі бұрғылау ерітінділерінде қолдану мүмкіндігін бағалау болып табылады. Жүгері крахмалын натрий монохлорацетатымен модификациялады. Жүгері крахмалы мен КМЖК құрылысы ЯМР және ИҚ-спектроскопия көмегімен анықталды. ЯМР-спектроскопиясы көмегімен анықталған жүгері крахмалының карбоксиметилдену дәрежесі 80% тең болды. Марк—Кун—Хаувинк теңдеуімен $[\eta]=K_{\eta} \cdot M^a$ табылған таза жүгері крахмалы мен КМЖК ортамассалық молекулалық массасы (M_{η}) сәйкесінше $2.15 \cdot 10^3$ г/моль және $2.75 \cdot 10^5$ г/моль тең болды. КМЖК температураға тәуелді тұтқырлығы суда Уббелод вискозиметрі көмегімен өлшенді, КМЖК реологиялық қасиеттері полимер концентрациясы және ерітіндінің иондық күшіне тәуелділігі реовискозиметрмен бағаланды. Үлгілердің жылу сипаттамалары дифференциалды сканирлеуші калориметрі (ДСК), термогравиметриялық (ТА) және дифференциалды термиялық анализаторы (ДТА) арқылы Eva Setaram (Франция) анықталды. Жүгері крахмалы мен КМЖК морфологиялық қасиеттері сканирлеуші электрондық микроскоп (СЭМ) арқылы зерттелді. Бұрғылау ерітінділерінің құрылымдық – механикалық, фильтрациялық және қабат түзу қасиеттері, КМЖК фильтрация көрсеткіші табылды.

Түйін сөздер: жүгері крахмалы, модификация, карбоксиметилденген жүгері крахмалы, орынбасу дәрежесі, ортамассалық молекулалық масса, тұтқырлық, реология, бұрғылау ерітінділері.

Ж.А. Нурахметова^{1,2}, Э.П. Курбашев³, Б. С. Селенова², Т. Борке⁴,
В. О. Асеев⁴, С. Е. Кудайбергенов^{1,2}

¹Институт полимерных материалов и технологий, Алматы, Қазақстан;

²Сәтбаев университеті, Алматы, Қазақстан;

³Алматынкі технологиялық университеті;

⁴Университет Хельсинки, Хельсинки, Финляндия

СИНТЕЗ И ХАРАКТЕРИСТИКА КАРБОКСИМЕТИЛИРОВАННОГО КУКУРУЗНОГО КРАХМАЛА

Аннотация. Целью данной работы является подготовка и исследование карбоксиметилированного кукурузного крахмала (КМКК) для потенциального применения в качестве буровых растворов. Кукурузный крахмал модифицировали монохлорацетатом натрия. Структура кукурузного крахмала и КМКК была установлена с помощью ЯМР и ИК-спектроскопии. Степень карбоксиметилирования кукурузного крахмала, определенная с помощью ЯМР-спектроскопии, была равна 80%. Средневязкостные молекулярные массы (M_n) чистого кукурузного крахмала и КМКК, рассчитанные по уравнению Марка-Куна-Хаувинка $[\eta]=K_n \cdot M^a$, равны $2,15 \cdot 10^3$ г/моль и $2,75 \cdot 10^5$ г/моль соответственно. Зависимость вязкости КМКК от температуры измерялась в воде с помощью вискозиметра Уббелюде, а реологические свойства КМКК в зависимости от концентрации полимера и ионной силы раствора оценивались реовискометром. Термические характеристики образцов определялись дифференциальным сканирующим калориметром (ДСК) и термогравиметрическим (ТГА) и дифференциальным термическим анализом (ДТА). Морфологические свойства кукурузного крахмала и КМКК были изучены сканирующей электронной микроскопией (СЭМ). Определены структурно-механические, фильтрационные и коркообразующие свойства буровых растворов и показатели потери жидкости КМКК.

Ключевые слова: кукурузный крахмал, модификация, карбоксиметилированный кукурузный крахмал, степень замещения, средневязкостная молекулярная масса, вязкость, реология, буровые растворы.

Information about authors:

Zh.A. Nurakhmetova - PhD student, Satbayev University, Institute of Polymer Materials and Technology, Almaty, Kazakhstan. Tel: +77757298304, e-mail: nurakhmetova86@mail.ru, ORCID: 0000-0003-2558-8579.

E. P. Kurbashev - student, Almaty Technological University, Almaty, Kazakhstan, e-mail: emirlank@gmail.com, ORCID: 0000-0002-1851-657X.

B.S. Selenova - Dr. of chemical sciences, Professor, Satbayev University, Almaty, Kazakhstan, e-mail: selen.b.s@mail.ru, ORCID: 0000-0001-7156-2703.

T. Borke - PhD, University of Helsinki, Helsinki, Finland, e-mail: tina.borke@gmx.net, ORCID: 0000-0001-8382-5195.

V.O. Aseyev - PhD, University lecturer, University of Helsinki, Helsinki, Finland, e-mail: vladimir.aseyev@helsinki.fi, ORCID: 0000-0002-3739-8089.

S.E. Kudaibergenov - Dr. of chemical sciences, Professor, Satbayev University, Director of Institute of Polymer Materials and Technology, Almaty, Kazakhstan, e-mail: skudai@mail.ru, ORCID: 0000-0002-1166-7826.

REFERENCES

[1] Fang Z. (2013) Pretreatment Techniques for Biofuels and Biorefineries, Green Energy and Technology, Springer-Verlag Berlin Heidelberg, DOI 10.1007/978-3-642-32735-3_2 (in Eng)

[2] Adeyanju O., Olademehin O. P., Hussaini Y., Nwanta U. C., Adejoh A. I., Plavec J. (2016) Synthesis and Characterization of CarboxymethylPlectranthusesculentusStarch. A Potential Disintegrant. J. Pharm. Appl. Chem. 2, 3:189-195. DOI: 10.18576/jpac/020309 Fang Z. (2013) Pretreatment Techniques for Biofuels and Biorefineries, Green Energy and Technology, Springer-Verlag Berlin Heidelberg, DOI 10.1007/978-3-642-32735-3_2 (in Eng)

[3] Zia-ud-Din, HanguoXiong, and Peng Fei (2017) Physical and chemical modification of starches: A review, Critical reviews in food science and nutrition, 57, 12:2691–2705. DOI: 10.1080/10408398.2015.1087379 (in Eng)

[4] Dias F., Souza R., Lucas E. (2013) Starch fatty esters for potential use in petroleum industry, Chemistry & chemical technology, 7(4): 451-456 (in Eng)

[5] Carolina S., Almeida M. (2015) Physicochemical properties, modifications and applications of starches from different botanical sources. Food Sci. Technol, Campinas, 35(2): 215-236 (in Eng)

[6] Manal A., El-Sheikh (2010) Carboxymethylation of maize starch at mild conditions. Carbohydrate Polymers, 79:875–881, DOI: 10.1016/j.carbpol.2009.10.013 (in Eng)

[7] Pfeiffer K., Heinze Th., Lazik W. (2002) Starch Derivatives of High Degree of Functionalization. Stepwise Carboxymethylation of Amylose, Chem. Pap, 56(4):261–266 (in Eng)

- [8] Masakuni T., Yukihiro T., Takeshi T., Yasuhito T. (2014) The Principles of Starch Gelatinization and Retrogradation. *Food and Nutrition Sciences*, 5, 280-291. DOI:10.4236/fns.2014.53035 (in Eng)
- [9] Karmakar, R., Ban, D., Ghosh, U. (2014). Comparative study of native and modified starches isolated from conventional and nonconventional sources. *International Food Research Journal* 21(2): 597-602 (in Eng)
- [10] Shintassova S. M., Baigazyeva G. I., Ermolayeva G. A., Mayemerov M. M., Moldakarimov A. A. (2018) Influence of ion-ozone explosive-cavitation on the protein and starch content in brewing barley. *News of the National Academy of Sciences of the Republic of Kazakhstan Series of Agricultural Sciences*, ISSN 2224-526X, 2(44):5 – 10. <https://doi.org/10.32014/2018.2224-526X> (in Eng)
- [11] Mbougoung P.D., Tenin D., Scher J., Tchiégang C. (2012) Influence of acetylation on physicochemical, functional and thermal properties of potato and cassava starches. *Journal of Food Engineering*, 108: 320–326. DOI:10.1016/j.jfoodeng.2011.08.006 (in Eng)
- [12] Bertoft E. (2017) Understanding Starch Structure: Recent Progress. *Agronomy*, 7, 56: 1-23. DOI:10.3390/agronomy7030056 (in Eng)
- [13] Minaev K. M., Martynova D. O., Zakharov A. S., Sagitov R. R., Ber A. A., Ulyanova O. S. (2016) Synthesis of Carboxymethyl Starch for increasing drilling mud quality in drilling oil and gas wells. *IOP Conf. Series: Earth and Environmental Science* 43. DOI:10.1088/1755-1315/43/1/012071 (in Eng)
- [14] Tadeusz S., Magdalena Z., Joanna K., Beata S. (2013) Carboxymethyl starch with high degree of substitution: synthesis, properties and application. *Polimery*, 58(7-8):501–630 (in Eng)
- [15] Ganorkar P. M., Kulkarni A.S (2013) Studies on preparation and functional properties of carboxymethyl starch from sorghum, *International Food Research Journal*, 20(5): 2205-2210 (in Eng)
- [16] Osundahunsi O. F., Mueller R. (2011) Functional and dynamic rheological properties of acetylated starches from two cultivars of cassava, *Starch*, 63:3–10 DOI: 10.1002/star.201000076 (in Eng)
- [17] Salcedo M., Hernández R., Fernández Q. (2016) *Rev.Fac.Nac.Agron.* 69(2): 7997-8006. DOI: 10.15446/rfna.v69n2.59144 (in Eng)
- [18] Stojanovic Z., Jeremic K., Jovanovic S., Lechner M.D. (2005) Comparison of Some Methods for the Determination of the Degree of Substitution of Carboxymethyl Starch, *Starch*, 57:79–83. DOI: 10.1002/star.200400342 (in Eng)
- [19] Jia L., Jian M., Weijin L., Guohua Zh. (2012) Synthesis, characterisation and in vitro digestibility of carboxymethyl potato starch rapidly prepared with microwave-assistance. *Food Chemistry* 133:1196–1205. DOI:10.1016/j.foodchem.2011.05.061 (in Eng)
- [20] Morgan J. T., Michael C. S., Daniel T., Christian S., Robert G. G. (2011) New ¹H NMR Procedure for the Characterization of Native and Modified Food-Grade Starches, *J. Agric. Food Chem*, 59:6913–6919. DOI:10.1021/jf201209z (in Eng)
- [21] Stepanets V. G., Levin V. L., Khakimzhanov M., Savelyeva N. A., Li E. S. (2018) [Problems of petrology of ultramafic rocks of karatargay river basin, northern ulytau \(central kazakhstan\)](https://doi.org/10.32014/2018.2518-170X). 1:6-25. <https://doi.org/10.32014/2018.2518-170X>

**Publication Ethics and Publication Malpractice
in the journals of the National Academy of Sciences of the Republic of Kazakhstan**

For information on Ethics in publishing and Ethical guidelines for journal publication see <http://www.elsevier.com/publishingethics> and <http://www.elsevier.com/journal-authors/ethics>.

Submission of an article to the National Academy of Sciences of the Republic of Kazakhstan implies that the described work has not been published previously (except in the form of an abstract or as part of a published lecture or academic thesis or as an electronic preprint, see <http://www.elsevier.com/postingpolicy>), that it is not under consideration for publication elsewhere, that its publication is approved by all authors and tacitly or explicitly by the responsible authorities where the work was carried out, and that, if accepted, it will not be published elsewhere in the same form, in English or in any other language, including electronically without the written consent of the copyright-holder. In particular, translations into English of papers already published in another language are not accepted.

No other forms of scientific misconduct are allowed, such as plagiarism, falsification, fraudulent data, incorrect interpretation of other works, incorrect citations, etc. The National Academy of Sciences of the Republic of Kazakhstan follows the Code of Conduct of the Committee on Publication Ethics (COPE), and follows the COPE Flowcharts for Resolving Cases of Suspected Misconduct (http://publicationethics.org/files/u2/New_Code.pdf). To verify originality, your article may be checked by the Cross Check originality detection service <http://www.elsevier.com/editors/plagdetect>.

The authors are obliged to participate in peer review process and be ready to provide corrections, clarifications, retractions and apologies when needed. All authors of a paper should have significantly contributed to the research.

The reviewers should provide objective judgments and should point out relevant published works which are not yet cited. Reviewed articles should be treated confidentially. The reviewers will be chosen in such a way that there is no conflict of interests with respect to the research, the authors and/or the research funders.

The editors have complete responsibility and authority to reject or accept a paper, and they will only accept a paper when reasonably certain. They will preserve anonymity of reviewers and promote publication of corrections, clarifications, retractions and apologies when needed. The acceptance of a paper automatically implies the copyright transfer to the National Academy of Sciences of the Republic of Kazakhstan.

The Editorial Board of the National Academy of Sciences of the Republic of Kazakhstan will monitor and safeguard publishing ethics.

Правила оформления статьи для публикации
в журнале смотреть на сайте:

www.nauka-nanrk.kz

<http://chemistry-technology.kz/index.php/en/arhiv>

ISSN 2518-1491 (Online), ISSN 2224-5286 (Print)

Редакторы: *М. С. Ахметова, Т. А. Апендиев, Аленов Д.С.*
Верстка на компьютере *А.М. Кульгинбаевой*

Подписано в печать 05.02.2019.
Формат 60x881/8. Бумага офсетная. Печать – ризограф.
4,6 п.л. Тираж 300. Заказ 1.