

## Comparative characteristics of microcrystalline cellulose obtained from the rice waste production of Kazakhstan

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Development of methods for effective processing of reconstructive biological resources and allocation of valuable materials refers to the main tasks of science and industry. The work determines the optimal hydro module and physico-chemical properties of microcrystalline cellulose (MCC), obtained by the method of organosolvent oxidation of rice husk (RH), grown in the southern (Kyzylorda region) and southeast (Almaty region) of Kazakhstan, and it was established that the yield and the qualitative indicators of the MCC depends on the climatic and geographical features of the region, where raw materials are grown to obtain cellulose. The effective hydro module for MCC obtained from Bakanas rice husk (B-RH) was found to be 1:12 g/mL and yield was 45.0%, whereas Kyzylorda rice husk (K-RH) the effective hydromodule was 1:10 g/mL and yield found to be equal to 52.58%. During organosolvent oxidation, the selected method did not require additional processing of raw materials. It was discovered that for delignification, it takes 120 minutes of time, and the yield of MCC will be 15-18% higher than the cellulose obtained by the alkali. Rice husk is a promising alternative raw material for cellulose production and the use of the organosolvent method for obtaining an MCC is an economically advantageous and environmentally friendly method.

**Keywords:** rice husks (RH); organosolvent oxidation; microcrystalline cellulose (MCC); FTIR; crystal structure.

## Қазақстандағы күріш өндірісі қалдықтарынан алынған микрокристалды целлюлозаның салыстырмалы сипаттамасы

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Қайта жаңартылатын биоресурстарды тиімді өңдеу әдістерін әзірлеу мен құнды материалдарды бөліп алу ғылым мен өндірістің ең басты міндеттеріне жатады. Бұл жұмыста Қазақстанның оңтүстік және оңтүстік-шығыс аймақтарында (Қызылорда облысы және Алматы облысы), өсірілген күріш қауызынан (RH) органосольвенттік тотықтыру әдісімен алынған микрокристалды целлюлозаның (MCC) тиімді гидромодулі және физико-химиялық қасиеттері анықталып, MCC-ның шығымы мен сапалық көрсеткіштері шикізат өсірілген аймақтың климаттық, географиялық ерекшеліктеріне тәуелді болатындығы зерттелді. Бақанас күріш қауызынан (B-RH) алынған MCC-ның тиімді гидромодулі 1:12 г/мл, шығымы 45.0%-ға тең болса, Қызылорда күріш қауызынан (K-RH) алынған MCC үшін тиімді гидромодуль 1:10 г/мл, шығымы 52.58%-ға тең болатындығы анықталды. Органосольвенттік тотықтыру барысында, таңдалған әдіс шикізатты қосымша өңдеуді қажет етпейтіндігі, делигнификациялауға 120 минут уақыт жұмсалатындығы анықталып, MCC-ның шығымы сілтілік жолмен алынатын целлюлозаға қарағанда 15-18%-ға жоғары болатындығы белгілі болды. Яғни, целлюлоза талшықтарын алуда күріш қауызы жоғары сұранысқа ие балама шикізат көзі екендігі және MCC алуда органосольвенттік әдісті қолдану, экономикалық және экологиялық жағынан тиімді болатындығы белгілі болды.

**Түйін сөздер:** күріш қауызы (КҚ); органосольвенттік тотықтыру; микрокристалды целлюлоза (МКЦ); ИҚ спектрометр; кристалдық құрылыс.

## Сравнительная характеристика микрокристаллической целлюлозы, полученной из отходов рисового производства Казахстана

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Разработка эффективных методов переработки реконструктивных биологических ресурсов и извлечения ценных материалов является одной из ключевых задач науки и производства. В данной работе определены оптимальные гидромодули и физико-химические характеристики микрокристаллической целлюлозы (МКЦ), полученной методом органосольвентного окисления рисовой шелухи (РШ), выращенной в разных регионах Казахстана: на юге (Кызылординская область) и юго-востоке (Алматинская область). Установлено, что выход и качественные показатели МКЦ зависят от климатогеографических особенностей региона, где произрастает исходное сырье. Для рисовой шелухи сорта Bakanas (РШ-Б) эффективный гидромодуль составил 1:12 г/мл, а выход МКЦ - 45,0%, в то время как для рисовой шелухи сорта Кызылордин (РШ-К) гидромодуль оказался равным 1:10 г/мл, а выход составил 52,58%. Процесс органосольвентного окисления не потребовал дополнительной предварительной обработки сырья. Было также установлено, что для делигнификации требуется 120 мин, при этом выход МКЦ в этом случае на 15-18% превышает выход целлюлозы, полученной щелочным методом. Таким образом, рисовая шелуха представляет собой перспективное альтернативное сырье для производства целлюлозы, а органосольвентный метод получения МКЦ является не только экономически эффективным, но и экологически чистым способом переработки.

**Ключевые слова:** рисовая шелуха (РШ); органосольвентное окисление; микрокристаллическая целлюлоза (МКЦ); ИК спектрометр; кристаллическая структура.



Article

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### 1. Introduction

The main task of modern scientific technological progress is to develop the use of resource shielding technologies that reduce environmental pollution and use natural sources [1]. In this context, utilizing annual plants that are high in hydrocarbon compounds, along with agricultural waste as a natural raw material, and extracting cellulose fibers from these sources holds both scientific and industrial significance [2]. This is the main reason that the opportunity for synthesis of biocomposite materials which provide biological resources and biological features of resources and raw materials [3]. One type of agricultural waste that serves as a natural raw material is rice husk (RH), produced during the processing of rice, which has potential as a source for cellulosic fiber production. The RH is about 20% of the mass of rice [4]. The studies have shown that the chemical composition is rich in hydrocarbons and can be divided into cellulose fibers up to 35-45% [5-6]. However, in Kazakhstan, there is no ready-made technology for using agricultural waste as a raw material base for obtaining natural polymers and other valuable materials, which makes the problem of rational use of natural resources still relevant [7]. Thus, until now, rice husk has primarily been used for pyrolysis, as biomass fuel, and in most cases as animal feed [8].

Rice production in Kazakhstan accounts for 89.4% of the total agricultural land in the country [9]. Accordingly, on average, remains 500 thousand tons of straw and 100 thousand tons of

husks per year [10]. This indicates that the reserves of renewable raw materials are accumulated significantly every year.

The study [11-12] revealed that the yield of cellulose from RH and its quality indicators depend on the rice variety, climatic, geographical distribution and method of production of cellulose. Therefore, the type and method of obtaining raw materials used in the production of cellulose, elimination of production and quality indicators, reducing the efficiency of production and energy consumption also leads to energy efficiency.

Currently, the widely used method of obtaining cellulose from rice husks is the method of alkaline hydrolysis. According to the results of the study [13-14], the obtaining cellulose from RH is carried out using the alkaline processing method by conducting additional bleaching. The resulting cellulose exit is 33-35%. In the work [15-16] an alkaline method was used for the extraction of cellulose from rice husks and by bleaching the obtained technical cellulose with additional reagents, cellulose was obtained with a yield of 30-35%. This method, in turn, is a two-stage method, and the yield of the obtained cellulose fibers is relatively low. In addition, due to the two-stage process, the costs of time, energy and additional reagents increase. Therefore, taking into account environmental, economic and energy costs, it is important to determine an effective method for obtaining cellulose fibers from the biomass of annual plants, as well as to study the effect of the type of raw material on the yield of cellulose and quality indicators.

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In this study, microcrystalline cellulose (MCC) was obtained from rice husk grown in «Bakanas» (Almaty region) and «Kyzylorda» (Kyzylorda region) regions of the Republic of Kazakhstan by a «soft» method based on the organosolvent oxidation method, and its yield and quality indicators, chemical structure, surface morphology, crystal structure and thermal decomposition were comparatively studied.

The samples obtained from the rice husk raw material used in the study were conventionally designated as «Bakanas» rice husk - B-RH, MCC obtained from it -  $MCC_{B-RH}$ , «Kyzylorda» rice husk - K-RH, and MCC obtained from it  $MCC_{K-RH}$ .

## 2. Experiment

### 2.1 Materials

Rice husks were obtained from Bakanas (Balkhash district, Almaty region, Kazakhstan) and Kyzylorda (Kyzylorda region, Kazakhstan). Hydrogen peroxide (15%,  $H_2O_2$ ), acetic acid ( $\geq 55\%$ ,  $CH_3COOH$ ), potassium permanganate (99%,  $KMnO_4$ ), ethanol (96%,  $C_2H_5OH$ ), sulfuric acid (98%,  $H_2SO_4$ ), orthophosphoric acid (98%,  $H_3PO_4$ ), sodium hydroxide ( $\geq 99\%$ , NaOH), potassium bichromate ( $\geq 99\%$ ,  $K_2Cr_2O_7$ ), sodium thiosulfate (99%,  $Na_2S_2O_3$ ), potassium iodide ( $\geq 99\%$ , KI) and starch were provided by Sigma-Aldrich (Bangalore, India). All other reagents were of analytical grade and were used without additional purification.

### 2.2 Methods

#### 2.2.1 Preparation of peroxyacetic acid (PAA)

Preparation of PAA was prepared according to the methodology in studies [17-18]. The obtained PAA was stored in a freezer at  $5 \pm 0.5^\circ C$ .

#### 2.2.2 Preparation of MCC from RH by organosolvent oxidation and determination of its yield

The scheme of obtaining MCC from RH by the organosolvent oxidation method is shown in Figure 1.

Extraction of MCC from RH was carried out according to the methodology described in studies [17-18]. That is, 10 g of each of B-RH and K-RH samples were measured, and RH:PAA and were obtained in hydromodule of: 1:8, 1:10, 1:12, 1:14, 1:16, 1:18, 1:20, 1:22, 1:24 g/mL, respectively. Obtaining MCC was carried out by boiling the raw material and delignifying agent in a flask with a rotary condenser at a temperature of  $90 \pm 2^\circ C$  with continuous intensive mixing for 2 hours. The obtained  $MCC_{B-RH}$  and  $MCC_{K-RH}$  were cooled to a temperature of  $25 \pm 2^\circ C$ , filtered using filter paper, and neutralized with distilled water until  $pH=7$ . The neutralized MSS was dried at a temperature of  $80 \pm 2^\circ C$  for 6 hours until it reached a constant mass, weighed on an analytical balance with an accuracy of 0.0001 g, and the yield was calculated using the following formula:

$$\eta = (m_{RH} - m_{MCC}) / m_{RH} \cdot 100\%$$

Where,  $m_{RH}$  is the mass of RH, g;  $m_{MCC}$  – the mass of obtained MCC, g.

#### 2.2.3 Determination of microcrystalline cellulose quality indicators

Moisture content of  $MCC_{B-RH}$  and  $MCC_{K-RH}$  was determined according to state standard -16932 (STST),  $\beta$ -cellulose content according to STST-6840, residual lignin content according to STST-11960, hemicellulose content according to STST-9002.

#### 2.2.4 Scanning electron microscopy (SEM)

The surface morphology of the MCC was examined using a Quanta 200i 3D SEM (FEI, Netherlands). Measurements were carried out in high vacuum mode using a secondary electron detector at an accelerating voltage of 15 kV. The surface of the MCC was coated with gold nanoparticles to improve the transfer of electrons, and the specimens were mounted onto aluminum pins with carbon tape.

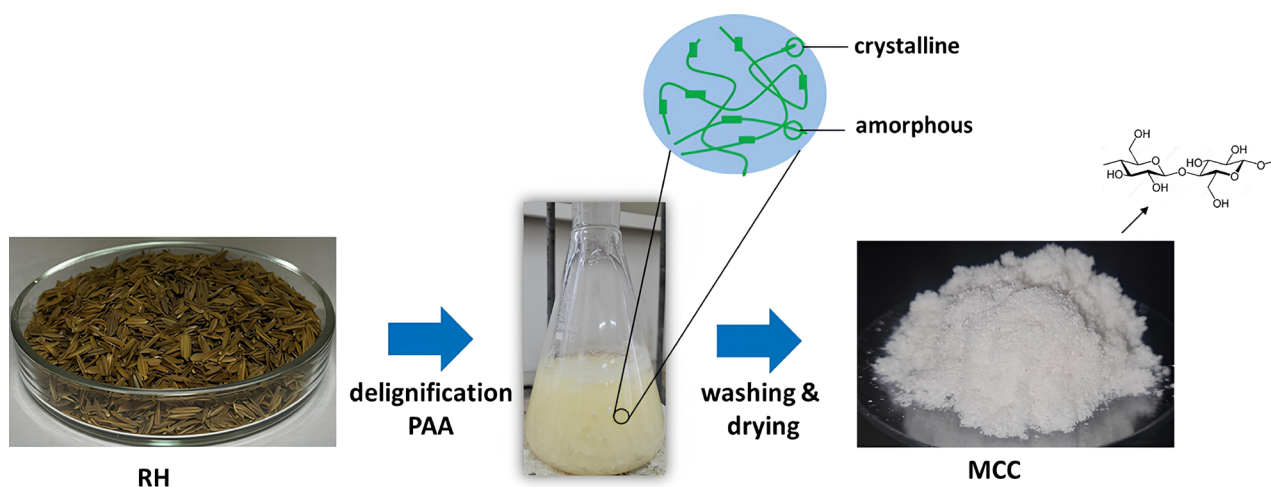


Figure 1 – Scheme of obtaining MCC from RH by the organosolvent oxidation method



**Figure 2** – Rice husks and MCC samples from RH: **a** – B-RH; **b** – K-RH; **c** – MCC<sub>B-RH</sub> (hydromodule 1:12); **d** – MCC<sub>K-RH</sub> (hydromodule 1:10)

### 2.2.5 FTIR spectroscopy

FTIR analysis was performed on a spectrometer FTIR FT-801 (Simex, Russia), with a resolution of  $1\text{ cm}^{-1}$  and a wavelength  $4500\text{--}4700\text{ cm}^{-1}$ , by placing the sample on the surface of the attachment with the method of internal and variable-diffuse reflection, at a temperature of  $25^\circ\text{C}$  and a number of scans of 100.

### 2.2.6 X-ray diffraction

The crystal structures of substances were studied by X-ray diffraction on X'PertPRO diffractometer (Malvern Panalytical Empyrean, Netherlands) using monochromatized copper ( $\text{CuK}\alpha$ ) radiation with a scan step of  $0.02^\circ$ ,  $\text{K-Alpha1}$  [ $\text{\AA}$ ] 0.1542. The measurement angle was  $10\text{--}45^\circ$ , the X-ray tube voltage was 45 kV, the current intensity was 30 mA, the measurement time at each step was 0.5 s and an aluminum rectangular multi-purpose sample holder (PW1172/01) was used for the measurement in reflection mode. The ICDD PDF-4/AXIOM database of XRD patterns was used for the analysis of the XRD.

### 2.2.7 Thermogravimetric analysis (TGA)

The thermal characteristics of the MCC were studied using a LabSysevo differential TGA (Setaram, France), in an argon atmosphere. The temperature range was  $30\pm 5\text{--}700\pm 5^\circ\text{C}$ , with a heating rate of  $10\pm 1^\circ\text{C}/\text{min}$ . The mass of the samples was found to be approximately  $25\pm 2\text{ mg}$ .

## 3. Results and Discussion

### 3.1 The MCC<sub>B-RH</sub> and MCC<sub>K-RH</sub> from RH by organosolvent oxidation method

Figures 2 a-d show rice husks from different regions (B-RH, K-RH) and MCC<sub>B-RH</sub> and MCC<sub>K-RH</sub> obtained from them. Although the raw materials B-RH and K-RH are yellow-brown in color, the MCC obtained from them is a fine-fibrous, completely porous and cotton-like soft mass (Figure 2 c and d). That is, as a result, it became known that it is possible to synthesize soft tissue, cotton-like MCC without additional processing of the raw material by the method of organosolvent oxidation. This, in turn, is time-saving and economically very effective.

### 3.2 The yield and quality indicators of MCC

Table 1 shows the yield and quality indicators of MCC<sub>B-RH</sub> and MCC<sub>K-RH</sub> obtained at different hydromodule of RH:PAA g/mL by the method of organosolvent oxidation under «soft» conditions. According to the results, the yield of MCC obtained in RH:PAA 1:12g/mL hydromodule for B-RH was 45.00%, moisture content was 4.14%,  $\beta$ -cellulose was 65.57%, residual lignin was 18.9%, hemicellulose was 19.2%, ash content ( $\text{SiO}_2$ ) was 33.4% and the size of the mentioned hydromodule



**Table 1** – Effect of RH:PAA hydromodule on MCC quality

| B-RH:PAA,<br>g/mL | Quality indicators of MCC <sub>B-RH</sub> , % |          |                    |                 |                |                                 |
|-------------------|---|----------|--------------------|-----------------|----------------|---------------------------------|
|                   | Yield of MCC                                  | Humidity | $\beta$ -cellulose | Residual lignin | Hemi-cellulose | Ash content (SiO <sub>2</sub> ) |
| 1:8               | 44.0±2  | 2.13±0.5 | 46.57±3            | 16.7±0.5        | 17.5±2         | 32.0±0.5                        |
| 1:10              | 44.6±2  | 2.01±0.5 | 64.26±3            | 17.6±0.5        | 18.9±2         | 32.9±0.5                        |
| 1:12              | 45.0±2  | 4.14±0.5 | 65.57±3            | 18.9±0.5        | 19.2±2         | 33.4±0.5                        |
| 1:14              | 40.8±2  | 1.75±0.5 | 56.3±3             | 21.9±0.5        | 22.1±2         | 31.9±0.5                        |
| 1:16              | 40.0±2  | 1.67±0.5 | 62.8±3             | 24.4±0.5        | 21.3±2         | 31.9±0.5                        |
| 1:18              | 42.86±2                                       | 1.87±0.5 | 54.33±3            | 23.2±0.5        | 23.7±2         | 32.1±0.5                        |
| 1:20              | 44.73±2                                       | 2.11±0.5 | 56.1±3             | 22.2±0.5        | 23.2±2         | 33.2±0.5                        |
| 1:22              | 39.8±2  | 2.25±0.5 | 49.43±3            | 16.3±0.5        | 22.1±2         | 33.1±0.5                        |
| 1:24              | 41.12±2                                       | 1.82±0.5 | 56.5±3             | 23.8±0.5        | 22.3±2         | 32.1±0.5                        |
| K-RH:PAA,<br>g/mL | Quality indicators of MCC <sub>K-RH</sub> , % |          |                    |                 |                |                                 |
|                   | Yield of MCC                                  | Humidity | $\beta$ -cellulose | Residual lignin | Hemi-cellulose | Ash content (SiO <sub>2</sub> ) |
| 1:8               | 46.7±2  | 3.41±0.5 | 40.86±3            | 17.4±0.5        | 17.0±2         | 30.0±0.5                        |
| 1:10              | 52.58±2                                       | 4.55±0.5 | 40.5±3             | 17.3±0.5        | 17.7±2         | 29.9±0.5                        |
| 1:12              | 50.89±2                                       | 3.41±0.5 | 41.3±3             | 19.1±0.5        | 21.1±2         | 29.4±0.5                        |
| 1:14              | 52.26±2                                       | 4.09±0.5 | 38.7±3             | 20.3±0.5        | 19.7±2         | 29.7±0.5                        |
| 1:16              | 52.13±2                                       | 4.81±0.5 | 38.13±3            | 23.6±0.5        | 22.9±2         | 30.1±0.5                        |
| 1:18              | 49.61±2                                       | 4.28±0.5 | 38.43±3            | 21.2±0.5        | 23.7±2         | 31.0±0.5                        |
| 1:20              | 49.71±2                                       | 3.39±0.5 | 38.5±3             | 22.4±0.5        | 22.2±2         | 32.2±0.5                        |
| 1:22              | 50.72±2                                       | 4.95±0.5 | 30.63±3            | 18.3±0.5        | 23.6±2         | 33.4±0.5                        |
| 1:24              | 50.55±2                                       | 3.83±0.5 | 34.4±3             | 20.7±0.5        | 21.3±2         | 30.8±0.5                        |

was recognized as the optimal indicator. And for K-RH, the optimum hydromodule of RH:PAA is equal to 1:10g/mL, yield of MCC is 52.58%, moisture content is 4.55%,  $\beta$ -cellulose is 40.5%, residual lignin is 17.3%, hemicellulose is 17.7%, ash content (SiO<sub>2</sub>) was equal to 29.9%. When analyzing the quality indicators of the obtained MCC, it can be noted that the organosolvent oxidation method increases the yield of cellulose by 15-18% compared to the alkaline and acid hydrolysis methods used in previous studies [19-20]. In addition, the environmentally friendly one-step oxidation of organic solvents in the biomass pretreatment process does not require additional bleaching steps. It is important to note that the oxidative-organosolvent technology enables the extraction of MCC from RH under mild conditions and at high productivity, without the need for excessive pressure or temperature [17,18]. This delignification method has shown significant effectiveness in extracting MCC from RH (Table 1).

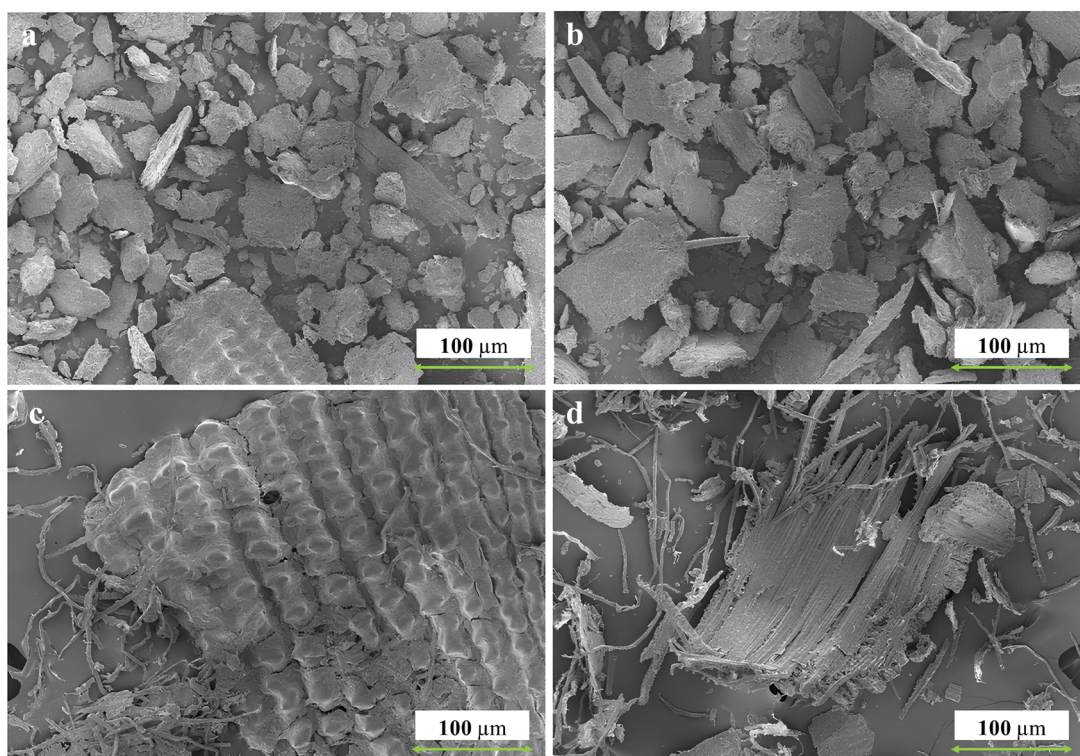
In addition, it was determined that the yield of MCC obtained from K-RH is 7.58% higher than that obtained from MCC obtained from B-RH, and the amount of PAA used in efficient hydromodules is 2 mL less. This may be related to the amount of SiO<sub>2</sub> in the cellulose obtained from K-RH. This is because silica is a key component of the cell walls of rice husks and helps increase their mechanical strength [21]. Thus, when pulp is cooked, silicon interacts with it, which can negatively

impact the yield of the pulp. Similar results were obtained in the study [22] and it was determined that increasing the amount of SiO<sub>2</sub> has a negative effect on the yield of cellulose. And the amount of SiO<sub>2</sub> in the primary raw material depends on the moisture content of the land used for agricultural purposes, and the chemical composition of the soil [23-24].

### 3.3 SEM analysis

Figure 3 compares the surface morphology of raw materials B-RH and K-RH (Figure a and b) and MCC obtained in an effective hydromodule (Figure 3 c and d). It can be seen that the surface morphology of the primary raw materials consists of granules of different shapes, the surfaces of which are covered with smooth wax materials. These are pectin, lignin, hemicellulose and other carbohydrate compounds covering the surface of cellulose fibers [22-23].

It can be seen that the surface morphology of MCC<sub>B-RH</sub> and MCC<sub>K-RH</sub> obtained in the effective hydromodule shown in Figures 3c-d, respectively, consists of ribbon-like fibrils. In addition, it is observed that the surface of cellulose fibers is not smooth (rough surface). This is due to the high content of silica in MCC [16, 24]. After delignification of MCC<sub>B-RH</sub> and MCC<sub>K-RH</sub> it is possible to observe that a certain amount of amorphous wax-like material was hydrolyzed, resulting in the release of crystalline cellulose fibers (Figure 3 c and 3). It can be seen that in the XRD

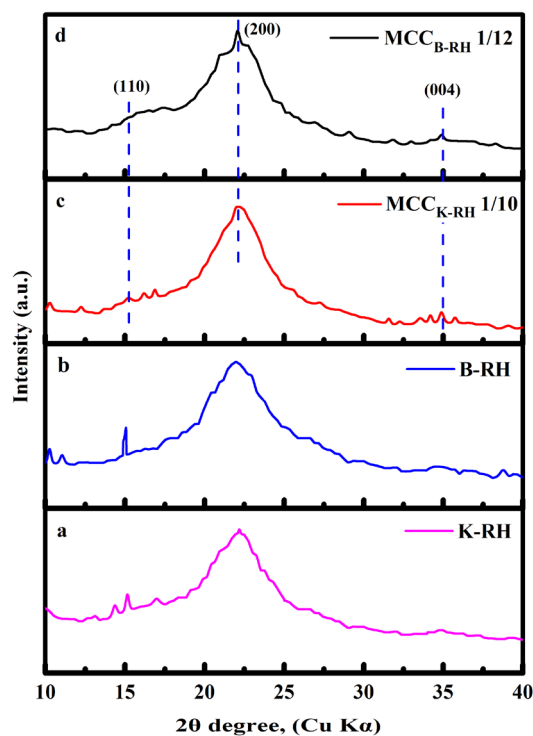


**Figure 3** – SEM images of: **a** – B-RH; **b** – K-RH; **c** – MCC<sub>B-RH</sub>; **d** – MCC<sub>K-RH</sub>

diffraction patterns in Figures 4c, d the diffraction reflection angle of  $2\theta=34.8^\circ$  corresponds to the increase in the signal intensity characteristic of the crystalline structure of cellulose. If we compare the surface morphology of the MCC, we can see that in MCC<sub>B-RH</sub> the hydrolysis of the amorphous layer was less effective, and the decomposition of cellulose into crystalline fibers was lower than that in MCC<sub>K-RH</sub> (Figure 3d). This is explained by the fact that the amount of silica in MCC<sub>B-RH</sub> is 4% higher than in MCC<sub>K-RH</sub>, totaling 33.4% (Table 1). That is, during delignification, silica interacts with cellulose and may inhibit the release of crystalline cellulose fibers. However, it was found that the organosolvent oxidation method is more efficient for producing MCC than alkaline or acid hydrolysis.

### 3.4 X-ray diffraction

X-ray diffraction analysis was performed to determine the crystal structure of the obtained MCC. Figure 4 compares the X-ray diffractograms of raw materials B-RH and K-RH and MCC<sub>B-RH</sub> and MCC<sub>K-RH</sub> obtained in an efficient hydromodule. The crystalline structure of cellulose was determined based on studies [12, 35, 36]. From the diffractograms of K-RH and B-RH in figures 4 a and 4 b, it is possible to observe peaks  $2\theta=15.1^\circ$  (110),  $22.1^\circ$  (200). The amorphous region of this raw material is intact, lignin, hemicellulose, etc. shows that hydrocarbons cover the crystalline part of cellulose [12-13]. Meanwhile, the X-ray diffraction patterns of MCC K-RH and MSS B-RH, according to the ICDD data for cellulose I $\beta$  (No. 00-056-1718), showed three



**Figure 4** – XRD diffractions of RH and MCC: **a**–K-RH; **b**–B-RH; **c**–MCC<sub>B-RH</sub> 1:12; **d**–MCC<sub>K-RH</sub> 1:10

registered diffraction peaks:  $2\theta = 15.30^\circ$  (110),  $22.30^\circ$  (200), and  $34.80^\circ$  (004) (Figure 4 c and d). That is, the crystal structure of the MCC molecule shows that it is a two-chain monoclinic, diffraction peaks characteristic of cellulose I $\beta$  [12, 33].

This indicates that the delignification process was successfully carried out during the organosolvent oxidation. In addition, it was found that the crystal structure of MCC did not change [12-13] in the studies, it was found that the crystal structure of MCC obtained from RH is consistent with the results of this research.

### 3.5 FTIR spectroscopy

The relative IR spectra of the initial raw materials B-RH and K-RH, as well as the chemical structures of MCC<sub>B-RH</sub> and MCC<sub>K-RH</sub> obtained in the effective ratio are shown in Figure 4. The symmetric and asymmetric long oscillation bands between 3500 and 3000  $\text{cm}^{-1}$  shown in the IR spectra of RH (Figure 5 a and b) indicate the presence of moisture in the raw material structure and the occurrence of dehydration reactions during pyrolysis [25]. In addition, the -OH groups in this region are due to the presence of signals (Si-OH) adsorbed on the RH surface [25-26]. The wave numbers at 1060  $\text{cm}^{-1}$ , 1517  $\text{cm}^{-1}$  and 1733  $\text{cm}^{-1}$  indicate long-range vibrations of C-O, C=C, C=O groups in RH, which are characteristic of cellulose, hemicellulose and lignin.

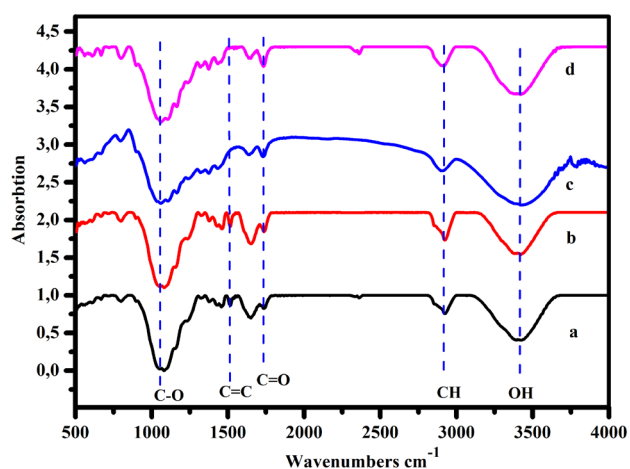


Figure 5 – FTIR spectra of: a – B-RH; b – K-RH; c – MCC<sub>B-RH</sub>; d – MCC<sub>K-RH</sub>

Figures 5 c and 5 d show the IR spectra of MCC<sub>B-RH</sub> and MCC<sub>K-RH</sub>, respectively. In all spectra, the absorption region starts from the out-of-plane vibration of the C-OH bond at 669.3  $\text{cm}^{-1}$  [28-29] and corresponds to absorbed water molecules at approximately 1641.7  $\text{cm}^{-1}$  [30]. And the wavelengths of 2902.8  $\text{cm}^{-1}$  and 3372.5  $\text{cm}^{-1}$  describe the long-term vibration of the CH group and the intermolecular hydrogen bond - OH group [29, 30, 31]. The high-intensity signal at 1059.9  $\text{cm}^{-1}$  indicates the long-term vibration of the C-O-C bond in the pyranose ring

defined as a  $\beta$  1,4-glycosidic bond [30, 32], while the signal at 1164.4  $\text{cm}^{-1}$  indicates the C-O and C-C bonds in the aromatic ring, 1316.1  $\text{cm}^{-1}$  shows C-H bond at 1333.4  $\text{cm}^{-1}$  and 1375.1  $\text{cm}^{-1}$ , C-H<sub>2</sub> bond at 1434.3  $\text{cm}^{-1}$  due to the crystalline nature of cellulose [29, 31]. Meanwhile, the weak absorption at 1508.9  $\text{cm}^{-1}$  and 1734.4  $\text{cm}^{-1}$  wave number indicates the long-term vibration of the aromatic C=C bond in the residual lignin molecule in MCC and the acetyl and ester C=O group in the hemicellulose molecule [33]. This will clarify the quantitative values of residual lignin and hemicellulose given in Table 1. The resulting absorption at 560.8  $\text{cm}^{-1}$  indicates the Si-O bond characteristic of silica in cellulose [34]. It can be observed that the FTIR absorption spectra of MCC<sub>RH</sub> in research works [12-13] are consistent with the results obtained in this study.

### 3.6 Thermogravimetric analysis of MCC

Comparative thermograms of thermal stabilities of MCC<sub>B-RH</sub> and MCC<sub>K-RH</sub> samples are shown in Figure 6. MCC<sub>B-RH</sub> lost 4% mass due to evaporation of absorbed moisture from air from room temperature to 120°C, while MCC<sub>K-RH</sub> lost 7% mass. And at temperatures from 120°C to 295°C, the first thermal degradation began, and the decomposition of the hemicellulose and lignin fraction in the samples took place [7]. According to studies [15-16], thermal decomposition of lignocellulosic materials takes place in the temperature range of 150-500°C, [37] it was found that hemicellulose mainly decomposes in the range from 150 to 350°C, cellulose in the range of 275-350°C, and lignin in the range of 250-500°C.

The second thermal degradation of cellulose took place in the temperature range of 295-400°C, MCC<sub>B-RH</sub> showed a 55% mass loss compared to MCC<sub>K-RH</sub> 60% loss. Meanwhile, in the temperature range of 400-600°C, 65% of MCC<sub>B-RH</sub> and 72% of MCC<sub>K-RH</sub> underwent thermal degradation, and the amount of degradation product SiO<sub>2</sub> was equal to 35% and 28% for MCC<sub>B-RH</sub> and MCC<sub>K-RH</sub>, respectively. From this, it was determined that the MCC in Table 1 corresponds to the numerical value of SiO<sub>2</sub> in the quality indicators.

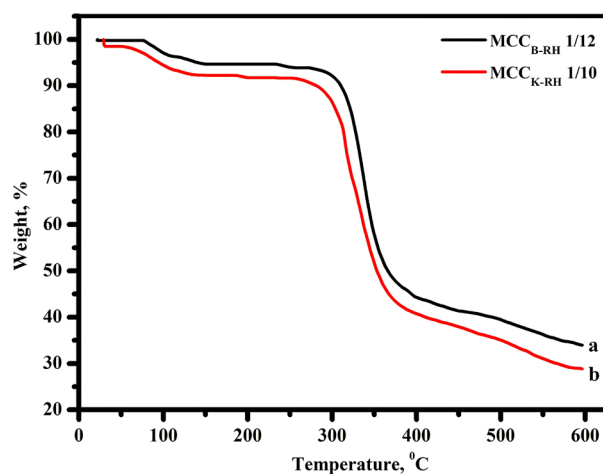


Figure 6 – TGA curves of: a – MCC<sub>B-RH</sub> and b – MCC<sub>K-RH</sub>

#### 4. Conclusion

In conclusion, in this study, the effective hydromodules RH:PAA necessary for obtaining microcrystalline cellulose (MCC) from rice husk grown in the southern and southeastern regions of Kazakhstan by the method of organosolvent oxidation were determined. The effective hydromodule for obtaining MCC by the method of organosolvent oxidation was equal to RH:PAA 1:12 g/mL for B-RH, RH:PAA 1:10 g/mL for K-RH, and the yield of MCC<sub>B-RH</sub> in this mode was 45%, the yield of MCC<sub>K-RH</sub> was equal to 52.58%. In addition, the yield of MCC<sub>K-RH</sub> was 7.58% higher than that of MCC<sub>B-RH</sub>, while the amount of  $\beta$ -cellulose was 2.23% less. It has been established that an increase in the ash content (SiO<sub>2</sub>) in MCC leads to a decrease in the yield of cellulose. That is, it was known that the yield, effective hydromodule and quality indicators of MCC obtained from RH are directly affected by the climatic and geographical conditions of the region where the primary raw material is grown, and the chemical composition of the soil. It was determined that the chemical structure of MCC obtained from B-RH and K-RH corresponds to cellulose, and that the surface morphology of cellulose consists of a fibrous structure. Additionally, it was found that the crystal structure remains intact during synthesis and that it is thermally resistant up to 600°C. That is, it has been found that RH is a raw material with high potential for producing biocomposite materials, such as biodegradable packaging and hydrogels, intended for industrial use, particularly in the fields of medicine and agriculture.

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