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A STUDY ON THE PREPARATION, STRUCTURE, AND PROPERTIES OF MICROCRYSTALLINE CELLULOSE

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Key Words: Microcrystalline; Cellulose; Colloid; Emulsion

ABSTRACT

The preparation, structure, and properties of microcrystalline cellulose (MCC) from rice straw were investigated by IR, x-ray, viscometry, polarizing microscope, SEM, etc. The results are as follows:

1. The leveling-off degree of polymerization (LODP) obtained from rice straw is about 80–150. The dimensions of MCC granules are 20–30 μm length, 0.5–0.8 μm thick, and the crystallinity is about 80%.
2. The aqueous suspension of a certain concentration of MCC can form a gel under the effect of shear force. The viscosity of MCC gel increased with an increasing content of MCC in water. A sharper increase of viscosity occurred in the 3–6% range.
3. The addition of one or two valence salts into the MCC gel increased the viscosity.
4. The viscosity of MCC gel has its maximum value at pH 8.
5. The MCC gel as an emulsifying agent can form a stable emulsion in the oil/water system when the ratio of oil/water is below 6/4.

INTRODUCTION

Microcrystalline cellulose (MCC) has been produced for 40 years. The product appeared commercially in the form of powder and was mainly used in the pharmaceutical industry for tableting. Battista et al. [1] found in 1962 that an aqueous suspension of MCC can form a suspension colloid (gel) under a strong shear force on the suspension. Later scientists [2–4] investigated its properties, morphology, and application. MCC gel has had a remarkable success in food and pharmaceutical uses during the 20 years since its commercialization as Avicel by FMC Corporation. The development of colloidal microcrystalline cellulose made available much finer particle forms of highly purified crystalline cellulose and more important aqueous suspensions of MCC particles. These have a smooth texture (like uncolored butter) and unique pseudoplastic properties, including a stable viscosity over a wide temperature range. In food industry, MCC is important for its heat stability, ability to thicken, favorable mouth feel, and flow control. It serves to extend starches, form sugar gels, stabilize foam, and control formation of ice crystals. However, MCC has not been used commercially on a large scale in China, especially MCC gel. Only some of it is used in the pharmaceutical industry for tableting. In this article we introduce our research results on the preparation, structure, and properties of MCC made from rice straw.

EXPERIMENTAL

Preparation of MCC

Rice straw cleaned of soil and dust was cooked in 1.5% NaOH at 120°C for 2 hours, then filtrated, washed with water until neutralization, dewatered by centrifuge, and dried. The cellulose obtained was subjected to acid hydrolysis in the following conditions: 2 mol/L HCl, 105°C, 15 minutes. Hydrolysis, washing, and centrifuging followed. To make the MCC gel, a suspension with a certain content of MCC granules was passed through a homogenizer for a certain time. The suspension became a butterlike suspension colloid.

Structure of MCC

A. The morphology of MCC granule.
Dimension measurement of MCC granule by SEM, S-430.
B. The crystallinity of MCC by x-ray, D/max-1200.

Properties of MCC Gel

A. Rheological properties by viscometer.
B. Emulsifying function by polarizing microscope.
C. Emulsion stability of MCC gel, including heat, cold, storage, pH, and salt added.

RESULTS AND DISCUSSION

The Effect of Cooking Conditions on Delignification of Rice Straw

To obtain cellulose from rice straw, the first important thing is to remove lignin from rice straw. The traditional process of delignification is to cook the rice straw in an alkali medium. The effect of NaOH concentration on delignification is shown in Fig. 1. For Curves 2 to 4, the concentration of NaOH is 1.5, 2, and 5%, respectively. The other cooking conditions are the same, i.e., temperature 80°C, time 2 hours. It is clear that even for Curve 2 the characteristic peaks for lignin, 1598 cm^{-1} (aromatic nuclei) and 1328 cm^{-1} (syringic group), have almost disappeared. This means that pure cellulose was obtained in these cooking conditions.

The Effect of Hydrolysis Conditions on the Morphology of MCC

Degradation of cellulose chain to reach the so-called LODP occurred during acid hydrolysis. The mechanism of hydrolysis is shown in Fig. 2 [5]. The degradation occurred in the glucosidic bonds of cellulose. The relationship between DP and hydrolysis time is shown in Fig. 3. After 2 hours the DP became constant. X-ray diffraction of MCC granule is shown in Fig. 4. A typical diffraction pattern of cellulose I was obtained, and the crystalline index was higher than that of the original straw cellulose. It can be seen from Fig. 5 that the morphology of the MCC

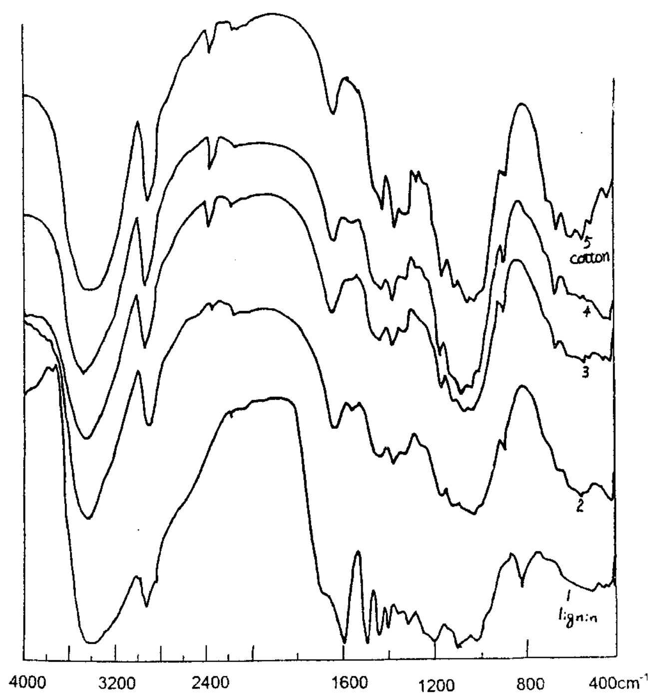


FIG. 1. The infrared spectra of lignin, cotton, and microcrystalline cellulose obtained in different cooking conditions.

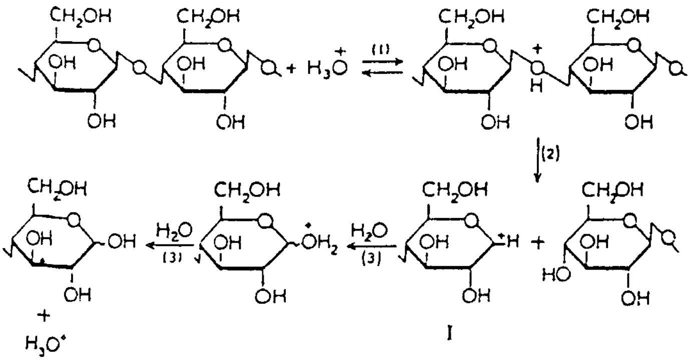


FIG. 2. The mechanism of cellulose hydrolysis.

granule differs at different stages of hydrolysis time from 50 to 20 μm. The fiber form became granular, as mentioned above, and created a suspension when the suspension was passed through a homogenizer for a certain time, a MCC gel formed. Many fine crystals separated from the MCC granules to form a network structure (microreticulation) [6] (see Figs. 6 and 7). The fine particles separated from MCC granules have more surface area and more free hydroxyl groups which link to each other in the manner of a hydroxyl bond, so much more water could be absorbed on the surface of the particles. The system became viscous, and finally the MCC gel formed.

The Rheological Properties of MCC Gel

Some scientists [7–10] investigated the rheological properties of MCC gel. They indicated that MCC gel is a thixotropic colloid. When the shear rate reaches a certain level (for example, 80 s^{-1}), the shear stress no longer increases. In our

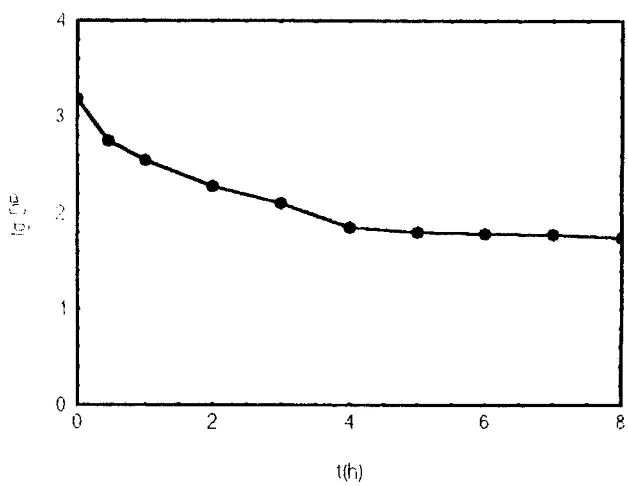


FIG. 3. The relationship between DP and hydrolysis time.

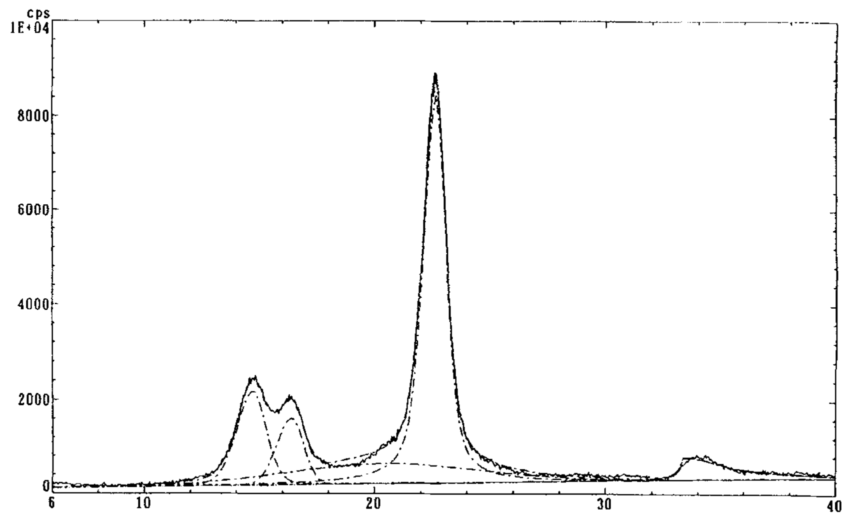


FIG. 4. X-ray diffraction pattern of MCC from rice straw.

experiments we found that the shear stress increased with increasing shear rate, but the viscosity decreased with increasing shear rate (see Figs. 7 and 8), which means that MCC gel is a shear diluted fluid. This property is very useful in food and paint. The MCC gel is very easy to stir or brush. As to the relationship between viscosity and concentration of MCC, it was found that the viscosity vs concentration curve has two slopes, one is in the 1-4% range and the other is above 8% (see Fig. 9). For industrial use as a thickener, the suitable concentration of MCC gel is in the 3-4% range. A heat stability test of MCC gel showed that the viscosity ratio at 90°C to 20°C was 0.30. This means that MCC gel has considerable stability to heat (see Fig. 10). In addition to its heat stability, MCC gel is also very stable during storage; the viscosity was almost unchanged after 1 year of storage (see Fig. 11). The other special properties of MCC gel are the influence of salts and pH on the viscosity. We

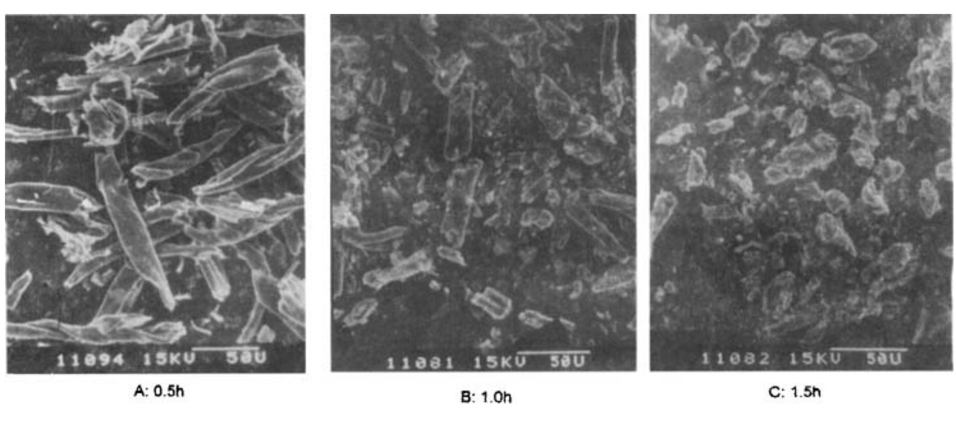


FIG. 5. SEM of MCC granules in different hydrolysis steps (HCl 2.5 mol/L, 30°C).

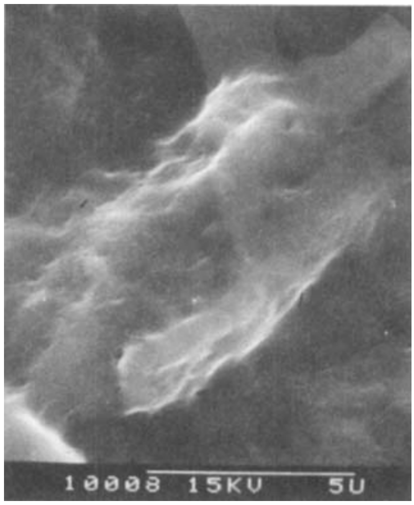


FIG. 6. Microreticulation of MCC.

found that no matter whether one valence salt (NaCl) or two valence salts ($CaCl_2$) were added, the viscosity increased with increasing salts content until the concentration of salts reach 0.10 mol/L. The reason may be that the metal ion hydrated with free water was not absorbed on the surface of MCC. So the smaller the free water in the MCC gel, the higher the viscosity, until saturation is reached (Fig. 12). The pH value considerably influenced the viscosity of MCC gel. Below pH 8, the viscosity increased with increasing pH. However, the viscosity suddenly dropped when pH > 8 (Fig. 13).

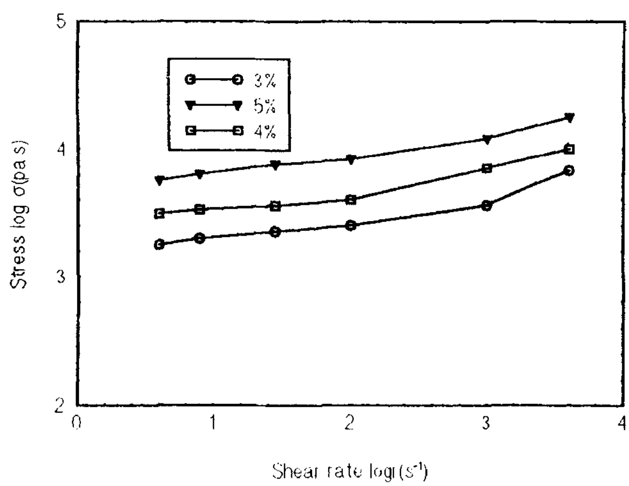


FIG. 7. The relationship between stress and shear rate.

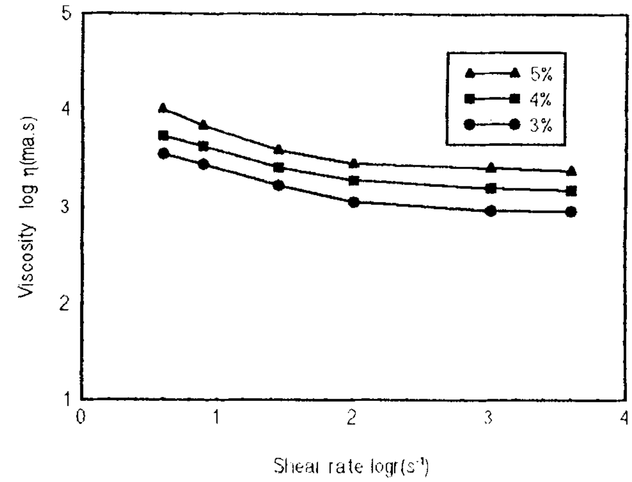


FIG. 8. Viscosity as a function of shear rate.

Emulsifying Function of MCC Gel

MCC gel not only has the effect of thickener, but also that of an emulsion. As an emulsifying agent, it must possess two kinds of functional groups on the molecule: one is hydrophilic and the other is hydrophobic. Cellulose cannot be dissolved in water or in oil, so why can MCC gel emulsify an oil in water system very well? (See Fig. 14.) From our experiments, we found that very fine particles (about 10 μm) separated from the MCC granule formed a network structure (see Fig. 15), water molecules filled in around the network structure. When the oil was separated into many small drops by stirring, these small oil drops would enter the network space. There were certain oilphilic sections on the cellulose molecule because the

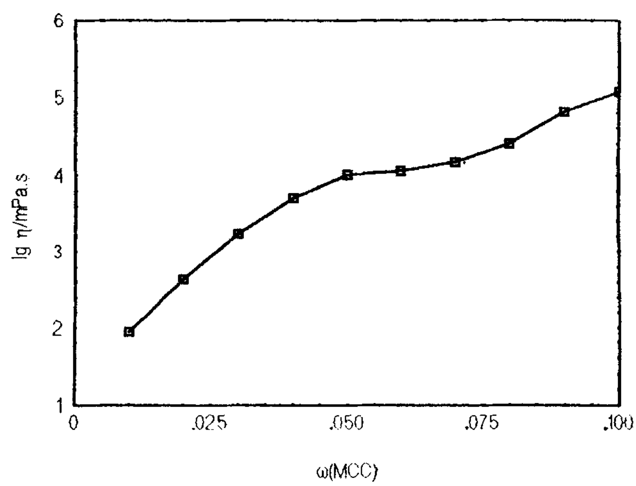


FIG. 9. The concentration of MCC gel effect on viscosity.

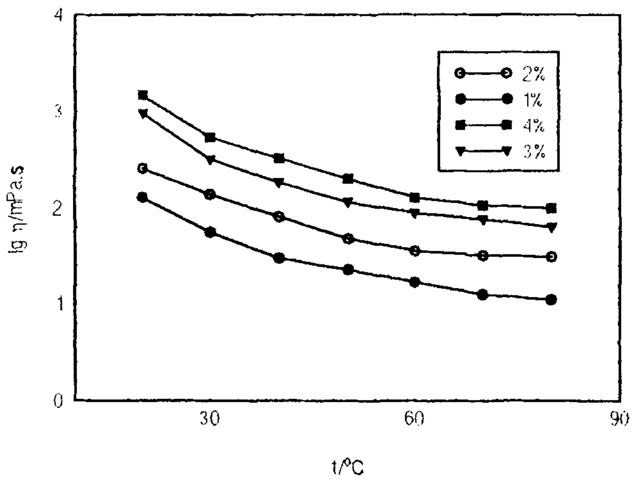


FIG. 10. Heat stability of different concentrations of MCC gel.

C—C, C—O—C, and C—H bonds were hydrophobic, so the fine oil drops could be absorbed on the cellulose chain. Therefore a very fine emulsion formed [see Fig. 16(1)-(4)]. For Figs. 16-(1) to 16-(3), the ratio of oil/water is 3/7, 4/6, and 5/5, respectively, and we can see that the oil drops (bright points) distributed homogeneously. Once the ratio of oil/water was higher than 5/5, the oil drops became bigger and bigger, and two phases appeared [see Fig. 16-(4)].

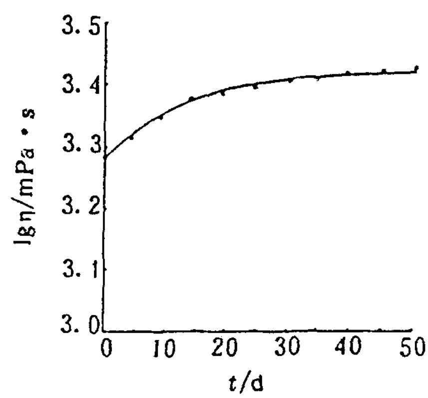


FIG. 11. The storage stability of MCC gel.

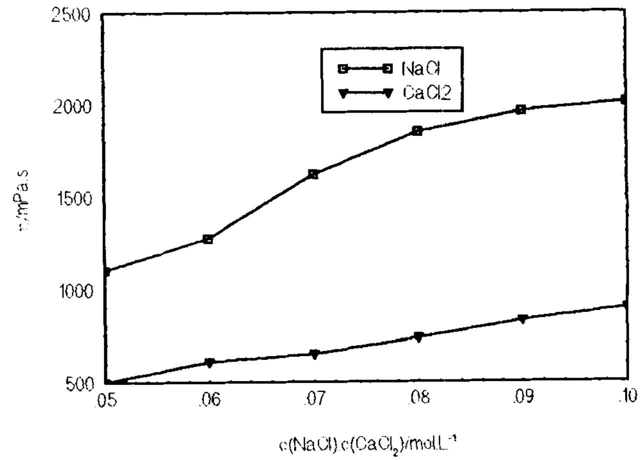


FIG. 12. Influence of the addition of salts on the viscosity of MCC gel.

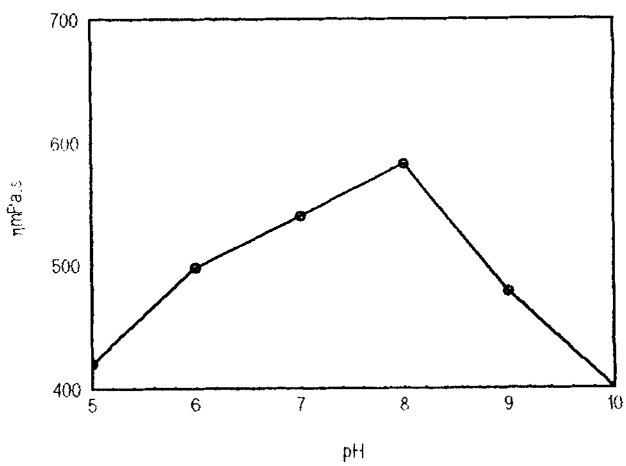


FIG. 13. Influence of pH on the viscosity of MCC gel.

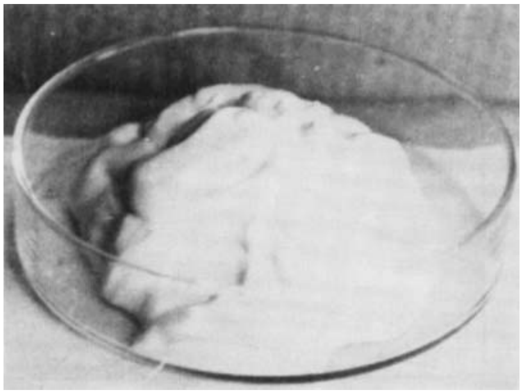


FIG. 14. Emulsion of MCC gel (oil/water = 3/7).

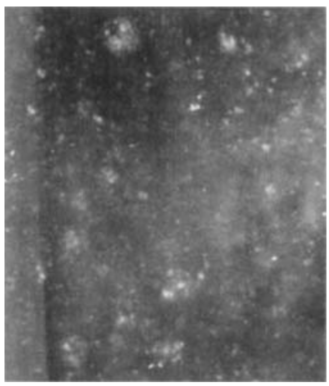
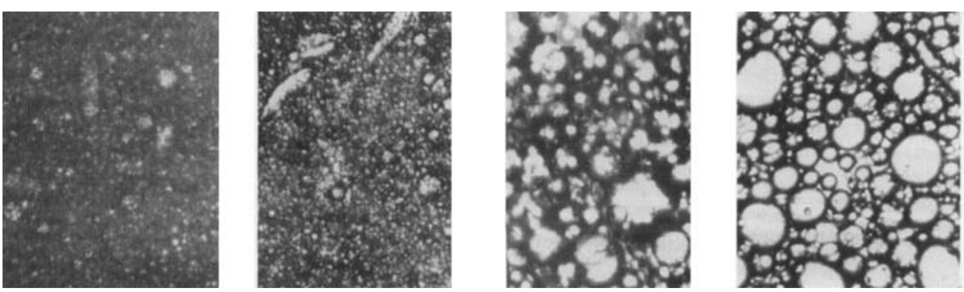


FIG. 15. Microphotograph of MCC gel.



[1] oil/water=3/7 [2] oil/water=4/6 [3] oil/water=5/5 [4] oil/water=6/4

FIG. 16. Micrographs of MCC emulsions.

TABLE 1. Complex Characteristics of MCC Gel Emulsion

	Sample								
Items	A	B	C	D	E	F	G	H	I
MCC content (%)	9	7	5	3	1	5	5	5	5
Oil/water ratio	3/7	3/7	3/7	3/7	3/7	3/7	4/6	5/5	6/4
Standing time until lamination	Over 1 year	Over 1 year	Over 1 year	1 year	8 months	Over 1 year	Over 1 year	6 months	30 minutes
Heat 15 minutes at 100°c, one or two phases	1	1	1	1	1	1	1	1	2
Chill 2 hours at −15°C, one or two phases	1	1	1	Little	2	1	1	1	2
Emulsion viscosity (mPa·s)	16,000	12,500	13,100	3,200	2,200	12,300	13,000	13,800	15,300
Centrifigue 3 minutes at 5000 r/min, one or two phase	2	2	2	2	2	2	2	2	2

Table 1 shows the comprehensive characteristics of a MCC emulsion. A MCC emulsion cannot be centrifuged because the MCC particles are not really soluble in water or oil.

CONCLUSION

1. MCC can be obtained from rice straw by cooking in alkali condition and then hydrolyzing in acid condition.
2. Aqueous MCC can form a gel under the effect of a strong shear force.
3. MCC gel is useful in industry because of its thickness and viscosity stability in heat, storage, and salts.

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