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Synthesis and Characterization of Microcrystalline Cellulose from Cotton Rag

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ABSTRACT

Synthesis of microcrystalline cellulose from cotton rag has been studied and reported in this work. The successful removal of lignin and hemicellulose has been confirmed through Fourier Transform Infra-red spectroscopic technique. X-ray Diffraction (XRD) technique has been used to measure the crystal size and crystallinity index. The FTIR analysis revealed that the acid hydrolysis had an effect on the crystalline of the fibre; however it did not influence the chemical components of the fibres. Scanning electron microscopic images depict the porous structure and agglomerate fibrous shape with hierarchical assembly of the microcrystalline cellulose produced. Pharmaceutical standard tests were done.

Key Words: Cotton rag, fibre, MCC, pharmaceutical, food.

1. Introduction

Microcrystalline cellulose is the crystalline part in the cellulose. It is the orderly oriented part in cellulose and is generally prepared by acid hydrolysis of α-cellulose at elevated temperature. Various fibre properties like absorbility or accessibility, swelling flexibility, fibre extension etc. are more or less dependent of the ratios of crystalline and noncrystalline parts of a fibre. Among these products, microcrystalline cellulose (MCC) has been prepared from different fiber. Rag pulp also constituted with crystalline and noncrystalline part as with other fibres. Crystalline and noncrystalline parts of cellulose have everything similar except in noncrystalline part there is some lignin and other noncarbohydric matter. And in noncrystalline part of fibre there is no periodicity of hydrogen bond as it occurred in crystalline part. Cotton rag is a good source to prepare MCC. Usages of MCC are wide. MCC has recently gained more interest owing to its renewability, non-toxicity, economic value, biodegradability, high mechanical properties, high surface area and biocompatibility. [1] It can be used in pharmaceutical industry, food industry, textile industry etc.

MCC is used as diluents in tablets prepared by wet granulation as well as filler for capsules and spheres [2]. The food industry is the second biggest user of MCC after the pharmaceutical sector. MCC has nutraceutical functions and impact positively on the gastrointestinal physiology as well weight management. MCC is a good candidate for emulsion stabilization and fat replacer in many food systems [3].

Waste management is one of the biggest problems faced by the human beings in industry as well as domestically. Garment and hosiery industries are having the abundant waste of the cotton rags, cuttings etc. during the manufacturing of garments. As cotton is having highest percentages (87 to 96 %) of cellulose, it can be used for manufacturing of value-added products like microcrystalline cellulose (MCC). MCC is obtained on industrial scale from wood and cotton cellulose, but also obtained from materials such as soybean husk [4], water hyacinth [5], coconut shells [6], sugar cane bagasse [6] and jute [7].

In the present work, MCC was prepared from cotton rags. It was characterized through infrared spectroscopy (FTIR), X-ray diffraction (XRD) and thermo gravimetric analysis (TGA). The objective of this article is to evaluate the possibility, scope, advantages and drawback of cotton rag MCC in pharmaceutical industries.

MCC was first commercialized in 1962 under the name Avicel®, which is marketed by FMC Corporation. Since then, an exponential number of researchers have focused their work on such material. Industrial scale MCC is manufactured through hydrolysis of cotton and wood cellulose using dilute mineral acids. MCC is characterized by a high degree of crystallinity, and the values typically range between 55% and 80% [8].

2. MATERIALS AND METHODS

The study was carried out from 1st July 2021 to 30 June 2022 in Applied Chemistry& Chemical Engineering Department of Dhaka University.

Cotton rags were obtained from local market shop of 100 % cotton. Most of the experimental works had been carried out in the Industrial Chemistry Laboratory, Chemistry Division, Bangladesh Jute Research Institute (BJRI), Dhaka and Applied Chemistry& Chemical Engineering Department of Dhaka University. All the chemicals are reagent grade (Merck), such as hydrochloric acid (HCl), and sulfuric acid (H_2SO4). Avicel PH 101 was used as standard. Very limited numbers of chemicals were used for low production cost. This study provides comprehensive scientific examination of the new production method for MCC, including its technological, economic and environmental aspects. The aim was to find a solution for the industrial scale manufacture of MCC while having low production costs that enable significant increase in product capacity and reducing the price of the final product, at the same time discovering new use targets and applications.

MCC preparation

The long cotton rag was cut into small pieces. Then 50 gm rag was treated for MCC preparation. There are two parts of MCC synthesis, isolation of cellulose (alpha cellulose) and micro crystallization of cellulose.

a) Isolation of cellulose

Isolation of cellulose were done by 3% 10.5 M HCl solution where cellulose: solution ratio was kept 1:15 i. e. for one gram of cotton rags and the amount of HCl solution is 15 ml. In this case, 50 g of cotton rags with 750 mL of HCl solution was kept in a closed reactor for 4.5 – 5 hours. The temperature of heating mantle was kept constant at 120ºC. After getting the mixture at room temperature, it was neutralized with water to get the neutral pH of the wash water. In this case, water to cellulose ratio is 10:1. We avoided chemical neutralization. The prepared cellulose was kept for drying at 50 to 60^{0}C. After complete drying, the cellulose was grinded to prepare cellulose powder. To prepare 100g cellulose powder, it takes 5 minutes.

b) Micro crystallization of cellulose

After isolation, cellulose was treated with different percentage of H_2SO_4 (25, 40, 50 and 64) of 18.4 M. It is kept in 50ºC along with stirring for 1hour. After treatment, it was neutralized with water to get the neutral pH of the wash water. Like previous, water to cellulose ratio is 10:1. We avoided chemical neutralization. After that, the product was subjected to mechanical shear with a centrifuge machine (7000 rpm) with 10 times water for 20 minutes. P^H was adjusted to 5.5 -7.0. Sonication was done at 60ºC, 1 hr. Finally freeze drying were performed at -51 ºC for 7hrs.

3. RESULT AND DISCUSSION

We categorized the samples according to hydrolysis with H_2SO_4 in different percentages. Here S1 represents treatment with 25% H_2SO_4. Similarly S2, S3 and S4 represents 40%, 50% and 64% H_2SO_4.

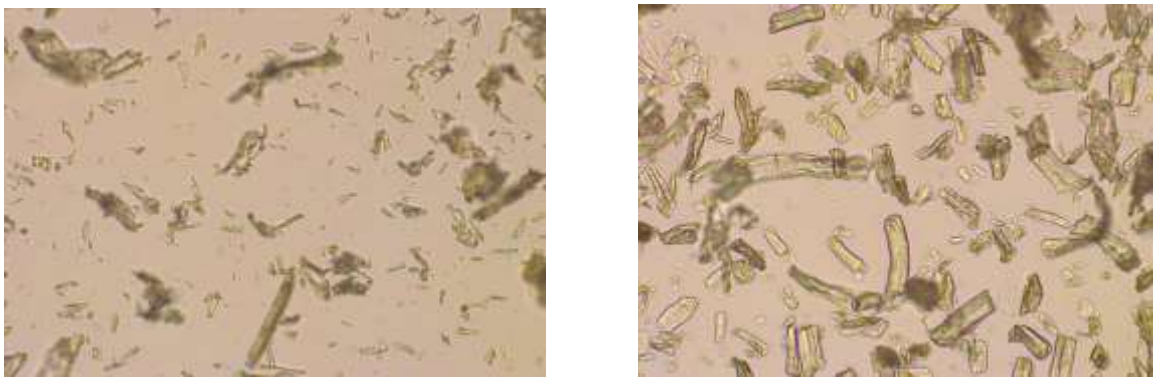
Scanning Electron Microscope (SEM)

The MCC obtained was prepared in the form of dried powder and sprinkled as thinly as possible on the Carbon Tabs. Then, the sample was coated with the Quorum Q150R ES Sputter Coater tool. Coating was carried out using gold material with 20 mA current sputter and sputter time 60 sec. The coated sample was then mounted in the stage for analysis. Picture was taken with SEM (JEOL JSM-6510 series). The detector used was secondary electron with a working distance of 9.0 mm and an EHT of 16 kV. The test was repeated using Avicel PH 101 as a standard. The produced MCC were analyzed for specific micrometer-level appearance (using SEM). The result of SEM analysis showed that microcrystals had been formed in MCC obtained. Based on SEM analysis results in Figure 1, the hydrolysis MCC particles were rods with cylindrical shapes with rough surfaces. Standard was found to exhibit uniform and more spheric particle size than the hydrolyzed sample [9]. Differences in MCC obtained and standard morphology may due to difference in raw material source and difference in MCC preparation methods.

Analysis of particle size

Particle size of MCC obtained is compared to particle size of Avicel PH 101 using Malvern Zetasizer ZS200. Preparation of the powder was performed by dispersing the crystal powder in an appropriate medium which can disperse sample powders and, in this study, distilled water was used.

Figure 1 shows the morphology of the samples. In the sample 1, there is no evidence of pore formation in the cotton rag where only carbonization of the raw material takes place without creating pores. In contrast, sample 4 indicates the formation of pores due to chemical activation. It is made very clear that the opening of the pores in the surface of the cotton rag should be due to the extraction of some materials, e.g., dissolution of lignin's and other mineral components during the impregnation process. As a result of the creation of pores, there is an increase in both the surface area and the pore volume, which are stably created in the carbon composite. The produced MCC were analyzed for specific micrometer-level appearance (using SEM),



a) S1 b) S4

Fig1: Microscopic view of MCC a) S1 and b) S4

Pharmaceutical Standard Tests

The MCC obtained was placed on a white base, and then the shape or appearance, color, taste, smell was observed.

Pharmaceutical standard test was done for purity and identification of MCC.

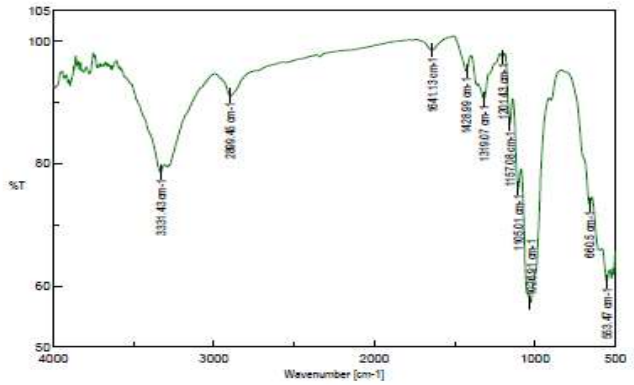
Parameters	**Acceptance Limit**	**Result**	
		Avicel pH-101	**MCC from rag**
Characters	A white or almost white, fine or granular powder	white and fine or granular powder	off white to white and granular powder
Solubility	Practically insoluble in water, acetone, ethanol, toluene and dilute acids and in a 50 g/l solution of sodium hydroxide. It completely dissolves in ammoniacal solution of copper tetrammine R	Compatible	Compatible
Color Reaction			
1.	Violet-blue color develops when addition of iodinated zinc chloride solution	Compatible	Compatible
2.	Red color is produced when addition of catechol in phosphoric acid	Compatible	Compatible
3.	A blue- purple color is produced when addition of sulphuric acid in iodine solution	Compatible	Compatible
pH	5-7.5	6.6	6.0
Starch and dextrin	No blue or brownish color is produced when addition of iodine	Compatible	Compatible
Loss on drying	Maximum 7.0 percent	5.50	8.42
Conductivity	Does not exceed the conductivity of the water by more than 75uScm^{-1}	21.7	51.7

Fourier Transform Infrared (FTIR)

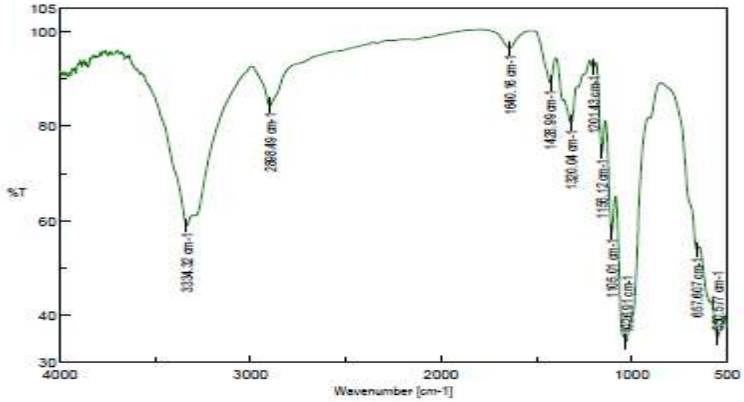
Infrared spectroscopy is a particularly powerful and reliable technique which is sensitive and rapid as well as inexpensive that is used to study polymers [8]. Fourier transform infrared spectroscopy is a measurement of the intensity and wavelength of the absorption of IR radiation by a sample. In this modern era, Fourier transform infrared spectroscopy has been used more in depth by monitoring the chemical structure and functional groups of lignocellulosic compounds [9,10,11]. For instance, various applications for biological, biochemical, and food industries are widely used in the mid-region at 4000–500 cm−1 where the band absorption involves transitions between vibrational energy states and rotational substrates of the molecule [12]. Figure 2 shows the FTIR spectra of MCC of the samples. Some peaks of S1 and S4 have similarities with the standard sample of Avicel pH 101. The C-H stretching vibration absorbance intensity in MCC (2893.66 cm^{-1}) upon acid hydrolysis of alpha- cellulose; this is due to the presence of –CH_2 moieties in

the samples. The peaks related to C-H or C-O bending vibrations for alpha cellulose (1317.14 cm^{-1}) in the polysaccharide aromatic rings is same in the spectrum of MCC. The band at 1024.98 cm^{-1} in cotton rag MCC corresponds with 1024.02 cm^{-1} in Avicel MCC are due to $–CH_2-O-CH_2-$ pyrans ring stretching vibration.

a)



b)



C)

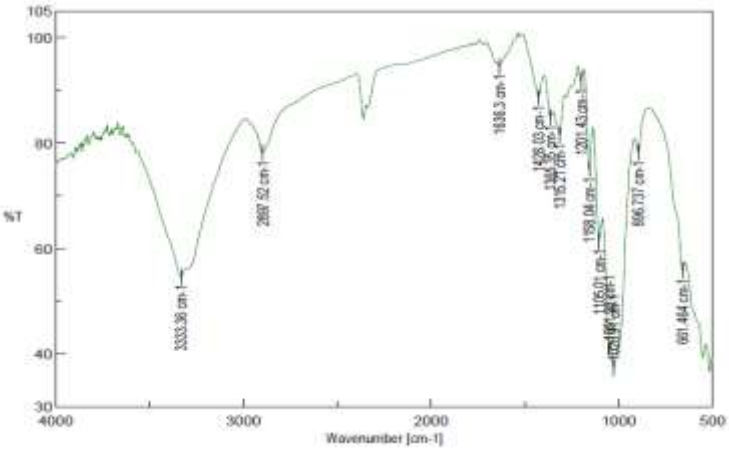


Fig2: FTIR spectra of MCC a) S1, b) S4 and c) Avicel pH 101

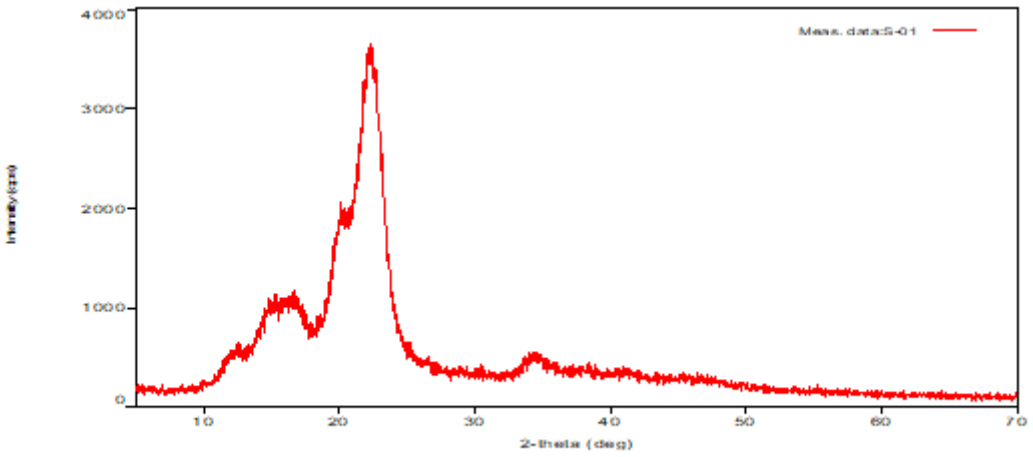
X-ray Diffraction

X-ray diffraction (XRD) is commonly used to analyze the crystalline solids based on their atomic- scale structure of materials [13-16]. About 2g of the pounded MCC obtained was placed and measured using XRD Bruker D8 Advance Eco Diffractometer. It was operated in reflection mode (40 kV, 35 mA) and used Cu-Kα radiation lamp (l1=1.54060 Å and l2=1.54439 Å). Figure 3 shows the XRD analysis of MCC samples.

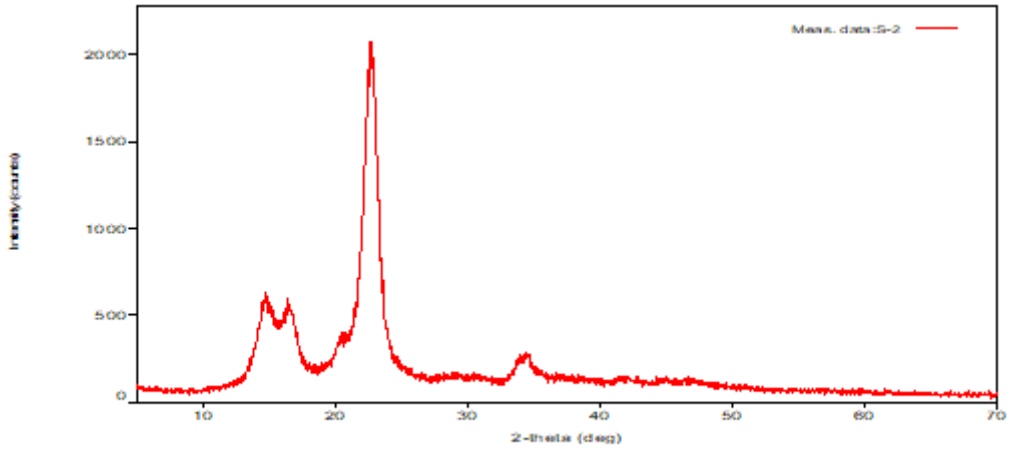
This higher crystallinity in MCC used to get by removal of amorphous regions of cellulose by hydrolysis process which instigates hydrolytic cleavage of glycosidic bonds and helps to re-arrangement of cellulose molecules [17- 18]. When the crystallinity size and index increase, Strength of cellulose structure exhibits good tensile strength towards fiber [19]. This higher tensile strength is hoping to higher the mechanical properties of composite materials

[20]. On the contrary, maximum percentage of lignin was removed during alkaline reaction which was then used for cellulose preparation while the exhausted amount of amorphous lignin was eliminated during acid hydrolysis of MCC [21].

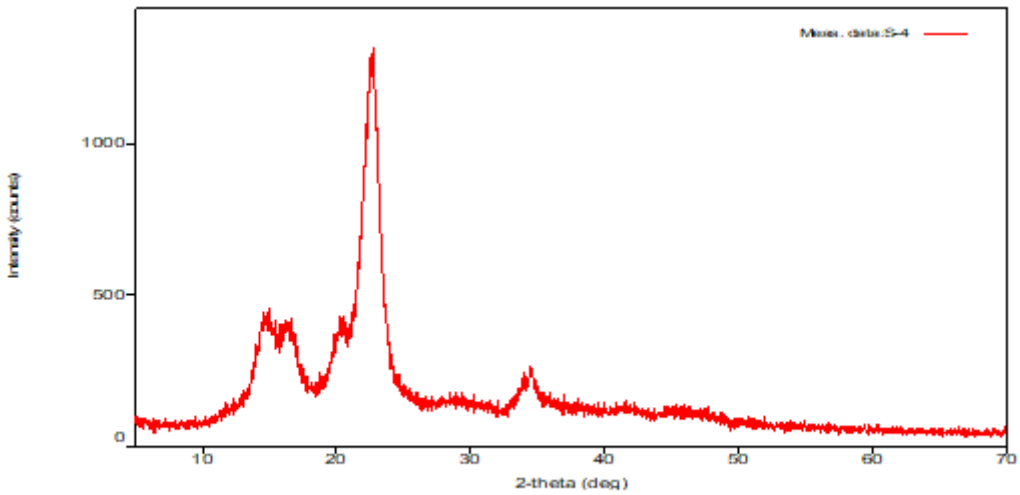
a) S1



b) S2



c) S3



d) S4

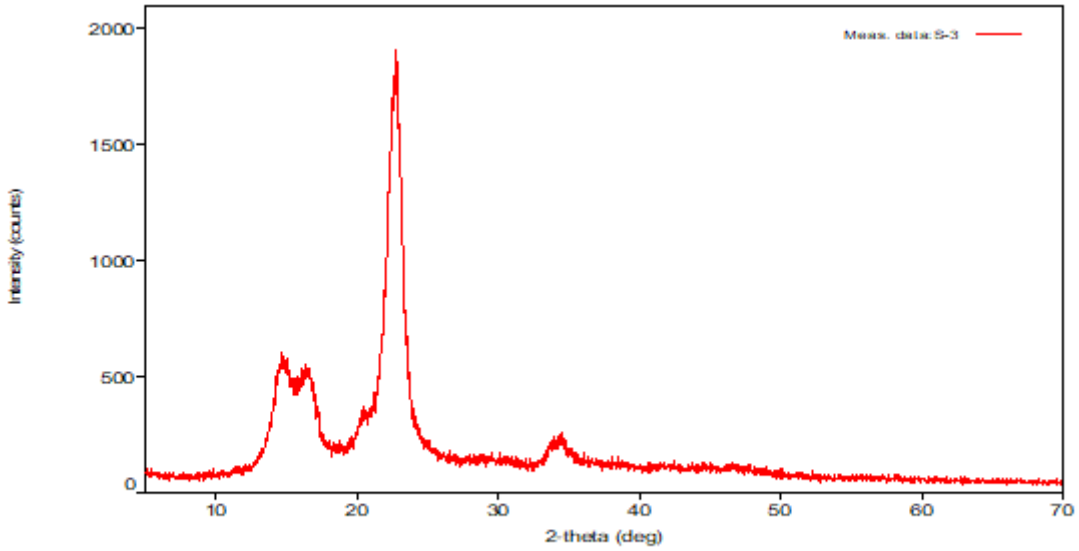
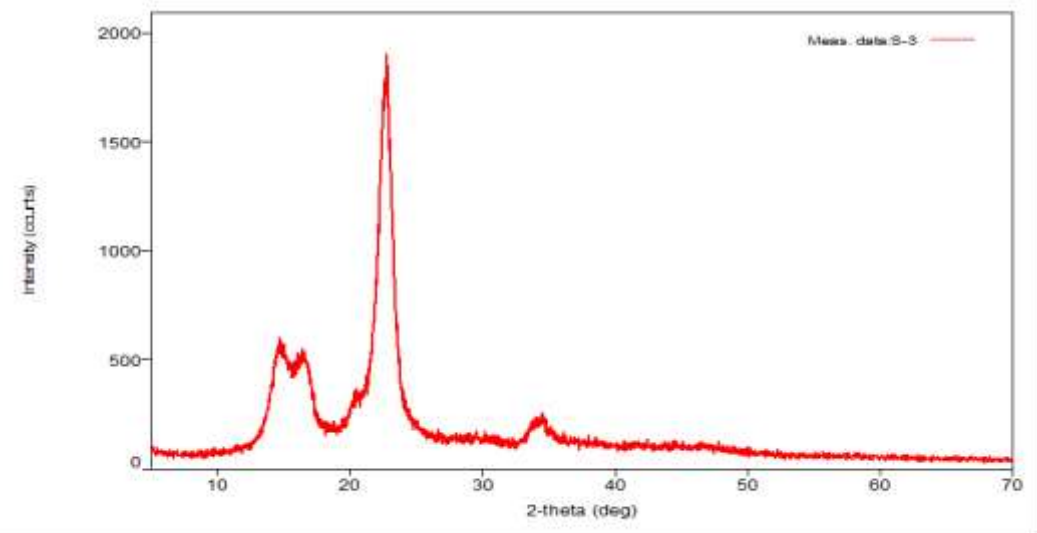


Fig3: XRD analysis of MCC a) S1, b) S2 c) S3 and d) S4



Thermo Gravimetric Analysis (TGA)

Figure 4 shows the thermal degradation pattern of microcrystalline cellulose produced from cotton rags at different percentage concentrations (40, 50 and 64) of H_2SO4. S1 and S2 have some similarities but S3 and S4 show some different characteristics than S1 and S2.

The TGA curves of S3 and S4 show lower thermal resistance properties for this product.

S3 and S4 started to decompose at around 110℃, sample S4 continued until reaching 200℃.

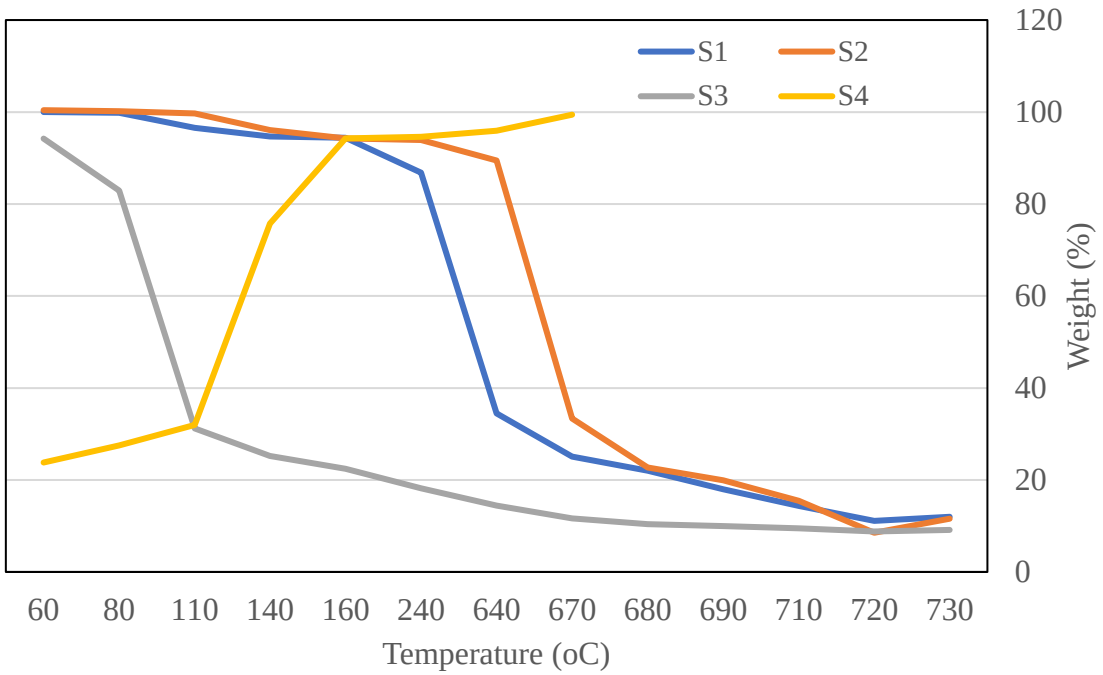


Fig.4 TGA curve of microcrystalline cellulose from cotton rags with S1 (blue), S2 (orange), S3 (ash) and S4 (yellow color).b when degradation increased again and leveled out at approximately 400°C. The lower decomposition point of S4, when compared to other samples (**Fig. 4**), probably originated from lignin. This was supported by the finding of Bartkowiak and Zakrzewski (2004) and Tejado et al. (2007) who studied kraft lignin originating from pine, and noted degradation starting at around 200°C. The thermal degradation of S1 (treated with 25% H_2SO_4) started at around 150°C, quickly increased to 250°C after leveling out. The TGA curve's form was sharp without gradual degradation phases. Werner et al. (2014) and Yang et al. (2007) measured the TGAs of different hemicellulose fractions finding degradation temperatures of 200 °C to 250°C. This fact matches well with the curve forms of **Fig.**4

Conclusion

The physicochemical properties and functions of MCC are influenced by its source and preparation methods. As source is very important factor, cotton rag here as taken source of preparation MCC. The aim was to find a solution for the industrial scale manufacture of MCC while having low production costs that enable significant increase in product capacity and reducing the price of the final product, at the same time discovering new use targets and applications. The implementation of a stand-alone type plant unit and a MCC plant integrated in a pulp mill is technically possible and also profitable.

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