



بسم الله الرحمن الرحيم

**Sudan University of Science and Technology**



**College of Graduate Studies**

**Synthesis and Characterization of Carboxymethylcellulose  
(CMC) from Rice husk**

**تخليق وتشخيص كاربوكسي ميثيل السليلوز من قشره الأرز**

Dissertation Submitted in Partial Fulfillment for the Requirements of Master Degree  
in Chemistry

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**June-2016**

# الآية

بسم الله الرحمن الرحيم

قال تعالى:

(إِنَّمَا أَمْرُهُ إِذَا أَرَادَ شَيْئًا أَنْ يَقُولَ لَهُ كُنْ فَيَكُونُ ﴿٨٢﴾ فَسُبْحَانَ الَّذِي بِيَدِهِ مَلَكُوتُ كُلِّ شَيْءٍ وَإِلَيْهِ تُرْجَعُونَ)

صدق الله العظيم

سورة يس الآية (82-83)

## **Dedication**

*To my beloved mother and father*

*To my sisters*

*To my best friend Najwa Fath Alrahman Alamin*

*I dedicate this research*

## **Acknowledgment**

Praise is to Allah, the Almighty who supported me and gave me strength to complete this work.

I would like to express my deep thanks and gratitude to my supervisor: **Dr. Adil Elhag Ahmed** for his precious guidance and advices in this project. My deepest thanks are extended to **Dr. Essa Esmail Mohammad Ahmed** for his unlimited helps.

Special thanks should be awarded for my respected family members for their kind assistance during my study.

Special thank for my uncle (Dr. Adil Suliman Madani) for his great efforts and help during this study.

## Abstract

This study focuses on the conversion of cellulose isolated from rice husk to CMC material which has wide industrial applications especially in the drilling fluids of petroleum wells. Alkaline extraction method was used for isolating the cellulose from rice husk then isolated cellulose was etherified onto sodium CMC (Na-CMC) by monochloroacetic acid (MCAA) in the presence of NaOH. Some reaction conditions were optimized, such as concentration of NaOH, solvent type, amount of MCAA and reaction time, for the production of CMC material of higher degree of substitution (DS). At optimum conditions, the as-synthesized CMC material was found to have a DS of 0.42.

The isolated cellulose and the as-synthesized CMC were characterized by FT-IR spectrometer and XRD powder diffractometer and the results indicated successful introduction of carboxymethyl species to the isolated cellulose occurred. Further proof was obtained by comparison with the FT-IR spectra of pure commercial CMC material. Rheological studies were conducted for the as-synthesized CMC and some commercially available carboxy methylated cellulosic materials such as PAC-LV and PAC-RV. The results showed that, the viscosity of as-synthesized CMC material is higher than that of PAC-LV but lower than that of PAC-RV. The variation could be attributed to the lower value of DS (0.42) associated with the synthesized material. However, the results of apparent viscosity, plastic viscosity, yield points and filter loss together, demonstrated that the synthesized CMC material could be classified as viscosifier rather than fluid loss controller.

## المستخلص

هذه الدراسة تركز على إمكانية تحويل السليلوز المستخلص من قشور الأرز الى كاربوكسي ميثيل السليلوز ذي التطبيق الواسع في الصناعة ومحاليل الحفر.

تم إستخدام طريقه الإستخلاص بالقلويات لإستخلاص السليلوز من قشور الأرز. ومن ثم تمت أثيرته بإستخدام حمض الخليك أحادي الكلور في وجود هيدروكسيد الصوديوم. تمت دراسة بعض الظروف المثلى للتفاعل وشملت تركيز هيدروكسيد الصوديوم ونوع المذيب وكمية حمض الخليك أحادي الكلور وزمن التفاعل , لإنتاج ماده كاربوكسي ميثيل السليلوز بأعلى درجه استبدال. في الظروف المثلى للتفاعل, وجد ان ماده كاربوكسي ميثيل السليلوز المخلوق له درجه استبدال تساوي 0.42 .

شخص السليلوز المستخلص وماده كاربوكسي ميثيل السليلوز المخلوق بمطيفيه الأشعه تحت الحمراء وتقنية حيود الأشعه السينيه وأشارت النتائج الى أن عمليه إدخال مجموعات الكاربوكسي ميثيل للسليلوز المستخلص قد تمت بنجاح. كما تم الحصول على إثبات إضافي من خلال المقارنه بأطياف الأشعه تحت الحمراء لماده كاربوكسي ميثيل السليلوز المخلوق مع اطياف الأشعة تحت الحمراء لماده كاربوكسي ميثيل السليلوز المخلوق مع اطياف الأشعة تحت الحمراء لماده كاربوكسي ميثيل السليلوز المتوفر تجاريا. أجريت دراسات ريولوجية (الإنسيابية) لماده كاربوكسي ميثيل السليلوز المخلوق وبعض مشتقات كاربوكسي ميثيل السليلوز المتاحة تجاريا (PAC-RV and PAC-LV) وأظهرت النتائج ان لزوجته ماده كاربوكسي ميثيل السليلوز المخلوق اعلى من مادة PAC-LV واقل من مادة PAC-RV. وهذا الإختلاف قد يعود الى القيمه المنخفضة لدرجه الإستبدال (0.42) للمادة التي تم تخليقها. من خلال نتائج اللزوجه الظاهرية ونقاط الناتج وكمية المرشح المفقودة صنفت ماده كاربوكسي ميثيل السليلوز المخلوقة على انه عامل لزوجه وليس عامل تحكم في فقدان السائل (المائع).

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## List of Abbreviations

<b>Term</b>	<b>Abbreviation</b>
RH	Rice husk
RHA	Rice husk ash
AGU	Anhydro glucose units
DP	Degree of polymerization
PG	Propyl gallate
IL	Ionic liquid
RTIL	Room-temperature ionic liquid
DS	Degree of substitution
BC	Bacterial cellulose
CMC	Carboxy methyl cellulose
MCA	Mono chloro acetate
MCAA	Mono chloro acetic acid
PAC- LV	Poly anionic cellulose - low viscosity
PAC-RV	Poly anionic cellulose - high viscosity
PPb	Pound per barrel
RPM	Revolution per minute

# **Chapter One**

**Introduction & literature review**



# Chapter One

## Introduction and literature review

### 1. Rice Husk

Rice husk is one of the most widely available agricultural wastes in many rice producing countries around the world. Globally, approximately 600 million tons of rice paddy is produced each year. On average 20% of the rice paddy is husk, giving an annual total production of 120 million tones (Giddel and Jivan, 2007) .In majority of rice producing countries much of the husk produced from processing of rice is either burnt or dumped as waste (Khatai *et al.*, 2015). Burning of RH in an ambient atmosphere leaves a residue, called rice husk ash. For every 1000 kg of paddy milled, about 220 kg (22 %) of husk is produced, and when this husk is burnt in the boilers, about 55 kg (25 %) of RHA is generated (Rao *et al.*, 2011).

Rice husk removal during rice refining, creates disposal problem due to less commercial interest. Also, handling and transportation of RH is problematic due to its low density. RHA is a great environment threat causing damage to land and surrounding area where it is dumped. Therefore, commercial use of rice husk and its ash is the alternative solution to disposal problem. Rice husk contains 75-90 % organic matter such as cellulose, lignin etc. and the rest are mineral components such as silica, alkalis and trace elements (Sarangi *et al.*, 2009).

Rice husk is unusually high in ash compared to other biomass fuels in the range of 10-20%. The ash is 87-97% silica (Rozainee *et al.*, 2008). Presence of high amount of silica makes it a valuable material for use in industrial application. Other constituents of RHA, such as  $K_2O$ ,  $Al_2O_3$ ,  $CaO$ ,  $MgO$ ,  $Na_2O$  and  $Fe_2O_3$ , are available in less than 1%. Various factors which influence ash properties are incinerating

conditions (temperature and duration), rate of heating, burning technique, crop variety and fertilizer use (Rozainee *et al.*, 2008). The silica in the ash undergoes structural transformations depending on the conditions of combustion such as time and temperature.

## **1.1 Application of Rice Husk**

Suitability of RH to be used for different applications depends upon the physical and chemical properties of the husk such as ash content, silica content etc. Direct use of rice husk as fuel has been seen in power plants. A detailed description related to application of rice husk in industrial sectors as well as other fields has been investigated and given in literature.

### **1.1.1 Fuel in Power Plant**

Rice husk is mostly used as fuel in boilers for processing paddy and generation of process steam. Heat energy is produced through direct combustion and/or by gasification. Small sector process industries use fixed low capacity boilers, which are manually fired using rice husk as a fuel. Partial and uneven fuel combustion lead to smoke emission and decrease the fuel efficiency. As husks are available virtually for free, the boiler efficiency and the degree of combustion were the issues receiving the latest attention. Plants with capacity 2-10 MW range can become commercially viable and this biomass resource can be utilized to a much greater extent than at present. It has been seen that to produce 1MWh, approximately 1 ton of rice husk is required. So, the technical and economic factors decide the effective use of rice husk as fuel for power generation. Also, rice husk has been used as useful and alternative fuel for household energy (Chandrasekhar *et al.*, 2003). RH is also used as fuel in brick kilns, in furnaces etc. (Chungsangunsit *et al.*, 2009).

### **1.1.2 Formation of Activated Carbon**

Due to presence of large amount of hydrocarbon such as cellulose and lignin content, rice husk can be used as a raw material to prepare activated carbons which are complex porous structures. They are obtained by two different processes: the physical or thermal activation and the chemical activation. In the former carbonization is followed by char activation; in the second one, carbonization and activation are performed in a single step, using a chemical agent. Physical activation of rice husk produces activated carbon that exhibits very low specific area. Activated carbons are effective adsorbents due to their microporous structure (Deiana *et al.*, 2008).

### **1.1.3 Source of Silica and Silicon Compounds**

Apart from organic component, presence of up to 20% silica makes rice husk a promising raw material source for a number of silicon compounds such as silicon carbide, silicon nitride, silicon tetrachloride, zeolite, silica, and pure silicon (Matori *et al.*, 2009).

The applications of such materials derived from rice husks are very comprehensive. The above compounds prepared in powder form are characterized by high purity and fine dispersity (Nayak and Bera, 2010).

### **1.1.4 Porous SiO<sub>2</sub>/C composite from RH**

During heat treatment of RH in inert atmosphere, organic compounds decompose and partly change to H<sub>2</sub>O, CO, CO<sub>2</sub>, and volatile compounds, remaining carbon and SiO<sub>2</sub> (Kumagai and Sasaki, 2009). The porous SiO<sub>2</sub>/C composites with a high surface area have been fabricated by heating the pellets in inert atmosphere. Porous SiO<sub>2</sub>/C composite was able to be fabricated through a simple one-step firing process. The pore characteristics of the products could be controlled by changing the

molding pressure, raw RH particle size, and heat treatment temperature. Heating at 1000° C displayed the optimal properties such as 87% porosity and 450 m<sup>2</sup>/ g specific surface area. Larger RH particles resulted in products with higher strength (Watari *et al.*, 2006).

### **1.1.5 Insulating fire brick using RH**

Bricks made using rice husk develop plenty of pores during heat treatment due to burning out of organic material. The more the percentage of rice husk in a brick, the more porous would be the brick and better thermal insulation. Presences of entrapped air in pores have thermal insulating characteristics and thus make the porous fire brick structure suitable for back up insulation (Ugheoke *et al.*, 2006).

## **1.2 Cellulose and Its Sources**

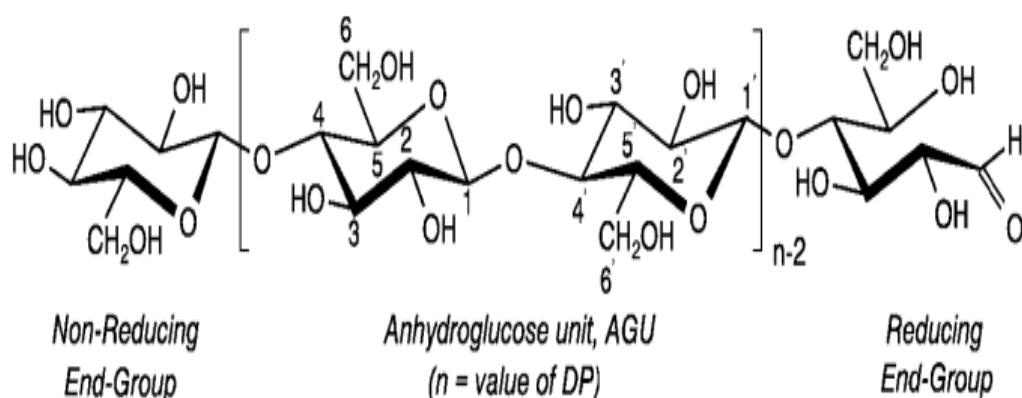
Cellulose, the most abundant renewable and biodegradable polymer, is the promising feedstock for the production of chemicals for their applications in various industries. Annual production of cellulose in nature is estimated to be 10<sup>11</sup>–10<sup>12</sup> t in two forms, partially in a pure form, for example seed hairs of the cotton plant, but mostly as hemicelluloses in cell wall of woody plants. The versatility of cellulose has been reevaluated as a useful structural and functional material. The environmental benefits of cellulosic have become even more apparent (Tang *et al.*, 1996). Cellulose is revered as a construction material, mainly in the form of intact wood but also in the form of natural textile fibers like cotton or flax, or in the form of paper and board. The value of cellulose is also recognized as a versatile starting material for subsequent chemical transformation in production of artificial cellulose based threads and films as well as of a variety of cellulose derivatives for their utilization in several industries such as food, printing, cosmetic, oil well drilling, textile, pharmaceutical, etc. and domestic life.

Cellulose can be derived from a variety of sources such as woods, annual plants, microbes, and animals. These include seed fiber (cotton), wood fibers (hardwoods and softwoods), bast fibers (flax, hemp, jute, ramie), grasses (bagasse, bamboo), algae (*Valonica ventricosa*), and bacteria (*Acetobacter xylinum*) (Nevell and Zeronian, 1985). A xylinum can synthesize extracellular pellicles of cellulose from glucose. Some simple marine animals such as tunicates deposit cellulose in their cell walls. Besides cellulose, these materials also contain hemicelluloses, lignin, and a comparable small amount of lignin. Wood and cotton are the raw materials for commercial production of cellulose. Cellulose serves as a structural material within the complex architecture of the plant cell walls with variation in its content. In wood, it constitutes about 40–50%; in leaf fibers: sisal fibers (55–73%), in bast fibers: flax 70–75%, hemp 75–80%, jute 60–65%, ramie 70–75%, kenaf 47–57%, in canes: bamboo 40–55%, bagasse 33–45%, and in cereal straw: barley 48%, oat 44–53%, rice 43–49%, rye 50–54%, wheat 49–54%. Cotton seed hairs, the purest source, contain 90–99% of cellulose (Hon, 1996, Han and Rowell, 1997).

### **1.2.1 Structure of cellulose**

Cellulose is a polydispersity linear homo polymer, consisting of regio- and enantioselectively  $\beta$ -1, 4- glycosidic linked D-glucofuranose units (so-called Anhydro glucose units [AGU]) (Figure 1-1), it has been shown by  $^1\text{H}$ NMR spectroscopy that the  $\beta$ -D-glucofuranose adopts the  $^4\text{C}_1$  chair conformation, the lowest free energy conformation of the molecule (Kester and Fennema, 1986). As a consequence, the hydroxyl groups are positioned in the ring plane (equatorial), while the hydrogen atoms are in the vertical position (axial). The polymer contains free hydroxyl groups at the  $\text{C}_2$ ,  $\text{C}_3$ , and  $\text{C}_6$  atoms. Based on the OH groups and the oxygen atoms of both

the pyranose ring and the glycosidic bond, ordered hydrogen bond systems form various types of supramolecular semi-crystalline structures.



**Figure 1.1:** Molecular structure of cellulose (Michell and Higgins, 1965).

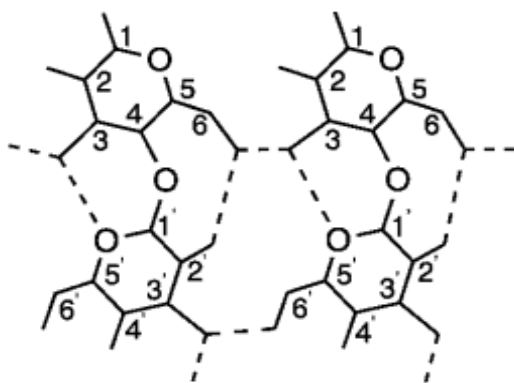
### 1.2.1.1 Hydrogen Bonding

Three hydroxyl groups are available for reaction in each repeating unit of cellulose, the structure of cellulose being largely affected by hydrogen bonds and van der Waals forces. Hydrogen bonding within neighboring cellulose chains may act to determine the straightness of the chain (O'SULLIVAN, 1997), and impart improved mechanical properties and thermal stability to the cellulose fibers. Inter-chain hydrogen bonds might introduce order or disorder into the system depending on their regularity (O'SULLIVAN, 1997). So, understanding hydrogen bonding within the I $\alpha$  and I $\beta$  structures is important as it governs the stability and properties of these polymorphs (Moon *et al.*, 2011) and of cellulose itself. With the hydroxyl groups being equatorial to the cellulose ring plane, intra- and inter chain hydrogen bonding is most prevalent within the (110) plane in the triclinic structure and within the (200) plane in the monoclinic structure, hence the name “hydrogen-bonded” plane (Moon *et al.*, 2011). On the other hand, intra-chain hydrogen bonding is dominated by strong

O<sub>3</sub>-H···O<sub>5</sub> bonds (O'SULLIVAN, 1997, Moon *et al.*, 2011), As shown in (Figure 1.1).

Inter-chain hydrogen bonding within the other planes (010), (100) in the triclinic structure and the planes (110) and (110) in the monoclinic structure is substantially lower and attractive van der Waals forces are believed to dominate the cohesion forces between cellulose chains (Moon *et al.*, 2011). Within these planes, the number of weak inter-chain hydrogen bonds in the I $\beta$  structure is believed to be larger than in the I $\alpha$  polymorph and it has been suggested that it would contribute to the higher stability of the I $\beta$  form, as compared to the I $\alpha$  form (Moon *et al.*, 2011, Hult *et al.*, 2003). The I $\alpha$  hydrogen bonds thermally degrade at lower temperatures, contributing to the lower I $\alpha$  thermal stability (Moon *et al.*, 2011).

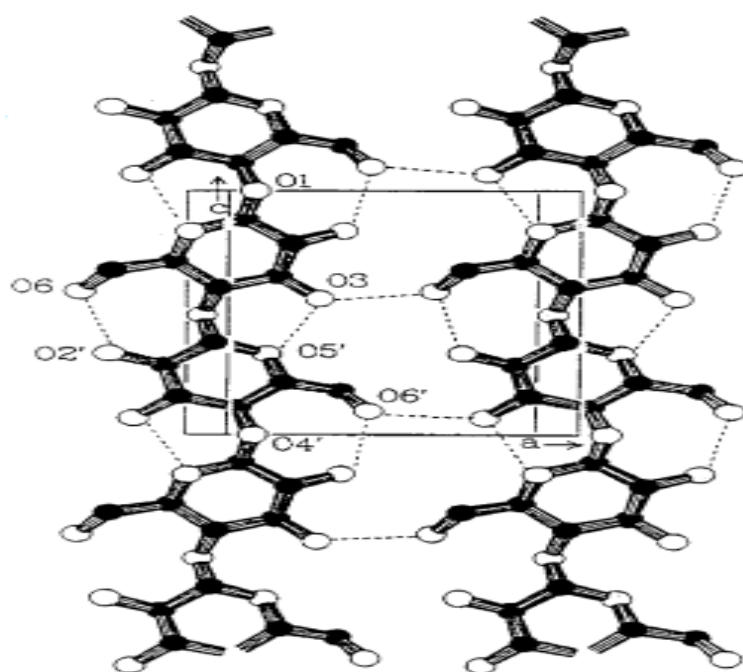
In this way, this study focuses on the characterization of structure and thermal properties of cellulose I, sometimes referred to as native cellulose. This work investigates the relationship between chemical structure, hydrogen bond interactions, crystallite size and crystallinity and the influence of these parameters on the thermal stability and decomposition kinetics of cellulose fibers obtained by two different pulping processes.



**Figure 1.2:** Hydrogen bond system of cellulose I (Fink *et al.*, 1995 b).

### 1.2.1.2 Crystal Structure

The order of the macromolecules in a cellulose fiber is not uniform throughout the whole structure. There exist regions of low order (so-called amorphous regions) as well as of very high crystalline order. The experimental evidence available today is adequately interpreted by a two-phase model, the fringed fibril model, assuming low-order (amorphous) and high-order (crystalline) regions and neglecting the rather small amount of matter with an intermediate state of order. The relative amount of polymer within the highly ordered regions is usually assessed from wide-angle X-ray scattering (WAXS) patterns or from the evaluation of a  $^{13}\text{C}$  CP-MAS NMR spectrum. The degree of crystallinity of cellulose (usually in the range of 40% to 60%) covers a wide range and depends on the origin and pretreatment of the sample (Klemm *et al.*, 2005 b).



**Figure 1.3:** Most probable bond pattern of cellulose I (Fink *et al.*, 1995 b).



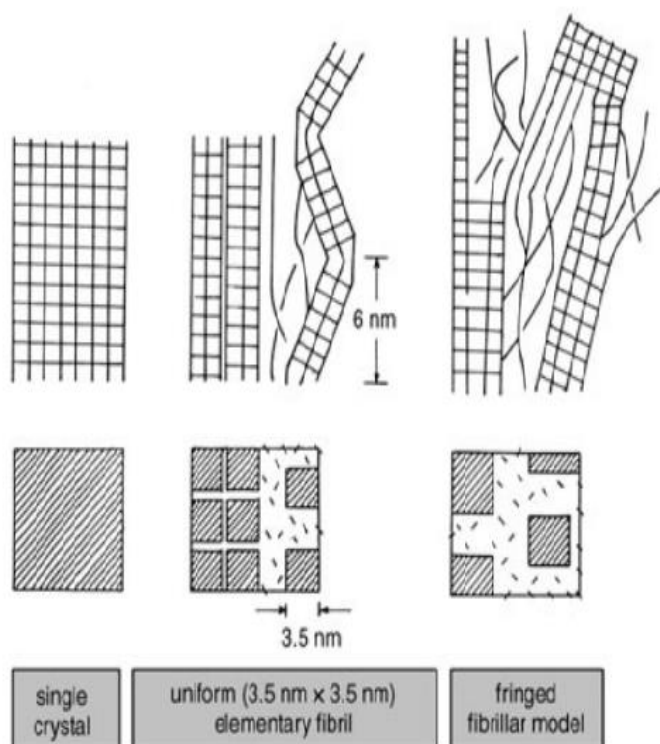
### 1.2.1.3 Morphology

The biological function and numerous applications of cellulose are based on its distinct fiber morphology. The morphological hierarchy is defined by elementary fibrils, micro fibrils, and micro fibrillary bands (Cheng *et al.*, 2011). The lateral dimensions of these structural units are between 1.5 and 3.5 nm (elementary fibrils), between 10 and 30 nm (micro fibrils), and on the order of 100 nm (micro fibrillary bands). The length of the micro fibrils is on the order of several hundred nm.

The fringed fibrillary model with crystalline regions of varying dimensions (crystallites) and monocrystalline regions have been proven successful for the description of the structure of micro fibrils and the partial crystalline structure of cellulose in connection with the reactivity of this polymer (Figure1-4) (Fink *et al.*, 1995 a). The degree of crystallinity of cellulose and the dimensions of the crystallites have been the subject of extensive investigations for many years (Ganster and Fink, 1999). Some results of X-ray diffraction measurements of native celluloses have been compiled in notably, the lateral crystallite dimensions of regenerated cellulose (cellulose II) are in the range of 4–5 nm regardless of the production process where as in native celluloses, values of up to 20 nm have been observed. The reasons for the formation of nearly uniform cross-sectional dimensions of these cellulose II crystallites from different structure-forming processes still have to be clarified.

The pore structure can be considered the counterpart to the fibril morphology of cellulose. It is considerably important for the accessibility in chemical reactions and enzymatic degradation (Westermarck, 2000, Crawshaw and Cameron, 2000, Brito *et al.*, 2012). The controlled variation of pore structures enables cellulose products to meet the needs of a wide range of applications, from highly specialized membrane

and carrier materials to consumer goods, such as nonwovens (Liu *et al.*, 2005), with excellent absorption properties.



**Figure 1.4:** Various models of the supramolecular structure of cellulose micro fibrils (Fink *et al.*, 1995 a).

### 1.2.2 Isolation

In the lignocellulosic materials, cellulose is embedded in a gel matrix composed of hemicelluloses, lignin, and other carbohydrate polymers (Hanley *et al.*, 1997, Yu *et al.*, 2005). The isolation of highly pure cellulose has been the subject of extensive studies for many years because of the complexity of cell wall structure (Brendel *et al.*, 2000, Sun and Hughes, 1998).

The combination of the chemical and the mechanical treatments is necessary for the dissolution of lignin's, hemicelluloses, and other non-cellulosic substances. A protocol based on acidified sodium chlorite is frequently applied to delignify woody materials as an initial step in the isolation of cellulose (Loader *et al.*, 1997). Alkali

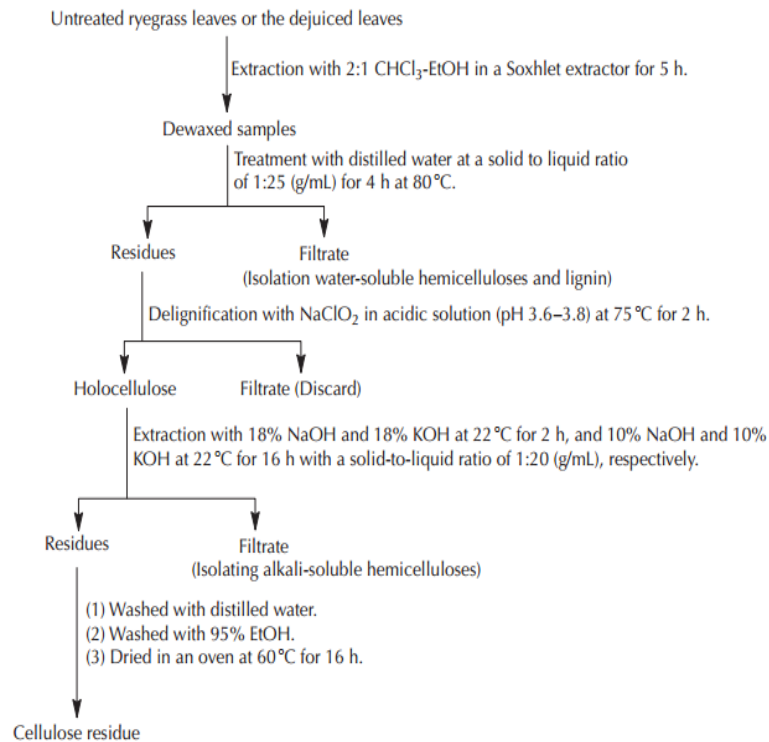
extraction to dissolve hemicelluloses before or after delignification is the common method (Sun *et al.*, 2004 a). It is well known that treatment of the lignocellulosic materials with chlorite can remove almost all of the lignin, and the following isolation of cellulose with alkali extraction can be performed at room temperature, which has been applied to isolate cellulose from woody materials for analysis for more than a century.

### **1.2.2.1 Delignification and Alkali Extraction**

Many effects have been made to isolate cellulose from various biomass sources, in which delignification and alkali extraction is considered as the most efficient method for separating cellulose from straws by releasing large amounts of lignin and hemicellulosic polysaccharides, respectively (Sun *et al.*, 2004 a). In particular, most of the lignin can be removed in a delignification step using chlorite. Delignification can significantly facilitate the extraction of the hemicelluloses during alkali treatment and therefore result in the residues of cellulosic polymers having a high purity. On the basis of the investigation of polysaccharides obtained from the delignified OAT (Organic Anion Transporters) tissues (Buchala *et al.*, 1972).

(Sun *et al.*, 1998 b) extracted cellulose from wheat straw holocellulose using 24% KOH and 2% boric acid at 20 °C for 2 h and obtained 41.8–43.0% of cellulose.

(Liu *et al.*, 2006) used delignification and alkali extraction to isolate cellulose from ryegrass shown in (Scheme 1.1). They found treatment at 22 °C with 18% NaOH and 18% KOH for 2 h and 10% NaOH and 10% KOH for 16 h yielded 28.2, 28.8, 22.7, and 23.4%, respectively, of cellulose residue from untreated ryegrass leaves and 35.7, 36.8, 32.8, and 34.6%, respectively, from the dejuiced ryegrass leaves. For each cellulosic fraction, the glucose content was 71.6, 69.6, 67.8, 66.7, 69.7, 68.6, 63.9, and 61.7%, respectively.

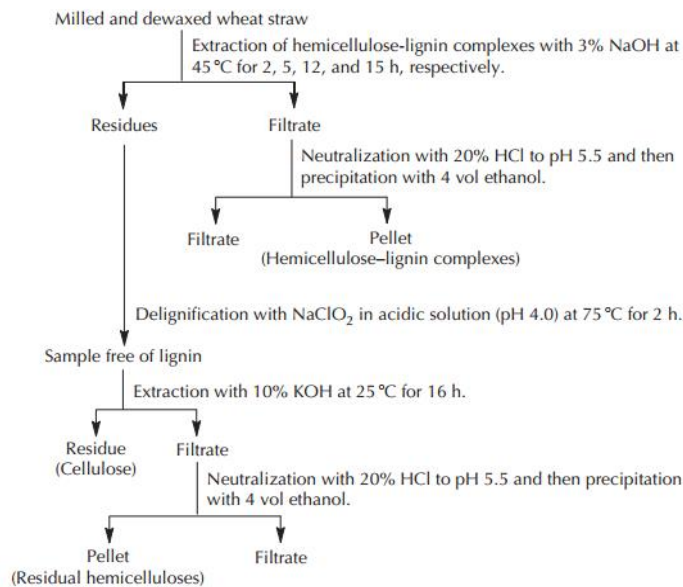


**Scheme 1.1:** Isolation of cellulose from untreated ryegrass leaves and the dejuiced leaves, (Liu *et al.*, 2006).

Sun *et al.*, (1998 a) isolated cellulose from dewaxed wheat straw after alkali extraction, followed by delignification and alkali extraction. Dewaxed wheat straw was first treated with 3% NaOH at 45 °C for 2–15 h with a low extract ant/sample ratio. The treatments resulted in the release of 32.7–41.5% hemicellulose-lignin complexes, which contained 9.3– 14.2% associated lignin. The residues of the treated straw were sequentially delignified with NaClO<sub>2</sub> and then extracted with 10% KOH at 25 °C for 16 h. The yields of cellulose ranged 38.0–39.9%. This procedure could be used to obtain cellulosic and hemicellulose polymers from straws and is listed in (scheme 1-2).

Adinugraha and Marseno, (2005) reported a method to isolate cellulose from Cavendish banana pseudo stem for further utilization. Cellulose preparations were obtained from the banana pseudo stem powder ground to pass 20 mesh after extraction with 8% NaOH at 100 °C for 3.5 h, followed by bleaching with 5% NaClO at 30 °C for 3 h ( Reddy and Yang, 2007) obtained single cells of cellulose fiber from wheat straw after dewaxing, alkali extracting with 2% NaOH solution at 95 °C for 45 min, and maceration with 10% (w/w) nitric acid and 10% (w/w) chromic acid solution.

Alemdar and Sain, (2008) extracted cellulose nanofibers from wheat straw by chemimechanical technique of alkali and acid treatment, followed by mechanical treatments of cry crushing, disintegration, and defibrillation.



**Scheme 1.2:** Isolation of cellulose and hemicelluloses from wheat straw,

(Sun *et al.*, 1998 a).

### 1.2.2.2 Steam Explosion

Steam explosion is one of the main methods developed last decade to isolate cellulose from straws, especially for the production of bioethanol (Cherian *et al.*, 2010). During the steam explosion, the significant amounts of hemicelluloses are partially hydrolyzed and some lignin species are depolymerized, resulting in sugars and phenolic compounds that are soluble in water. The hydrolysis of glycosidic linkages in hemicelluloses and the  $\beta$ -O-4 ether bonds in lignin are catalyzed by acetic acid formed at high temperature from acetyl groups present in hemicelluloses (auto hydrolysis). On the other hand, in auto hydrolysis, the depolymerized lignin fragments remain in the proximity of condensation sites in the biomass matrix (Josefsson *et al.*, 2001). The residue consists mainly of cellulose and lignin and also has some hemicelluloses. In this process, cellulose is also depolymerized and defibrillated and undergoes a change in its crystallinity, and the resulting product is more susceptible to the hydrolytic enzymes. The lignin and residual hemicelluloses may be removed by a subsequent alkali extraction and can be recovered and used for the production of various chemicals. Therefore, the steam explosion process is generally followed by a fractionation step, such as alkaline extraction, to separate the main cellulose component. Some of the possible end products of steam-exploded lignocellulosic materials are dissolving pulp, paper pulp, ethanol, xylitol, lactic acid, and furfural or furfural derivatives (Josefsson *et al.*, 2002), it has been reported that steam explosion pretreatments improve the digestion of resulting residues and shred the fibers into many individual fragments. A two-stage process proposed by (Sun *et al.*, 2005 c), was based on the steam explosion pretreatment followed by the alkaline peroxide post-treatment for the isolation of cellulose from wheat straw.

### 1.2.2.3 Alkaline Peroxide Extraction

This reaction has been explained through the reactions of the hydro-peroxide anion ( $\text{HOO}^-$ ), formed in an alkaline medium. On the other hand, depending on the pH, hydrogen peroxide acts as either a nucleophilic or an electrophilic species, it is stable under acidic conditions. Above pH 6.0, it is unstable and readily decomposes, particularly in the presence of certain transition metals such as iron, copper, and manganese. Decomposition of the hydrogen peroxide forms molecular oxygen and more active radicals such as the hydroxyl radicals ( $\text{HO}$ ) and superoxide anion radicals ( $\text{O}_2^-$ ), which in turn react with lignin in a variety of ways, thus resulting in delignification by both degradation and dissolution (Sun *et al.*, 1998 b). Alkaline peroxide extraction exhibits good performance in isolation of cellulose from straws, but less effective from wood. Recently, one of the most important approaches to cellulose isolation from straws is based on the hydrogen peroxide treatment in alkaline solution.

Sun *et al.*, (2003) found that the extraction of the dewaxed wheat straw using 2%  $\text{H}_2\text{O}_2$ –2%  $\text{NaOH}$  aqueous solution for 5 h at 45 °C and 50 °C resulted in dissolution of 85 and 86% of the original lignin and 75 and 76% of the original hemicelluloses, respectively, and left 53.8 and 53.3% cellulose.

Fang *et al.*, (2000) compared the extraction of water-treated rye straw with alkali and alkaline peroxide to isolate cellulose and hemicelluloses. The results showed that the treatment of the straw with a dilute alkaline solution at pH 11.5 for 12 h at 50 °C in the absence of  $\text{H}_2\text{O}_2$  yielded only 7.3% of the original hemicelluloses and 7.4% of the original lignin, whereas extraction with 2%  $\text{H}_2\text{O}_2$  at pH 11.5 for 12 h at 20–70 °C released 44.2–71.9% of the original hemicelluloses and 52.7–87.8% of the original lignin.

#### 1.2.2.4 Organic Solvent Extraction

Organic acid pulping such as acetic acid pulping has been proved to be an effective method to delignify and fractionate straws (Pan and Sano, 1999 b, Pan and Sano, 1999 c, Pan and Sano, 1999 a, Pan *et al.*, 1999).

Lam *et al.*, (2001) Studied rice straw pulping using formic acid. Approximately 85% of delignification with a cellulose pulp yield of 44.4% was obtained under relatively mild cooking conditions (temperature, 100 °C; cooking time, 60 min; and formic acid concentration, 90%). They thought the advantage of this technique compared with cooking in basic environments was that most of the silicon derivatives remain in the pulp. One of the developments in acetic acid pulping is the FORMACELL process, based on the addition of 5–10% formic acid to aqueous acetic acid, resulting in improved selectivity of delignification (Lehnen *et al.*, 2002).

Sun *et al.*, (2004 c) found that wheat straw lignin and hemicelluloses were degraded in the medium containing 80% acetic acid and 0.92–13.5% nitric acid. The treatment with 80% acetic acid and 0.92% nitric acid as a catalyst at 120 °C for 20 min resulted in more than 81% original hemicelluloses and 92% original lignin degradation. As the nitric acid concentration increased to 8.5%, more than 96% original hemicelluloses and approximately 98% original lignin were degraded and yielded the cellulose approaching 96% purity.

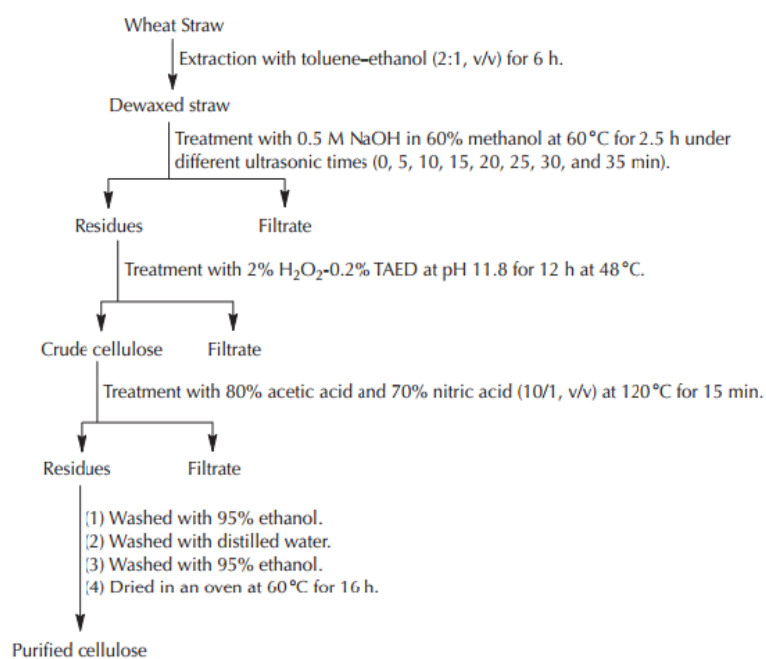
Xu *et al.*, (2006) and Xu *et al.*, (2005) used this procedure to isolate cellulose from wood and cereal straws. The results showed that the treatment using 80% acetic acid with 2.0–8.0% (w/w) nitric acid as a catalyst led to the significant degradation of lignin and hemicelluloses, the slight acetylation of cellulose, and an increase in the degree of crystallinity of cellulose. Glucose was comprised with more than 90% of the



total neutral sugars of the isolated cellulose preparations, revealing the relatively high purity of cellulose samples.

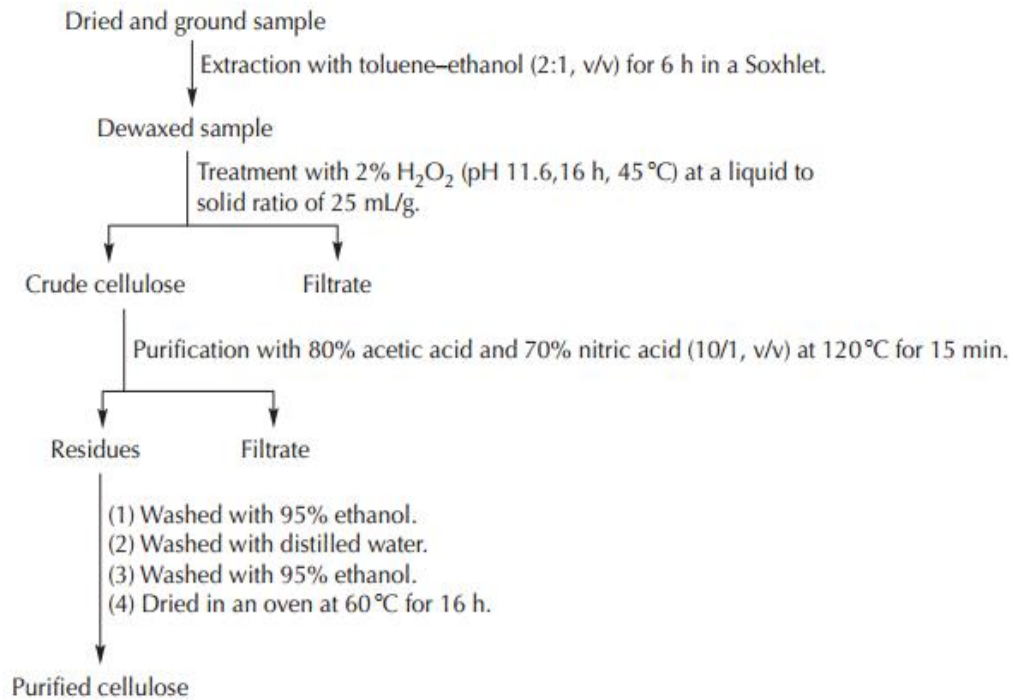
Sun *et al.*, (2004 b) proposed a sequential totally chlorine-free procedure for isolation of cellulose from wheat straw based on the alkaline extraction in organic alcohol, peroxide treatment, and purification with 80% acetic acid–70% nitric acid. It was shown that pretreatment with 0.5 M NaOH in 60% methanol at 60 °C for 2.5 h, under ultrasonic irradiation for 0 –35 min, and subsequent post-treatment with 2% H<sub>2</sub>O<sub>2</sub>–0.2% TAED at pH 11.8 for 12 h at 48 °C solubilized 85.3–86.1% of original hemicelluloses and 91.7–93.2% of the original lignin, respectively. Dry wheat straw contained cellulose between 46.2 and 49.2% in addition to 11.2–12.2% residual hemicelluloses and 2.5–2.9% remaining lignin. Further treatment of the corresponding crude cellulosic preparations with 80% acetic acid–70% nitric acid yielded 36.8–37.7% of the cellulose with high purity. This procedure is shown in (scheme 1-3).

Sun *et al.*, (2005 b), Sun and Tomkinson, (2005), Sun *et al.*, (2005 a) adopted Sun *et al.*, (2004 b) procedures to isolate cellulose from many kinds of lignocellulosic materials including barley straw, oil palm frond fiber, poplar wood, maize stems, wheat straw, rice straw, and rye straw, as shown in (scheme 1.4). Highly purified cellulose preparations were obtained by pretreatment with 2.0% H<sub>2</sub>O<sub>2</sub> at 45 °C and pH 11.6 for 16 h and sequential purification with 80% acetic acid–70% nitric acid (10/1, v/v) at 120 °C for 15 min.



**Scheme 1.3:** Isolation of crude and purified cellulose from wheat straw,

(Sun *et al.*, 2004 b).



**Scheme 1.4:** Isolation of crude and purified cellulose from dewaxed barley straw, oil palm frond fiber, poplar wood, maize stems, wheat straw, rice straw, and rye straw, (Sun *et al.*, 2005 a).

#### 1.2.2.5 Other Isolation Methods

There are many other methods, including acid hydrolysis and biological treatment, for the isolation of cellulose from straws.

Zhao *et al.*, (2008) proposed an integrated process for the isolation of nearly pure cellulose from rice straw based on treatment with dilute acid to decompose hemicelluloses followed by delignification with sulfo methylation reagents.

Bhattacharya *et al.*, (2008) isolated cellulose microfibrils from SCB using a conventional pulping process to eliminate lignin and hemicelluloses, mechanical homogenization, and acid hydrolysis. Hydrolysis of the cellulose fibers with 60% (w/v) sulfuric acid for 2.5 h at 60 °C was found to be optimum and resulted in the

removal of most of the amorphous domains without any significant damage to the crystal structure.

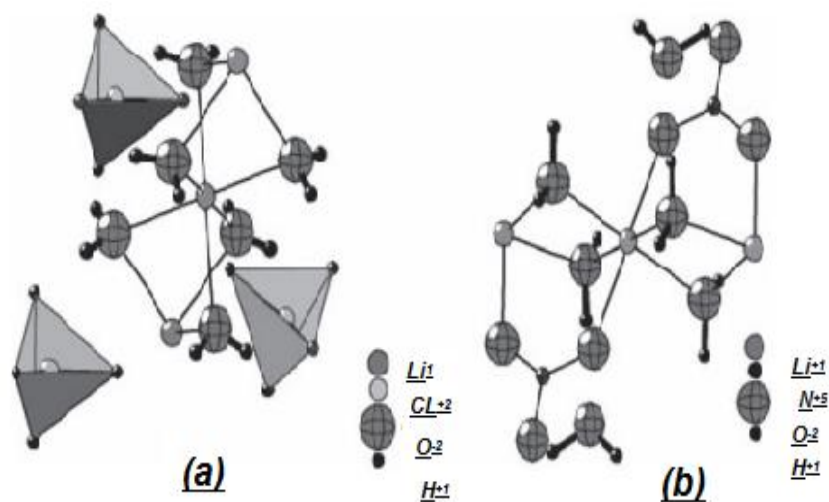
Fungal pretreatment a kind of white rot fungi, was applied to wheat straw before kraft-AQ pulping, the so-called bio-kraft process. The results indicated that kraft-AQ pulps from wheat straw exhibited better characteristics than the other pulp samples, such as lower lignin content, higher carbohydrate content, higher paper strength properties, and better bleach ability. The highest kappa number, viscosity, and fiber coarseness were found for organosolv pulp samples; however, these pulps had the lowest carbohydrate contents and strength values and poor bleaching properties (Liu and Sun, 2010).

### **1.3 Dissolution of Cellulose**

The solvents for efficient cellulose dissolution have been searched for the confirmation of cellulose molecules. To date, a number of solvent systems, such as inorganic molten salts like  $\text{LiClO}_4 \cdot 3\text{H}_2\text{O}$  (Fischer *et al.*, 2003), N-methyl morpholine-N-oxide (NMMO) (Rosenau *et al.*, 2003), NaOH/urea (Cai and Zhang, 2005), and ionic liquids (ILs) (Swatloski *et al.*, 2002), have been found efficient for cellulose dissolution.

#### **1.3.1 Inorganic Molten Salts**

Inorganic molten salts can be used as efficient solvents for cellulose in a wide range of DP (Fischer *et al.*, 1999). The characteristics that mainly determine the dissolution power toward cellulose are recognized as acidity, water content of the melts, and properties of the coordination sphere of the cations. The structures of  $\text{LiClO}_4 \cdot 3\text{H}_2\text{O}$  and  $\text{LiNO}_3 \cdot 3\text{H}_2\text{O}$  are shown in (Figure 1.5).



**Figure 1.5:** Crystal structure of  $\text{LiClO}_4 \cdot 3\text{H}_2\text{O}$  (a) and  $\text{LiNO}_3 \cdot 3\text{H}_2\text{O}$  (b)

### 1.3.2 N-Methyl morpholine-N-Oxide

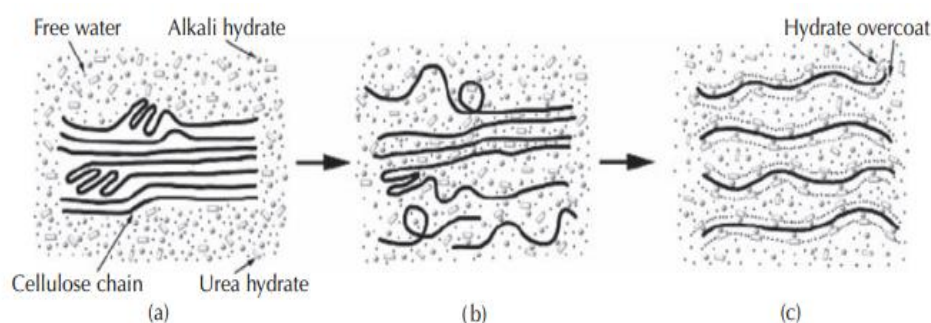
Apart from being widely applied as an oxidant in organic synthesis, N-methyl morpholine-N-oxide (NMMO) has attracted major interests due to its ability to dissolve cellulose. NMMO is used as direct solvent for cellulose in the commercial Lyocell process as a modern industrial fiber-making technology (Rosenau *et al.*, 2003, Lewandowski, 2000, Rosenau *et al.*, 2002, Fink *et al.*, 2001).

Main features of Lyocell process are the direct dissolution of cellulose without chemical derivatization and the almost complete recovery of the NMMO. The organic substance NMMO can dissolve cellulose due to the high polarity of its N–O bond, which breaks the hydrogen bond network of the cellulose and forms new hydrogen bonds with the solute (Kuo and Lee, 2009).

### 1.3.3 NaOH/urea and LiOH/urea

In last few years, Cai *et al.*, (2007) developed a novel solvent system for cellulose based on an NaOH/urea aqueous solution precooled to  $-12\text{ }^{\circ}\text{C}$ , in which the dissolution of cellulose could be achieved rapidly at ambient temperatures (below  $20\text{ }^{\circ}\text{C}$ ). Interestingly, cellulose with a relatively high molecular weight could not be dissolved in the solvent without being precooled to  $-12\text{ }^{\circ}\text{C}$  or without urea being added. The addition of urea and the low temperature play an important role in the improvement of the cellulose dissolution because low temperature creates a large inclusion complex associated with cellulose, NaOH, urea, and  $\text{H}_2\text{O}$  clusters, which bring cellulose into aqueous solution, even at relatively high cellulose concentrations (Kosan *et al.*, 2008). Moreover, the cellulose dope could remain in a liquid state for a long period at about  $0$  to  $5\text{ }^{\circ}\text{C}$ .

(Cai and Zhang, 2005, Swatloski *et al.*, 2002, Kuo and Lee, 2009, Cai *et al.*, 2007 systematically studied rapid dissolution of cellulose in LiOH/urea and NaOH/urea aqueous solutions. The schematic dissolution process of the cellulose is shown in (Figure 1.6).



**Figure 1.6:** Schematic dissolution process of the cellulose in LiOH/urea and NaOH/urea aqueous solutions precooled to  $-10\text{ }^{\circ}\text{C}$ : (a) cellulose bundle in the solvent, (b) swollen cellulose in the solution, (c) transparent cellulose solution (Cai and Zhang, 2005).

### 1.3.4 Ionic Liquids and Ionic Liquid Analogues

The first example of the cellulose dissolution and processing using ILs might be dated back to 1934. In a patent, (Zhu *et al.*, 2006) discovered that molten N-ethyl pyridinium chloride, in the presence of nitrogen-containing bases, could dissolve cellulose. Unfortunately, this did not attract significant attentions due to the lack of knowledge on this kind of substances at that time and relatively high melting points of the pyridinium salts, 118–120 °C. Later, it has been shown that the melting point can be lowered to 77 °C by mixing the IL with 50% N, N-dimethyl formamide (DMF) or dimethyl sulfoxide (DMSO); the mixtures thus obtained dissolve cellulose (Swatloski *et al.*, 2002).

### 1.4 Syntheses of cellulose derivatives

Cellulose is a versatile starting material for several applications. It is directly linked to the paper industry in which cellulose is used in a conventional way, as a structural material for paper and cardboard products. However, even though this is the current major use of cellulose, only the imagination is the limit for the utilization of this extremely versatile and adaptable material. Cellulose can be chemically modified to yield derivatives which are used widely in different industrial sectors in addition to conventional applications. As an example, in 2003, 3.2 million tons of cellulose was used as a raw material in the production of regenerated fibers and films in addition to cellulose derivatives (Klemm *et al.*, 2005 a). Derivatives are further used as coatings, laminations, optical films and absorbents. Additionally, cellulose derivatives can be found as additives in building materials and also in pharmaceutical, food and cosmetic products.

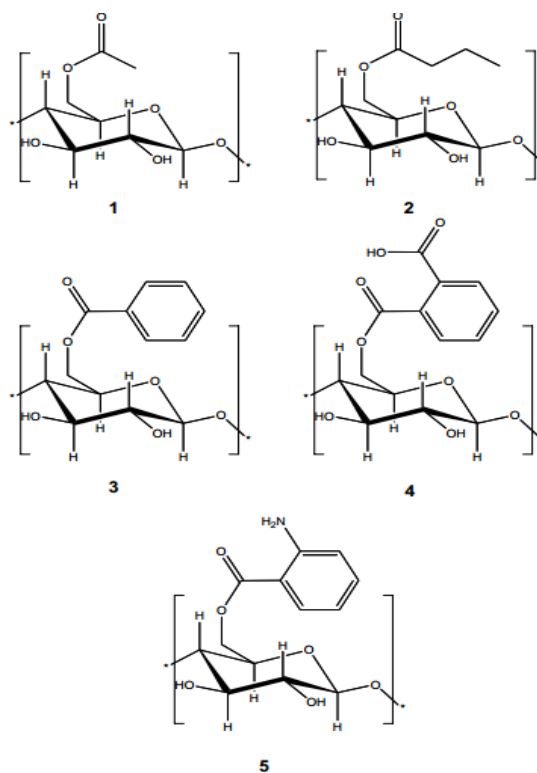
Commercial cellulose esters and ethers are produced under heterogeneous reaction conditions by using acids and acid anhydrides as reagents. On the other hand,

the main synthetic route for ethers is Williamson ether synthesis method (Klemm *et al.*, 1998). Major drawbacks of heterogeneous phase reactions are the limited reaction rates and lack of region-selectivity in certain reactions. The ramifications of these drawbacks are that the accessibility of free hydroxyl groups of cellulose is the determining factor for selectivity and for the degree of substitution (DS). In contrast, when carrying out reactions in homogeneous solutions, the region-selectivity of the reaction is determined by the reactivity differences among the free hydroxyl groups on the cellulose molecules, not by their accessibility. In addition to controllable selectivity of the reaction, the DS values can be tuned varying from low DS derivatives to highly substituted compounds.

#### **1.4.1 Esterification of cellulose**

The first types of ionic liquids used in the esterification of cellulose were N-alkyl pyridinium halides, especially N-ethyl pyridinium chloride and N-benzyl pyridinium chloride (Pasquini *et al.*, 2008). These solvents had high melting points and were therefore diluted with organic solvents, such as DMSO, DMF or pyridine (Pasquini *et al.*, 2008). These mixtures provided a homogeneous reaction media and several derivatives were synthesized using carboxylic acid anhydrides or chlorides and pyridine as a base. These derivatives include acetates (1), butyrates (2), benzoates (3), phthalates (4) and anthranilic (5) acid esters of cellulose (Figure 1-7) (Pasquini *et al.*, 2008). However, the DS values have not been reported for these derivatives and thereby, the efficiencies of these reactions were found to be difficult to judge.

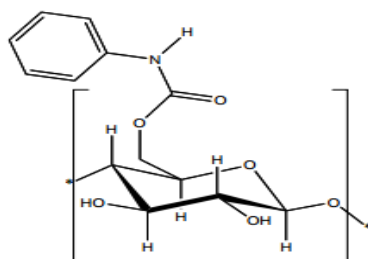




**Figure 1.7:** Schematic structures of cellulose acid esters synthesized in *N*-benzylpyridinium chloride/pyridine used as early IL: acetate (**1**), butyrate (**2**), benzoate (**3**), phthalate (**4**) and anthranilic (**5**) acid esters of cellulose (Pasquini *et al.*, 2008).

#### 1.4.2 Carbanilation of cellulose

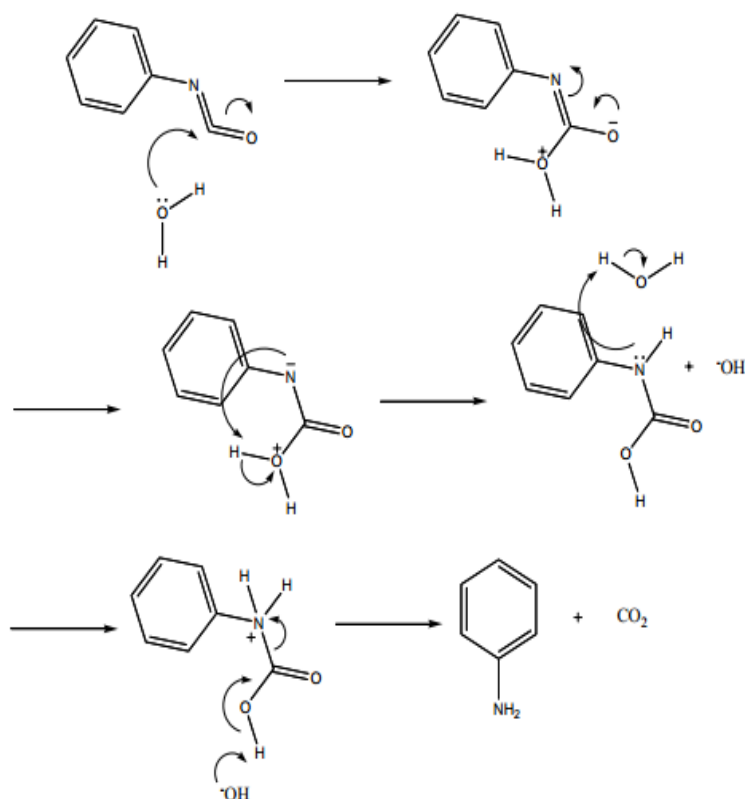
Cellulose tri carbanilate with various functional groups on their aromatic rings are reported to form lyotropic liquid crystalline phases, and can be used to separate enantiomers (Evans *et al.*, 1991, Mormann and Kuckertz, 2002, Yashima *et al.*, 1995).



**Figure 1.8:** Structure of cellulose carbanilate

Carbanilation of cellulose using both low and high DP cellulose sources including: MCC, cotton linters, pulp and bacterial cellulose (BC), have been conducted in [Bmim] Cl (Barthel and Heinze, 2006, Schluffer *et al.*, 2006). This reaction has also been studied earlier under homogeneous conditions using DMA/LiCl (Terbojevich *et al.*, 1995). In [Bmim] Cl solution the reaction yielded cellulose carbanitrile with a DS range of between 0.26 and 3.0, independent of the DP and source of cellulose (Schluffer *et al.*, 2006). However, the high DP cellulose containing hemicelluloses had a low reactivity and hence, required longer reaction times with increased amounts of reagents. The difference in reactivity between the cellulose sources was explained by the presence of hemicellulose in the pulp. The solubility of the products was dependent on the DS values of the products; DS > 2.4 were completely soluble in DMSO, DMF and THF.

It is known that carbanilation liberates CO<sub>2</sub> under normal reaction conditions. However, with ILs, it was observed that CO<sub>2</sub> was indeed being liberated but additionally, the formation of aniline was evident and verified by <sup>13</sup>C NMR (Schluffer *et al.*, 2006). This side-reaction originates from the presence of water. The formation of aniline by the reaction of phenyl isocyanate and water is plausible by considering the following putative reaction mechanism (Figure1.9).



**Figure 1.9:** Proposed reaction mechanism of the side reaction forming aniline and  $\text{CO}_2$  (Granström, 2009).

### 1.4.3 Etherification of cellulose

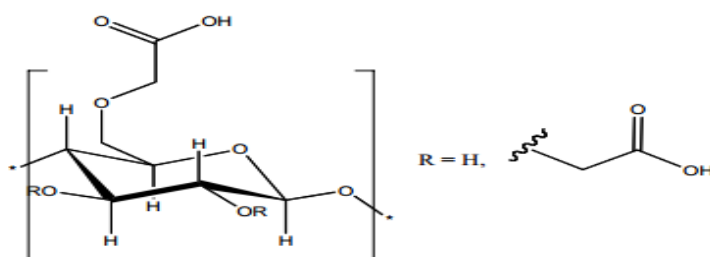
#### 1.4.3.1 Carboxymethylation, -ethylation and -propylation

Carboxymethylation of cellulose in a wide variety of ionic liquids (ILs) was reported by Granström, 2009. Carboxymethylation of cellulose in [Bmim] Cl was achieved by diluting the cellulose-IL solution with DMSO to effect suitable mixing (Heinze *et al.*, 2005).

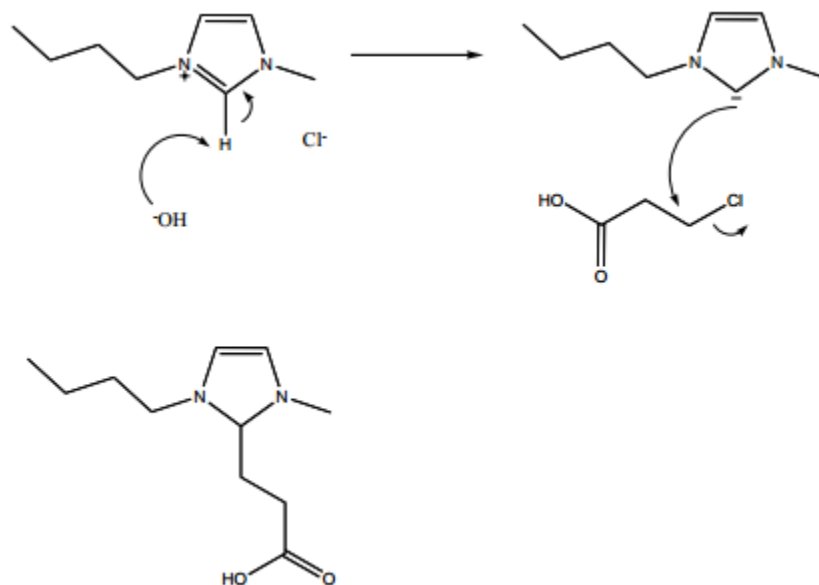
A solution of NaOH and sodium mono-chloroacetate dissolved in DMSO was added into the cellulose-IL-DMSO solution, which formed a gel-like mixture. Carboxymethyl cellulose (CMC) was obtained with a DS of 0.49 when an equivalency of 1:1 was used (Figure 1.10). In spite of the increased equivalency of reagents to 1 (AGU):3, the DS did not increase. The authors did not discuss this point further and the spectral data was not interpreted in enough detail to explore the

possible side products from the reaction. Nonetheless, they later reported a lack of reproducibility of the reaction due to the reaction between the base and IL (Liebert and Heinze, 2008). Moreover, the reaction is not homogeneous as NaOH is not soluble in IL and the cellulose precipitates from the solution during the course of the reaction.

It is generally perceived that strong bases such as NaOH cannot be used with imidazolium-based ILs that have C-2 protons as this results in side-reactions. The C-2 proton is fairly acidic with a dissociation constant ( $pK_a$ ) of 24 in DMSO (Nishida *et al.*, 1971), and is deprotonated by strong bases to form carbene (Figure 1.11). The presence of carbene in the reaction mixture inhibits the reaction from proceeding further due to its reaction with the monochloroacetate (Figure 1.11).



**Figure 1.10:** Schematic structure of carboxymethyl cellulose (CMC)  
(Granström, 2009).



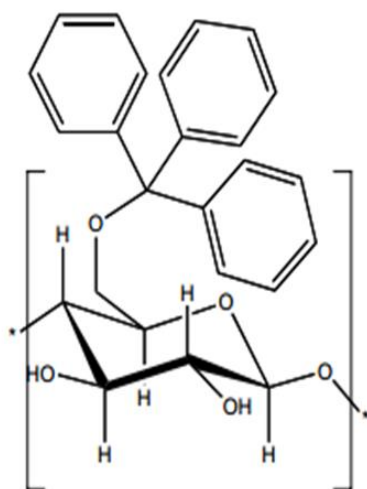
**Figure 1.11:** Formation of carbene in the presence of a strong base such as NaOH (Granström, 2009).

In contrast to reaction in ILs, the carboxymethylation of cellulose under homogeneous conditions in conventional solvent systems, namely Ni (tren) OH<sub>2</sub>, NMMO and melt of LiClO<sub>4</sub>•3H<sub>2</sub>O proceeds fairly well resulting in higher DS values (Heinze *et al.*, 1999) . For MCC in Ni (tren) OH<sub>2</sub> solvent a DS of 0.54 was obtained with a large excess of reagents (1:20 NaOH: 10 monochloroacetate). The DS could be increased to 0.71 by a stepwise addition of reagents. Spruce pulp was used as a cellulose source for the reaction in NMMO with same amount of reagents that yielded a DS of 1.26, whereas the reaction carried out in a melt of LiClO<sub>4</sub>•3H<sub>2</sub>O gave a DS of only 0.69.

Carboxymethylation and propylation of cellulose has also been studied in [Bmim] Cl and in [Amim] Cl, but the reactions yielded relatively low DS values that ranged from 0.01 to 1.53 (Heinze *et al.*, 1999).

### 1.4.3.2 Tritylation

Tritylation of cellulose is a well-known reaction that produces regioselectively of C-6 substituted cellulose derivatives leaving positions C-2 and C-3 available for subsequent modifications (Figure 1.12) (McCormick and Callais, 1987, Hearon *et al.*, 1943, Gómez *et al.*, 1996, Harkness and Gray, 1990, Dawsey and McCormick, 1990, Yue and Cowie, 2002, Tsunashima *et al.*, 2001). Regioselectively substituted cellulose derivatives are of increasing interest due to their unique properties as compared to those of statistically substituted analogues.



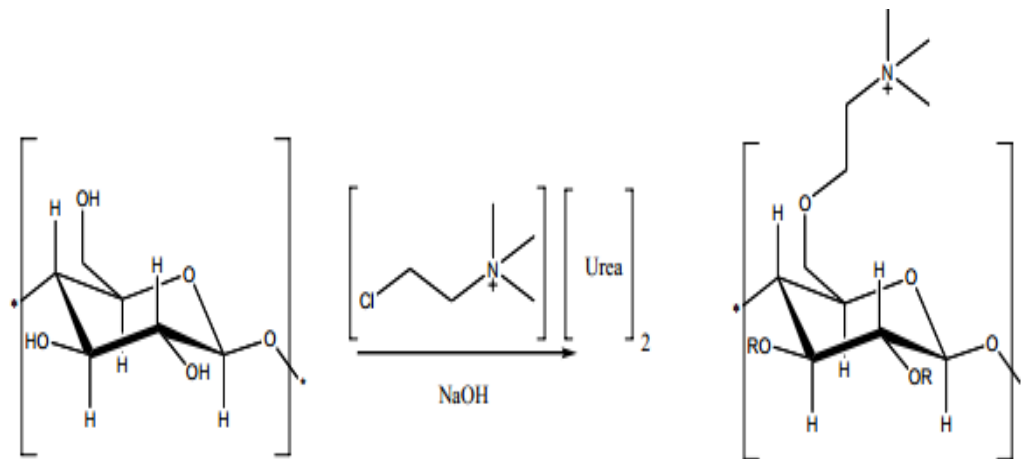
**Figure 1.12:** Structure of trityl cellulose (Granström, 2009).

Reactions involving the use of ILs in tritylation were carried out in molten salts using pyridine as a solvent and/or inorganic base (Pasquini *et al.*, 2008), these reactions were reported in the quite apart years, in 1934 and then much later in 2005 (Pasquini *et al.*, 2008). Tritylation of cellulose in a ‘real’ IL was investigated using [Bmim] Cl as a reaction medium with tri phenyl methyl chloride (trityl chloride, TrCl) in the presence of pyridine (Erdmenger *et al.*, 2007).

### 1.4.3.3 Cationic functionalization

Cationic cellulose derivatives are industrially very important compounds and have many applications in the paper industry, cosmetics, textiles, flotation and flocculation and in drilling fluids (Trombino *et al.*, 2008), these substances are also utilized in the removal of acidic dyes from aqueous effluent produced by the textile industry thereby reducing the environmental impact of the processes (Blackburn and Burkinshaw, 2003).

Previously, cationic cellulose derivatives have been prepared by the etherification of cellulose using glycidyl ammonium salts or alkylene epoxides in the presence of suitable alkaline catalyst, usually NaOH (Abbott *et al.*, 2006). Cationic substitution values of between 0.034 and 0.5 moles per quaternary nitrogen per mole of glucose unit have been reported in these reactions (Stone and Rutherford, 1969). However, these reactions give low yields and require large amounts of organic solvents (Trombino *et al.*, 2008), but eutectic mixture of choline chloride and urea, was used for heterogeneous cationic functionalization of cellulose (Figure 1.13). Moreover, this has the advantages of being non-toxic, biodegradable and has no Lewis acidity, though it has a poor solubilizing capacity for cellulose. In the reaction with cellulose, it functions as both reagent and a solvent. However, it does not provide homogeneous reaction conditions as it is not capable of dissolving cellulose and therefore, the reaction may be regarded as heterogeneous. Maximum DS of 0.19% was obtained in this heterogeneous cationic functionalization.



**Figure 1.13:** Cationic functionalization of cellulose with a choline derivative and urea in the presence of NaOH. R represents the cationic substituent (Abbott *et al.*, 2006).

### 1.5 Carboxymethylcellulose

Cellulose is commonly converted into useful derivatives by etherification. Among these, Carboxymethyl cellulose (CMC) is the most important water soluble derivative, with many applications in the food, cosmetics, pharmaceutical and detergents industries, etc. The modified cellulose is a linear, long chain, water-soluble, anionic, man-modified polysaccharide. Purified CMC is a white to cream colored, tasteless, odorless, free flowing powder (Ghannam and Esmail, 1997).

CMC is useful in systems where hydrophilic colloids are involved, and they show ability to suspend solids in aqueous media, stabilize emulsions, absorb moisture from the atmosphere, solubilize proteins (milk proteins, egg proteins), thicken solutions (sugar solutions, paints) and form films. CMC gives good enteric coatings for powders and tablets (Dapia *et al.*, 2003).

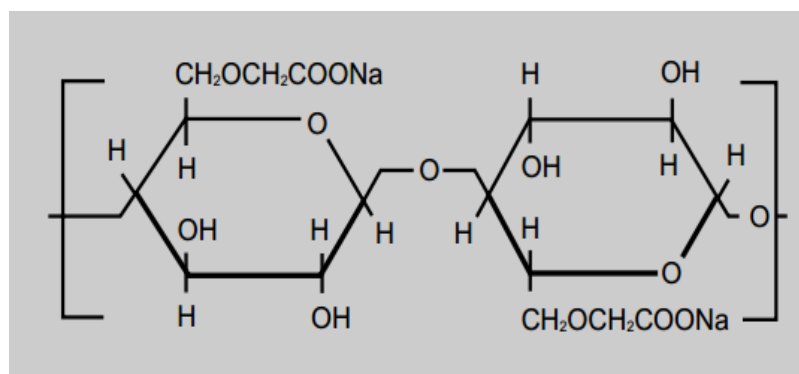
Production of cellulose derivatives is done by reacting the free hydroxyl groups in the Anhydro glucose units (AGU) with various chemical substitution groups. The introduction of the substituent disturb the intermolecular and intramolecular hydrogen bonds in cellulose, which leads to liberation of the



hydrophilic character of the numerous hydroxyl groups and restriction of the chains to closely associate (Toğrul and Arslan, 2003). However, substitution with alkyl groups reduces the number of free hydroxyl groups.

In principal, all hydroxyl groups (HO-2, HO-3, and HO-6) in the Anhydro glucose unit can be substituted, and the maximum degree of substitution (DS) is being 3 (Salmi *et al.*, 1994).

Bono *et al.*, 2009 studied the production of CMC using palm kernel cake. The cellulose was converted to CMC through carboxymethylation process using William Etherification technique in heterogeneous system. CMC was characterized in terms of DS and viscosity.



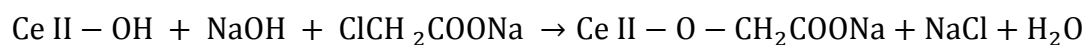
**Figure 1.14:** Molecular structure of CMC with a DS of 1.0 ([http:// www. Ashland. Com / Ashland / static / documents / AAFI / PRO – 250 – 10 H – Aqualon – CMC Pd](http://www.Ashland.Com/Ashland/static/documents/AAFI/PRO-250-10H-Aqualon-CMC-Pd) – retrieved on 15/5/2016 at 4:17 pm).

### 1.5.1 Synthesis of Carboxymethylcellulose (CMC)

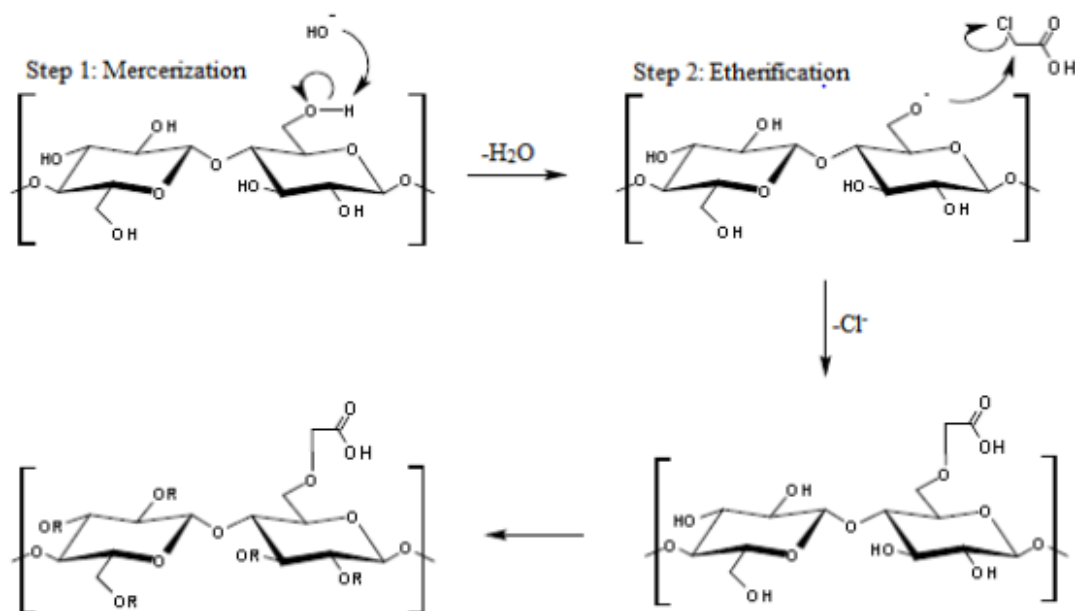
Sodium carboxymethylcellulose (Na-CMC) was produced by conversion of alkali cellulose swollen in aqueous NaOH and a surplus of organic solvent (e.g. isopropanol, ethanol) with monochloro acetic acid (MCAA) or its sodium salt (Na-

MCA). The hydroxyl groups in cellulose are usually replaced by the carboxymethyl groups in the order of C2>C6> C3 (Kutsenko *et al.*, 2005).

In practice, the manufacturing of CMC involves two steps (Scheme 1.5). In the first step, the cellulose is treated with NaOH, often in the presence of inert solvent, which act as both swelling agent and a dilatant and thus facilitate good penetration of NaOH into the cellulose structure (Latif *et al.*, 2007). The alkali cellulose is accessible and reactive toward MCA, which is added to reaction in the second step. The reaction between alkali cellulose and the etherification agent carried out in aqueous system. According to the following reaction:



A considerable amount of the etherifying agent, up to 30%, is consumed in side reaction with the aqueous NaOH forming predominantly sodium glycolate by hydrolysis of chloroacetate. The CMC can be neutralized and dried immediately to give a technical grade or neutralized and washed to give a purified grade (Adinugraha and Marseno, 2005).



**Scheme 1.5:** Carboxymethylation reaction where R could be H or  $\text{CH}_2\text{COOH}$  if the carboxymethylation progresses (Stigsson *et al.*, 2001).

### 1.5.2 Applications of purified CMC

Cellulose derivatives being of natural origin have diverse physicochemical properties because of substituents DS, Molecular weight and degree of polymerization (DP) are reversed for their large scale use mainly as additives of fine / special chemicals in textile, pharmaceuticals, cosmetics, Food and backing industries.

CMC is non-toxic and it is currently finding an increasing number of applications in pharmaceutical, medical and food industries. It is a key component in control drug –release pills and in the manufacture of personal care products. It is also used in gels applied as protecting agent during heart throat and cornea surgery, most of the CMC application based on it is rheological properties. The ability of CMC to function as a thickener or flow-controlled agent depends largely on its degree of substitution, molecular weight and stiffness of the cellulose backbone (Akzo, 2011).

Applications of CMC span wide range of products and industries. CMC is used as thickening agent and purified CMC is used as a stabilizer in foods,

particularly in dairy products such as ice cream, yogurt, and milk drinks, other food applications include beverages, syrups, baked goods, and pet foods. Other major industrial consumers that use purified CMC for its properties as a binder and thickener include producers of paper, the ceramics industry, and the textiles industry. Crude/unrefined CMC is used in laundry detergents as soil antired position aid, tobacco, cosmetics, foods, pharmaceuticals, adhesives, Aerial-drop fluids, Coatings and lithography (Pushpamalar *et al.*, 2006).

Some applications for purified CMC illustrated in the following tables (<http://www.Ashland.Com/Ashland/static/documents/AAFI/PRO-250-10H-Aqualon-CMC-Pd> – retrieved on 15/5/2016 at 4:17 pm).

**Table 1.1:** Applications of CMC in Cosmetics industries:

Specific application	Properties utilized
Toothpaste	Thickener; flavor stabilizer; suspending aid; binder
Shampoos; foamed	Suspending aid; thickener; foam stabilizer; high water- binding capacity
Creams; lotions	Emulsion stabilizer; film former; thickener
Gelled products	Thickener; gelling agent; film-former
Denture adhesives	Wet tack; long-lasting adhesion

**Table 1.2:** Application of CMC in Pharmaceuticals industries:

<b>Specific application</b>	<b>Properties utilized</b>
Ointments; creams; lotions	Stabilizer; thickener; film-former
Jellies; salves	Thickener; gelling agent; protective colloid; film-former
Tablet binder; granulation aid	High-strength binder
Bulk laxatives	Physiologically inert; high water-binding capacity
Syrups	Thickener
Suspensions	Thickener; suspending aid

**Table 1.3:** Applications of CMC in Aerial drop fluids and Coatings industries:

<b>Specific application</b>	<b>Properties utilized</b>
Insecticides	Thickener; binder; suspending aid
Drift-control agent	Thickener
Latex paints; paper coatings	Rheology control; suspending aid; protective colloid
Foundry core wash	Binder; thickener; suspending aid

**Table 1.4:** Applications of CMC in Foods industries:

Specific application	Properties utilized
Frozen desserts; soft-serve	Controls ice crystal growth; improves mouthfeel; body; and texture
Pet food	Water binder; gravy thickener; extrusion aid; binder of fines
Protein foods	Retains water; improves mouthfeel
Baked goods	Batter viscosifier; improves moisture retention and texture
Beverages	Suspending aid; rapid viscosifier; improves mouthfeel and body; protein stabilizer in acidified drinks
Desserts; icings; toppings	Odorless and tasteless; thickens; controls sugar crystal size; improves texture; inhibits syneresis
Low-calorie foods	No caloric value (2); thickens; imparts body and mouthfeel
Syrups	Clear; thickens; imparts favorable mouthfeel and body
Dressings; sauces	Thickener and suspending aid; imparts mouthfeel
Animal feed; extrusion Products	Lubricant; binder; film-former

**Table 1.5:** Applications of CMC in Detergents and Lithography and Tobacco industries:

Specific application	Properties utilized
Laundry	Whiteness retention through soil suspension
Fountain and gumming solutions	Hydrophilic protective film
Water-based inks	Binder; rheology control; suspending aid
Cigar and cigarette adhesive	Good wet tack; high film strength
Reconstituted sheet	High -strength binder and suspending aid

### 1.6 Literature review

Many studies were handled for converting cellulose extracted from different natural resources to carboxymethylcellulose (CMC). Many parameters were considered to optimize the yields, Degree of substitution (DS) value and rheological behavior of the synthesized CMC material.

Pushpamalar *et al.*, (2006) isolated cellulose from sago waste and converted it to CMC by etherification using sodium monochloroacetate in the presence of sodium hydroxide. The reaction was optimized against temperature, concentration of NaOH and reaction time. The optimized product has a large value of DS of 0.821. The optimized DS value was obtained using pure isopropyl alcohol as the solvent medium, reaction period of 180 min, 6.0 g of sodium monochloroacetate, 10 mL of 25% NaOH aqueous solution and a reaction temperature of 45 °C. Fourier Transform Infrared (FT-IR) spectra were used to characterize the CMC product.

Adinugraha and Marseno, (2005) studied the synthesis and characterization of Na-CMC from Cavendish banana pseudo stem. The cellulose powder was extracted using an aqueous solution of 8% NaOH at 100 °C for 3.5 h, and then bleached with an

aqueous solution of 5% NaOCl at 30 °C for 3 h. The cellulose was then alkalinized with 5–30% NaOH at 25 °C for 1 h then variable quantities of 3-7 g of ClCH<sub>2</sub>COONa were added per 5 g cellulose. The results showed that the cellulose alkalinized by 15% NaOH gave CMC of the optimum properties, i.e. DS of 0.75, viscosity of 4033 cps, purity of 98.63 % and crystallinity of 38.33 %.

Aguir and M'henni, (2006) studied the production of CMC from bleached cellulose pulps obtained from *Posidonia oceanica*. The carboxymethylation reaction was carried out with NaOH and monochloro acetic acid (MCA) as the reagent. The highest DS (2.75) was obtained with *n*-butanol at an optimum temperature of 80 °C. The best molar ratios of cellulose/NaOH and cellulose/MCA were 1/3.

Hutomo *et al.*, (2012) studied the synthesis and characterization of Na-CMC from pod husk of Cacao. The optimum conditions used to produce CMC of higher DS value of 0.75 were 15% NaOH, temperature 55.93°C, 4g NaMCA and 3h reaction period. The aqueous solution of CMC of the highest DS value (0.75) exhibited viscosity of 206.10 cps.

Varshney *et al.*, (2006) synthesized CMC from cellulose isolated from *Lantana camara*, using optimized set of conditions include 20% NaOH aqueous solution, an amount of MCA of 2.05 mol/AGU, carboxymethylation time of 3.5 h, temperature of 55 °C and isopropyl alcohol as a solvent medium. The resulting CMC had a viscosity of 600 cps (1% solution) and 7500 cps (2% solution) and DS value of 1.22.

Haleem *et al.*, 2014 studied the synthesis of CMC from waste of cotton ginning (CGW) industry. The isolated cellulose was converted to CMC by etherification reaction using Na-MCA and different concentrations of sodium hydroxide (NaOH) (5 – 40 g/100 mL). The optimum NaOH concentration for the



carboxymethylation reaction was found to be 20 g/100 mL NaOH which provided the highest DS value (0.874). The aqueous solution of optimized CMC exhibited the highest viscosity.

Mat Som, (2004) studied the preparation and characterization of CMC from oil palm empty fruit bunch fibers. The work involved manipulation of three variable parameters namely, reaction temperature (55, 60 and 70 °C), time of reaction (4, 6, 8, 16, 18 and 20 h) and concentration of sodium hydroxide (2.6 moles and 3.4 moles per mole of monochloro acetic acid). Thirty-six grades of CMC material were produced and characterized. The findings showed that the percent yield of CMC, moisture content, DS, purity, viscosity and ash content were in the range of 49.76 – 58.62%, 7.3 – 8.8%, 0.74 – 0.95, 85.5 – 99.5%, 116 – 2217 cps and 15.2 – 20.2%, respectively. Overall judgment on the selection of the best processing conditions was preferably of 55 °C, 2.6 moles NaOH and 4 h reaction time. The conversion of cellulose to CMC material was indicated from the FT-IR spectra of as-synthesized and commercial CMC materials. Both materials exhibited similar patterns with the presence of peaks at the fingerprint regions between 1300 and 1580  $\text{cm}^{-1}$  due to the presence of carboxymethyl group.

Latif *et al.*, (2007) studied the synthesis and characterization of CMC from rayon grade wood pulp and cotton linter. The dried cellulose was alkalized using 40% NaOH solution at 25 °C for 1.5 hour. The carboxymethylation reactions were conducted using various amounts of Na-MCA (5-7g) per 5 g of cellulose, a temperature of 55 °C, reaction time of 3.5 h and isopropyl alcohol solvent. The optimum DS value of the synthesized CMC was found to be 1.9.

Heydarzadeh *et al.*, (2009) studied the catalyst-free conversion of alkalized cellulose to fine CMC at mild conditions. The preparation of CMC was conducted

using sodium hydroxide solution in sequential reactions involve MCA species at desired conditions. CMC has been successfully synthesized in a batch reactor with DS value of 0.15 to 0.7 and excellent purity of 99.3% at pH 7. The maximum DS of 0.7 was obtained using 40% monochloroacetate (MCA) and 30% NaOH. The samples of CMC were characterized by SEM and FT-IR spectroscopic techniques. The synthesized CMC was easily dissolved in water and was found to be of pharmaceutical and food grade.

Joshi *et al.*, (2015) studied the synthesis and characterization of CMC from mixed office waste papers (MOW). After deinking, the cellulosic pulps of MOW papers were functionalized with carboxymethyl group to give CMC of high value of DS. The carboxymethylation process was completed using NaOH and ClCH<sub>2</sub>COONa in an alcoholic medium. Maximum DS value of 1.07 was obtained by conducting the reaction process at 50 °C for 3 hours using solutions of 0.094 M NaOH and 0.108 M ClCH<sub>2</sub>COONa.

## 1.7 Objectives

The main objectives of this study were:

- To extract cellulose from rice husk.
- To convert the extracted cellulose to CMC.
- To optimize the carboxymethylation conditions for the production of CMC of high degree of substitution (DS).
- To investigate and characterize the isolated cellulose and as-synthesized CMC.
- To investigate some rheological properties of as-synthesized CMC.

# **Chapter Two**

## **Experimental**

## **Chapter Two**

### **Experimental**

#### **2.1 Materials and Equipment**

Distilled water, Clorox (Aqueous solution of 5% Sodium hypochlorite), Sodium Hydroxide pellets (Min assay: 97%, CDH, India), Iso-propanol (Min assay: 99.0%, ALPHA CHEMIKA, India), n-Butanol (Min assay: 99.0%, ALPHA CHEMIKA, India), Ethanol (Min assay: 99.9%, DUKSAN, Korea), Methanol (Min assay: 99.5%, ALPHA CHEMIKA, India), Mono chloro acetic acid (Min assay: 99.0%, BDH, England), Acetic acid (Min assay: 99.9%, ALPHA CHEMIKA, India), Nitric acid (Min assay: pure 69-72%, LOBA Chemie, India), Hydrochloric acid (Min assay: 35-38%, LOBA Chemie, India), Phenolphthalein, Potassium bromide (FT-IR grade, CDH, India ), PAC-RV (Min assay: 99%, API, Dubai – U.A.E). PAC-LV (Min assay: 99%, API, Dubai – U.A.E), Rice husk, Extracted cellulose, as- Synthesized CMC.

Manual Mortar and Pestle, Oven, Magnetic stirrer, Water bath, Litmus papers, Sensitive balance, Transparent disk, Hamelton mixer, Viscometer cup.

#### **2.2 Synthesis Methods**

##### **2.2.1 Preparation of the sample**

The rice husks raw materials were collected from Gezira State (Sudan) and were washed and air-dried then ground using manual mortar and pestle.

##### **2.2.2 Extraction of cellulose from rice husk fibers**

The sample was soaked with suitable quantity of water in 1L beaker for about 30 minutes then decanted after that, the rice husk fibers were cooked in 1 M NaOH at ratio of sample to solvent 1:20 (w/v) for one hour at 80 °C several times. The obtained

slurry was filtered then washed using distilled water and bleached with white Clorox solution (contains 5% NaOCl) for one hour at 80 °C four times. The bleached cellulose was washed again using distilled water until the order of hypochlorite could no longer be detected then washed with ethanol and dried at 60 °C in the oven (Adinugraha and Marseno, 2005)

### **2.2.3 Synthesis of sodium carboxymethylcellulose**

A quantity of 2.5 grams of extracted cellulose was suspended in 80 ml of (iso-propanol, n-Butanol, Ethanol, Methanol) and stirred continuously. 10 mL of aqueous NaOH solution (20%, 30%, 40%) (w/v) were added drop wise over a period of 30 min. The mixture was stirred for one hour at room temperature. (1.5g, 2.5g, 3.5g) of mono chloro acetic acid were dissolved in 10 mL of solvent (iso propanol, n-Butanol, Ethanol, Methanol) and were added to the alkalized cellulose, the temperature was raised to 55 °C. The reaction was allowed to continue for (2, 3, 4 hour) then neutralized with 90% acetic acid and filtered. The obtained CMC solid was washed by 70% ethanol five times to remove undesirable by products then dried at 60 °C in an oven (Adinugraha and Marseno, 2005).

For purification, the dried CMC was dispersed on 60 mL of 95% ethanol and stirred for 5 minutes. Then 10 mL of 2M nitric acid were added and the mixture was agitated for 2 min. The mixture was then heated to boiling for 5 min and agitated further for 15 min and left to settle. After the solution had settled, the supernatant liquid was filtered and discarded. The precipitate was washed with 80 mL of 95% ethanol and further wash was applied with hot 80% ethanol at 60 °C, until the acid and salts were removed. The precipitate was washed with methanol and transferred to a beaker and heated until the alcohol was removed. The beaker with the precipitate was dried in the oven at 105 °C for three hour (Pushpamalar *et al.*, 2006).

## 2.2.4 Synthesis of sodium carboxymethylcellulose at optimum conditions

For fabrication of CMC at optimum reaction conditions all the procedure mentioned in section 2.2.3( pg. 45) was followed, at 55°C, 2.5g MCAA, 3h, 30% NaOH and iso-propanol alcohol which were found to optimum conditions (Pushpamalar *et al.*, 2006).

## 2.3 Characterization Methods

### 2.3.1 Infrared spectroscopy

The infrared spectroscopic analysis was carried out for isolated cellulose and as-synthesized CMC materials using the KBr method. The samples were dried in an oven at 60 °C. Few milligrams of the sample were mixed with sufficient amount of KBr, and compressed to a form a transparent disk. The infrared spectra of samples were recorded with Fourier transform infrared spectrometer, FT-IR, Shimadzu (model 8400S - Japan) between 400 - 4000  $\text{cm}^{-1}$  (Pushpamalar *et al.*, 2006).

### 2.3.2 Determination of degree of substitutions

Absolute values of degree of substitution (DS) of all samples were determined by back titration method. An amount of 0.25 g of as- synthesized CMC was weighed in 250 mL conical flask and 50 mL distilled water were added and stirred. A volume of 12.5 mL of 0.5 N NaOH aqueous solution was added and boiled for about 15 min, and then the hot solution was titrated against a solution of 0.3 N hydrochloric acid using phenolphthalein as an indicator. The carboxy methyl content and the degree of substitution were calculated based on the equations 2.1 and 2.2.

$$\text{Carboxy methyl content (\%CM)} = [(V_o - V_n) \times N \times 0.058 \times 100] / M \quad (2.1)$$

$$\text{DS} = 162 \times \% \text{CM} / [5800 - (57 \times \% \text{CM})] \quad (2.2)$$

Where  $V_o$  = the volume (in mL) of HCl used to titrate the blank.

$V_n$  = the volume (in mL) of HCl used to titrate the sample material.

$N$  = normality of HCl used,  $M$  = the amount (g) of sample taken for analysis. 58 = the molecular weight of carboxymethyl group (Pushpamalar *et al.*, 2006).

### 2.3.3 X-ray diffraction analysis

A quantity of about 3g from the as-synthesized CMC was taken separately and ground finely. The X-R diffractometer instrument (Asset No 00921, Brand and model No MP210, serial No 20029001) was operated and the diffraction pattern was recorded. (Adinugraha and Marseno, 2005).

## 2.4 Rheological studies

### 2.4.1 Determination of plastic viscosity, apparent viscosity and yield point

Concentrations of 3.5 ppb and 7 ppb aqueous solutions from the synthesized- CMC, PAC-LV and PAC-RV were made and agitated for 5 minutes by Hamelton mixer in 700 mL Viscometer cup. The cup of each was located under sleeve of Fann model 355A Viscometers. The rotor sleeve was raised and lowered until it was immersed in the sample to scribed line. The sample was stirred for 5 seconds at 600 RPM and then at 300, 200, 100, 6 and 3 RPM. The dial reading and RPM were recorded after the dial reading stabilized. The rheological parameters were calculated depending on equations 2.3, 2.4 and 2.5.

#### Plastic viscosity (in centipoise-up):

$$\text{Plastic viscosity } (\mu_P) = 600 \text{ RPM reading} - 300 \text{ RPM reading} \quad (2.3)$$

#### Apparent viscosity (in centipoise-up):

$$\text{Apparent viscosity } (\mu_a) = \frac{600 \text{ Rpm Reding}}{2} \quad (2.4)$$



**Yield point (in 1b/100 ft<sup>2</sup>):**

$$\text{Yield point (YP)} = 300 \text{ RPM reading} - \text{plastic viscosity} \quad (2.5)$$

(Pete, 2003).

**2.4.2 Filter loss**

Well agitated water solution of synthesized CMC of 7 ppb concentration was introduced into cup assembly and clamped to the filter press frame. A pressure of 100 PSI was applied at room temperature for 30 minutes. The filtrate was collected by graduated cylinder and measured (Pete, 2003).

# **Chapter Three**

## **Results and Discussion**

## Chapter Three

### Results and Discussion

#### 3.1 Yields of extracted Cellulose and as-synthesized CMC

The cellulose was extracted from rice husk fibers and then converted to carboxymethylcellulose (CMC) material by carboxymethylation using monochloro acetic acid (MCAA) as etherification agent. The results of the extracted cellulose and the produced CMC materials are presented in Table 3.1.

**Table 3.1:** The results of obtained cellulose and CMC at optimum condition:

<b>Weight of rice husk fibers (g)</b>	<b>Percentage of obtained cellulose (%)</b>
100	59
<b>Weight of cellulose (g)</b>	<b>Weight of CMC (g)</b>
2.5	4.5

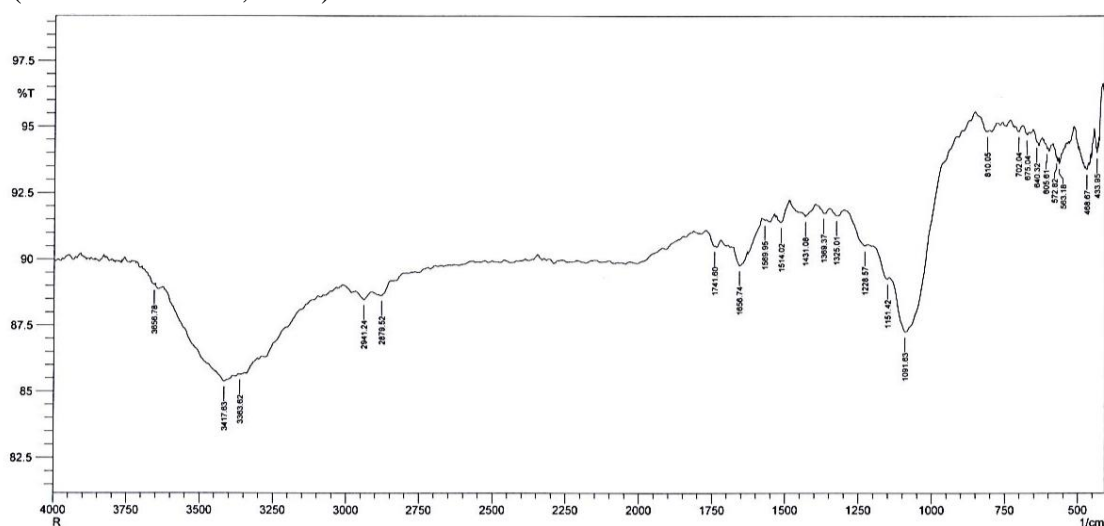
It is very obvious that raw rice husk fibers gave yield of cellulose almost 60%. This percentage is consistent with the values reported in literature. As it is already known, cellulose usually occurs in the cell wall of plants and is generally associated with other substances such as lignin and hemicellulose, which make it difficult to find in pure form. Plants contain on a dry basis between 40 – 55% cellulose, 15 – 35% lignin and 25 – 40% hemicellulose.

The result of this study showed the weight of as-synthesized CMC was 4.5 g, which is considered almost double that of cellulose (2.5g). This drastic increment in cellulose weight after conversion to CMC could be assigned to the attachment of carboxymethylcellulose substituents to cellulose macro-molecules. According to theoretical calculations, this weight of the produced CMC can be twice or more than

the weight of cellulose precursor. Hence, this result might indicate a lower value of DS (0.42) of the produced material. Deep study on the structure of cellulose and CMC is needed to support this rational assumption.

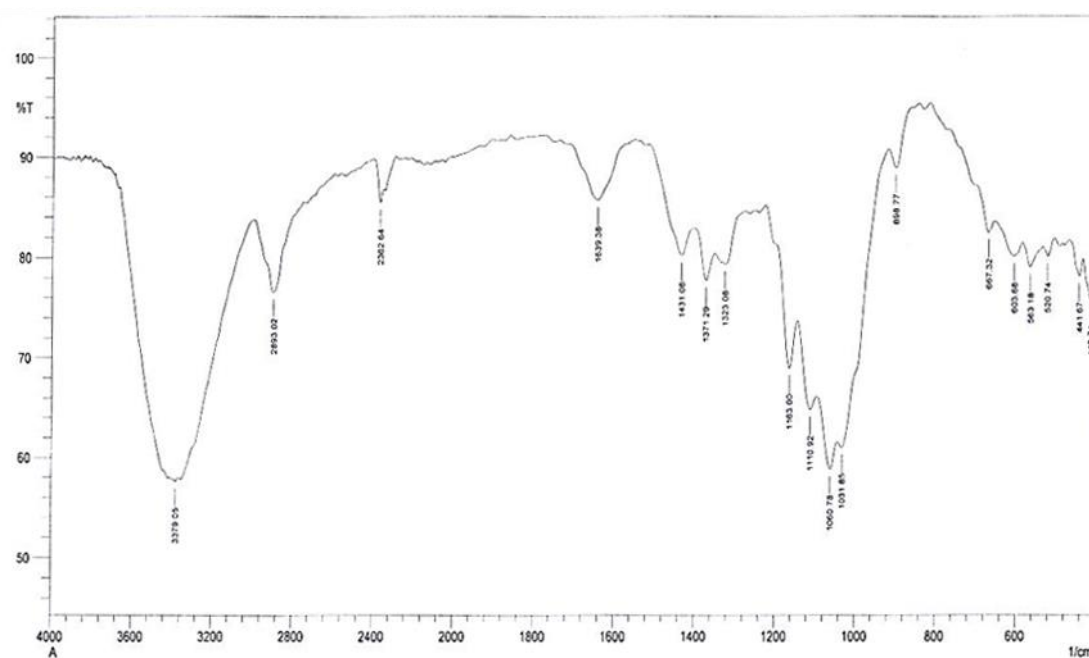
### 3.2 FT-IR spectroscopic analysis

FT-IR spectroscopy was used to indicate the extraction of pure cellulosic material from rice husk. It was also used to examine the changes in the chemical composition of the cellulose fibers as a result of carboxymethylation reaction. The FT-IR spectra of rice husk fiber, cellulose and as-synthesized CMC were obtained according to the method prescribed earlier in section 2.3.1 (pg. 46). The notable peak at  $1741\text{ cm}^{-1}$  that is found in the spectrum of the untreated rice husk fibers (Fig. 3.1) can be attributed either to the acetyl and ester group of the hemicellulose. Whereas, the peak at frequency of  $1514\text{ cm}^{-1}$  is due to  $\text{C}=\text{C}$  stretching vibration of the aromatic rings of lignin. The peak at  $1431\text{ cm}^{-1}$  is assigned to  $-\text{CH}_2-$  bending vibration, and peaks in the region from  $1228 - 810\text{ cm}^{-1}$  are due to  $-\text{C}-\text{O}-$  stretching. The  $-\text{C}-\text{O}-$  pyranose ring skeletal vibration gives a notable band at  $1091\text{ cm}^{-1}$  (Elanthikkal *et al.*, 2010).



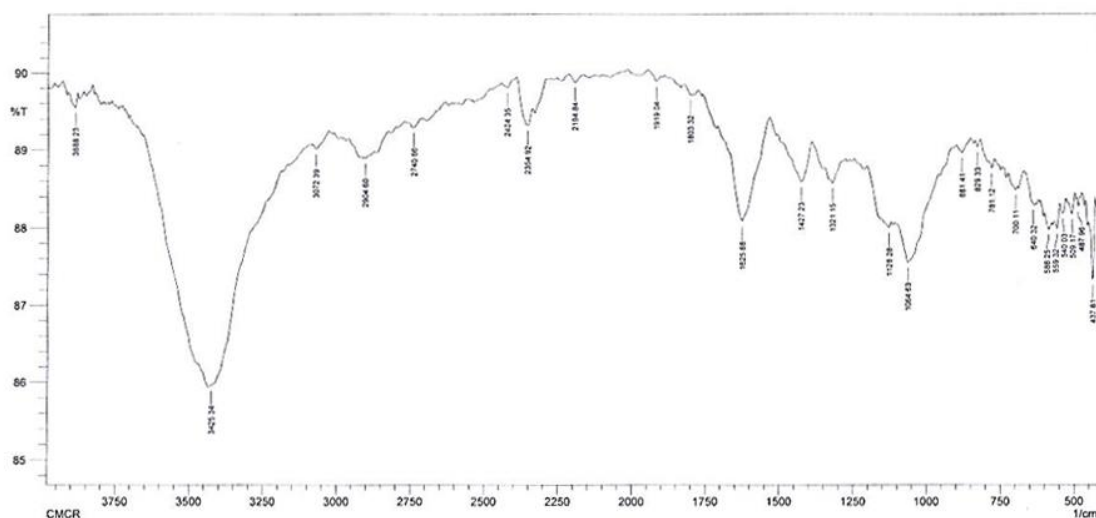
**Figure 3.1:** The FT-IR spectrum of untreated rice husk fibers

Figure 3.2 shows the FT-IR spectrum of cellulose extracted from rice husk fibers. It is evident that the broad absorption band at  $3379\text{ cm}^{-1}$ , is due to the stretching frequency of the  $\text{-OH}$  group as well as intra-molecular and intermolecular hydrogen bonds. The band at  $2893\text{ cm}^{-1}$  is due to  $\text{C - H}$  stretching vibration, whereas, the bands of frequencies centered at  $1431$  and  $1323\text{ cm}^{-1}$  are assigned to  $\text{-CH}_2$  scissoring and  $\text{-OH}$  bending vibrations, respectively. The band at  $1060\text{ cm}^{-1}$  is due to  $\text{OCH - O - CH}_2$  stretching (Kondo, 1997). Figure 3.2 also shows the absence of carbonyl group ( $\text{C=O}$ ) of hemicellulose at  $1741\text{ cm}^{-1}$  and aromatic  $\text{-C = C -}$  stretching of the aromatic ring of lignin at  $1515\text{ cm}^{-1}$  indicating an almost pure cellulosic material was successfully extracted from rice husk (Kondo, 1997).



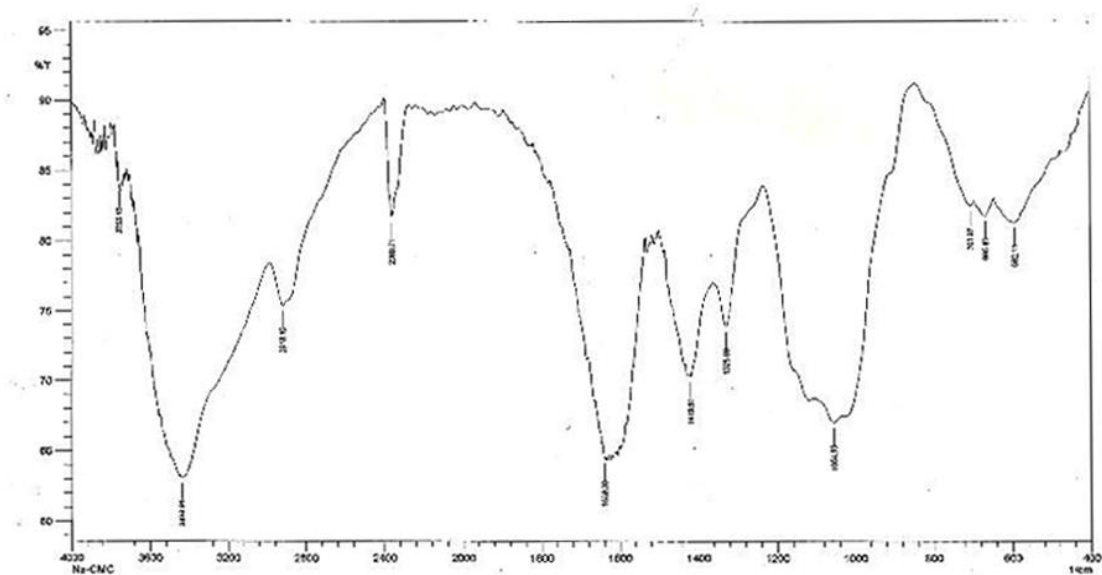
**Figure 3.2:** The FT-IR spectrum of cellulose extracted from rice husk fibers

The FT-IR spectrum of the as-synthesized CMC with DS value of 0.42 is depicted in Figure 3.3. The peaks at wave number of 1625-1427  $\text{cm}^{-1}$  indicated of presence of carboxymethyl substituent. It is clearly evident that a broad absorption band at 3425  $\text{cm}^{-1}$  is due to stretching frequency of  $-\text{OH}$  group and a band at 2904  $\text{cm}^{-1}$  attributable to C-H stretching vibration. The presence of a new and strong absorption band at 1625  $\text{cm}^{-1}$  confirms the presence of  $\text{COO}-$  group. The bands around 1427 and 1321  $\text{cm}^{-1}$  are assigned to  $-\text{CH}_2$  scissoring and  $-\text{OH}$  bending vibration, respectively. The band at 1064  $\text{cm}^{-1}$  is due to  $>\text{CH}-\text{O}-\text{CH}_2$  stretching (Biswal and Singh, 2004).



**Figure 3.3:** The FT-IR spectrum of as-synthesized CMC of optimum DS (0.42)

Figure 3.4 shows the FT-IR spectrum of commercial CMC, which shows the typical absorption bands of the cellulose backbone as well as the presence of the carboxymethyl groups at 1620 and 1423  $\text{cm}^{-1}$ . It is clearly evident that the broad absorption band at 3433  $\text{cm}^{-1}$  is assigned to the stretching frequency of  $-\text{OH}$  group, whereas, the band at 2923  $\text{cm}^{-1}$  is attributable to C-H stretching vibrations. The presence of a new and strong absorption band at 1620  $\text{cm}^{-1}$  confirms the presence of  $\text{COO}^-$  group. The bands around 1423 and 1326  $\text{cm}^{-1}$  are assigned to  $-\text{CH}_2$  scissoring and  $-\text{OH}$  bending vibration, respectively. The band at 1056  $\text{cm}^{-1}$  is due to  $\text{OCH} - \text{O} - \text{CH}_2$  stretching (Biswal and Singh, 2004). This spectrum was found almost similar to that shown in Figure 3.3, with minor differences such as, absence of peaks at wave numbers of 2194 and 2354  $\text{cm}^{-1}$  in commercial CMC. These extra peaks in synthesized CMC material could solo be assigned to impurities or combination band from waters (Adinugraha and Marseno, 2005).

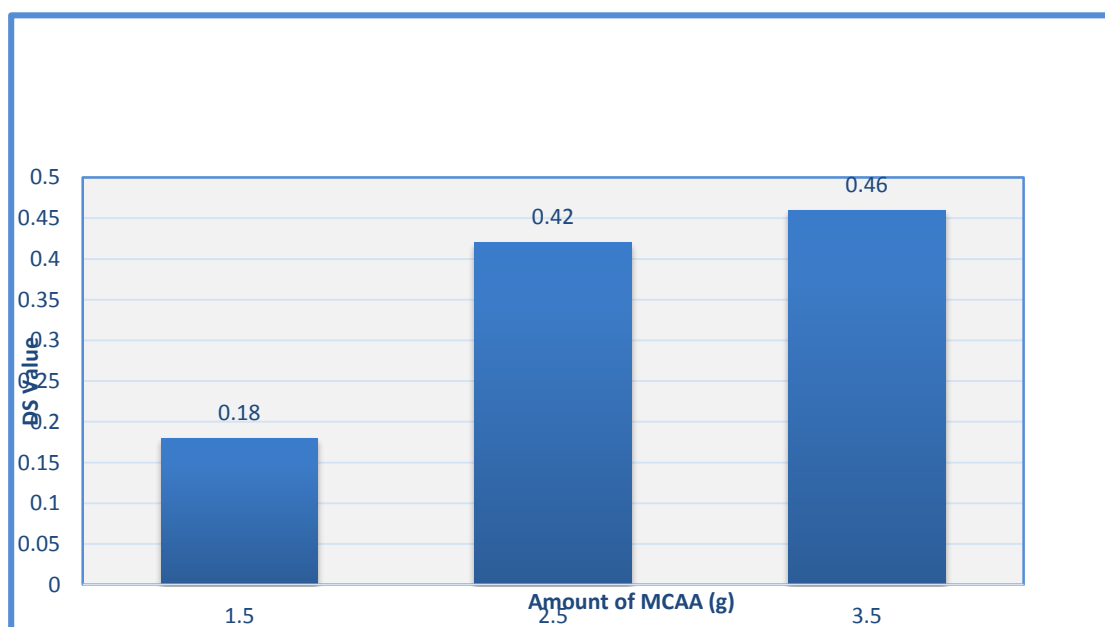


**Figure 3.4:** The FT-IR spectrum of commercial CMC

### 3.3 Effects of different parameters on carboxymethylation reactions

#### 3.3.1 Effect of amounts of Monochloroacetic acid (MCAA)

The amount of MCAA was varied to study its effect in the value of DS (section 2.2.3, pg. 45). As shown in Figure 3.3, maximum DS value of 0.46 was obtained when 3.5 g of MCAA were used when other effective parameters were kept constant i.e, 2.5 g of cellulose, 30% NaOH alkalization solution, 55°C reaction temperature and iso propanol solvent. The general trend shows there is an increase in the value of DS with increasing the amount of MCAA. This proportional relationship could be attributed to the availability of acetate ions at higher concentrations in the proximity of cellulose molecules (Bhattacharyya *et al.*, 1995). However, only minor reduction in DS (0.42) was observed when the amount of MCAA was minimized to ~ 70% (2.5 g), hence the amount of 2.5 g was considered as an optimum weight to study the subsequent parameters.

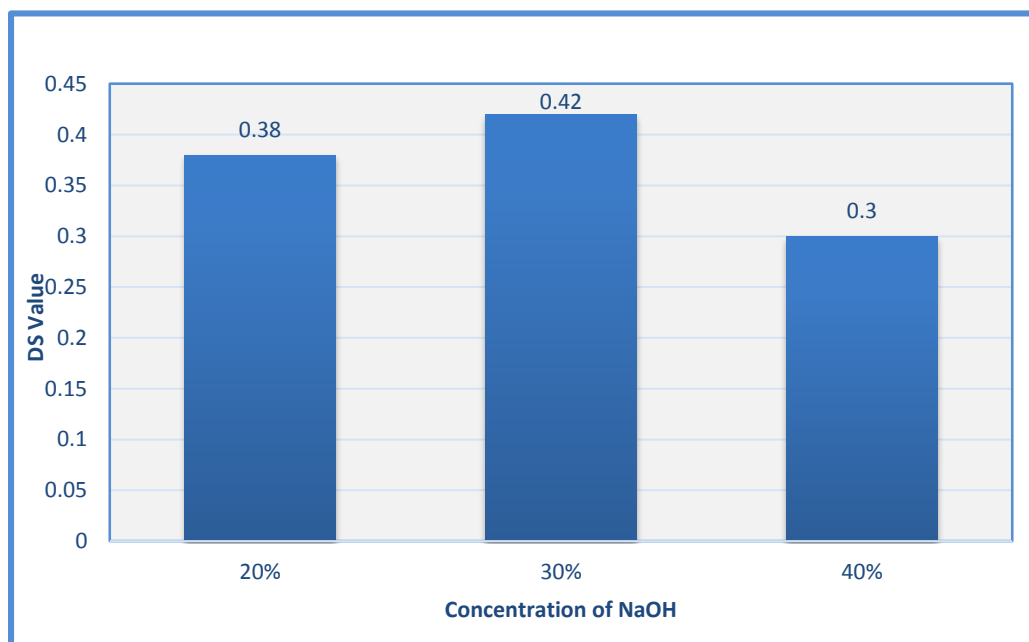


**Figure 3.5:** The effect of various amounts of MCAA on the DS value



### 3.3.2 Effect of the concentration of sodium hydroxide solution

The effect of the concentration of NaOH aqueous solution on the value of DS was also studied while neutralizing the effect of other parameters. It is depicted in Figure 3.6 that as the concentration of NaOH aqueous solution was increased the DS value increased as well. A maximum value of DS (0.42) was obtained when a concentration of 30% NaOH was applied, but when the concentration of NaOH was increased beyond 30%, an obvious decrease in DS value was observed. The results obviously indicated the significance of NaOH in the carboxymethylation process at limited levels. However, when its concentration goes beyond these levels, it could promote the degradation of the glycosidic bonds of the cellulose forming sodium glycolate by product. The same phenomenon was observed and reported by Pushpamalar *et al.* (2006).

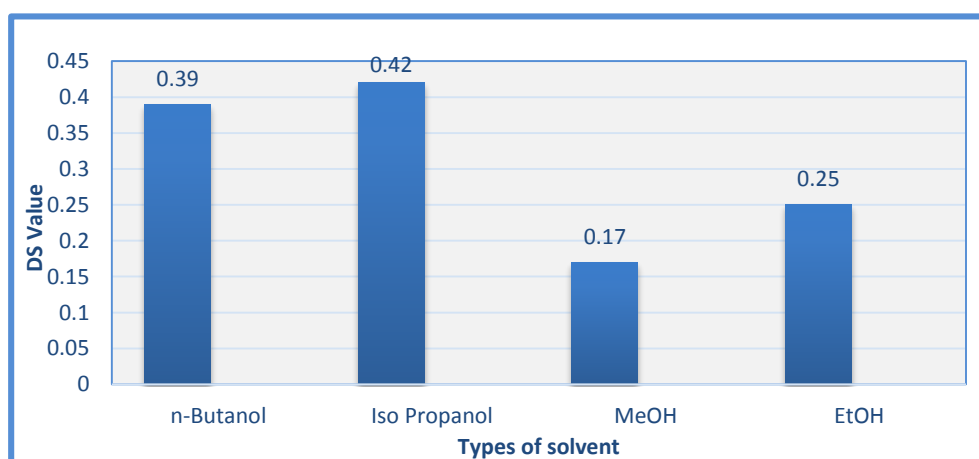


**Figure 3.6:** The Effect of various concentrations of NaOH on the DS value

### 3.3.3 Effect of various solvents

The effect of solvent on the DS was studied at optimum reaction conditions (i.e. at 55°C and 2.5 g of MCAA) using four types of alcoholic solvents. The highest value of DS (0.42) was obtained when isopropanol was applied as reaction medium. It is already known that the role of the solvent in the carboxymethylation reaction is to provide miscibility and accessibility of the etherifying reagent (MCAA) to the reaction centers of cellulose chain rather than glycolate formation (Toğrul and Arslan, 2003). Therefore, it is considered promoter for CMC and inhibitor for glycolate formation (Toğrul and Arslan, 2003).

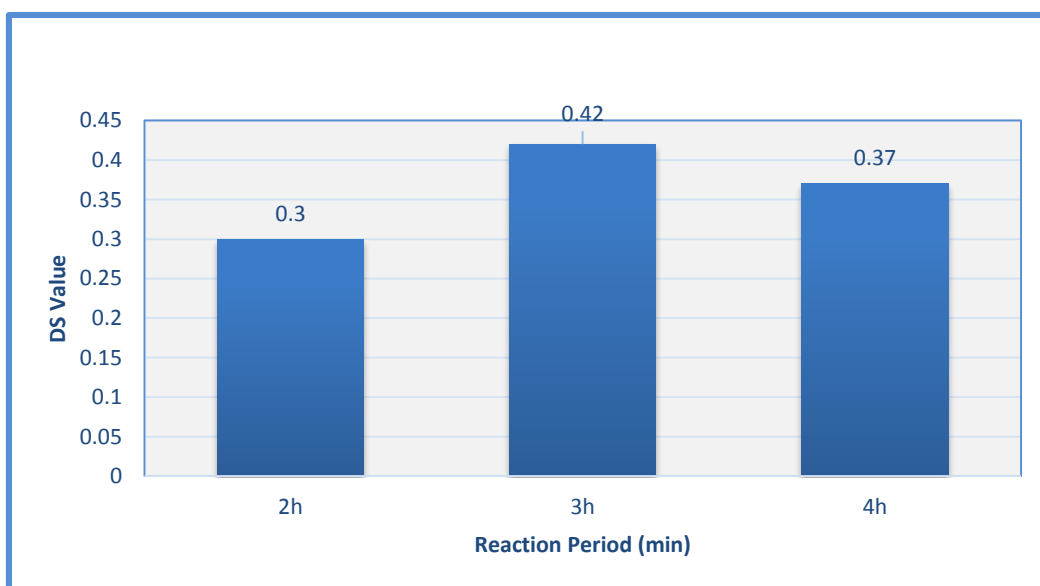
The divergences in the extent of carboxymethylation in the presence of some alcohols can be illustrated by taking in consideration their solvent polarities and stereochemistry. The reaction adequacy increases as the polarity of the solvent decreases (Barai et al., 1997). Figure 3.7 shows the values of DS over various alcohols used for the carboxymethylation reactions. The trend in DS values was in a good agreement with the literature but the solvents isopropyl alcohol and n-butyl alcohol, with almost similar polarity, did not produce the CMC with the same DS value. Isopropyl alcohol was the best choice which is in agreement with the research reports issued by Bhattacharyya et al. (1995) and Khalil et al. (1990).



**Figure 3.7:** The effect of various solvents on the DS value

### 3.3.4 Effect of reaction period

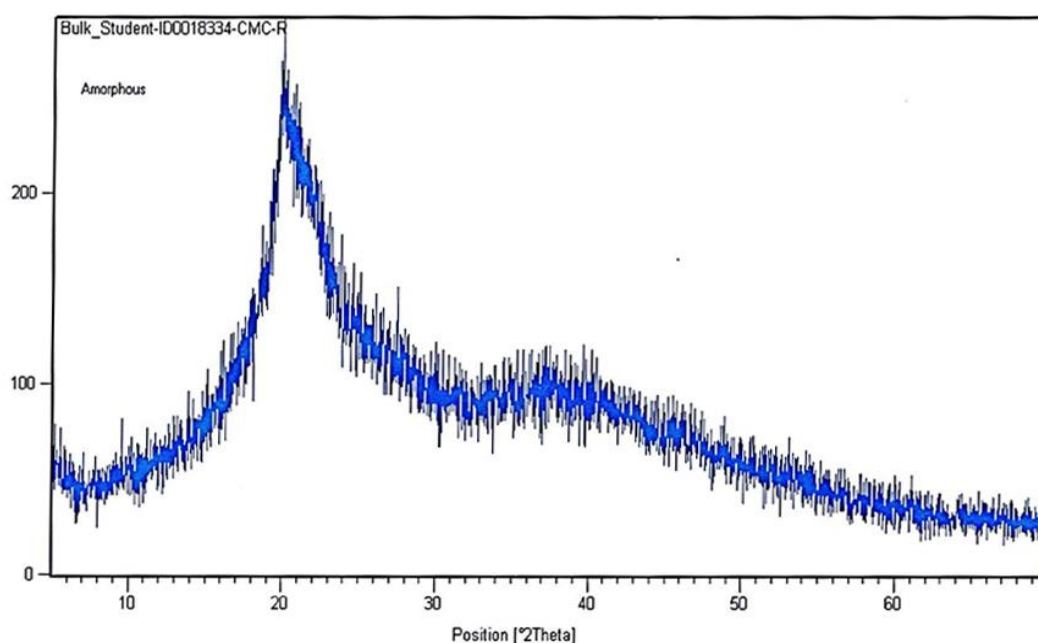
The influence of time on the value of DS was also considered in the carboxymethylation of extracted cellulose at optimum conditions. As illustrated in Figure 3.8, it is very clear that the value of DS increased with reaction time until three hours (180 min) then decreased beyond this time. The depression in DS could be assigned to the degradation of glycosidic bonds. This degradation was expected when such high concentration of NaOH was applied. It occurs at low rates but its effect accumulated with time and hence became obvious over long reaction periods (Pushpamalar *et al.*, 2006).



**Figure 3.8:** The effect of various reaction period on the DS value

### 3.4 The XRD of pattern of as- synthesized CMC

The XRD diffraction analysis was applied to the as-synthesized CMC material of an optimum value of DS (0.42). It is well known in literature that the arrangement of pure cellulose in a crystalline form was assisted by inter- and intra-molecular hydrogen bonds in the macro molecule (Elanthikkal *et al.*, 2010). As depicted in Figure 3.9, this arrangement, i.e. degree of crystallinity, decreased as a result of treatment with 30% NaOH aqueous solution. It was further reduced after cleaving the remaining hydrogen bonds through attacking by carboxy methyl species at hydroxyl positions in the cellulose molecule. XRD pattern of CMC (DS 0.42) presented in Figure 3.9 shows a main broad peak of CMC at 22° a Bragg angle of (002) plane. The absence of sharp peaks at lower or higher angles indicates the amorphous nature of CMC material (Adinugraha and Marseno, 2005).



**Figure 3.9:** The XRD of pattern of as- synthesized CMC of the highest DS

### 3.5 Rheological studies

Sodium carboxymethylcellulose (Na-CMC) is primarily a fluid loss reducer, it also produces viscosity in fresh water and saline muds whose salt content does not exceed 50,000 mg/L. CMC is along chain molecule that can be polymerized to produce different molecular weights and in effect, available in different viscosity grades. It is generally available in a high or low viscosity type. Either grade provides effective fluid- loss control. The temperature limit of CMC is 121 °C, and is not subjected to bacterial degradation (Kumar *et al.*, 2003).

#### 3.5.1 RPM readings

Fann VG meter was used as instrument to obtain RPM readings for rheological measurements. The sample is contained in the annular space between the two concentric cylinders .There is a small gap and the distance of the gap will determine the constants to obtain shear rate and shear stress. Six shear rates were set by the apparatus in revolutions per minute: 3 rpm, 6 rpm, 100 rpm, 200 rpm, 300 rpm and 600 rpm. The reading is taken using the highest rpm so that the viscosity will not skew due to the gel strength when a low rpm is set. The outer cylinder rotates at a constant rate (revolutions per minute) which is set.

The results of RPM are tabulated in Tables 3.2 and 3.3.

**Table 3.2:** RPM readings for 3.5 ppb aqueous solutions of carboxycellulosic materials at room temperature

Materials	RPM	600	300	200	100	6	3
As-synthesized CMC	Readings	25.7	14.3	12.0	8.0	2.0	1.5
PAC – LV		18.0	10.0	6.0	3.0	1.0	0.4
PAC – RV		69.0	47.0	38.0	25.0	4.0	2.0

**Table 3.3:** RPM readings for 7 ppb aqueous solutions of carboxycellulosic materials at room temperature

Materials	RPM	600	300	200	100	6	3
As-synthesized CMC	Readings	73.0	53.5	47.2	30.0	7.0	5.0
PAC – LV		45.0	24.0	17.0	9.0	1.0	0.3
PAC – RV		190.0	145.0	124.0	90.0	18.0	11.0

The RPM readings of as-synthesized and commercial PAC-LV and PAC-RV are presented in Tables 3.2 and 3.3. The results show an obvious increase in RPM readings with increasing the concentration of CMC. This increase is an indicative of increase in the viscosity of the CMC aqueous solution refers (Elemam *et al.*, 2014).

### 3.5.2 Viscosities and Yield points

The results of viscosity and yield points or 3.5 ppb solutions of as-synthesized CMC and commercial PAC materials are listed in Table 3.4. The as-synthesized CMC showed a plastic viscosity of 11.4 centipoise-up, apparent viscosity of 12.8 centipoise-up and yield point of 2.9 lb/100 ft<sup>2</sup>. The PAC-LV showed a Plastic viscosity of 8.0 centipoise-up, apparent viscosity of 9.0 centipoise-up and yield point of 2.0 lb/100 ft<sup>2</sup>. Whereas, PAC-RV showed a Plastic viscosity of 22.0 centipoise-up, apparent viscosity of 34.5 centipoise-up and yield point of 25.0 lb/100 ft<sup>2</sup>.

**Table 3.4:** Plastic viscosity ( $\mu_p$ ), apparent viscosity ( $\mu_A$ ) and Yield point (YP) for 3.5 ppb aqueous solution of carboxycellulosic materials

Material	$\mu_p$ (CP)	$\mu_A$ (CP)	YP (lb/100 ft <sup>2</sup> )
CMC	11.4	12.8	2.9
PAC – LV	8.0	9.0	2.0
PAC – RV	22.0	34.5	25.0

When the concentration of as-synthesized CMC, PAC-LV and PAC-RV was enhanced to 7 ppb, drastic increments in rheological parameters and yield points were observed. The results are listed in Table 3.5, the as synthesized CMC showed plastic viscosity of 19.5 centipoise-up, apparent viscosity of 36.5 centipoise-up, yield point of 34.0 lb/100 ft<sup>2</sup>. The PAC-LV showed a Plastic viscosity of 21.0 centipoise-up, apparent viscosity of 22.5 centipoise-up and yield point of 3.0 lb/100 ft<sup>2</sup>. And PAC-RV also showed a Plastic viscosity of 45.0 centipoise-up, apparent viscosity of 95.0 centipoise-up and yield point of 100.0 lb/100 ft<sup>2</sup>. And filter loss of the as- synthesized CMC was found to be 24.8 cm<sup>3</sup> per 30 min.

**Table 3.5:** Plastic viscosity ( $\mu_p$ ), apparent viscosity ( $\mu_A$ ) and Yield point (YP) for 7 ppb aqueous solution of carboxycellulosic materials

<b>Material</b>	$\mu_p$ (CP)	$\mu_A$ (CP)	YP (lb/100 ft <sup>2</sup> )
<b>CMC</b>	19.5	36.5	34.0
<b>PAC – LV</b>	21.0	22.5	3.0
<b>PAC – RV</b>	45.0	95.0	100.0

We can conclude from the results of Tables 3.4 and 3.5 that, apparent viscosity, plastic viscosity and yield point increase with increase in concentration of CMC, PAC- LV and PAC- RV. For as- synthesized CMC material, the reason for this is that the carboxy group in CMC causes water dispersion, as result, friction between particles increases, and the shearing stress required to induce unit rate of shear increases and hence apparent viscosity, plastic viscosity and yield point increase. The other reason is that the dissociation of Na<sup>+</sup> from CMC creates negative sites along the chain. Mutual repulsion between the charges causes the randomly coiled chains to stretch linearly, thereby increasing viscosity. Gel strength increases at the beginning and becomes stable at higher concentrations of CMC (Kumar *et al.*, 2003).

### **3.5.3 Filter loss**

According to fundamental theory, the filter loss decreases while the concentration of CMC increases (Elemam *et al.*, 2014). The filter loss of the as-synthesized CMC (7 ppb) was found to be 24.8 mL per 30 minutes. Whereas, the standard filter loss is 10 cm<sup>3</sup> per 30 minutes, hence the as-synthesized CMC can be classified as a viscofier rather than filter loss controller.



## Summary

The sodium (CMC) was synthesized successfully from carboxymethylation of cellulose isolated from rice husk using pure isopropanol as a solvent. The effect of reaction time and amount of monochloro acetic acid (MCAA) and concentration of NaOH were investigated. The optimum conditions were attained at reaction temperature of 55 C, sodium concentration of 30% and amount of MCAA of 2.5 g per 2.5 g of cellulose and reaction period of 3 h. The CMC product at optimum conditions was found to have a DS value of 0.42. The CMC fabricated from rice husk was characterized by FT-IR spectrometer and XRD diffractometer. Rheological studies were conducted for the as-synthesized CMC and commercially available carboxy methylated cellulosic materials (i.e. PAC-LV and PAC-RV). The results of viscosity showed that, the viscosity of as-synthesized CMC material is higher than that of PAC-LV but lower than that of PAC-RV. The variation could be attributed to the lower value of DS (0.42) associated with the synthesized material.

### **Suggestion for further research work**

According to the findings of this research, CMC can be prepared from rice husk at reasonable conditions. However, more studies are recommended to overcome or minimize the problems associated with fabrication of CMC from rice husk. These problems can be summarized as follow:

- ✓ Study the possibility of introducing some chemicals to leach out all impurities.
  
- ✓ The possibilities of using minimum quantity of (MCAA) (minimize the cellulose/MCAA molar ratio).
  
- ✓ Study the possibility of getting CMC material of high DS from reactions in the presence of cheaper and less hazardous alcohols such as ethanol.
  
- ✓ Deep investigations on the effect of temperature are also needed for the possibility of conducting the reaction at lower temperatures.

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