



بسم الله الرحمن الرحيم

Sudan University of Science and Technology



College of Graduate Studies

**Synthesis and Characterization of Carboxymethylcellulose
from Wheat Stalks**

تخليق وتشخيص كاربوكسي ميثيل السليلوز من سيقان القمح

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

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الآيه

بسم الله الرحمن الرحيم

قال تعالى:

(لَقَدْ أَرْسَلْنَا رُسُلَنَا بِالْبَيِّنَاتِ وَأَنْزَلْنَا مَعَهُمُ الْكِتَابَ وَالْمِيزَانَ
لِيَقُومَ النَّاسُ بِالْقِسْطِ وَأَنْزَلْنَا الْحَدِيدَ فِيهِ بَأْسٌ شَدِيدٌ وَمَنَافِعُ
لِلنَّاسِ وَلِيَعْلَمَ اللَّهُ مَنْ يَبْصُرُهُ وَرُسُلَهُ بِالْغَيْبِ إِنَّ اللَّهَ قَوِيٌّ
عَزِيزٌ)

سورة الحديد الآية (25)

صدق الله العظيم

Dedication

To

My parents,

Husband,

Brother,

Sisters and

My best friend Reem Taj Elsir

Acknowledgment

First of all I would like thank **Allah**, Almighty for helping me 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 advice in this project. My deepest thanks are extended to **Dr. Essa Esmail Mohammad Ahmed** for his unlimited support.

Thanks to my family and friends for their continue support.

Abstract

This study focuses on conversion of cellulose isolated from wheat stalks to carboxy methyl cellulose(CMC).This material has wide industrial applications especially as adriilling fluidin petroleum wells. Alkaline extraction method was used for isolating the cellulose from wheat stalks the isolated cellulose was etherified onto sodium CMC (Na-CMC) by monochloro acetic 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 yield was found to have a DS of 0.39.

The isolated cellulose and the as-synthesized CMC were characterized by FT-IR spectrometer and X-ray diffraction. The results indicated successful introduction of carboxy methyl group to the isolated cellulose. Rheological studies were conducted for the as-synthesized CMC and some commercially available carboxymethylated 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 (0.39) of the synthesized material. However, the results of apparent viscosity, plastic viscosity, yield points and filter loss together, demonstrated that synthesized CMC material could be classified as viscosifier rather than fluid loss controller.

المستخلص

هذه الدراسة تركز على إمكانية تحويل السليلوز المستخلص من سيقان القمح الى كاربوكسي ميثيل السليلوز هذه المادة ذات تطبيق واسع في الصناعة كمحاليل للحفر.

تم استخدام طريقه الإستخلاص بالقلويات لإستخلاص السليلوز من سيقان القمح. السليلوز المستخلص تمت أثيرته باستخدام حمض الخليك أحادي الكلور في وجود هيدروكسيد الصوديوم. بعض الظروف المثلى للتفاعل تمت دراستها وشملت تركيز هيدروكسيد الصوديوم ونوع المذيب وكمية حمض الخليك أحادي الكلور وزمن التفاعل ، لإنتاج مادة كاربوكسي ميثيل السليلوز بأعلى درجة استبدال. في الظروف المثلى للتفاعل، وجد ان مادة كاربوكسي ميثيل السليلوز المخلوق له درجة استبدال تساوي 0.39 .

شخص السليلوز المستخلص وماده كاربوكسي ميثيل السليلوز المخلوق بمطيافيه الأشعه تحت الحمراء وجهاز حيود الأشعه السينيه وهذه النتائج تشير الى أن عمليه إدخال مجموعات الكاربوكسي ميثيل للسليلوز المستخلص قد تمت بنجاح. أجريت دراسات عن الريولوجية (الإنسيابية) لمادة كاربوكسي ميثيل السليلوز المخلوق وبعض مشتقات كاربوكسي ميثيل السليلوز المتاحة تجاريا (PAC-RV and PAC-LV). أظهرت النتائج ان لزوجه ماده كاربوكسي ميثيل السليلوز المخلوق اعلى من مادة PAC-LV واقل من مادة PAC-RV. وهذا الإختلاف قد يعود الى قيمه المنخفضة لدرجه الإستبدال (0.39) للمادة التي تم تخليقها. من خلال نتائج اللزوجه 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

Term	Abbreviation
AGU	Anhydro glucose units
DP	Degree of polymerization
PG	Propyl gallate
IL	Ionic liquid
RTIL	Room-temperature ionic liquid
DS	Degree of substitution
CMC	Carboxy methyl cellulose
MCA	Mono chloroacetate
MCAA	Mono chloro acetic acid
PAC- LV	Polyanionic cellulose- low viscosity
PAC-RV	Polyanionic cellulose- high viscosity
PPb	Pound per barrel
RPM	Revolution per minute

Chapter One

Introduction and literature review

Chapter one

Introduction and Literature review

1.1 Wheat

Wheat is a cereal grain, originating from the Levant region of the Near East but now cultivated worldwide. Wheat was the second most-produced cereal in 2009, the world production in that year was 682 million tons, after maize (817 million tons), and with rice as a close third at 679 million tons (Hanji *et al.*, 2015). In 2013, world production of wheat was 713 million tons, making it the third most-produced cereal after maize (1,016 million tons) and rice (745 million tons). World trade in wheat is greater than for all other crops combined (Curtis, 2002). Globally, wheat is the leading source of vegetable protein in human food, having a higher protein content than other major cereals, maize (corn) or rice ("Nutrient data laboratory"). In terms of total production tonnages used for food, it is currently second to rice as the main human food crop and ahead of maize, after allowing for maize's more extensive use in animal feeds.

There are six wheat classifications: hard red winter, hard red spring, soft red winter, durum hard, hard white and soft white wheat. The hard wheat's have the highest gluten content and are used for making bread, rolls and all-purpose flour. The soft wheat is used for making flat bread, cakes, pastries, crackers, muffins, and biscuits. A high percentage of wheat production in the EU is used as animal feed, often surplus to human requirements or low-quality wheat (<http://www.feedipedia.org/node/223>).

Wheat is planted to a limited extent as a forage crop for livestock, although the straw cannot be used as feed (Henry and Morrison, 1922). Its straw can be used as a construction material for roofing thatch (Smith, 1995, Bridgwater, 1959). The whole grain

can be milled to leave just the endosperm for white flour. The by-products of this are bran and germ. The whole grain is a concentrated source of vitamins, minerals, and protein, while the refined grain is mostly starch.



Figure 1.1: Photographs of wheat corps and stalks

1.2 Cellulose

Cellulose is the most abundant compound in plants cell wall and woods. Payen (1842) was the first to determine the elemental composition of cellulose, that it had the empirical formula $C_6H_{10}O_5$ (Payen, 1842). It was also found that on hydrolysis it yields cellobiose and finally glucose. The nature of the bonds between the atoms in the glucose units and between the glucose units were recognized by Haworth, but it was Staudinger who reported a proof of the polymeric nature of the cellulose molecule (Hon, 1994). The chain-like, linear, macromolecular structure proposed by Haworth in the 1920s is generally, accepted, today Figure 1.2. The glucose units are linked together by β -(1, 4)-glucosidic bonds between carbon C_1 and C_4 of adjacent glucose units. Cellulose is actually a β -(1, 4)-polyacetal of cellobiose. The terminal hydroxyl groups at each end of the polymer chain differ in chemical nature. The C_1 hydroxyl is an aldehyde hydrate group with reducing activity and originates from the formation of the pyranose ring through an intramolecular hemiacetal reaction. The hydroxyl on carbon C_4 is an alcoholic hydroxyl

and therefore non-reducing. The β -glucosidic bonds are sensitive to hydrolytic attack. At the super molecular level cellulose chains are held together by hydrogen bonds. The resulting cellulose aggregates can be ordered as crystalline cellulose or unordered, amorphous cellulose. Several polymorphs of crystalline cellulose are known; cellulose I, II, III, and IV.

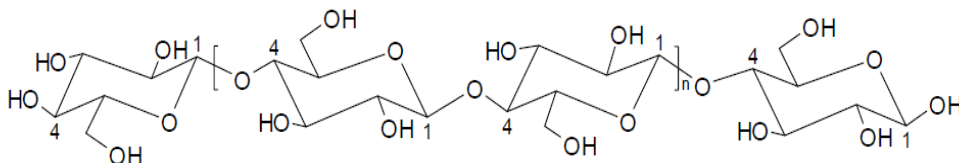


Figure 1.2: Cellulose, β -(1, 4)-polyacetal of cellobiose (Elg Christoffersson, 2004).

1.2.1 Occurrence

Cellulose is the most abundant polymer available worldwide with an estimated annual natural production of 1.5×10^{12} tons and considered as an almost inexhaustible source of raw material (Klemm *et al.*, 2005, Cao *et al.*, 2009). As a raw material of an enormous underutilized energy resource for the production of paper, panel products, chemicals, and other industrial products, cellulose has received much attention world wide. In general, nonwood materials such as cereal straws, grasses, and sugarcane bagass (SCB) are composed of single fiber cells that are only about 0.5–3.0 mm in length, whereas bast fibers such as flax can have single cells as long as 77 mm (Reddy and Yang, 2005). Cellulose is the main constituent of cell wall in lignocellulosic plant, and its content depends on the plant species, growing environment, position, growth, and maturity. Generally, cellulose content in lignocellulosic plant is 23–53% on a dry-weight basis, less

than that in cotton, which is almost made of pure fibrous cellulose (Knauf and Moniruzzaman, 2004).

1.2.2 Structure and Properties of Cellulose in the Solid State and in Solution

The hierarchical structure of cellulose, formed by the hydrogen bond network (Figure 1.3) between hydroxy groups, has been the subject of intense research for more than 100 years, marked with frequent controversy over results and a consistent supply of new insight (Atalla, 1987, osullivan, 1997, Zugenmaier, 2001). Directly from the beginning, progress was closely connected with the introduction and continued development of structure-analysis methods, such as X-ray diffraction, electron microscopy, high-resolution ^{13}C solid state NMR spectroscopy, and neutron diffraction analysis. Detailed analysis and modeling of the various structural levels of cellulose is essential for synthetic reaction procedures, and for controlled structure formation and properties of cellulose-based chemical products (man-made cellulosic).

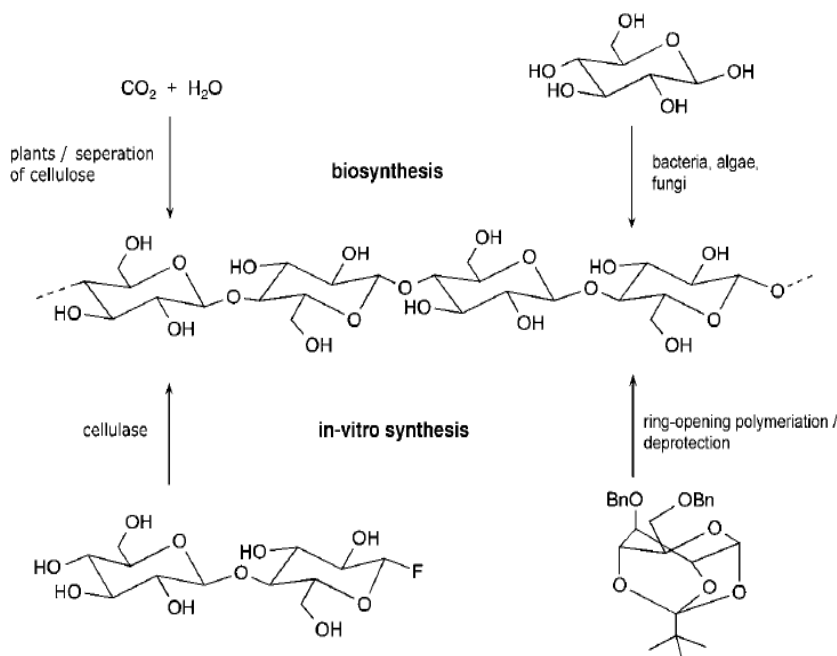


Figure 1.3: Principle pathways to cellulose formation (Klemm *et al.*, 2005).

1.2.2.1 Solid-State Structures of Native Cellulose

The molecular structure (Figure 1.4) shows hydroxy groups of β -(1, 4)-glucan cellulose are placed at positions C₂ and C₃ (secondary, equatorial) as well as C₆ (primary). The -CH₂OH side group is arranged in a trans-gauche (tg) position relative to the O5-C5 and C4-C5 bonds. As a result of the supra molecular structure of cellulose in the solid state, is represented by areas of both high order (crystalline) and low order (amorphous).

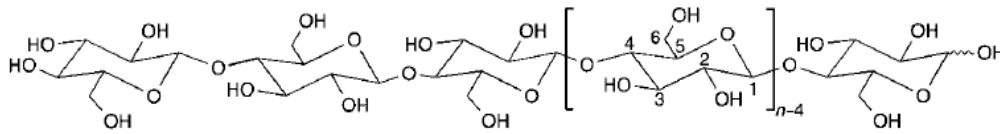


Figure 1.4: Molecular structure of cellulose (n=DP, degree of polymerization)

(Kobayashi *et al.*, 2001).

1.2.2.2 Crystal Structure

As a first approximation, the crystal structure of native cellulose (cellulose I) determined by X-ray diffraction can be described by a monoclinic unit cell (space group P21) which contains two cellulose chains in a parallel orientation with a twofold screw axis (Gardner and Blackwell, 1974). In the 1980s, ¹³C-CP/MAS NMR spectroscopy was used in the initial discovery that native cellulose is present in two different crystalline cellulose modifications (I_α and I_β), which can be found alongside each other; the I_α/I_β ratio depends on the origin of the cellulose (Atalla and Vanderhart, 1984). Finkenstadt and Millane (1998) revealed that the corresponding crystalline structures have triclinic (I_α) and monoclinic (I_β) unit cells. Figure 1.5 shows a schematic representation of the I_β crystal structure. In the side view (Figure 1.5 b) of the central chains of a unit cell, two intra-

molecular, chain-stiffening hydrogen bonds are revealed. Notably, one of the most recent reports on the I_{β} structure describes different conformations for neighboring chains as well as different H-bonding systems inside neighboring molecular layers (Nishiyama *et al.*, 2002). Apart from the thermodynamically less stable cellulose I, cellulose may occur in other crystal structures (cellulose II, III, and IV) of which cellulose II (Figure 1.5) is the most stable structure of technical relevance (Krässig, 1993, Hon, 1996, Klemm *et al.*, 1998, Hon and Shiraishi, 2001, Richter and Klemm, 2003, Klemm *et al.*, 2005, Nishio, 2006). Cellulose II is formed from cellulose I by treatment with aqueous sodium hydroxide (mercerization) or by dissolution of the cellulose and subsequent precipitation/regeneration, as is done in the formation of fiber and film. This monoclinic crystal structure with two antiparallel chains in the unit cell is characterized by the specific unit cell geometry with a modified H-bonding system (Langan *et al.*, 2001). The alkalization of cellulose is of considerable importance to commercial-scale cellulose production as a method for increasing the reactivity (activation) of subsequent reactions as well as for the mercerization of cotton. Depending on the concentration of lye, temperature, and mechanical load, it is possible to convert cellulose I into various crystalline alkali forms, each with a different crystal structure and variable NaOH and water content (Okano and Sarko, 1985, Fink *et al.*, 1995, Fink *et al.*, 1995). All forms are then converted into crystalline “hydrate cellulose” (water cellulose) during washout, and to cellulose II through drying. It is not yet understood how the parallel chain arrangement of cellulose I undergoes transition into the antiparallel orientation of cellulose II without an intermediate dispersion of cellulose molecules. There are currently only few reports on the structure of noncrystalline random cellulose chain segments (O. Ellefsen and Norman, 1960, Fink *et*

al., 1987, Paakkari *et al.*, 1989). More knowledge in this area is required, as these structure elements have significant influence on the accessibility and reactivity of cellulose, as well as on the properties of man-made cellulose fibers.

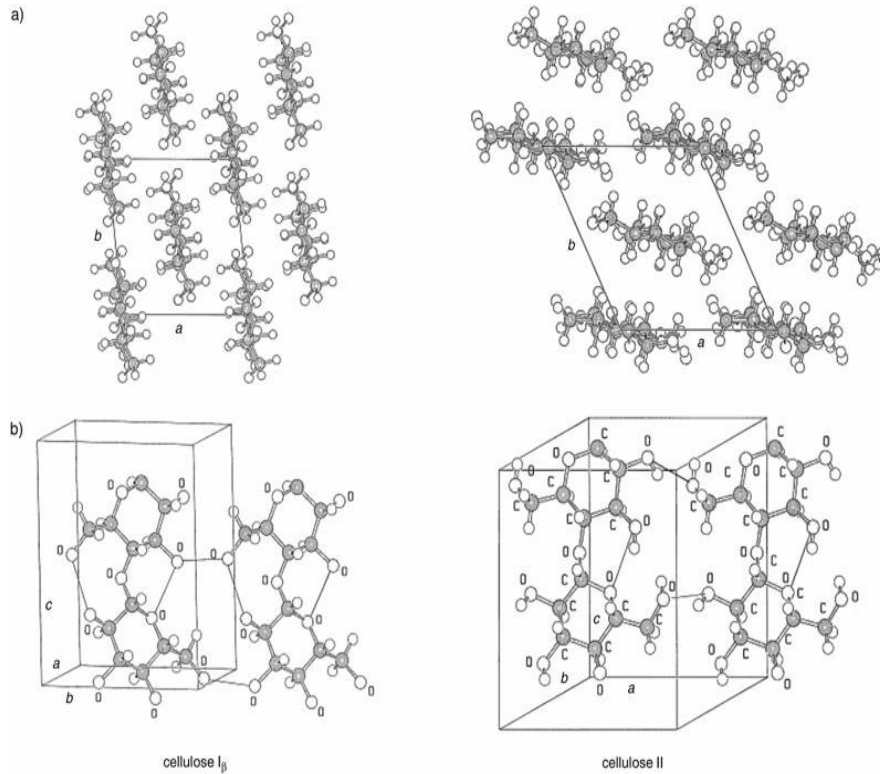


Figure 1.5: Crystal structures of cellulose Ib and cellulose II: a) projection of the unit cell (UC) along the a–b plane; b) projection of the UC parallel to the (100) lattice plane (cellulose I) and the (010) lattice plane (cellulose II)

1.2.2.3 Morphology

The biological function and numerous applications of cellulose are based on its distinct fiber morphology. The morphological hierarchy is defined by elementary fibrils, microfibrils, and microfibrillar 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

(microfibrils), and on the order of 100 nm (microfibrillar bands). The length of the microfibrils is on the order of several hundred nm. The fringed fibrillar model with crystalline regions of varying dimensions (crystallites) and noncrystalline regions has proven successful for the description of the structure of microfibrils (Figure 1:6) and the partial crystalline structure of cellulose related to the reactivity of this polymer (Fink *et al.*, 1995).

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 whereas 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).

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.

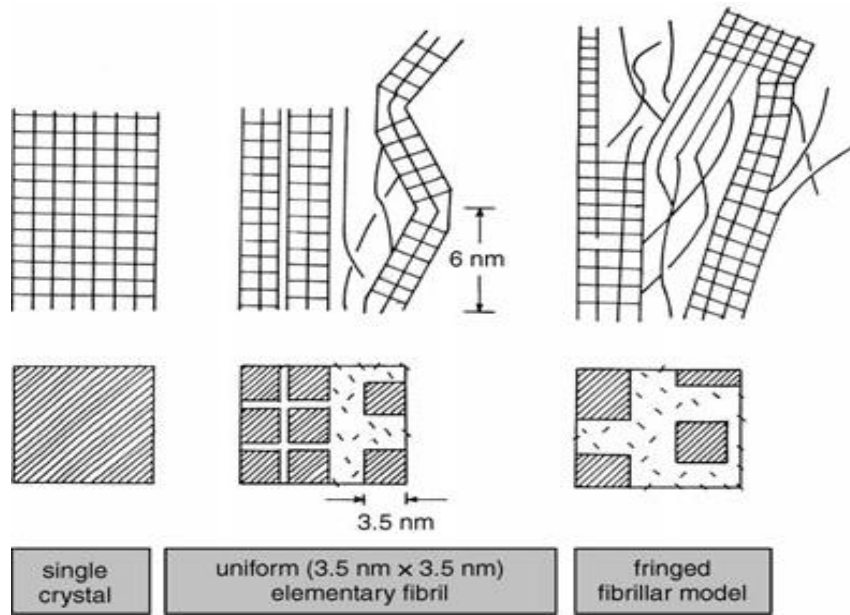


Figure 1.6: Various models of the supra molecular structure of cellulose microfibrils (Fink *et al.*, 1995).

1.2.2.4 Solution Structures of Cellulose and Cellulose Derivatives

An understanding of the structure of cellulose and cellulose derivatives in solution is not only a matter of scientific interest, but has great practical importance as well. Examples include the shaping of cellulose from spinning solutions, modification of the synthesis of cellulose derivatives and properties of water-soluble cellulose ethers, which are all dependent on the solution structure (Schurz, 1949, Gruber, 1979, Treiber and Uneback, 1988, Karstens, 1988, Fink *et al.*, 2014). For this reason, questions regarding the structure of cellulose in solution have been the subject of intense research and discussion over the past decades. According to Schurz, 1949, a differentiation is made initially between molecularly dispersed and network solutions, to which a portion of gel particles may be added. As a rule, cellulose derivatives with free OH groups are not molecularly

dispersible. Investigations with partially substituted cellulose carbanilates and benzoates revealed, however, that aggregate-free solutions can occur through specific polymer–solvent (e.g. DMF) interactions (Zugenmaier and Schmidt, 2000). On the other hand, completely substituted products (such as cellulose tricarbanilates) can be molecularly soluble or, owing to strong intermolecular interactions, insoluble as is the case with trimethylsilyl cellulose with DS 3.0. Whereas highly, diluted solutions have been used for fundamental research of solution structures, applied practices, such as the viscous process, employ concentrated systems with polymer concentrations of 8–12%, which are described as network solutions with gel-particle portion in accordance with model assumptions (Gruber, 1979, Treiber and Uneback, 1988). Apart from rheological examinations, gel-particle characterizations are also normally carried out to determine the quality of a given spinning solution (Schurz, 1949, Gruber, 1979, Treiber and Uneback, 1988, Karstens, 1988, Fink *et al.*, 2014). Over the past few years, the research group of Burchard, in particular, has carried out extensive fundamental research into the structure of cellulose and cellulose derivatives in solution using static and dynamic light scattering (Burchard, 1994, Burchard, 2003). With regioselective modified cellulose ethers, new insight was gained into the entropy effect during the dissolution of cellulose derivatives (Burchard, 1994, Zugemaier and Schmidt, 2000, , Burchard, 2003). The initial research results on the solution state of cellulose in N-methylmorpholine-N-oxide (NMMO) monohydrate as a technically relevant system substantiate the presence of bimodal molecule aggregations with up to 1000 chains, which can be attributed to incomplete dissolution of crystal structures of the starting cellulose material (Morgenstern and Röder, 1998, Röder and Morgenstern, 1999). In the first approximation, the average number of molecules in the

smaller aggregates corresponds to that of crystallites (50–100), whereas the average number of molecules in larger aggregates correlates with the number of molecules found in a microfibril (Fink *et al.*, 2001). In a ternary solvent system composed of NMMO, water, and diethylenetriamine [bis-(2-aminoethyl)-amine], cellulose is molecularly soluble within a temperature range of 25 – 60 °C. Therefore, the average molar mass and other properties of dissolved molecules could be determined using light scattering (Drechsler *et al.*, 2000).

1.2.3 Isolation of cellulose

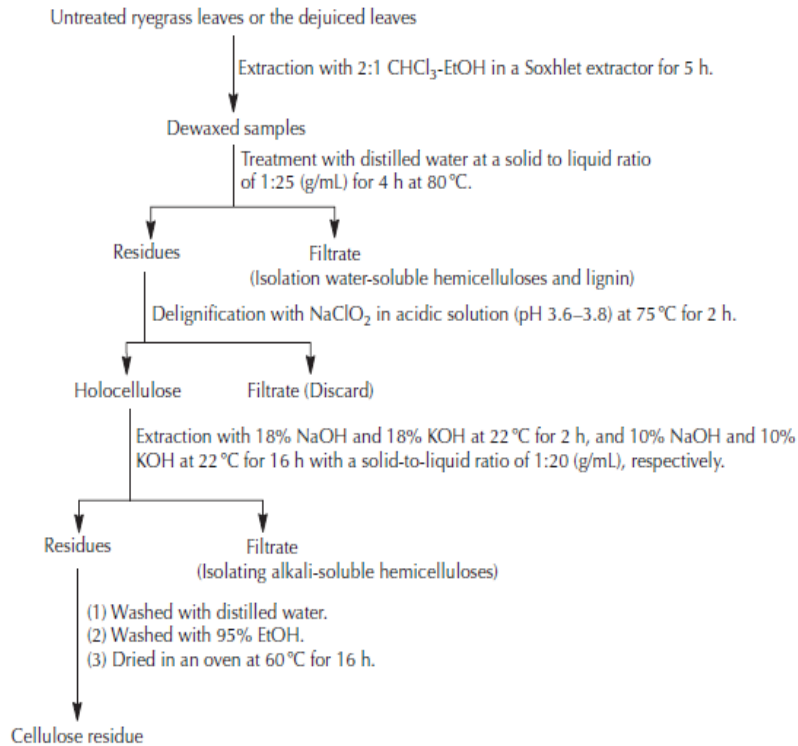
In the lignocellulosic materials, cellulose is embedded in a gel matrix composed of hemicelluloses, lignins, and other carbohydrate polymers (Hanley *et al.*, 1997, Yu *et al.*, 2005). The isolation of highly pure cellulose has been the subject of extensive studies for many years because of the complexity of cell wall structure (Sun and Hughes, 1998, Brendel *et al.*, 2000). The combination of chemical and mechanical treatments is necessary for the dissolution of lignins, hemicelluloses, and other noncellulosic 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). It is well known that treatment of lignocellulosic materials with chlorite remove almost all the lignins, and the following alkali isolation of cellulose is performed at room temperature.

1.2.3.1 Delignification and Alkali Extraction

Many efforts 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 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 from 61.7 to 71.6%.



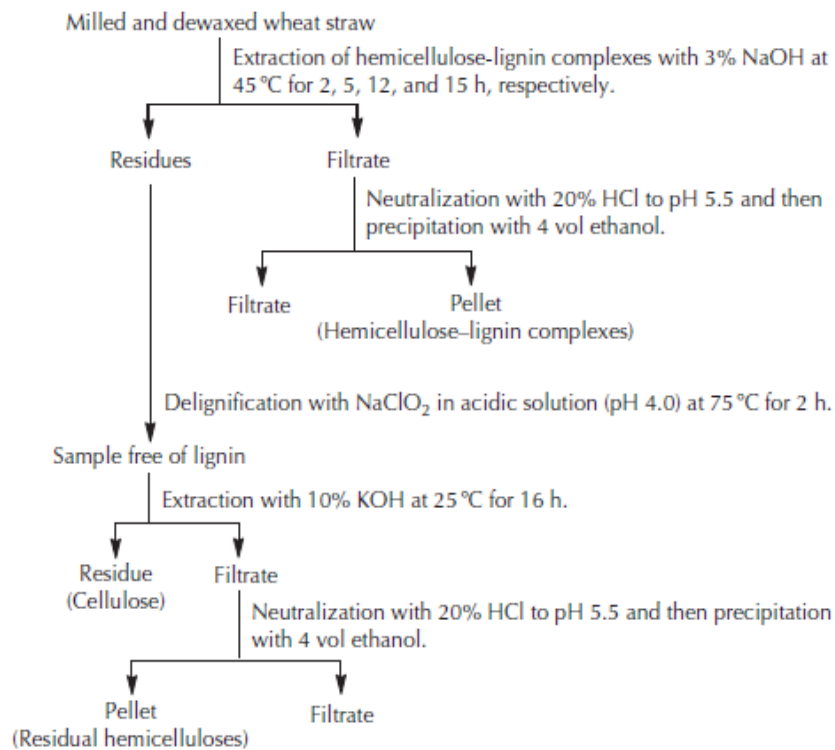
Scheme 1.1: Isolation of cellulose from untreated ryegrass leaves and the dejuiced leaves (Liu *et al.*, 2006).

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 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 NaClO₂ and then extracted with 10% KOH at 25 °C for 16 h. The yields of cellulose ranged between 38.0 to 39.9%. This procedure could be used to obtain cellulosic and hemicellulose polymers from straws and listed in (scheme 1-2).

Adinugraha *et al.*, (2005) reported a method to isolate cellulose from Cavendish banana pseudo stem for further utilization. Cellulose preparations were obtained from

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 dry crushing, disintegration, and defibrillation.



Scheme1.2: Isolation of cellulose and hemicelluloses from wheat straw (Sun *et al.*, 1998).

1.2.3.2 Steam Explosion

Steam explosion is one of the main methods recently developed to isolate cellulose from straws, especially for the production of bioethanol. During the steam explosion, the significant amounts of hemicelluloses are partially hydrolyzed and some lignins are depolymerized, in to, water soluble sugars and phenolic compounds. Hydrolysis of glycosidic linkages in hemicelluloses and β -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, depolymerized lignin fragments remain in the proximity of condensation sites in the biomass matrix (Josefsson *et al.*, 2001). The residue consist mainly of cellulose, lignin and some hemicelluloses. In this process, cellulose is also depolymerized and defibrillated and undergoes a change in its crystallinity, the resulting product is more susceptible to hydrolytic enzymes. Lignin and residual hemicelluloses are removed by 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 main cellulose components. 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 improves digestion resulting residues and shred fibers into many individual fragments .A two-stage process proposed by (Sun *et al.*, 2005) was based on the steam explosion pretreatment followed by the alkaline peroxide post-treatment for the isolation of cellulose from wheat straw.

1.2.3.3 Alkaline Peroxide Extraction

This reaction has been explained through the reactions of the hydro-peroxide anion (HOO^-), formed in an alkaline medium. On the other hand, depending on the pH, hydrogen peroxide acts as either a nucleophile or an electrophile. 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 hydrogen peroxide forms molecular oxygen and more active radicals such as the hydroxyl radicals (HO) and superoxide anion radicals (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, Xiao *et al.*, 2001). 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 hydrogen peroxide treatment in alkaline solution.

Sun *et al.*, (2003) reported that the extraction of dewaxed wheat straw using 2% H_2O_2 –2% 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 dilute alkaline solution at pH 11.5 for 12 h at 50 °C in the absence of H_2O_2 , yielded only 7.3% of hemicelluloses and 7.4% of lignin, whereas extraction with 2% H_2O_2 at pH 11.5 for 12 h at 20–70 °C released 44.2–71.9% of hemicelluloses and 52.7–87.8% of lignin.

1.2.3.4 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%). The advantage of this technique compared to 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, where the addition of 5–10% formic acid to aqueous acetic acid, results in improved selectivity of delignification (Lehnen *et al.*, 2002).

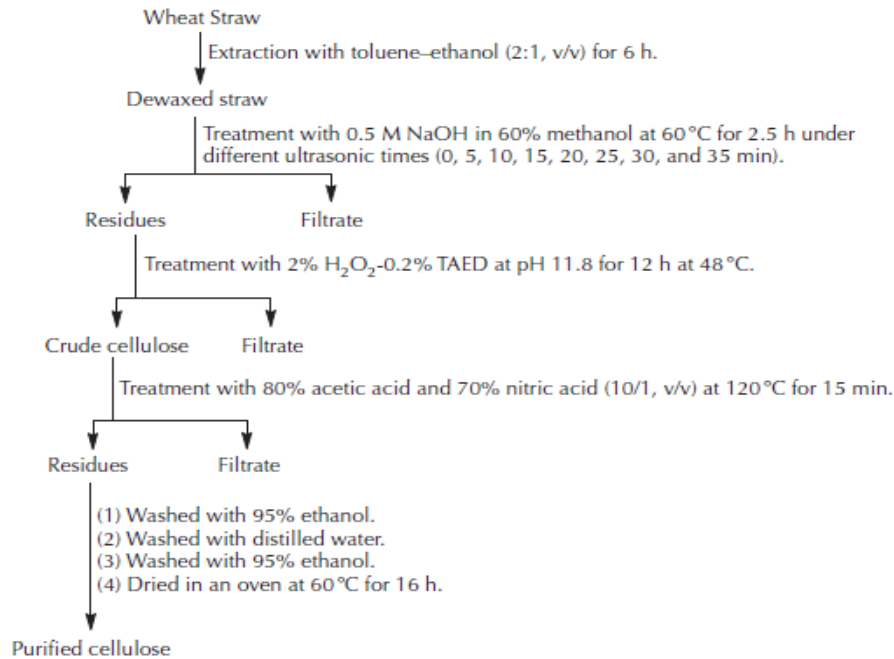
Sun *et al.*, (2004 c) reported that wheat straw lignin and hemicelluloses were degraded in a medium containing 80% acetic acid and 0.92–13.5% nitric acid. The treatment with 80% acetic acid and 0.92% nitric acid as a catalyst at 120 °C for 20 min resulted in more than 81% hemicelluloses and 92% lignin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

Xu *et al.*, (2005 and 2006) 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 a significant degradation of lignin and hemicelluloses, slight acetylation of cellulose, and an increase in the degree of crystallinity of cellulose.

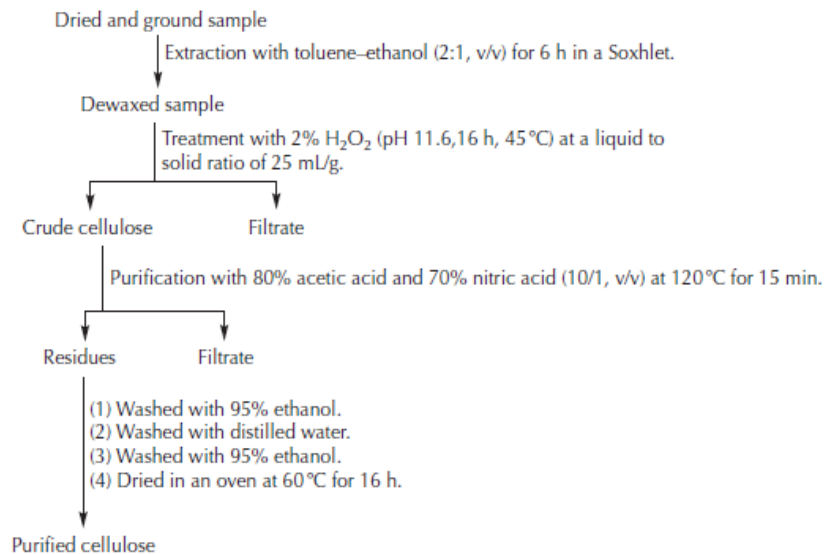
Glucose was comprised with more than 90% of the total neutral sugars of the isolated cellulose preparations, revealing the relatively high purity of cellulose samples.

Sun *et al.*, (2004 b) proposed a chlorine-free procedure for isolation of cellulose from wheat straw based on the alkaline extraction in alcohol, peroxide treatment, and purification with 80% acetic acid and 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% H₂O₂–0.2% TAED at pH 11.8 for 12 h at 48 °C solubilized 85.3–86.1% of hemicelluloses and 91.7–93.2% of lignin, respectively. The dry wheat straw contained 46.2 - 49.2% cellulose, 11.2–12.2% residual hemicelluloses and 2.5–2.9% remaining lignin. Further treatment of the corresponding wheat straw with 80% acetic acid and 70% nitric acid yielded 36.8–37.7% of the cellulose with high purity scheme 1.3.

Sun *et al.*, (2005 b), Sun and Tomkinson, (2005), Sun *et al.*, (2005 a) adopted Sun *et al.*, (2004) 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 scheme 1.4. Highly purified cellulose preparations were obtained by pretreatment with 2.0% H₂O₂ 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).



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).

1.2.3.5 Other Isolation Methods

There are many other isolation 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 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 content strength values and poor bleaching properties (Liu and Sun, 2010).

1.2.4 Chemical Modification and Its Utilization

Cellulose is used for many centuries not only as a construction material, but also as a versatile starting material for subsequent chemical modification to a variety of

cellulose derivatives (ethers and esters) to be used in the form of fibers, films, food casings, membranes, and sponges in many areas of industries and life (Roy *et al.*, 2009). Effective utilization of straw cellulose not only reduces the consumption of the limited fossil resources but also protects the environment of the Earth. Due to the three hydroxyl groups available for modification within one AGU and the polymeric character of the cellulose, a great variety of chemical modifications, such as esterification with linear and cyclic anhydrides, etherification including carboxymethylation and quaternization, tosylation, tritylation, and carbanilation are possible (Potthast *et al.*, 2006). In the past decade, chemical modification of cellulose has gained much attention, especially in homogeneous reaction media with the development of novel green solvents for cellulose. For the homogeneous cellulose derivatization reaction, suitable solvent systems that can dissolve cellulose and provide a feasible reaction environment. Several solvents for cellulose have been developed over the past, and a few of them are suitable for the chemical functionalization of the cellulose. These solvents include DMAc/LiCl (El Seoud *et al.*, 2000, Regiani *et al.*, 1999, Marson *et al.*, 1999) DMSO/TBAF (Heinze *et al.*, 2000, Hussain *et al.*, 2004), some molten salt hydrate, such as $\text{LiClO}_4 \cdot 3\text{H}_2\text{O}$ and $\text{LiSCN} \cdot 2\text{H}_2\text{O}$, and ILs (Fischer *et al.*, 2002, Fischer *et al.*, 2003).

1.2.4.1 Acetylation of cellulose

During the past decade, there has been strong emphasis on developing new cellulose-based materials because of the biodegradability and renewable aspects of these

materials (Biswas *et al.*, 2005). Acetylation of cellulose with acetyl chloride or acetic anhydride has been known for a long time. Cellulose acetate (as shown in Figures 1.7 and 1.8) is one of the most commercially important cellulose derivatives. It is widely used in textiles because of its low cost, toughness, glossiness, high transparency, natural feel, and other favorable aesthetic properties. Cellulose acetate fibers in cigarette filters are designed to absorb vapors and accumulate particulate smoke components. Cellulose acetate is also used as a carrier for photographic negatives, motion picture film (celluloid), microfilm, microfiche, and audio tape (Edgar *et al.*, 2001, Biswas *et al.*, 2005, Biswas *et al.*, 2007). In addition, the acetylation of cellulose is also widely used for the protection of hydroxyl groups and the purification and structural elucidation of natural products. The often-used cellulose acetates include diacetates having an average degree of substitution (DS) in the range from 2.2 to 2.7 and triacetates having an average DS above 2.8 (Heinze and Liebert, 2001). Various methods have been developed for producing cellulose acetates, in which acetic anhydride and acetyl chloride are commonly used as acetylating agents. Industrially, cellulose acetates are often produced by reaction of cellulose with an excess of acetic anhydride in the presence of sulfuric acid or perchloric acid as catalysts (Hummel, 2004). Biswas *et al.* (2006) acetylated cellulose, from agricultural residues, with acetic anhydride and catalytic amount of sulfuric acid to make cellulose acetate. They followed the hydrolysis process with dilute acid at a moderate temperature to remove hemicelluloses. The results showed that the pretreatment used to hydrolyze hemicelluloses was useful for the production of cellulose acetate and the conversion rate increased to about 25 wt. % after pretreatment.

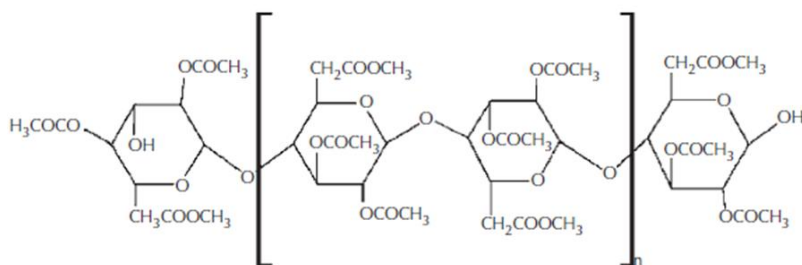


Figure 1.7: Structure of cellulose triacetate, (Biswas *et al.*, 2006).

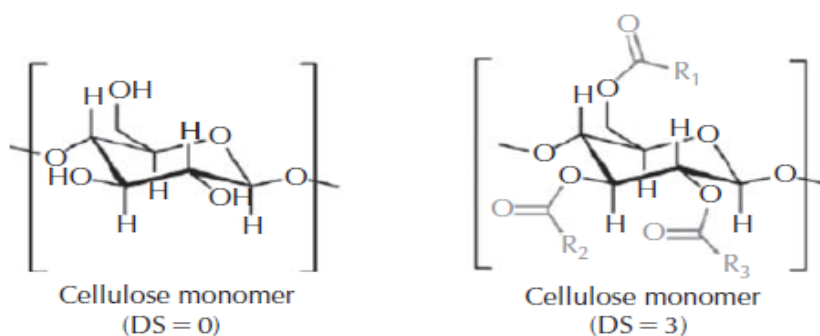


Figure 1.8: Structure of cellulose monomer and related cellulose triacetate (de María and Martinsson, 2009).

Biswas *et al.* (2005), Edgar *et al.* (2001) and Biswas *et al.* (2007) developed a process for esterification of cellulose with acetic anhydride in the presence of a novel catalytic amount of iodine to produce cellulose triacetate (Figure 1.9). The results showed that the acetic anhydride in the presence of a catalytic amount of iodine was an excellent acylating reagent for cellulose. The reaction time required for complete esterification at room temperature was 12 h; however, it was reduced to 10 min when the reaction was conducted at 100 °C. Iodine activates the carbonyl group of acetic anhydride making the latter more reactive, as shown in Figure 1.10. Acetic anhydride– iodine combination works only in the absence of a solvent. When cellulose was heated with a mixture of acetic acid

and iodine instead of acetic anhydride, no acetylation occurred. Due to the heterogeneous nature of the aforementioned reaction, it is impossible to synthesize partially substituted cellulose acetates directly. Homogeneous derivatization of cellulose has three main advantages over the heterogeneous path (Heinze and Liebert, 2001, Heinze *et al.*, 2003). First, the DS of the cellulose derivative can be effectively controlled by adjusting reaction conditions, such as the reaction time, the temperature, and the molar ratio of derivatizing agent to cellulose. Second, substituent groups are introduced regularly along the cellulose backbone. Third, the physicochemical properties of products thus obtained are controlled better than those prepared under heterogeneous conditions. Several molten inorganic salt hydrates were applied as media for the homogeneous acetylation of cellulose. The acetylation in molten thiocyanate leads to the formation of amorphous cellulose acetate. The formation of cellulose acetate depends on the used molten salt hydrate itself as well as on the water content of the melt. However, the only melt in which the acetylation was successful was the eutectic mixture of NaSCN and KSCN with addition of 10% LiSCN·2H₂O. The most important condition for the reaction was the minimization of the water content of the melt.

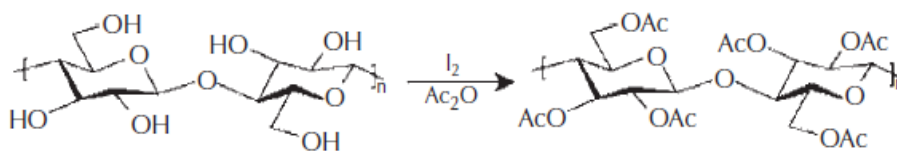


Figure 1.9: Conversion of cellulose to cellulose triacetate (Biswas *et al.*, 2007).

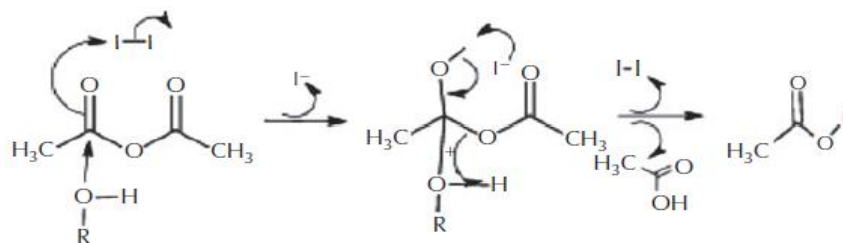


Figure 1.10: Mechanism of iodine catalyzed acetylation (Biswas *et al.*, 2005).

Acetylation at 130 °C in excess of acetic anhydride (50–100%), and a short reaction time (0.5 – 3 h), cellulose acetate with a DS in the range between 1 and 2.5 was obtained under homogeneous reaction conditions, e.g., in LiCl/DMAc. The reaction proceeded in three steps including activation, dissolution, and subsequent reaction with the derivatizing agent. Activation can be carried out by solvent exchange, e.g., treatment with water, methanol, and DMAc, by distillation of part of the solvent and by heating native cellulose under reduced pressure. Solubilized cellulose is then derivatized, e.g., by reaction with an acetylating agent with or without catalyst. El Seoud *et al.* (2000) successively acetylated cellulose from cotton linters, sisal, and SCB under homogeneous reaction conditions in the presence of DMAc/LiCl solvent (Figure 1.11). The attractive feature of this procedure is the ease of controlling the reaction conditions and the high reproducibility of DS. Additional advantages were found to be the elimination of base catalyst, the negligible degradation of the natural polymer, and the recycling of high purity DMAc and acetic anhydride. Heinze *et al.* (2005) found that it was very easy to synthesize cellulose acetate with high DS in good yield within a short time using different ILs such as [C₄mim]Cl as reaction media and using acetyl chloride or acetic anhydride as acetylation reagent without

any catalysts. The reaction of three free hydroxyl groups in cellulose at the C2, C3, and C6 positions all occur during homogeneous modification in ILs, and the order of reactivity is C6-OH > C3-OH > C2-OH similar to that observed in acetylation in DMAc/LiCl system.

Cao *et al.* (2007) prepared cornhusk cellulose acetates with DS ranging from 2.16 to 2.63 in AmimCl. The resultant cellulose acetates readily dissolve in organic solvents, such as acetone and DMSO. The distribution of the acetyl moiety among the three OH groups of the AGU revealed a preference at the C6 position.

Barthel and Heinze, (2006) investigated different ionic liquids as reaction media for homogeneous acylation of cellulose. They found that cellulose acetates with DS in the range from 2.5 to 3.0 were accessible in [C₄mim] Cl within 2 h at 80 °C in a complete homogeneous procedure. Ionic liquid analogues based on choline chloride (ChCl; HOCH₂CH₂N (Me)₃ Cl) and zinc chloride have been successfully used for a variety of reactions (Abbott *et al.*, 2002, Morales *et al.*, 2004, Thomas, 2005).

Thomas (2005) studied the acetylation reaction of cellulose with acetic anhydride for 3 h at 90 °C using Lewis acidic ionic liquid based on choline chloride and zinc chloride. The results showed that cellulose acetate was formed but with low levels of functionalization (<20% acetylation).

Because of its limited solubility, cellulose triacetate has not been used in a great number of commercial applications, whereas cellulose diacetates after deacetylation of triacetate are industrially more important. Acidic properties of the molten inorganic hydrates could be used for the cleavage of functional groups. Cellulose triacetate deacetylation was carried out in molten ZnCl₂·4H₂O. After a reaction time of 21 h, DS of 1.81 and PDS (C6) of 0.53 were obtained (Leipner *et al.*, 2000). Furthermore, molten

ZnCl₂·4H₂O or LiClO₄·3H₂O was applied as medium for deprotection of triphenylmethyl cellulose. A complete deprotection occurred in the comparatively short reaction time of 3–5 h (Fischer *et al.*, 2001).

1.2.4.2 Acylation with Other Linear Anhydrides or Chlorides

Many reports exist in the literature pertaining to the preparation of esters of cellulose with the ultimate aim of significantly increased hydrophobic properties of the polymer and imparting suitable mechanical characteristics such as to render it more useful as engineering materials than the precursor polymer, which could be achieved by acylation with linear anhydrides or chloride. (El Seoud *et al.*, 2000) successively acylated cellulose samples from cotton linters, sisal, and sugar cane bagasse to prepare cellulose esters including acetate, propionate, butyrate, and acetate/ butyrate in DMAc/LiCl under homogeneous reaction conditions according to the procedure shown in Fig.1.11

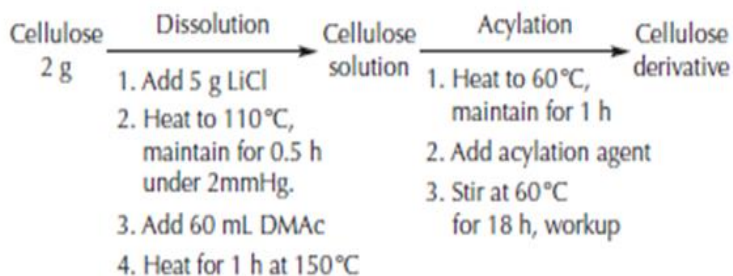


Figure 1.11: Procedure for cellulose acetylation in DMAc/LiCl system (El Seoud *et al.*, 2000).

The reproducibility of DS is easily attainable in homogeneous acylation of cellulose in DMAc/LiCl solvent system, which is very difficult in heterogeneous

derivatization. Barthel and Heinze, (2006) prepared cellulose laureates with DS from 0.34 to 1.54 using lauroyl chloride in ILs. They found that acylation started homogeneously and continued heterogeneously in [C₄mim] Cl. The acylation efficiency of cellulose with lauroyl chloride decreased compared with acetylation. Efficiency of cellulose with lauroyl chloride decreased compared with acetylation.

1.2.4.3 Esterification with Cyclic Anhydrides

One of the key properties required for the cellulose materials intended for use in hygienic products is their ability to absorb liquids. Absorbent hydrogels are lightly cross-linked hydrophilic polymers capable of absorbing large amounts of water as much as 10–1000 times their own weight. Therefore, these hydrogel materials have been widely used in various applications such as disposal diapers, sanitary napkins, additives for soil in agriculture, and medicine for drug delivery systems. Acylation of cellulose fibers with cyclic anhydrides results in cellulose derivatives with carboxylic acid group attached onto cellulose molecule, which has the potential as water absorbents for soil in agriculture, natural absorbents for the removal of heavy metal ions in wastewater treatment, medicine for drug delivery systems, thermoplastic materials, and superabsorbent hydrogels (Yoshimura *et al.*, 2006, Hadano *et al.*, 2003).

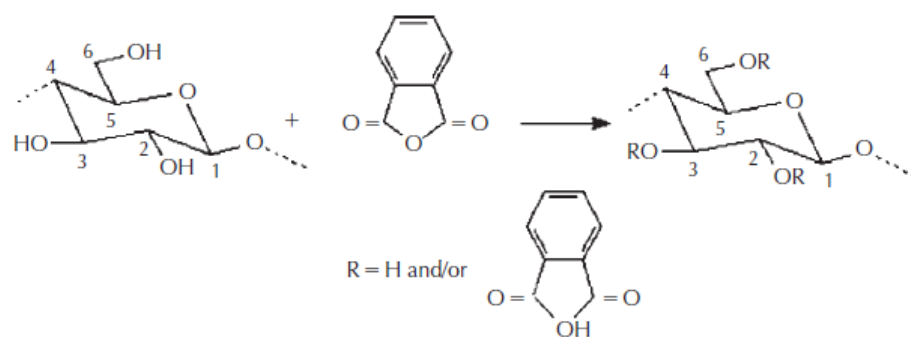


Figure 1.12: Reaction of SCB cellulose with phthalic anhydride (Liu *et al.*, 2007, Liu *et al.*, 2007).

Homogeneous chemical modification of cellulose with succinic anhydride was investigated in a solvent containing [C₄mim]Cl and DMSO using N-bromosuccinimide (NBS) as a catalyst. Figure 1.13 shows the reaction of SCB cellulose with SA using NBS as a catalyst in [C₄mim] Cl/DMSO. The possible mechanism of NBS in cellulose succinylation in ILs is shown in Figure 1.14.

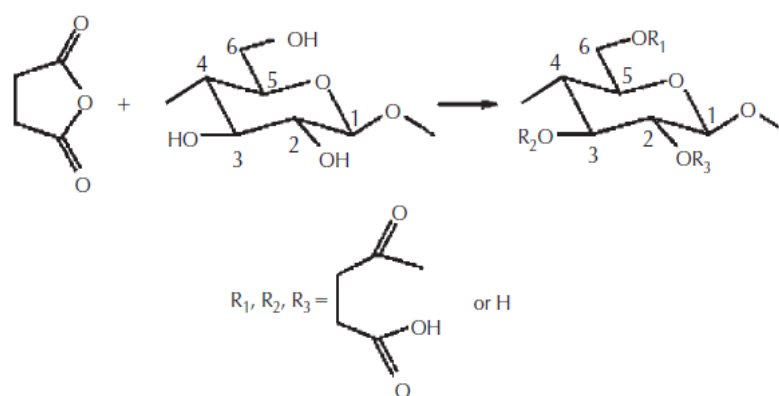


Figure 1.13: Reaction of SCB cellulose with SA using NBS as a catalyst, (Liu *et al.*, 2009).

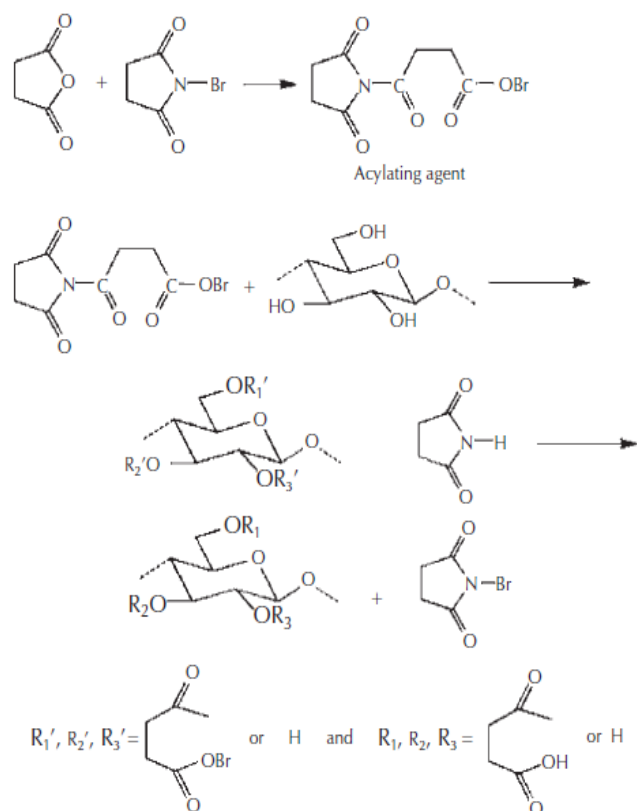


Figure 1.14: Mechanism of succinylation of cellulose using NBS as a catalyst

(Liu *et al.*, 2009).

1.2.4.4 Carboxymethylation

Carboxymethylation is one of the most versatile functionalization procedures as it provides access to bio-based materials with valuable properties such as filming, emulsification, suspension, water maintaining, and binding (Ren *et al.*, 2008). Carboxymethylated polymers have been used for many applications, such as printing dyeing, medicine, food, textures, toilet, oil drilling, electrical elements, and papermaking. Sodium carboxymethylcellulose (CMC), is a linear, long-chain, water-soluble, anionic, man-modified cellulose derivative. Purified CMC is a white-colored to cream-colored,

tasteless, odorless, free-flowing powder. In general, sodium CMC was produced by conversion of alkali cellulose swollen in aqueous NaOH and a surplus of organic solvent (e.g. isopropanol or ethanol) with monochloroacetic acid or its sodium salt (Heinze *et al.*, 1999). In this case, hydroxyl groups in cellulose are usually replaced by carboxymethyl groups in the order of $C_2 > C_6 > C_3$ (Tezuka *et al.*, 1996).

Adinugraha *et al.* (2005) prepared CMC from Cavendish banana pseudo stem cellulose according to the conventional procedure. The results showed that CMC with the highest DS, viscosity, purity, and crystallinity was obtained by the alkalization using 15% NaOH and etherification using 1.2 g (w/w) $\text{ClCH}_2\text{COONa}$. Homogeneous carboxymethylation of cellulose in Inorganic molten salts such as $\text{LiClO}_4 \cdot 3\text{H}_2\text{O}$ is possible using sodium monochloroacetate in the presence of NaOH (Heinze and Pfeiffer, 1999).

Fischer *et al.* (2003) investigated the carboxymethylation of cellulose in different inorganic molten salts. (Heinze *et al.*, 1999) Investigated carboxymethylation of cellulose in different solvents including $\text{Ni}(\text{tren})(\text{OH})_2$ [tren = tris(2-aminoethyl)amine], $\text{LiClO}_4 \cdot 3\text{H}_2\text{O}$, and NMMO. In the case of $\text{Ni}(\text{tren})(\text{OH})_2$, a totally homogeneous carboxymethylation of cellulose with sodium monochloroacetate in the presence of an aqueous NaOH solution is possible. The results revealed the functionalization of the hydroxyl groups in the order $C_6 \geq C_2 > C_3$. The carboxymethylation of cellulose in $\text{LiClO}_4 \cdot 3\text{H}_2\text{O}$ was shown to be possible and yielded products of a statistic functionalization pattern as well. Carboxymethylation of cellulose in pure NMMO or NMMO/DMSO mixtures yielded CMC samples with a nonstatistical distribution of functional groups along with the polymer chain. This result is comparable to the earlier findings that etherification reactions start from a solution of cellulose in DMA/LiCl or from cellulose intermediates in

DMSO. Carboxymethylation of cellulose in IL [C₄mim]Cl was proposed by Heinze *et al.*, (2005). However, carboxymethylated cellulose obtained according to this method had relatively low DS, and an increase in DS was not observed along with the increase in the dosage of carboxymethylating reagent. The reason for this unusual result is still unclear.

1.2.4.5 Other Chemical Modification

Beside acylation with linear anhydride and linear chloride, esterification with cyclic anhydrides, and carboxymethylation, there are several other chemical modifications of cellulose reported in recent years, including tritylation, tosylation, quaternization, carbanilation, and so on. These modifications provide the novel utilization of cellulose, the protection of hydroxy groups, and the structural elucidation of cellulose products. Erdmenger *et al.* (2007) performed the tritylation of cellulose in [C₄mim]Cl using pyridine as base, Figure 1.15. A DS of around 1 was obtained after the reaction time of 3 h using a six-fold excess of trityl chloride. Granström *et al.* (2008) performed a series of cellulose modification including esterification with pyro-phosphoribide activated with N,N'-carbonyldiimidazole (CDI).

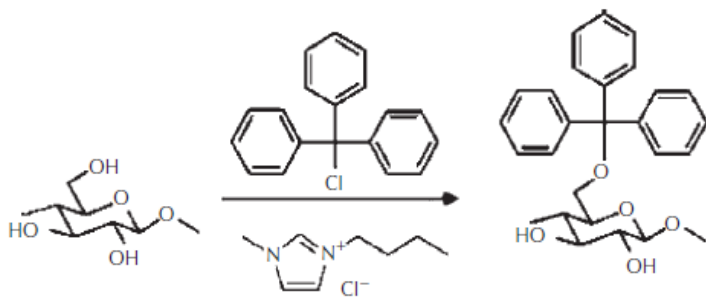


Figure 1.15: Tritylation of cellulose in [C₄mim]Cl using pyridine as base (Erdmenger *et al.*, 2007).

Esterification with stearic acid activated with 1-ethyl-3-(3'-dimethylaminopropyl) carbodiimide hydrochloride (EDCI), triacetylation with acetic anhydride catalyzed with pyridine, and tosylation with tosyl chloride catalyzed with pyridine using AmimCl as solvents and etherification of tosylcellulose with 11-Bromoundecanol in DMF. Cellulose derivatives with DS of 0.07, 0.16, 2.99, 0.84, and 0.73, respectively, were obtained. Abbott *et al.*, (2006) resorted on found the efficient cationic functionalization of cellulose using an ionic liquid analogue, based on a eutectic mixture of a chlorine chloride (ClCl) derivative and urea, as both solvent and reagent. The results showed that all available hydroxyl groups on cellulose had been quaternized at 90 C for 15 h. The derivatization reaction of cellulose with cationic functionalities is shown in Figure 1.16 Using the solvent DMSO/TBAF as reaction medium. Homogenous modification of cellulose, including acylation with acetic anhydride, vinyl acetate, vinyl butyrate, vinyl laurate, and benzoate, tosylation with tosylchloride in the presence of triethylamine, and carboxymethylation with sodium monochloroacetate, was comparatively studied. Cellulose esters obtained from modification with acetic anhydride, vinyl acetate, vinyl butyrate, vinyl laurate, and vinyl benzoate had the DS of 0.83, 1.04, 0.86, 1.47, and 0.95, respectively.

Barthel and Heinze (2006) investigated the homogeneous carbanilation of cellulose in different ionic liquids (IL). The synthesis of cellulose carbanilates succeeded in the IL [C₄mim]Cl without any catalyst and cellulose carbanilate with DS in the range of 0.26 to 3.0 were obtained.

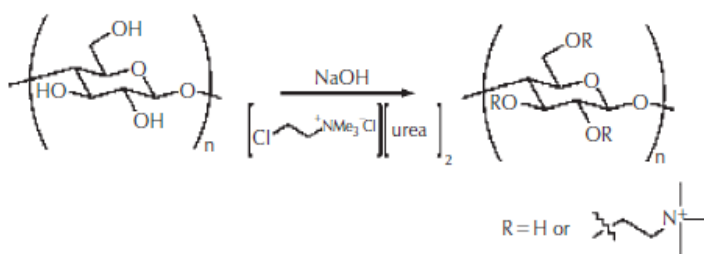


Figure 1.16: Cellulose quaternization in ClChCl/urea at 90 °C for 15 h (Abbott *et al.*, 2006).

1.3 Carboxymethylcellulose (CMC)

The industrial manufacture of carboxymethylcellulose (CMC) is carried out principally by reacting alkali cellulose with monochloroacetic acid (MCA) or sodium chloroacetate and the annual production is about 360,000 metric tons. The degree of substitution (DS) of CMCs (typically in the range 0.5–1.4 for commercial products) is a key parameter controlling their final applications. CMCs are useful in systems where hydrophylic colloids are involved, and show ability to suspend solids in aqueous media, stabilize emulsions, absorb moisture from the atmosphere, help to solubilize proteins (soy protein, casein from milk or egg white proteins) and stabilize their solutions. Feddersen and Thorp (1993) thicken solutions (sugar solutions, paints. . .) and form films (Baird and Speicher, 1962, Meltzer, 1968, Moreau, 1983). For this reason, CMCs were found to have more applications in industry as stabilizers in frozen food, beverages and ice creams due to their tasteless and odourless properties, as well as an additive in low-caloric foods (Boursier *et al.*, 1985). CMC gives good enteric coatings for powders and tablets, being insoluble in stomach acid but soluble in alkaline intestinal fluids (Allen, 1961) it is also employed in pharmaceuticals (Koyama, 1988), pesticides (Lee and Farre Torras, 1993), paper (Seiichi and Shosuke, 2000), textiles (Kniewske *et al.*, 1994), ceramics (Sanchez *et*

al., 1999, Soper, 1991) adhesives (Gayrish *et al.*, 1989), detergents (Leupin and Gosselink, 1999) and cements (Ernandes, 2000).

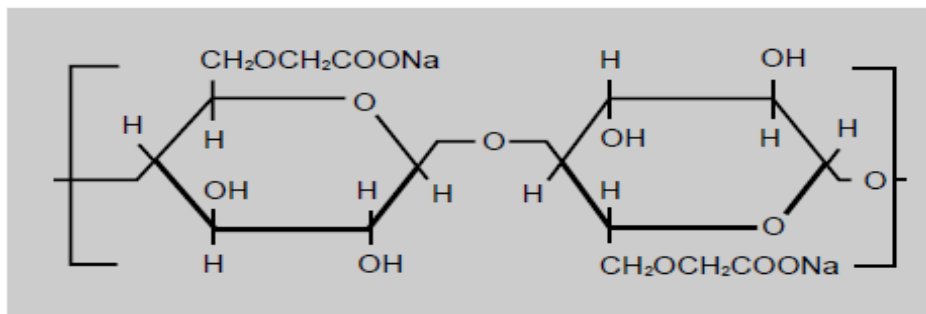
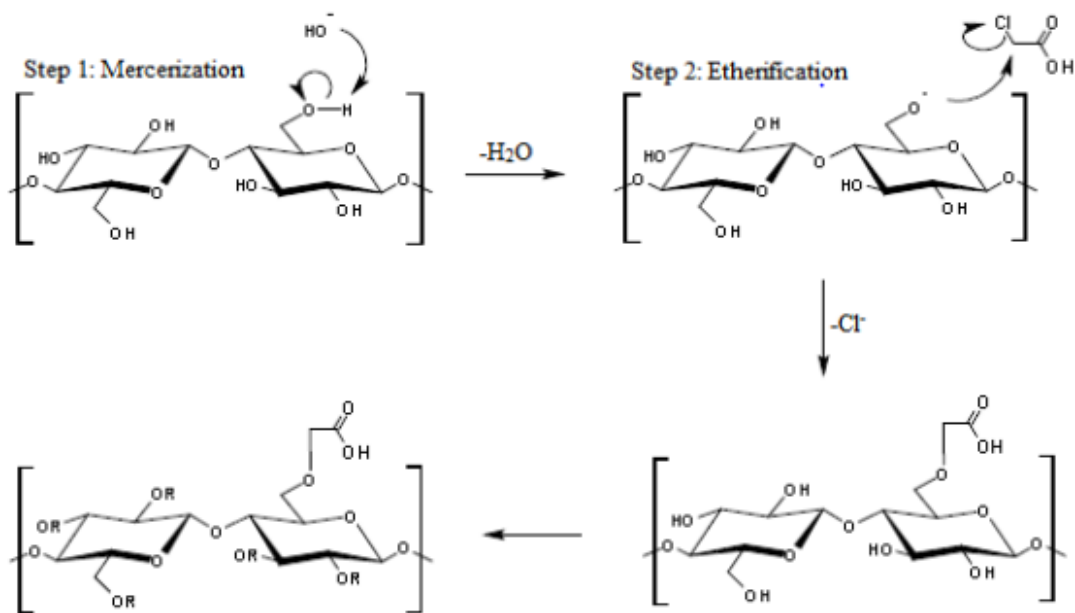


Figure 1.17: Structure of carboxymethylcellulose ([http:// www. Ashland. Com / Ashland / static / documents / AAFI / PRO – 250 – 10 H – Aqualon – CMC pd](http://www.Ashland.Com/Ashland/static/documents/AAFI/PRO-250-10H-Aqualon-CMCpd) – retrieved on 15/5/2016 at 5:17 pm)

1.3.1 Synthesis of Sodium Carboxymethylcellulose

The synthesis of the CMC was conducted in two steps, namely alkalization and etherification of cellulose under heterogeneous conditions. Alkalization is a pre-treatment step for etherification reaction. The reaction was conducted in a temperature controlled water bath to maintain an exact reaction temperature. A motor running stirrer was also used to homogenize the solution and speed up the reaction. The product was oven dried. The dried product was blended into powder form for the DS analysis. Pure cellulose in adequate amount was suspended in 100 ml of ethanol: isopropanol in an appropriate ratio under mechanical stirring. Ten milliliters of aqueous sodium hydroxide, as swelling agent, were added drop-wise and the solution was stirred for an hour at room temperature (Pushpamalar *et al.*, 2006). Carboxymethylation reaction was started with an addition of sodium monochloroacetate (SMCA) with the reaction mixture placed in a temperature controlled

water bath. The reaction mixture was then heated up to the reaction temperature and stirred for three hours (Pushpamalar *et al.*, 2006). This period of time is the optimum time for inducing better contacts between the etherifying agent and cellulose. Prolonged time increased degradation of the polymer which will lower the value of DS (Bhattacharyya *et al.*, 1995). The slurry was neutralized with 90% acetic acid and then filtered. The CMC was purified by washing it with 70% ethanol four times to remove undesired by products. CMC was filtered and dried at 60 C (Pushpamalar *et al.*, 2006).



Scheme 1.5: Carboxymethylation reaction where R could be H or CH_2COOH (Stigsson *et al.*, 2001).

1.3.2 Applications of CMC

Cellulose derivatives 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 s thickener or flow-controlled agent depends largely on it is degree of substitution, molecular weight and stiffness of the cellulose back bone (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 industrial applications of purified CMC are illustrated in Tables 1.1 – 1.5, (<http://www.Ashland.Com/Ashland/static/documents/AAFI/PRO-250-10H-Aqualon-CMC.pdf> – retrieved on 15/1/2016 at 4:17 pm).

Table 1.1: Application 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: Applications of CMC in Pharmaceuticals industries

Specific application	Properties utilized
Ointments, creams and 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

Specific application	Properties utilized
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 Tobaccindustries

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

1.4 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.

Adinugraha *et al.*, (2005) studied the ynthesis and characterization of sodium carboxymethylcellulose from Cavendish banana pseudo stem. They found that CMC of high DS value could be synthesized from carboxymethylation of Cavendish banana pseudo

stem cellulose, using 15% NaOH and 6 g NaMCA per 5 g cellulose. The CMC material at optimum conditions was observed to exhibit good physicochemical properties ca. DS of 0.75, viscosity of 4033 cps, purity of 98.63% and crystallinity of 38.33%.

Pushpamalar *et al.*, (2006) prepared CMC with DS of 0.821 from cellulose isolated from sago waste. The optimum conditions for Carboxymethylation of cellulose were pure isopropyl alcohol as the solvent medium, reaction period of 180 min, 6.0 g of sodium monochloroacetate, NaOH concentration of 10 mL of 25% and reaction temperature of 45 °C.

Varshney *et al.*, (2006) synthesized CMC from α -cellulose isolated from Lantana camara, using optimized set of conditions included concentration of aqueous NaOH 3.24 mol/AGU, 20% (w/v), concentration of MCA 2.05 mol/AGU, carboxymethylation time 3.5 h and temperature 55 °C with isopropyl alcohol as solvent. The resulting CMC exhibited viscosity of 600 cps (1% solution) and 7500cps (1% solution) and DS of 1.22.

Hutomo *et al.*, (2012) studied the synthesis and characterization of sodium carboxymethylcellulose from pod husk of Cacao. The CMC material with optimum DS of 0.75 and high viscosity (206.10 cps) was obtained from a carboxymethylation reaction for 3 h using aqueous solution of 15% NaOH, temperature of 55.93 °C, and 4g of sodium monochloroacetate (NaMCA).

Dapi'a *et al.*, (2005) studied the rheological behaviour of CMC manufactured from TCF-bleached Milox pulps. CMC samples with different DS were obtained from Eucalyptus globulus pulps made in formic acid-peroxyformic acid medium (Milox delignification) and subjected to chlorine-free bleaching. This type of CMC, obtained by reaction in media made up of 2-propanol and mixtures of NaOH:MCA:cellulose was

classified as medium-viscosity type. The purity of CMC samples was higher than 99.2% and hence they were considered to be of pharmaceutical and food grades.

Bhandari *et al.*, (2012) studied the carboxymethyl cellulose was prepared using a continuous, reduced solvent, reactive extrusion process with a short reaction time. The effects of the amounts of NaOH (30 g, 40 g and 50 g), water: ethanol ratio (100%, 70%, 50%, 30% and 10% H₂O) and their interactions on the physical, chemical and morphological properties of carboxymethyl cellulose. X-ray diffraction analyses revealed higher degrees of crystallinity and fractions of cellulose. The degrees of substitutions decreased with increasing amounts of NaOH and tends to increase with increasing alcohol concentrations.

Mastrantonio *et al.*, (2015) studied the synthesis of CMC adopting the slurry process at ambient temperature using different amounts of sodium hydroxide and various incubation times. The synthesized CMC material was characterized by FT-IR spectroscopy, X-ray diffraction, DS, average degree of polymerization, rheological properties and apparent viscosity. The reaction yield and DS both decreased when the initial concentration of NaOH was increased from 7.0 g/mL to 10.5 g/mL. The CMC obtained was darker and had low hydration properties than commercial samples.

Qi *et al.*, (2009) studied the carboxymethylation of cellulose in an alkaline cellulose solvent, 7 wt.% NaOH/12 wt.% urea aqueous solution, was investigated. Carboxymethyl cellulose (CMC) samples were characterized with FT-IR, NMR, HPLC, and viscosity measurements. Carboxymethylation of cellulose in NaOH/urea leads to a polymer with the lowest DS value for water solubility (0.20) of CMC known. The total DS

of CMC could be controlled by varying the molar ratio of reagents and NaOH to AGU and the reaction temperature.

Mansouri *et al.*, (2014) studied the effect of the degree of substitution (DS) and the purity of sodium carboxymethyl cellulose (Na-CMC) prepared from Tunisian vine stem on the absorption and retention of water. Vine stem was first delignified using souda-anthraquinone, then bleached and finally chemically modified, in order to synthesize different (Na-CMC) derivatives. Carboxymethylation was carried out in presence of NaOH (40 %) and monochloro acetic acid (ClCH_2COOH), in *n*-butanol as a reaction solvent. The obtained (Na-CMC) derivatives were characterized using different tools such as the DS, Fourier transforms IR techniques, CP-MAS, ^{13}C -NMR. The performance of (Na-CMC) derivatives was compared with that achieved by commercial counterparts and it was concluded that the prepared ones exerted higher efficiency.

Saputra *et al.*, (2015) studied the Carboxymethyl Cellulose (CMC) can be obtained from water hyacinth cellulose using isopropyl-isobutyl mixture as reaction medium (20 ml: 80 ml, 50 ml: 50 ml, 80 ml: 20 ml) and the variations of NaOH concentration (5%, 10%, 20%, 30% and 35%) and the temperature of carboxymethylation process at 55 ° C. Increasing NaOH concentration and decreases DS. The optimum condition to increase DS of CMC (2.33) from water hyacinth cellulose is at composition of reaction medium isobutyl-isopropyl alcohol (20 ml: 80 ml) and NaOH concentration at 10%.

1.5 Objectives

The main objectives of this study were:

- To isolate cellulose from wheat stalks.
- To convert the isolated cellulose to CMC.
- To optimize the carboxymethylation conditions for the production of CMC of high degree of substitution (DS).
- To characterize the isolated cellulose and as-synthesized CMC materials using various physicochemical techniques.

Chapter Two

Materials and Methods

Chapter Two

Materials and Methods

2.1 Materials and Equipment

Wheat stalks collected from Gezira state(Sudan),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: 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), Wheat stalks, Extracted cellulose, as- Synthesized CMC.

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

2.2 Methods

2.2.1 Preparation of the sample

The wheat stalks raw materials were washed, air-dried and ground using mortar and pestle.

2.2.2 Extraction of cellulose from wheat stalks

The sample was soaked with suitable quantity of water in 1L beaker for about 30 minutes then decanted. The wheat stalks fibers were cooked in 1 M NaOH in sample to solvent ratio of 1:20 (w/v) for h 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 1 h at 80 °C four times. The bleached cellulose was washed again with distilled water until the order of hypochlorite could no longer be detected then washed with ethanol and oven dried at 60 °C (Adinugraha *et al.*, 2005).

2.2.3 Synthesis of sodium carboxymethylcellulose (CMC)

2.5 grams of extracted cellulose were suspended in 80 mL of (iso-propanol, n-Butanol, Ethanol, Methanol) and stirred continuously. A volume of 10 mL of aqueous NaOH solution (20%, 30% and 40% w/v) was added drop wise over a 30 min period. The mixture was stirred for 1 hour at room temperature. A quantity (1.5g, 2.5g and 3.5g) of mono chloro acetic acid (MCAA) were dissolved in 10 mL of solvent (isopropanol, n-Butanol, Ethanol and ethanol). The solution of MCAA was added to the alkalinized cellulose and the temperature was raised to 55 °C. The reaction was allowed to continue for certain time (2, 3 or 4 hours) then neutralized with 90% acetic acid and filtered. The CMC obtained was washed with a solution of 70% ethanol five times to remove undesirable by products then oven dried at 60 °C (Adinugraha *et al.*, 2005).

For purification purpose, the dried CMC was dispersed in 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 further washed with methanol and transferred to a beaker and heated until the alcohol was removed. The precipitate was oven dried in the at 105 C for 3 h then cooled to a room temperature in a desiccator and weighed (Pushpamalar *et al.*, 2006).

2.2.4 Optimum conditions for the synthesis of sodium carboxymethylcellulose (CMC)

In order to determine optimum reaction conditions for the synthesis all the procedure mentioned in section 2.2.3(pg.48) were followed, at 55 C, 2.5g MCAA, 3h, 30% NaOH and iso-propanol alcohol which were found to be optimum conditions (Pushpamalar *et al.*, 2006).

2.3 Characterization Methods

2.3.1 Infrared spectroscopy

Infrared spectroscopic analysis was carried out for isolated cellulose and as-synthesized CMC materials using the KBr method. The samples were oven dried at 60 C. 0.2 mg of a sample and 2 mg of KBr were mixed finely ground and the mixture was compressed to a form a transparent disk. Infrared spectra of samples were recorded with Fourier transform infrared spectrometer, FT-IR, Shimadzu (model 8400S- Japan) between 400- 4000 cm^{-1} (Pushpamalar *et al.*, 2006).

2.3.2 Determination of degree of substitution (DS)

Absolute values of degree of substitution (DS) of all samples were determined by conventional 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. 12.5

mL aqueous sodium hydroxide (0.5 N) were added and boiled for about 15 min. The hot solution was titrated against a solution of 0.3 N hydrochloric acid using phenolphthalein indicator. The carboxymethyl content and the DS were calculated using equations 2.1 and 2.2 below.

$$\text{Carboxy methyl content (CM \%)} = [(V_0 - V_n) \times N \times 0.058 \times 100] / M \quad (2.1)$$

$$\text{DS} = [162 \times (\text{CM \%})] / [5800 - (75 \times (\text{CM \%}))] \quad (2.2)$$

Where V_0 = 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, and 58 = the molecular weight of carboxymethyl group (Pushpamalar *et al.*, 2006).

2.3.3 X-ray diffractometer (XRD) powder

. 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 *et al.*, 2005).

2.4 Rheological studies

2.4.1 Plastic viscosity, apparent viscosity and yield point

Concentrations of 3.5 ppb and 700 ppb aqueous solutions of CMC, PAC-LV and PAC-RV were prepared and agitated for 5 minutes by Hamelton mixer in 700 mL Viscometer cup. The cup of each solution was located under sleeve of Fann model 355A Viscometers. The rotor sleeve was immersed in the sample to scribed line. The sample was stirred for 5 seconds at 600 RPM and then at d 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):

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

Yield point (in 1b/100 ft²):

$$\text{Yield point (YP)} = 300 \text{ RPM reading} - \text{plastic viscosity (Pete, 2003)} \quad (2.5)$$

2.4.2 Filter loss

Well agitated water solution of synthesized CMC of 7 ppb concentration was introduced to the 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 Discussions

3.1 Yields of extracted Cellulose and as-synthesized CMC

The cellulose was extracted from wheat stalks fibers and then converted to carboxymethylcellulose (CMC) material by carboxymethylation using monochloro acetic acid (MCA) 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 in optimum condition

Weight of wheat stalks fibers (g)	Percentage yield cellulose (%)
100	48
Weight of cellulose (g)	Weight of CMC (g)
2.5	4.5

It very obvious that raw wheat stalks 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, the weight of produced CMC can be twice or more than the weight of cellulose precursor.

3.2 FT-IR spectroscopic analysis

FT-IR spectroscopy was used to indicate the extraction of pure cellulosic material from wheat stalk. It was also used to examine the changes in the chemical composition of the cellulose fibres as a result of carboxymethylation reaction. The FT-IR spectra of wheat stalks fiber, cellulose and as-synthesized CMC were recorded. The prominent peak at 1660 cm^{-1} that is seen in the spectrum of the untreated wheat stalks fibers (Fig. 3.1) can be attributed to either acetyl or ester group of the hemicellulose. Whereas, the peak at frequency of 1515 cm^{-1} is due to $\text{C} = \text{C}$ stretching vibration of the aromatic rings of lignin. The peak at 1433 cm^{-1} is assigned to $-\text{CH}_2-$ bending vibration, and peaks in the region from $1244 - 933\text{ cm}^{-1}$ are due to $-\text{C}-\text{O}-$ stretching. The $-\text{C}-\text{O}-\text{C}$ pyranose ring skeletal vibration gives a prominent band of 1043 cm^{-1} (Elanthikkal et al., 2010).

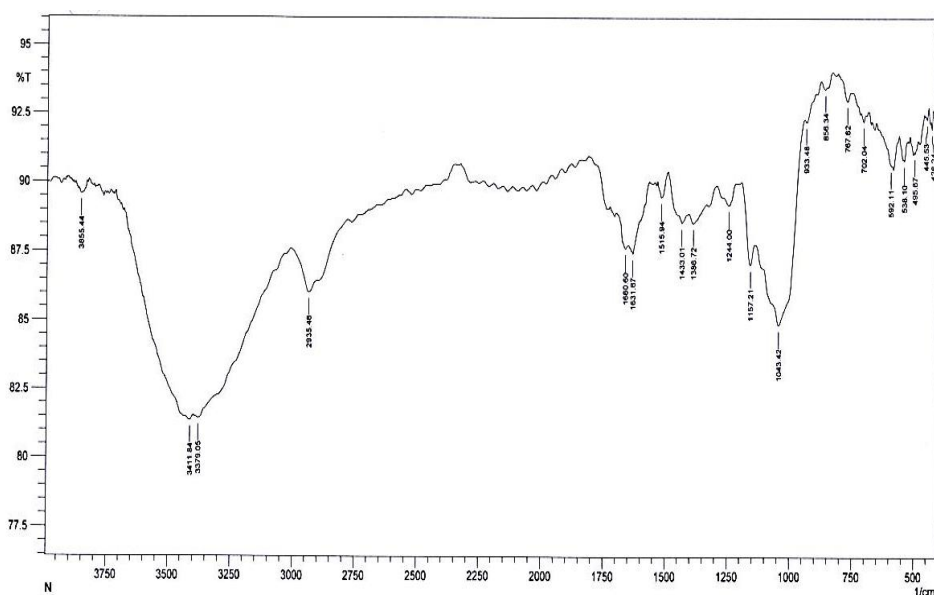


Figure 3.1: The FT-IR spectrum of untreated wheat stalks fibers

Figure 3.2 shows the FT-IR spectrum of cellulose extracted from wheat stalks fibres. The broad absorption band at 3404 cm^{-1} is due to the stretching frequency of the -OH group as well as intra-molecular and intermolecular hydrogen bonds. The band at 2896 cm^{-1} is due to C-H stretching vibration, whereas, the bands of frequencies centered at 1429 and 1319 cm^{-1} are assigned to -CH_2 scissoring and -OH bending vibration, respectively. The band at 1058 cm^{-1} is due to OCH-O-CH_2 stretching (Kondo, 1997). Figure 3.2 also shows the lack of aromatic -C=C- stretching of the aromatic ring of lignin at 1515 cm^{-1} and carbonyl group -C=O of hemicellulose at 1660 cm^{-1} indicating an almost pure cellulosic was successfully extracted from wheat stalks (Kondo, 1997).

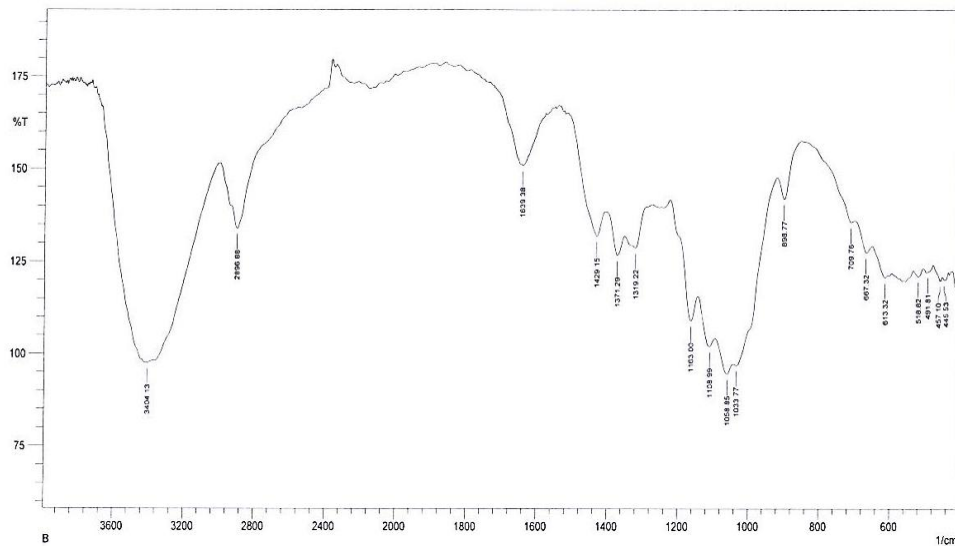


Figure 3.2: The FT-IR spectrum of cellulose extracted from wheat stalks fibers

The FT-IR spectrum of as-synthesized CMC, which is depicted in Figure 3.2, shows typical absorption bands of the cellulose back bone as well as the presence of the carboxymethyl groups at 1616 and 1425 cm^{-1} . It is clearly evident that the broad absorption band at -OH group and a band at 2912 cm^{-1} are attributable to C-H at 2896 cm^{-1} stretching vibration. The presence of a new and strong absorption band at 1616 cm^{-1} confirms the presence of COO^- group. The bands around 1425 and 1325 cm^{-1} are assigned to -CH_2 scissoring and -OH bending vibration, respectively. The band at wave number 1060 cm^{-1} is due to OCH-O-CH_2 stretching (Biswal and Singh, 2004).

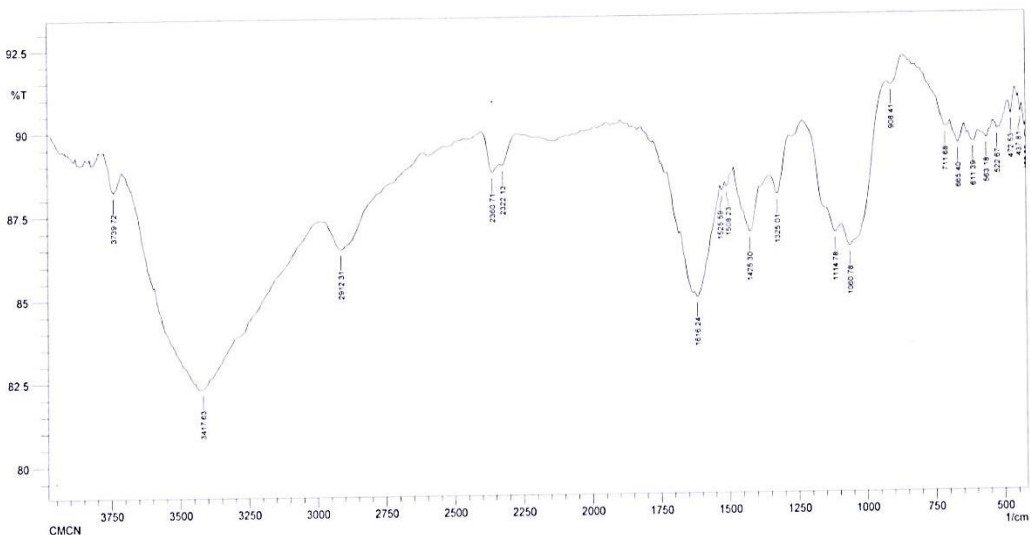


Figure 3.3: The FT-IR spectrum of as-synthesized CMC of optimum DS (0.39)

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 investigate its effect in the value of Degree of Substitution (DS). As illustrated in Figure 3.3, maximum DS value of 0.43 was obtained when 3.5 g of MCAA were used while other parameters were kept constant i.e., 2.5 g of cellulose, 30% NaOH alkalization solution, 55 C reaction temperature and iso propanol solvent. There was an increase in the DS with increasing amount of MCAA. This 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 (3.9) 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.

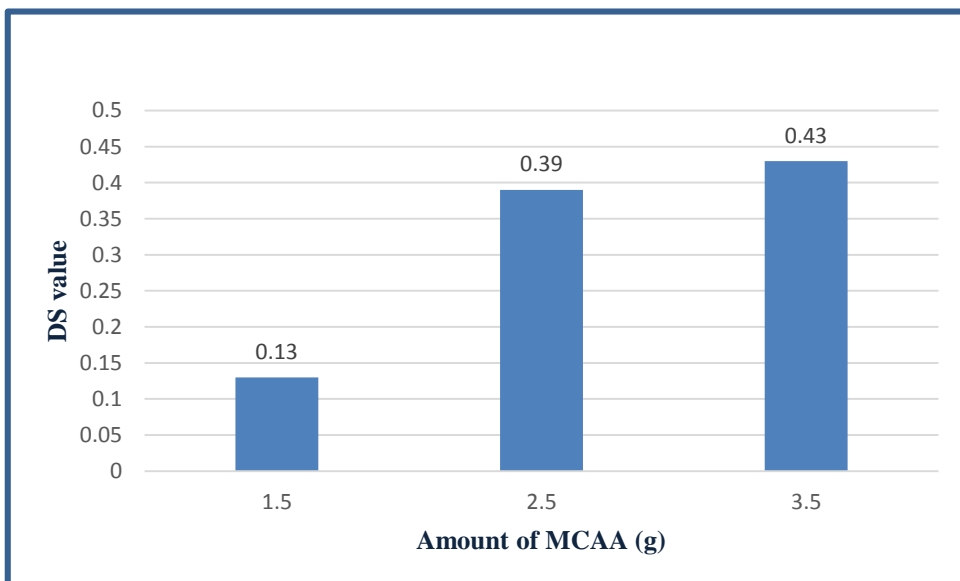


Figure 3.4: The effect of various amounts of MCAA on the value of DS

3.3.2 Effect of the concentration of sodium hydroxide solution

The effect of the concentration of NaOH aqueous solution on the value DS was also studied keeping other parameters constant. Figure 3.5 shows a direct proportional relationship between the DS and the concentration of NaOH aqueous solution used for alkalization. A maximum DS value of 0.39 was obtained when a concentration of 30% NaOH was applied. However, when the concentration of NaOH was increased beyond 30%, an obvious decrease in DS value was observed. The results clearly indicate that NaOH is significant for carboxymethylation reaction, but when its concentration reached higher levels it could promote the degradation of the glycosidic bonds of cellulose forming sodium glycolate by product. The same phenomenon was observed and reported by Pushpamalar *et al.* (2006).

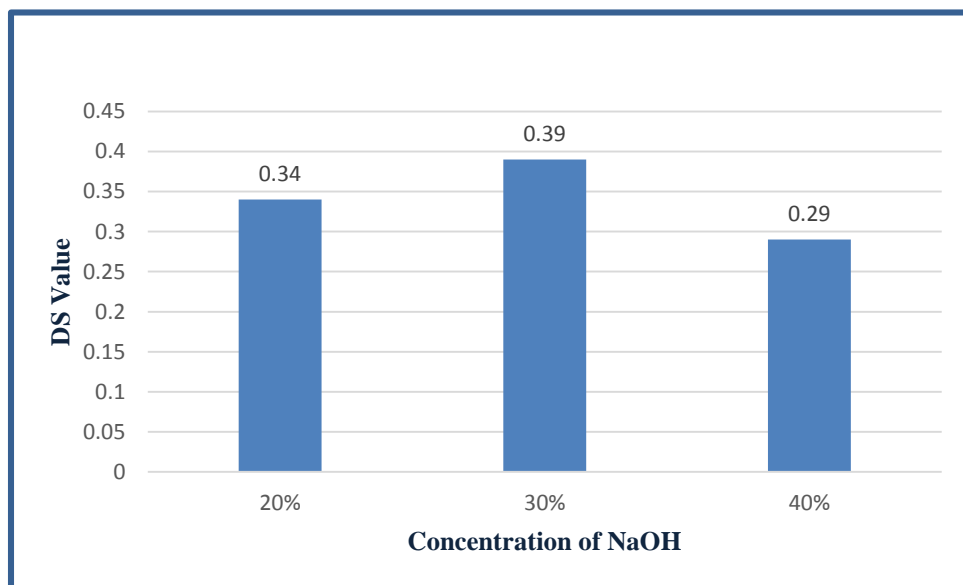


Figure 3.5: Effect of various concentration of NaOH on the DS

3.3.3 Effect of various solvents

The effect of solvent on the degree of substitution was investigated using four different alcohols (section 2.2.3) Higher DS value of 0.39 was obtained using isopropyl

alcohol as a solvent while fixing other reaction parameters. It is important to note that the principle 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. It is therefore, considered promoter for CMC production and inhibitor for glycolate formation (Toğrul and Arslan, 2003).

The variation in the extent of carboxymethylation with different alcoholic solvents could be clarified by taking into consideration their solvent polarities and stereochemistry. The reaction efficiency increases as the polarity of the solvent decreases (Barai et al., 1997). Figure 3.6 depicts the results of DS over various alcohols used as solvents for the carboxymethylation reactions. Interestingly, the obtained results were in perfect agreement with the literature (Bhattacharyya *et al.*, 1995, Khalil *et al.*, 1990) but the solvents isopropyl alcohol and butanol, with almost similar polarity, did not produce CMC with the same DS value. Considering its availability and low price as well as its wide uses as common solvent in literature for this reaction, isopropanol was selected as an optimum solvent to study the subsequent parameters (Bhattacharyya *et al.*, 1995, Khalil *et al.*, 1990).

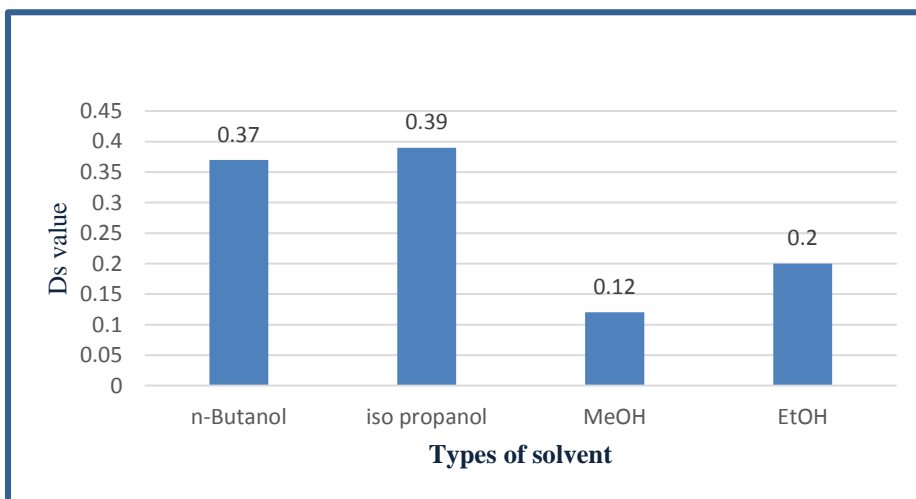


Figure 3.6: The effect of various solvents on the value of DS

3.3.4 Effect of reaction time

The effect of various reaction times was also considered in this study at optimum reaction conditions. It is very clear in Figure 3.7 that the value of DS increased with reaction time until three hours (180min) then decreased beyond this time. The decrease in DS value could be attributed to the degradation of glycosidic bonds. This degradation was expected since such high concentration of NaOH was applied. It occurs at low rates but its effect becomes obvious over long reaction periods (Pushpamalar *et al.*, 2006).

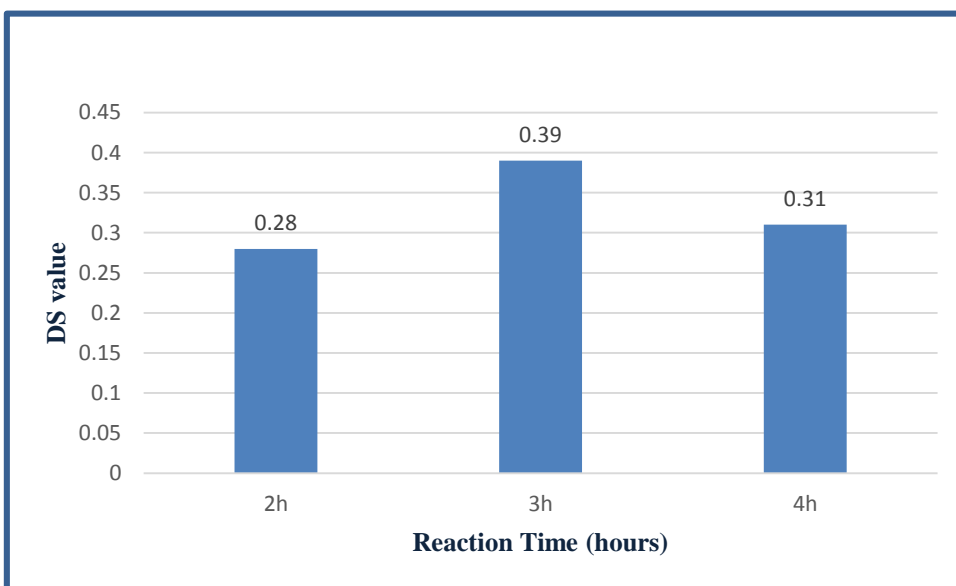


Figure 3.7: The effect of various reaction times on the DS

3.4 The XRD of pattern of as- synthesized CMC

The XRD diffraction analysis was conducted for CMC of an optimum value of DS (0.39). As it is already established that the crystallinity of cellulose was associated with inter- and intra- molecular hydrogen bond of cellulose (Elanthikkal *et al.*, 2010). As manifested in Figure 3.8, this arrangement, i.e. degree of crystallinity, decreased as a result of treated with 30% NaOH. 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 3.9) presented in Figure 3.8 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 *et al.*, 2005).

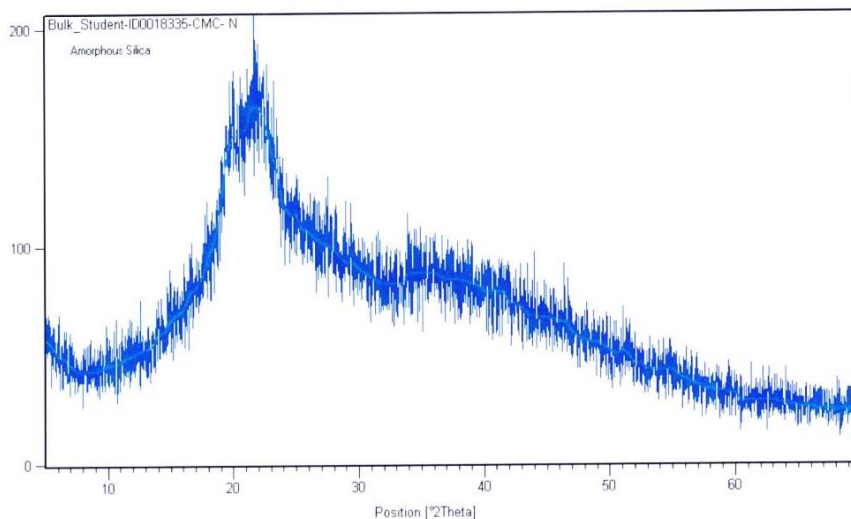


Figure 3.8: The XRD of pattern of as- synthesized CMC of highest DS

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).

Polyanionic cellulose (PAC) is used primarily as a fluid-loss reducer for fresh water and salt water muds and it also acts as a viscosifier of the system. PAC is available in two

types (high or low viscosity type), both of which impart the same degree of fluid- loss control but different degrees of viscosity. Temperature stability of PAC is 149 °C and is not subjected to bacterial degradation. Rheological studies were conducted for the CMC material to study its efficiency as an alternative and competitive viscofier and/or fluid loss controller (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	21.8	13.6	10.9	7	1.2	1
PAC – LV		18	10	6	3	1	0.4
PAC – RV		69	47	38	25	4	2

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	66.5	48.2	41.0	27.9	5.0	3.8
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 of 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 8.2 centipoise-up, apparent viscosity of 10.9 centipoise-up and yield point of 5.4 lb/100 ft². 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 ft². 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 ft².

Table 3.4: Plastic viscosity (μ_p), apparent viscosity (μ_A) and Yield point (YP) for 3.5 ppb aqueous solution of carboxycellulosic materials

Material	μ_p (CP)	μ_A (CP)	YP (1b/100 ft ²)
CMC	8.2	10.9	5.4
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 18.3 centipoise-up, apparent viscosity of 33.2 centipoise-up, yield point of 29.9 1b/100 ft². 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 1b/100 ft². 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 1b/100 ft². And filter loss of the as- synthesized CMC was found to be 21 cm³ per 30 min.

Table 3.5: Plastic viscosity (μ_p), apparent viscosity (μ_A) and Yield point (YP) for 7 ppb aqueous solution of carboxycellulosic materials

Material	μ_p (CP)	μ_A (CP)	YP (1b/100 ft ²)
CMC	18.3	33.2	29.9
PAC – LV	21.0	22.5	3.0
PAC – RV	45	95	100

It is possible to 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⁺ 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 21 mL per 30 minutes. Whereas, the standard filter loss is 10 cm³ per 30 minutes, hence the as-synthesized CMC can be classified as viscofier rather than filter loss controller.

Conclusion

- The sodium (CMC) was successfully synthesized from carboxymethylation of cellulose isolated from wheat stalks using pure isopropanol as a solvent.
- 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 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 (0.39) associated with the synthesized material.

Recommendations

According to the findings of this research, CMC can be prepared from wheat stalks at reasonable conditions. However, more studies are recommended to overcome or minimize the problems associated with fabrication of CMC from wheat stalks. 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.
- Investigations off the effect of temperature are also needed for the possibility of conducting the reaction at lower temperatures.

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