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SCHOOL OF GRADUATE STUDIES

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PRODUCTION AND OPTIMISATION OF CARBOXYMETHYLCELLULOSE FROM WASTE CARTONS

By

Abebe Hailu

A Thesis Submitted to the School of Graduate Studies of Addis Ababa University, Institute of Technology, in Partial Fulfilment of the Requirement for the Degree of Masters of Science in Chemical Engineering (Process Engineering)

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List of Acronyms

AGU- Anhydroglucose unit

ANOVA- Analysis of variance

CCD- Central composite design

CMC- Carboxymethyl cellulose

DCM- Dichloromethane

DS-Degree of substitution

GHC-Green house gas

GPC- Gel permeation chromatography

H-CMC- Acid form of CMC

HEH- hypochlorite bleaching, caustic extraction, hypochlorite bleaching sequence

MCA-Monochloro acetate

NaCMC- Sodium carboxymethyl cellulose

PHK-Pre-hydrolysis kraft

RSM-Response surface methodology

SMCA-Sodium monochloroacetate

ABSTRACT

Lignocellulosic materials (e.g. Waste cartons) can be utilized to produce carboxymethyl cellulose, a water soluble, biodegradable anionic polymer. This study involved production and optimization of carboxymethyl cellulose from waste cartons. The conversion of waste cartons to CMC can be achieved mainly by three process steps: extraction of cellulose from waste cartons, alkalization of the extracted cellulose and etherification of the alkali cellulose into CMC. The central composite experimental design (CCD) method involving response surface methodology was chosen to optimize the alkalization, etherification reaction and to determine the effect of three operating variables: NaOH concentration, amount of monochloroacetic acid and temperature (T). For the response surface methodology involving CCD, a total of 20 experiments were conducted for three factors at two levels with three replicates at center point. An optimization was carried out to optimize the alkalization and etherification reaction parameters so as to determine the best NaOH concentration, sodium monochloroacetic acid dosage, and etherification temperature that resulted optimum degree of substitution (DS) of the CMC. The statistical analysis showed that the degree of substitution of CMC of 0.767 was obtained at optimised alkalization & etherification variables of 13.53%w/w NaOH conc., 0.4 w/w of monochloroacetic acid to cellulose, and 41.62°C etherification temperature. The value of degree of substitution of CMC obtained from experiment at the optimized conditions of sodium hydroxide concentration of 13%, monochloroacetic acid concentration of 0.4w/w and etherification temperature of 41°C was 0.767. It is concluded that the waste cartons can be a good source of cellulose that can be modified by etherification reaction to carboxymethylcellulose with a medium degree of substitution of about 0.767.

INTRODUCTION

1.1 BACKGROUND OF THE STUDY

Commercially carboxymethyl cellulose (CMC) is produced from virgin cellulosic plants like cotton linter and wood pulp which are very costly agricultural products and also their use aggravates the deforestation and environmental problems. Globally, 140 billion metric tons of biomass is generated every year from agriculture. This volume of biomass can be converted to an enormous amount of energy and raw materials. Equivalent to approximately 50 billion tons of oil, agricultural biomass waste converted to energy can substantially displace fossil fuel, reduce emissions of greenhouse gases and provide renewable energy to some 1.6 billion people in developing countries, which still lack access to electricity. As raw materials, biomass wastes have attractive potentials for large-scale industries and community-level enterprises (UNEP, 2009). Biomass takes the form of residual stalks, straw, leaves, roots, husk, nut or seed shells, waste wood and animal husbandry waste. Widely available, renewable, and virtually free, waste biomass is an important resource. With the global campaign to combat climate change, countries are now looking for alternative sources of energy and materials to minimize green house gas (GHG) emissions. Aside from being carbon neutral, the use of biomass for energy and materials reduces dependency on the consumption of fossil fuel; hence, contributing to energy security and climate change mitigation. (UNEP, 2009).

Currently, because of the economic growth seen in Ethiopia, the consumption of chemicals and additives has increased and much of the demand is met from imported products. One of these chemicals is carboxymethyl cellulose, which is a cellulose derived water soluble polymer, widely used in the liquid detergent formulation.

On the other hand, economic growth, and changing consumption and production patterns are resulting into rapid increase in generation of waste papers and cartons in the world in general and in Ethiopia in particular. The world's annual consumption of paper and paperboard materials is anticipated to grow from 300 million tonnes to over 490 million tonnes by the year 2020, which is expected to raise the cost of pulp wood (Agnihotri et al., 2010). This implies that on one hand, more resources are being used to meet the increased demand of papers and, and on the other hand, more papers and cartons waste is being generated at the end of their useful life. The increasing demand coupled with environmental concerns, have increased interest in alternative feedstocks and processes for more efficient, integrated use of the raw material according to the "zero waste" context (Kamm and Kamm, 2004).

Carboxymethyl cellulose (CMC) is a cellulose derivative produced by alkalyzation and carboxymethylation. There are many researches which studied the production of CMC from agricultural waste as a cellulose sources. CMC from sugar beet pulp cellulose and rheological behaviour of CMC was studied by Togrul and Arslan (2003). Adinugraha et al. (2005) synthesized and characterized sodium CMC from cavendish banana pseudo stem. Alkalization, using 15% NaOH provided the highest DS value of CMC (Adinugraha et al.,2005). Pushpamalar et al. (2006) investigated the optimization of reaction conditions for preparing CMC from sago waste. Yalew (2011) synthesized carboxymethyl cellulose from sugarcane bagasse. Asep et al.(2014) synthesized and characterized carboxymethyl cellulose (CMC) from water hyacinth using ethanol-isobutyl alcohol mixture as the solvents. These studies and references therein report the possibility of synthesizing carboxymethyl cellulose from lignocellulosic biomass. In cognizant of the importance of meeting the countries demand of CMC and resource efficiency, this research work aims at producing carboxymethyl cellulose from waste cartons.

In this study, the production of CMC using cellulose extracted from waste cartons was investigated. The cellulose was converted to CMC through carboxymethylation process using William Etherification technique in heterogeneous system. The synthesized CMC was characterized in terms of DS.

1.2 PROBLEM STATMENT

In modern world, the consumption of disposable materials has increased and hence, the load on the environment has increased dramatically. On the other hand, chemical products are produced from virgin materials, the consumption of which has great impact on the resource depletion and environment. In this context, development of products and processes that convert waste materials to useful products is of great importance and need to be prioritised.

In this regard the consumption and disposition of cartons has increased in Ethiopia and in parallel to that the import of carboxymethl cellulose (CMC) has increased in the last few years. Therefore the main objective of this thesis is to extract cellulose from waste cartons, and to produce carboxymethyl cellulose. The study also aims at the optimization of the process conditions.

1.3 OBJECTIVES OF THE STUDY

1.3.1 GENERAL OBJECTIVES

The general objective of this thesis is the production and optimization of the reaction conditions of carboxymethyl cellulose from waste cartons.

1.3.2 SPECIFIC OBJECTIVES

The specific objectives of the research were listed as follows:

- To extract cellulose from the waste cartons.
- To carry out alkalization and etherification reactions to produce carboxymethyl cellulose.
- To optimize the alkalization, & etherification reaction parameters like concentration of NaOH, concentration of monochloroacetic acid and temperature against the degree of substitution.
- To perform preliminary economic analysis of the process.

1.4 SIGNIFICANCE OF THE STUDY

The proposed benefits of using waste cartons as chemical feedstock were three-fold: economic, social and environmental which are the three pillars of sustainability.

- This study contributes to a significant improvement in the efficient resource utilization by converting waste to wealth.
- It contributes to the development of green economy effort by reducing deforestation in search of virgin material.
- It also contributes to the economic benefit by promoting the import substitution policy of the country by producing input materials locally.
- It will create job opportunity and income generation to the people who participate in the collection of waste cartons and production of carboxymethyl cellulose.

2. LITERATURE REVIEW

2.1 Raw materials for CMC production

Chemical functionalization of cellulose aims to adjust the properties of macromolecule for different purposes, particularly, as a chemical feedstock for production of cellulose derivatives for a variety of applications. In theory, all cellulosic materials can be used for the production of modified celluloses such as carboxymethyl cellulose. This is because it is possible to extract the cellulose from cellulosic materials (Yalew, 2011). The conventional sources of cellulose include cotton linters and wood pulp which now-a-days are discouraged on account of the cost of the former, availability, easy of delignification and environment conservative regulations associated with the latter. Further, renewable raw materials are gaining considerable importance because of the limited existing quantities of fossil supplies. In this regard, cellulose-rich biomass derived from the nonconventional sources such as weeds, fibers, bamboos, and wastes from agriculture and forests, etc. acquires enormous significance, as alternative chemical feedstock, since it consists of cellulose, hemicellulose, and lignin, which contain many functional groups suitable to chemical functionalization (Yalew, 2011).

Table2.1. Composition of common lignocellulosic raw materials and wastes (wt % on dry material)

Source	**Cellulose (%)**	**Hemicelluloses (%)**	**Lignin (%)**	**Extracts (%)**
Hardwood stems	45-50	24-40	18-25	
Softwood stems	45-50	24-40	18-25	
Corn cobs	45	35	15	
Wheat straw	30	50	15	5
News paper	40-55	25-40	15-30	
Bagasse	40-50	23-35	18-24	
Cotton	95	2	1	0.4
Waste cartons	68.4	11	11.4	

Source: Cheung & Anderson (1997); Mandal Chakrabarty (2011); Francou et al. (2008)

2.2 Cellulosic polymers

Cellulosic polymers (or: cellulosics) are produced by chemical modification of natural cellulose. The main representatives are cellophane, a type of regenerated cellulose used for films, cellulose acetate, an ester derivative (for moulding, extrusion and films); and regenerated cellulose for fibres (including viscose/rayon and Lyocell). Cotton fibers and wood are the primary raw materials for the production of industrially used cellulose (Krässig, 1993).

Cellulose is one of the main cell wall constituents of all major plants, both nonlignified (such as cotton) and lignified (such as wood) and constitutes as such the major portion of all chemical cell components. It is also found in the cell walls of green algae and the membranes of most fungi. So-called bacterial cellulose is synthesized by *Acetobacter xylinum* on nutrient media containing glucose (Krässig, 1993).

Cellulose was first used as a basis for polymer production in the mid- to late-19th century, when applications in both films and fibres were developed. One of the first cellulosic films was cellulose nitrate, which was introduced as a base material for photographic emulsions. Due to its flammability, it was later replaced by cellulose triacetate. Other important early cellulose-based films were derived from cellulose acetate and cellulose hydrate. Until the 1950's, cellulose hydrate films (cellophanes) dominated the packaging field. In particular, cellophane coated with cellulose nitrate or poly(vinylidene chloride) found extensive applications due to its low permeability to water vapor and oxygen, coupled with desirable sealing properties.

Following the introduction of polyolefin films in the 1950's with their extensive processability, durability and good mechanical properties, films from cellulosic polymers lost their market dominance. Cellulosics, with their relatively high price compared to petrochemical polymer replacements, were relegated to comparatively low volume or niche applications. This is evidenced by statistics for the global production of man-made cellulosic fibres (IVC, 2003) from the period 1970 to 2000, showing the relative stagnation of cellulosic fibres compared to a tenfold increase in man-made synthetic fibres. Although, there have been improvements recently in regenerated cellulose technology (e.g. lyocell, rayon/viscos, cellulose coating technologies), there it seems unlikely that cellulosics will attain sufficient competitiveness to grow their market share over other polymers and may even lose further ground to newly developing bio-based polymer alternatives.

2.2 Cellulosic Biomass

Cellulose is a polymer consisting of glucose units and is the main component in plant cell wall structure, which typically represents approximately 35 to 50 % of plant dry weight. It is produced by some animals (e.g. tunicates) (Coffey et al,1995) and a few bacteria [Lynd et al., 2002]. Therefore, cellulosic biomass is an abundant organic matter (e.g. carbohydrate molecules) reserved in earth that has aroused research interest in its re-utilization, as it can be obtained from a variety of sources such as agricultural,forestry residues, municipal and industrial solid wastes.

However cellulose fibre, usually found in a mixture with other biopolymers, primarily hemicellulose, lignin and other substances such as pectin, waxes and organic acids, which need to be removed by physical, chemical or biological treatment before to gain access to cellulose chains (Abdel-Monem et al.,1984).

The cellulose is a polymer composed of a long chain of glucose, between hundreds to several thousand residues depending upon the source, linked by β-1, 4-glucosidic bond [Van Wyk, 2000].The individual chains adhere to each other along their lengths by hydrogen bonding in a way that forms a matrix called crystalline cellulose that strengthens plants. Crystalline cellulose represents approximately 50-90% of the total cellulose polymer [Fujita et al, 2004]. Consequently, the success of the hydrolysis method depends on the effectiveness in breaking the β-1, 4-glucosidic bonds. However, in the cellulose matrix ,there exists some remainder chain units, which present a disorganised array and are known as amorphous cellulose [Fujita et al, 2004].

This structure contains tens of glucan chains in parallel orientation. Their reducing chain ends at one terminus, and their nonreducing chain ends at the other terminus. The reducing end is a latent aldehyde and responds to both reduction and oxidation process, making it stable and less accessible to water.

In the chain-like extended linear macromolecule, the glucose units are linked together by β-1, 4-glucosidic bonds formed between the carbon atoms C1 and C4 of adjusted glucose units. On formation of the glucosidic linkage of a single oxygen atom linked to two carbons, a molecule of water is eliminated. Consequently, the glucose unit in the cellulose polymer is referred to as an anhydroglucose unit (AGU). The cellulose chain has a non-reducing (alcoholic) hydroxyl end group and a reducing (aldehyde) hydrate end group that show different patterns of behavior (Krässig 1993; Klemm et al. 2001a).

The chemical character of the cellulose molecule is determined by the sensitivity of the β-glucosidic link between the glucose repeating units to hydrolysis and by the presence of three reactive hydroxyl groups, i.e. the primary OH-6 and the two secondary OH-2 and OH-3 in each glucose unit. The hydroxyl groups can undergo etherification and esterification reactions. The reactivity of the hydroxyl groups is to a certain extent dependent on solvent and decreases in the order OH-2 > OH-6 > OH-3 in the cellulose molecule when producing CMC in isopropanol, determined by H-NMR (Baar et al. 1994).

The cellulose molecule has a strong tendency to form intra-molecular (within the same molecule) and intermolecular (between neighbouring molecules) hydrogen bonds (Klemm et al. 2001a). The intra-molecular hydrogen bonds are the main reason for the stiffness and rigidity of the cellulose molecule. It has been proposed that it also exists within hydrophobic interactions between the cellulose molecules (Lindman et al. 2010). Cellulose is hard to dissolve in aqueous solutions due to the existence of large quantities of inter- and intra-molecular hydrogen bonds and the hydrophobic interactions between the cellulose molecules.

2.3. Reactivity viewed at the molecular and supermolecular levels

Cellulose accessibility and reactivity have been the topic of great interest for years. Even today, they have not lost their significance and are some of the most important quality parameters for dissolving pulps. These parameters, which are associated with the accessibility and reactivity of chemicals (solvents and reagents) to the cellulose, are considered to be completely dependent on the structure and morphology of the cellulose fibers (Krässig, 1993). Furthermore, it has been suggested that cellulose reactivity is more related to the dissociation of fibril aggregates into elementary fibrils than to crystallinity (Fahmy and Mobarak ,1971).

Cellulose exhibits a compact and complex network characterized by the arrangement and deposition of cellulose molecules in fibrils and fibril aggregates in the cell wall, resulting in more- or less-ordered regions formed by the hydrogen bonds within the cellulose chains (Fengel and Wegener 1984; Klemm et al. 2002). The hydrogen bonds, together with dipole interactions and van der Waals bonds, produce rather strong inter-chain forces that are responsible for the limited accessibility of cellulose to solvents and reagents. Therefore, only the cellulose molecules located on the surfaces and within the fibrils and aggregates are accessible.

The accessibility of cellulose depends mainly on the number and size of the pores in the cellulose structure, the size and type of solvent or reagent, the internal surface that is

accessible (as determined by the size of fibrils or fibril aggregates), and the structure of the cellulose molecules (which determines which hydroxyl groups are accessible). Therefore, to increase cellulose accessibility, the pores must be opened and both the fibril aggregates and the highly ordered regions must be altered (Krässig,1993).

The accessibility and reactivity of cellulose are also affected by the hornification. Hornification occurs upon drying or water removal from the pulp, which causes a partial irreversible collapse of the polymer structure by shrinking the internal fiber volume and, therefore, a reduction in its reactivity. Hemicelluloses have shown to hinder the hornification effect (Oksanen et al. 1997). However, dissolving pulps demand a low amount of hemicelluloses. Thus, when hemicelluloses are removed, hornification is likely to occur.

In recent years, several studies have proposed optimal treatments, either alone or in combination, to activate cellulose and, therefore, increase its accessibility and reactivity. Activation methods include degradative treatments (e.g., hydrolysis, oxidation and thermal treatments), mechanical treatments (e.g., wet milling and dry milling), and swelling treatments (e.g., interfibrillar and intrafibrillar action) (Krässig 1993). For instance, it has been reported that different aqueous solvents, such as sodium hydroxide, have been used as swelling solvents (Bochek 2003; Ye and Farriol 2005; Bui et al. 2008), as well as the combination of sodium hydroxide and urea (Kunze and Fink 2004). In addition, enzymatic treatments have been shown to activate cellulose by enhancing cellulose accessibility and reactivity. They have become a very promising environmentally friendly alternative to other treatments (Jeffries, 1992; Pere et el., 1995).

2.4. Dissolving Grade Pulp

2.4.1 Introduction

Dissolving pulp refers to the pulp of high cellulose content which is used to manufacture various cellulose-derived products such as regenerated fibres or films (e.g., Viscose, Lyocell), cellulose esters (acetates, propionates, butyrates, nitrates) and cellulose ethers (carboxymethyl-, ethyl-, methyl-celluloses). The wood-derived celluloses which account for about 85–88% of the total dissolving pulp market are made by the pre-hydrolysis kraft and acid sulfite processes comprising additional purification stages such as hot and cold caustic extraction. The residual amount of dissolving pulps is based on cotton linters. The linters fibres, being attached to the cotton seeds, are removed by the deliniting process, producing fibres of different lengths. The shortest fibres or second-cut linters are used as chemical feedstock. Purification is accomplished by a combination of mechanical and chemical steps comprising mild alkali treatment at elevated temperature to remove proteins, waxes, pectins

and other polysaccharides and bleaching to achieve the required brightness level. Purified cotton linters represent the dissolving pulp of highest cellulose purity particularly used for manufacturing acetate plastics and high-viscosity cellulose ethers.

Production of dissolving pulp is carried out by acid sulfite and prehydrolysis kraft processes. The acid sulfite process is the most common and benefits of this technique include high recovery rates of the inorganic cooking chemicals and the totally chlorine free (TCF) bleaching. One disadvantage is that it results in pulps with a broad molecular weight distribution of cellulose (Sixta et al. 2004). Organosolv processes have been suggested as alternative pulping methods. The original one only using a mixture of water and ethanol. New acid pulping processes such as Acetosolv, Formacell and Milox have also shown promising results (Vila et al. 2004; Puls et al. 2006). Comparisons of the pulps produced by these different methods have presented by some researchers (Fink et al. 2004; Sixta et al. 2004). In the cited studies, the process ability of the pulps regarding viscose staple fibre preparation and NMMO treatment were tested. The pulp was characterized in terms of their chemical properties and structure by microscopy, NMR spectroscopy and X-ray scattering. Another area of great interest is the potential of biosulfite pulping in dissolving pulp production (Christov et al. 1993).

When using softwoods and hardwoods as a raw material, more drastic conditions in pulping and bleaching operations are required in order to obtain a high quality dissolving pulp. However, even least amounts of residual impurities such as resins or inorganic compounds can adversely affect the filterability of viscose, and some residual non-cellulosic carbohydrates can promote yellowing of cellulose acetate spinning dope. Since complete removal of non-cellulosic impurities would be very expensive and, moreover environmentally harmful (high yield loss, high chemical charges, additional equipment, etc.), the main emphasis is placed on adjusting the refining processes on the demands of each cellulose product.

The suitability of dissolving pulps can be adequately determined only by simulating the conversion processes to the final products (e.g., to regenerated fibres or cellulose derivatives) on a small scale. Sometimes, even pilot plant or mill-scale tests are needed to approve the dissolving pulp for further processing. This is particularly true in the case of new applications such as the Lyocell process. Since the early days of cellulose research, much effort has been undertaken to develop analytical methods that provide rapid and reliable assessment of the quality of dissolving pulp. There are many established methods for evaluating pulp quality, but they are insufficient to provide a full picture of the dissolving pulps′ properties (Treiber, 1971; Treiber, 1974). The relationships between

structure, chemical composition and behaviour with regard to topochemical reactions are too complex. The difficulty of reliable cellulose characterization has been expressed appropriately by L.E. Wise, an important pioneer of cellulose chemistry and technology, by the statement that “Cellulose is a system, not a pure individual” (Treiber, 971).

The process ability of a dissolving pulp is often characterized as its reactivity towards derivatizing chemicals or solvents. Reactivity is related to the accessibility of chemicals to the cellulose, which virtually means the relative ease by which the hydroxyl groups can be reached by the reactants. The structure and morphology of cellulose is responsible for the homogeneity of the conversion process and the final product quality. A reliable analysis of the property profile of dissolving pulps involves the extensive characterization of the cellulose structure at three different levels: (a) the molecular level of the single macromolecule; (b) the supramolecular level of aggregation of macromolecules to highly ordered structural entities; and (c) the morphological level comprising the architecture of well-organized fibrillar elements. Moreover, the pore system providing access to the molecular structure is an important characteristic of dissolving pulps. Finally, the qualitative and quantitative determination of organic and inorganic impurities completes the analytical characterization of a dissolving pulp.

2.4.2 Dissolving Pulp Characterization

2.4.2.1 Pulp Origin, Pulp Consumers

Despite much effort to develop alternative pulping routes, dissolving pulp is still solely produced by acid sulfite and prehydrolysis kraft processes. The most promising alternative processes under development are organosolv processes such as that originally proposed by Kleinert in 1931 (Sixta, 2006) and further developed by Peter and Höglinger (Sixta, 2006) using only a mixture of ethanol and water. Other approaches include the recently evaluated Formacell procedure, as well as the prehydrolysis- ASAM (alkaline sulfite with anthraquinone and methanol) and prehydrolysis- ASA (alkaline sulfite process) processes which enable the manufacture of high purity, high viscosity dissolving pulps due to their high purification and delignification selectivity. The progress in kraft cooking during the past two decades owing to the principles of modified cooking has formed the basis for the development of the new Visbatch© and VisCBC processes, both of which combine the advantages of displacement technology and steam pre-hydrolysis. These new environmentally friendly pulping processes are characterized by their short cover-to-cover times, low energy requirements and very homogeneous and high product quality, and

promote a gradual shift from traditional softwood sulfite pulps to hardwood pre-hydrolysis kraft pulps (Sixta et al,2004).

Despite the world production of dissolving pulp having been reduced constantly in the past, the latest forecasts reveal a slight change in this trend. A stabilization of the production amounts, followed by a pronounced growth until the year 2006 is predicted, mainly due to new installations of Viscose (and presumably also Lyocell) plants manufacturing regenerated cellulose fibres in Asia (Sixta et al,2004).

Alkaline and acid processing routes constitute the main applications of dissolving pulps. The former comprises the viscose and etherification processes, which involve steeping of the pulp in aqueous solutions of high NaOH concentration (18–25 wt. %) , followed by the addition of appropriate chemicals for subsequent derivatization (e.g., CS_2 for xanthation or alkylhalides for cellulose ethers). The acidic esterification processes yield cellulose nitrate and cellulose acetate. The latter, more important, conversion process involves a pre-treatment with acetic acid prior to esterification to triacetate on the addition of acetic anhydride and a catalyst, usually sulfuric acid. In a second step, the triacetate is hydrolyzed to the so called secondary acetate (DS between 1.8 and 2.5) on dilution with water and precipitation of the flakes. These are then dissolved in acetone to a spinning dope (polymer concentration above 30%) from which fibres (e.g., filter tow, textile filaments), lacquers or plastic are processed.

Since the commercialization of the Lyocell process in 1992, the direct solution of pulp in an organic solvent without the formation of an intermediate cellulose derivative represents a new processing route for dissolving pulp comprising challenging demands on pulp quality.

For over 80 years, regenerated fibres of high quality and special uses have also been spun from a cuprammonium solution (cupram), a metal complex solvent for cellulose. Less than 2% is estimated for cuprammonium rayon within the world rayon production. The high demand on process ability and pulp quality requires the use of high-purity cotton linters which, compared to the viscose process, is not a decisive cost factor.

2.4.2.2 Chemical Properties

2.4.2.2.1 Chemical Composition

Organic Compounds

Hemicelluloses (short-chain alkali-soluble carbohydrates)

One of the main objectives of dissolving pulp production is the removal of non-cellulosic carbohydrates which constitute the major part of the short-chain material in the polymer. The available purification processes – particularly the hot and cold caustic extraction processes – contribute to a considerable increase in production costs, mainly due to high yield loss and high chemical charges. Therefore, the extent of purification is adjusted to the demands on the particular further processing. However, even small amounts of alien polysaccharides may influence the process ability and properties of the final product.

During steeping, the first step of alkaline processing of dissolving pulps for the viscose and etherification procedures, alkali-soluble hemicelluloses are removed to an extent depending on pulp quality, the process conditions and the equilibrium concentration level in the recycled steeping liquor. In this definition, the hemicelluloses consist of both alkali-soluble degraded cellulose and heteropolysaccharides such as degraded xylan or mannan. The accumulation of hemicelluloses in the steeping lye inhibits cellulose degradation during ageing due to the additional oxygen consumption through these degraded carbohydrates. In addition, they react preferentially with carbon disulfide in the subsequent xanthation process, thus leading to inhomogeneously substituted cellulose which consequently adversely affects viscose filterability. A good quality of viscose solution, characterized by low particle content (< 3 lm) and good viscose filterability, is governed by a low content of non-cellulosic impurities, particularly pentosans, certain inorganic substances, and resins (Sixta,2006).

Hemicelluloses also contribute to discoloration of the resulting cellulose products during both alkaline (e.g., Viscose) and acidic conversion (e.g., acetate) steps. The chromophore formation of the hemicelluloses under alkaline conditions is closely associated with the presence of carbonyl and carboxyl groups.

Acid processing generally requires pulps of higher purity as compared to alkaline processes. Acetate pulps are high-purity pulps containing hemicelluloses in an amount less than 1.5% and no detectable residual lignin. Experimental findings strongly suggest that even very small amounts of certain hemicellulose fractions play an important role in the formation of

haze and color of cellulose triand diacetate solutions. Glucomannan from both acid sulfite and prehydrolysis kraft (PHK) pulps is a major source for diacetate haze, false viscosity, and poor filtration. False or anomalous viscosity determines production capacity, and is defined as the percent increase in dope viscosity compared to that of a dope prepared from cotton linters diacetate of the same composition and intrinsic viscosity. The effect of the pulp mannan content on false viscosity and filterability of a diacetate solution in acetone is illustrated in Fig. 2.1.

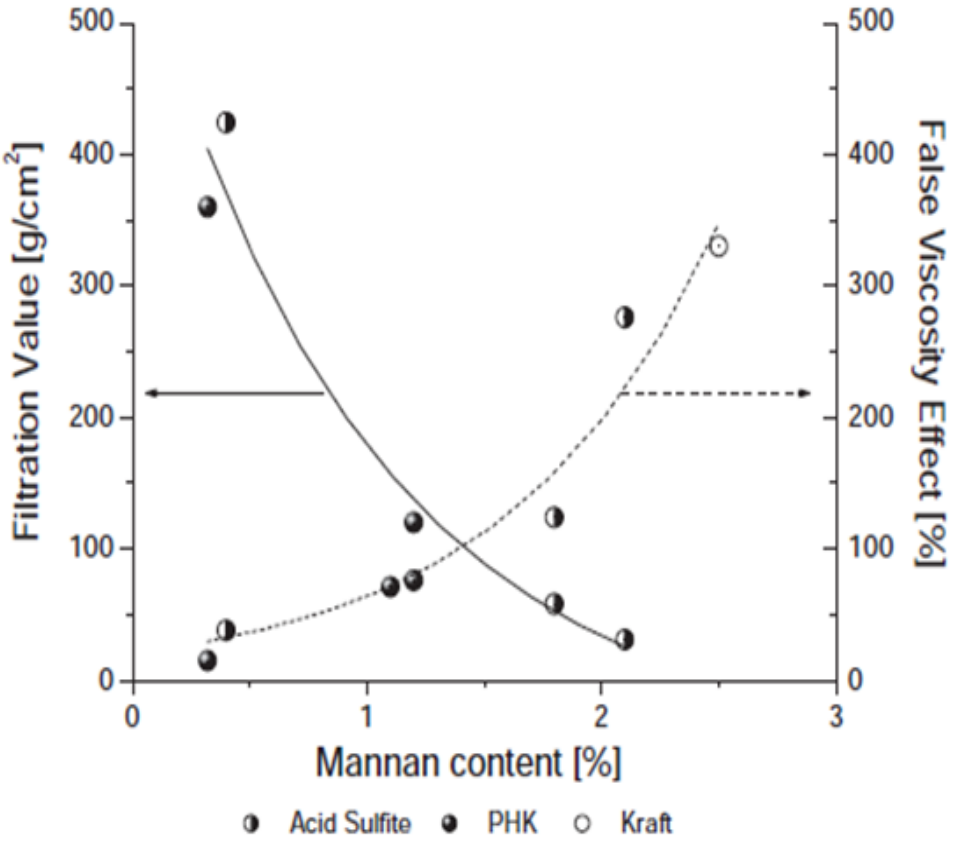


Figure 2.1 Effect of mannan content in various pulps on diacetate filterability and false viscosity (Sixta, 2006).

Extractives, resins

Pulp resins, determined as acetone or dichloromethane (DCM) extractives, play an ambivalent role in dissolving pulp processing. When exceeding a certain threshold concentration, resins may cause severe problems along the process chain such as precipitation (preferably taking place through sudden changes from alkaline to acid pH), haze in the viscose, clogging of the spinnerets, and yellowing of the yarn. On the other hand, the presence of resins considerably improves the accessibility of reagents to the cellulose substrate (e.g., alkali cellulose) due to lowered surface tension. The amount of extractives in

the dissolving pulp is determined by both the wood species used and the pulping and bleaching operations.

Acid sulfite cooking is rather sensitive to wood that is rich in resins. The major problems arise with phenolic extractives originating from pine, larch, Douglas fir and other extractive-rich wood species, which tend to undergo condensation reactions with reactive lignin structures. The formation of high molecular-weight resinous products may cause uncontrollable pitch problems in subsequent operation steps. These may be largely overcome by applying a two-stage process with an initial bisulfite or neutral sulfite stage. Thereby, the most reactive groups of lignin are protected by sulfonation. Hardwoods are generally better suited for acid sulphite pulping than softwoods. In the case of some resinous hardwoods, such as birch or some aspen species, the delignification of parenchyma cells with a high content of resins remains incomplete. Subsequent chlorine-free bleaching sequences – particularly those containing ozone stages – contribute significantly to reducing the resin content. Additionally, the short parenchymal cells may be removed by fractionation, though this is connected with high yield loss (Sixta, 2006).

Kraft cooking is less sensitive to wood raw materials that are rich in resins because most acidic extractives, together with part of the neutral lipophilic compounds, are dissolved in the cooking liquor, leaving little resin in the unbleached pulp. However, if the fraction of unsaponifiable compounds is high (as with many hardwoods), the fatty acid soaps formed do not possess sufficient micellar-forming properties to carry less polar compounds into solution. During PHK pulping of Eucalyptus globulus L., nearly all polyphenols, phenols, fatty acids are dissolved. Two-thirds of the neutral compounds are left in the unbleached pulp, while two thirds consists of b-sitosterol. During bleaching, the unsaponifiables are modified to more polar compounds containing carboxyl groups; these compounds, together with other polar extractives such as fatty acids, are favorable as surface active agents in the viscose process and account in part for good filtration of the viscose prepared from this pulp (Sixta, 2006).

Resins derived from pulps of high resin content – and particularly those containing higher amounts of non-polar neutral substances such as hydrocarbons and waxes – show a tendency to accumulate in the spinnerets. The deposits of resin inside the holes in the spinnerets increase the adhesion of precipitated zinc sulfide, and this ultimately leads to clogging of the spinnerets. In times of conventional bleaching, chlorination of extractives caused viscose turbidity, which was closely associated with spinning jet clogging. The introduction of hydrophilic groups by means of oxidation during bleaching operations (O, D, Z, P) improves the dispersibility of pulp resin in sodium hydroxide.

Residual lignin, brightness

The residual lignin content in dissolving pulps is generally very low. The kappa number, which specifies the amount of oxidizable (by KMnO4) structures containing double bonds in the pulp, is typically between 0.2 and 0.5 units which translates to a residual lignin content of about 0.05% . The main reason for aiming at a low kappa number is the high demand on optical properties. Residual lignin structures strongly contribute to yellowing of the cellulosic products. The highest demands on brightness and brightness stability are given for viscose, lyocell, and acetate pulps. Similar brightness levels are required for dissolving pulps converted to cellulose ethers for application in foodstuff and pharmaceuticals. Residual lignin is, however, not the only factor determining the optical properties of cellulosic substances. Therefore, the relationship between pulp brightness and brightness of the final product is also dependent upon the processing conditions, especially in the case of alkaline derivatization procedures (e.g., viscose, ethers). In industrial operations using constant conditions, pulp brightness is clearly reflected in the brightness of the final product.

Brightness – and thus residual lignin – is not a concern for pulps used for technical- grade cellulose ethers (major applications: textile, paper, drilling muds, ceramics, etc.). Nevertheless, bleaching to brightness levels of about 70–75% ISO is necessary to improve pulp reactivity and prevent precipitation of lignin compounds in subsequent processing steps (Sixta, 2006).

The residual lignin is not only a concern for optical properties, but also governs the processability of dissolving pulps. It is reported that viscose filterability (determined by the clogging constant) gradually deteriorates when increasing the residual lignin content from about 0.17 to 0.36%.

Inorganic Compounds

The presence of certain inorganic compounds such as silicates, Ca salts, and catalytically active transition metal ions (Fe, Mn, Co, etc.) clearly impairs the filterability and spinnability of a cellulose spinning dope (e.g., viscose or lyocell type of fibres). Moreover, pulp contamination with inorganic compounds leads to a gradual clogging of the spinnerets, and this alters the uniformity of the fibre titer. In particular, the cations Ca^{2+} and Fe^{2+}, as well as silicates, are considered to be detrimental in this respect. Although Fe(II), and to a lesser extent Cu(II), promote light-induced yellowing, both cations are involved in detrimental degradation reactions in the presence of hydrogen peroxide bleaching (Fenton-type reaction). Thus, all necessary measures must be undertaken (acid wash, chelation stage, etc.) to remove catalytically active cations.

Surprisingly, most of the harmful ash components are not distributed homogeneously in the pulp, but are present as particulates in certain cell fractions, particularly in the parenchyma cells. Therefore, the only promising way to reduce the amount of harmful ash components is an efficient mechanical pulp treatment which applies combined pressure screening of unbleached pulp and centrifugal cleaning after bleaching. This treatment ensures the removal of extremely small debris such as sand, bark specks, and shives. Again, the best way to control inorganic compounds is to reduce them to the lowest level economically feasible.

2.4.2.3 Overview of Pulp Specification

The suitability of dissolving pulps can be adequately determined by simulating the conversion processes to the final products, at least on a laboratory scale. The most important property of virtually all dissolving pulps can be expressed by the term “chemical reactivity. Pulp reactivity, however, cannot be described by a single structural feature, but rather by both the physical structure of the cellulosic material and the type of chemical interaction with the reagent. Additionally, all three structural levels – the molecular, supramolecular, and fibrillar – must be considered when using the term reactivity.

Reactivity is related to the accessibility of chemicals to the cellulose, which means the relative ease by which the hydroxyl groups can be reached by the reactants. Structure and morphology of the fibre determines the homogeneity of the conversion process and final product quality.

One of the most informative parameters in commercial specification sheets (quality card) is that of alkali solubility tests at room temperature. Here, the pulps are subjected to extractions with 10% (highest alkaline solubility) and 18% NaOH (concentration of steeping lye), respectively. Thereby, differentiation must be made between methods based on the gravimetric determination of the extraction residue (R-values) and determination of the soluble fraction (S-values) using potassium dichromate oxidation of the filtrate, followed by titration. The results are specified as a percentage based on the dry starting material. The concentration of NaOH is given as a subscript index (R10, R18 or S10, S18). The alkali resistances are directly related to alkaline processing of dissolving pulps, as for viscose and etherification processes. There, the R18 or (in some cases preferred) R21.5 values have been cited as being representative of the yield of alkaline-processed products (viscose fibre and cellulose ether) (Schenker and Heath, 1959). It has been shown that the cellulose content corresponds well with the R18 value. For sulfite pulps with low molecular weight, the R18 value lies below the cellulose content, because low molecular weight material becomes

dissolved. For PHK pulps and high-viscosity sulphite pulps (ether application), the R18 value exceeds the cellulose content because high molecular-weight, alkali-stable hemicelluloses remain in the pulp (Patt & Wang, 1987). The difference between the two extraction results is sometimes used as a measure for low molar mass cellulose (R18 – R10 or S10 – S18).

Moreover, the S18 or (100 – R18) values are good indicators for estimating the organic wastewater load associated with the production of viscose fibres or cellulose ethers.

2.5. Kraft vs. Dissolving Pulp

The essential difference between dissolving pulp and Kraft pulp is the lower hemicelluloses content of the former in the final product (Kraft:10%;Dissolving:3%). For this reason the conversion to a dissolving operation requires a pre-hydrolysis stage to remove the hemicellulose before cooking. A neutralisation step is also required to restore the alkalinity of the chips from the acidic hydrolysis stage (both water and steam hydrolysis are acidic). These additional steps increase the total reaction time and reduce the yield of the dissolving pulp (dissolving pulp:38%;Kraft 48%). As a consequence, the maximum pulp production is reduced during the conversion. The bleaching chemicals must also be changed to meet the target pulp specification for dissolving pulp grade.

2.6 Pre-Hydrolysis Method

There are several pre-hydrolysis methods that could be implemented in a dissolving pulp mill: steam (auto-hydrolysis), hot water, acidic or alkaline medium. Each of the pre-treatment method has its own advantage and disadvantage (Sixta et al, 2004).

2.6.1 Hot water Hydrolysis

Hot water hydrolysis is carried out at 150-180˚C. The cleavage of the acetyl group causes the release of acetic acid which is used as a catalyst to hydrolyse the glycosidic bonds (Sixta et al, 2004). The resulting PH of the prehydrolysate is between 3 and 4. This low PH is the reason for the need of a neutralisation step before cooking (alkaline). The advantage of this method is that degraded hemicelluloses are solubilised in water and can be extracted from the digester. These degraded hemicelluloses are mainly in their oligomeric form and may have to convert to their monomer form depending on the type of the value added product to be produced. The pressure in the digester is normally released to drain the prehydrolysate, however, this causes the formation of resinous products with a high tendency for

precipitation and stickiness. Therefore, the extraction of hemicelluloses following water pre-hydrolysis requires maintaining the pressure to avoid lignin products precipitation.

Hot water pre-extraction of hemicelluloses from lignocellulosic material is of interest because it is cheap and environmentally friendly, corrosion problems are limited and results in simpler downstream processes, i.e. no sludges are generated compared to dilute acid and alkaline methods (Walton et al., 2010). However, the implementation of hot water pre-extraction processes is hindered by low hemicelluloses (sugar) solubilisation under the too mild conditions (Lei et al., 2010). The mechanism of hydrolysis and subsequent dissolution of lignocellulosic material is promoted by acetic acid formed from hydrolysis of acetyl groups and uronic acid substitutions removed by hydronium ions coming from water auto-ionisation, both lowering the pH of the extract to the range of 3-4 (Garrote and Parajo, 2002). Considering hardwoods and nonwoods as feedstocks, acetylated glucuronoxylan is the major hemicelluloses; the application of hot water extraction to these feedstock would generate a separate value added stream mainly consisting of xylooligosaccharides. The hot water hydrolysis is selective to hemicelluloses whereas cellulose is retained in solid residue and shows improved susceptibility to further treatments due to the structural changes of the lignocellulosic matrix (Garrote and Parajo, 2002; Lei et al., 2010).

2.6.2 Steam Hydrolysis

Steam hydrolysis is carried out at 170˚c. Essentially, this method follows the same principles as the water hydrolysis, however most of the hemicelluloses remains within the chips (Kemp, 2007). The subsequent step is neutralisation using an alkaline solution. The hemicelluloses will be degraded in the subsequent alkaline stage. This degradation makes it impossible to recover and convert the sugars initially present in the chips.

Therefore, steam hydrolysis is probably preferred if the aim is to only produce dissolving pulp. However, if hemicellulose extraction is also a goal, water hydrolysis is advantageous.

2.7. Carboxymethylcellulose (CMC)

With a production of approx. 230 000 tons p.a., CMC is the economically most important cellulose ether (Thielking & Schmidt, 2006) Commercial CMCs are produced with a degree of substitution (DS) between 0.2 and 1.5. Carboxymethyl cellulose (CMC) is a cellulose derivative with carboxymethyl groups (- H_2-COOH). It is often used as its sodium salt, sodium carboxymethyl cellulose (Bogati, 2011). It is derived from cellulose, which is made water-soluble by a chemical reaction. The water-solubility is achieved by introducing

carboxymethyl groups along the cellulose chain, which makes hydration of the molecule possible.

The substituents are irreversibly linked to the cellulose backbone with ether bridges, and thus, CMC belongs to the group of substances called cellulose ethers. It is important to note that the carboxymethyl group has an acid function meaning that CMC is an anionic polyelectrolyte. CMC has many interesting properties when dissolved in aqueous solutions, but this will depend on the CMC grade and the solution conditions.

This water-soluble polymer was invented in 1918, with the first patent being granted in 1921 (DE 332203). CMC is manufactured by reacting sodium monochloroacetate with alkali cellulose. It is almost always distributed as the sodium salt, but instead of using the longer name, sodium carboxymethyl cellulose (Na-CMC), it is usually designated simply carboxymethyl cellulose (CMC) (Stigsson et al., 2006). In this thesis, CMC or carboxymethyl cellulose is used as a short name for NaCMC or sodium carboxymethyl cellulose.

2.7.1 Production or Synthesis of Carboxymethyle Cellulose

Cellulose derivatization in industrial scale is a heterogeneous process. CMC is produced in a Williamson ether synthesis from alkali cellulose with monochloroacetic acid (MCA) or its sodium salt (Na-MCA) in an aqueous or aqueous alcoholic medium (slurry).

In practice, the manufacture of CMC involves two reaction steps. First, cellulose is treated with NaOH (2.1). This activation (mercerisation) is of immense importance, as it modifies and widens the crystalline structure of cellulose. The hydrogen bonds are partially broken and the AGUs become more easily accessible to the nucleophile.

$$Cell{-}OH + NaOH \rightarrow Cell{-}O^{-}\,Na^{+} + H_2O \quad (2.1)$$

This so-called alkali cellulose is now accessible for MCA, which is added in the second step (2.2)

$$Cell{-}O^{-}Na^{+} + NaOH + ClCH_2COOH \rightarrow Cell{-}O{-}CH_2COONa + NaCl + H_2O \quad (2.2)$$

As a side reaction, hydrolysis of MCA occurs (2.3), forming glycolate and sodium chloride and hydrochloric acid, respectively.

$$NaOH + ClCH_2COONa \rightarrow HO\text{-}CH_2COONa + NaCl \quad (2.3)$$

The first continuous process for carboxymethylation was used by Wyandotte Chem. Corp. in 1947, but it had no washing stage and was therefore only suitable for unpurified CMC (Hader et al, 1952). In current CMC production, cellulose is processed batch wise either as a suspension (for a low mass fraction of cellulose) or in mixers as slurry (for high mass fraction). Both processes use short-chain alcohols as reactand-transfer and heat-exchanging media and as suspending agents, respectively. For high mass fraction processes, ethanol is usually used as slurry medium, whereas isopropyl alcohol is used in suspension-type processes (Stigsson et al, 2001; Donges, 1997).

Carboxymethylation is exothermic and takes place between 50 °C and the boiling point of the slurry or suspension medium under appropriate system pressure. The reagent efficiency is between 65 % and 80 %. Depending on the required purity, the product is washed with alcohol-water mixtures, preferably with the same alcohol used in synthesis. Before drying, suspension agents and washing liquids are collected and reprocessed either by distillation and extraction or membrane processes (Thielking & Schmidt, 2006).

The use of ethanol during the mercerisation stage causes a homogeneous system of sodium hydroxide, water, and ethanol whereas by the use of isopropanol a nonhomogeneous system occurs, forming a layer around the fibre composed of a highly concentrated sodium hydroxide water phase, caused by the low solubility of sodium hydroxide in unpolar systems (Yokota,1985). The sodium hydroxide concentration is therefore high around the fibre. The use of isopropanol in CMC synthesis is reported to generate less sodium glycolate, as the less polar solvent provides an environment for MCA whereas NaOH is enriched in the aqueous phase (Klemm et al,1998).

Various other solvent systems, like acetone, benzene and LiCl/ DMAc (LiCl / N,Ndimethylacetamide) show cellulose dissolving properties (Cheng et al,1996;Heinze et al,1999), but those are usually only used in laboratory scale.

Even a clear solution is not a sufficient condition for a homogenenous reaction, as cellulose is not necessarily molecular dispersed. It may still contain aggregates of ordered cellulose molecules (Fink et al,1985;Fink et al,1990;Krassig & Schurz,1986). These aggregates, so-called fringed micelles/fibrils, consist of aligned chains forming a compact core, thus do not interact with the solvent, and of solvated amorphous outer chains.

Fink et al. (1995) studied the influence of the surrounding alkali concentration on the cellulose state using X-ray and solid state 13C-NMR. They observed that in aqueous alkaline systems phase transitions occur above 10 % NaOH, while below this level the original crystalline structure is preserved. (Dapía et al,2003) presented their study on CMC

preparation from pulp of *Eukalyptus glubulus.* They found that concentrations of NaOH and MCA strongly affected the DS of the resulting CMC and concluded that the MCA concentration should not be too high while the NaOH concentration could be very high. These results do not agree with those obtained by Stigsson et al.2001, who concluded an optimum in NaOH concentration.

One of the most important properties of the cellulose raw material used in the manufacture of CMC is its reactivity. The literature shows that approximately 35 to 50% of the hydroxyl groups can be etherified in cotton or dissolving pulps (Krässig 1993). Carboxymethylation is a uniform reaction; it occurs only at accessible hydroxyl groups, followed by the slow penetration of the ordered surfaces (Borsa et al. 1992). Cellulose reactivity in a heterogeneous alkali medium depends not only on the cellulose structure at molecular, supermolecular and morphological levels, but also on the reaction medium employed. It is known that the reaction rate in ethanol is lower than that in isopropanol since ethanol is better at dissolving sodium hydroxide (Olaru and Olaru 2001). The crystallinity and polymorphism of the cellulose change during the mercerization step; the organic solvent acts as a swelling-restrictive agent and does not permit full hydration of the cellulose chain (Yokota 1985). Isopropanol is a poorer solvent for sodium hydroxide compared with ethanol, and a two-phase system therefore occurs. Only small amounts of the Na^+ and the OH^- ions enter the alcohol phase, favoring a higher concentration of NaOH in the vicinity of the cellulose. This results in substantial decrystallization and change of polymorphism from cellulose to Na-cellulose during mercerization. It is also reported that different solvent systems affect the characteristics of CMC during its manufacture. For example, when isopropanol is present during the mercerization stage substitution is more uneven; tri-substituted units occur and substitution on the C_6 carbon is increased (Stigsson et al. 2006).

Sodium carboxymethyl cellulose is produced from a heteregenous reaction where its rate is dependent upon the diffusion rate of the reagents NaOH and $CHClCH_2COONa$ inside the cellulose particles. This means that the aggregation state of the cellulose particles act as a decisive role. The crystalline structure of the particles should be destroyed adequately so that the particles become looser thus increasing the reaction rate. If the crystalline aggregation cannot be destructed then the NaOH and $ClCH_2COONa$ will remain in the solvent rather than diffuse into the crystalline aggregration when carrying out the carboxymethylation for cellulose. That is the reason as to why, NaOH as well as $ClCH_2COONa$ is added slowly and is to be stirred at a very high speed so that the reaction will take place. In addition, by having complete reactions, it would lessen the production of by-products such as sodium glycolate and also decreasing the availability of monochloroacetic acid.

Accounting for 30-40 percent of the resulting reaction mixture, are removed in a series of alcohol washes and separations. The purification process washes out the majority of those impurities, such that one round of purification will result in a product that is approximately 90 percent pure CMC. After purification is complete, the particle size of the CMC is adjusted using physical means such as grinding, sieving and agglomeration.

The functional properties of CMC depend on the degree of substitution of the cellulose structure also the chain length of the cellulose backbone structure and the degree of clustering of the carboxymethyl substituent.

Production of CMC is simpler than that of most other cellulose ethers because all reactions are operated at atmospheric pressure using commercially available reagents. The etherifying reagent, sodium monochloroacetate, is easy to handle and very efficient. For these reasons, CMC has become the largest industrial cellulose ether. Large quantities are produced in crude commercial grades without any refining for use in detergents, oil drilling, and in the paper industry. High-purity grades are also employed as food additives (Dahlman et al, 2003).

2.7.2 Properties of CMC in aqueous solution

CMC is a water as well as alkali soluble even at low degree of substitution. Trivedi et al.,1981 studied the effect of degree of substitution, polymer concentration and size of the counter ions from the dissociation constant of CMC potentiometrically. The solubility of CMC depends on the pH as well as degree of substitution. At low pH values CMC precipitates due to intermolecular hydrogen bond formation between the undissociated carboxymethyl groups as shown in Fig. 2.2.

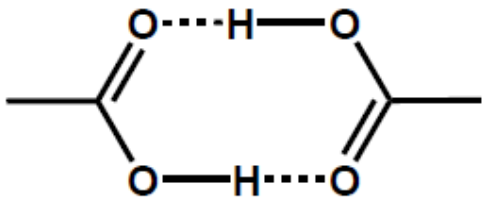


Fig. 2.2: Hydrogen bond formation between two carboxylic acid groups at low pH values (Adopted from Trivedi et al., 1981)

These H-bonds are very strong. With 1.64 Å the length of H···O between two acetic acid molecules is in the range of the covalent C-OH bond (1.33 Å) (Jeffrey et al,1994). At DS values of 0.3 - 0.5, precipitation occurs at pH-values below 3, higher substituted CMC with DS values between 0.7 and 0.9 precipitates at pH < 1. With rising pH, the amount of

carboxylate and thus repulsion increases. At pH > 12, the repulsion between the negatively charged CM-groups decreases due to the presence of alkali-metal cations like sodium. Consequently, the CMC molecules form a coil resulting in a drop of viscosity. Heavy-metal salts like Cu^{2+}, Ag^{+} or Pb^{2+} and trivalent cations such as Al^{3+}, Fe^{3+} or Cr3+ may form insoluble salts or complexes and hence CMC precipitates. With divalent cations (e.g. Ca^{2+}) these effects depend largely on the substituent to salt ratio (Kauper, 1998).

In neutral solutions, molecular dispersed molecules are arranged in uncoiled linear structures, but CMC may also form aggregates in aqueous solution. Burchard intensively studied the behaviour of cellulose (Schulz et al, 2000) and its aliphatic ethers (Burchard,2003) in solution. He suggests that the crystalline sections in cellulose are not fully destroyed but form a bundle of aggregated chains with dangling outer chains. These outer chains bind water molecules extensively. Residual crystalline cellulose sections are responsible for aggregation and discrete gel particle formation in aqueous CMC solutions according to the fringed micelle model (Francis, 1961).

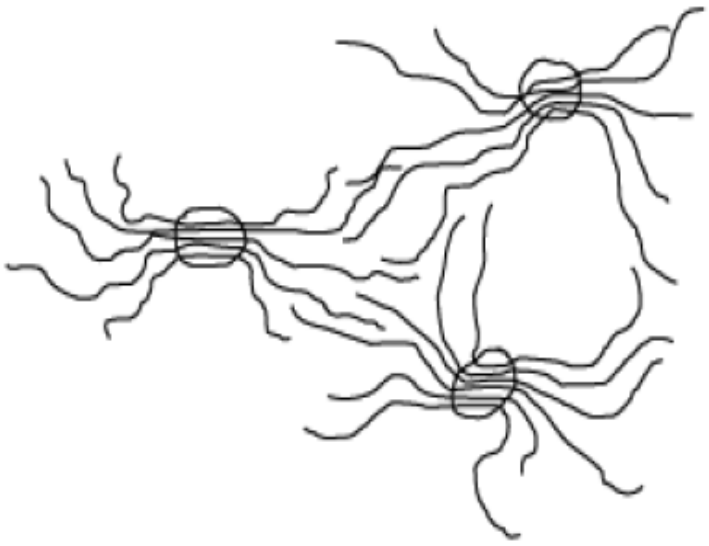


Fig. 2.3 Aggregate formation of CMC in aqueous media according to the fringed fibril model (Francis,1961;Liebert et al,2005)

2.7.3 Uses

CMC is used primarily because it has high viscosity, is non-toxic, and is hypoallergenic. It has wide application food sector, pharmaceutical and dentifrice (toothpaste). It is used as soil carrier and redeposition inhibitor in detergents as anionic dirt particles are repelled by the anionic charges of the dissociated CM-group. It is used in deep-well drilling as flotation

aid in drilling mud. Purified products are used in surface coatings and e.g. in paper industry due to the affinity of CMC to cellulose for coatings and pulp sizing to improve fiber retention, filler/pigment/dye yield as well as paper strength. CMC also improves the printability and smoothness of paper. Together with gelatine CMC is used as a coacervate to encapsulate ink in the production of non-carbon copy papers. Building applications use its high water retention. CMC stabilizes e.g. aqueous solutions of clay and helps control adhesion by providing bonding strength and improves workability.

In cosmetics and pharmaceutical industries extra purified grades are used for instance as fat-free ointment base or as tablet filling matrix. Mixed esters of CMC like CMC acetate butyrate (CMCAB) showed zero-order release of the active component when used as filling matrix for drug-delivery agents (Pose-Dowty et al, 2007).

In food-grade purity, Na-CMC is commonly known as “cellulose gum” or as food additive E 466. In Europe, its use is regulated by law. By the order EG 178/2002 of the Parliament and the Council of Europe the regulations for food, animal feed, and food contact materials, and consumer products in the European Union are defined. The German implementation of this European regulation is the “Lebensmittel- and Futtermittelgesetzbuch, LFGB”. Based on the LFGB, the “Zusatzstoff-Zulassung-Verordnung (ZZulV)” regulates the use of food additives hence the use of CMC. In annex 4 to §§ 5.1 and 7 ZZulV the terms for the application of CMC in food are regulated. Though no maximum permissible quantities are named (“quantum satis”), its use is restricted to certain applications. An addition of CMC is forbidden e.g. for honey, butter or minced meat.

In food applications, CMC improves consistency, and emulsion stability and controls and provides e.g. freeze-thaw stability of deep-frozen products. CMC is neither digested nor resorbed in the human intestinal tract (Scherz, 1996)

CMC is applied in various levels of purity. “Unpurified” CMC, used for technical applications up to “highly purified” CMC for pharmaceutical- and food-grade applications are commercially available (Table 2.2).

Table 2.2 Carboxymethyl cellulose (CMC) grades and typical applications (Stigsson et al, 2001)

Quality	**Examoles of application areas**	**Content of CMC (%)**	**Content of salt (%)**
Technical	detergent,mining and floating	<75	>25

semi-purified	oil and gas drilling muds	75-85	15-25
purified	paper coating,textile sizing and printing,ceramic glazing	>98	<2
extra purified (cellulose gum)	food,tooth paste,pharmaceuticals	>99.5	<0.5

2.7.4. Market Demand and Supply

Carboxymethyl cellulose has a wide range of application in various industries. It is used in detergent, soap, food products (especially dietetic foods and ice-cream), where it acts as water binder, thickener, suspending agent and emulsion stabilizer, sizing agent, coating agent in paper and paper board to lower porosity, emulsion paints, pharmaceuticals and cosmetics. The country's requirement for the product is met through imports. The quantity of imports of the product during the period 2000 – 2006 is shown in the following Table 2.3:

Table 2.3: Imported quantity of carboxymethyl cellulose from 2000-2006

Year	Import quantity [tons]	Percent increment/decrement
2000	12.5	
2001	0.02	
2002	15.4	
2003	20.3	31.8
2004	15.9	-21.67
2005	12.7	-20.1
2006	27.7	118.1

Source: Customs Authority, External trade statistics

During the above periods imports exhibited substantial fluctuations and averaged at 14.9 tones. Given, the substantially considerable fluctuations in the supply of the product, which comprises of only imports, the average annual supply during the last five years (2002 – 2006) is considered as the effective demand for the product for the other years. Accordingly, the projected demand for the product is thus estimated as.

$$\text{Average percent increment} = \frac{[31.8 + (-21.67) + (-20.1) + 118.1]}{4}$$

$$\text{Average percent increment} = 27\%$$

$$\text{Import average} = \frac{15.4 + 20.3 + 15.9 + 12.7 + 27.7}{5}$$

$$\text{Import average} = 23 \text{ tones}$$

The future demand for CMC is a function of growth of the end-user industries. The market oriented economic policy has been hastening the rate of investment in different economic sectors of the country including the manufacturing sector. Considering the present favourable conditions will stay for the future an annual growth rate of 27% is considered for projecting the demand for the product. The projected demand is presented in the Table 2.4:

Table 2.4: Projected demand of CMC from the given data

Year	Demand in tones
2007	29.21
2008	37.10
2009	47.10
2010	59.80
2011	75.95
2012	96.46
2013	122.50
2014	155.60
2015	197.60
2016	250.95
2017	318.71
2018	404.76
2019	514.05
2020	652.84

3. Materials and Methods

3.1 Time and Place of the Study

The study was conducted from May 2015 to December 2015 at Addis Ababa Institute of Technology, School of Chemical and Bio-Engineering.

3.2 Materials

The raw materials and reagents needed for CMC synthesis were:

- Carton boxes-used as feedstock to extract cellulose
- Reagent grade monochloroacetic acid –used to etherify the cellulose
- Reagent grade sodium hydroxide flake-used to alkalise the cellulose
- Iso-propanol solutions-used as a diluent and swelling agent of the cellulose while alkalizing
- Methanol and ethanol-used to wash and purify the CMC
- Acetone,HCl, Methanol, NaOH, Distilled water, phenolphthalein indicator – used for determination of degree of substitution.

Equipment and devices needed for CMC synthesis were:-

- Cutting mill to grind waste carton boxes in smaller pieces
- Autoclave for water hydrolysis and kraft pulping or cooking
- Analytical balance,
- Flask with circular bottom,
- Water bath-to bleach, alkalize and etherify at constant temperature
- Oven –to dry
- pH meter-to adjust the ph of the CMC after washing and purification
- Beakers, 250 ml Erlenmeyer flask, Spatula, Glass rod, Filter paper,

3.3. Methods

3.3.1 Overall experimental framework

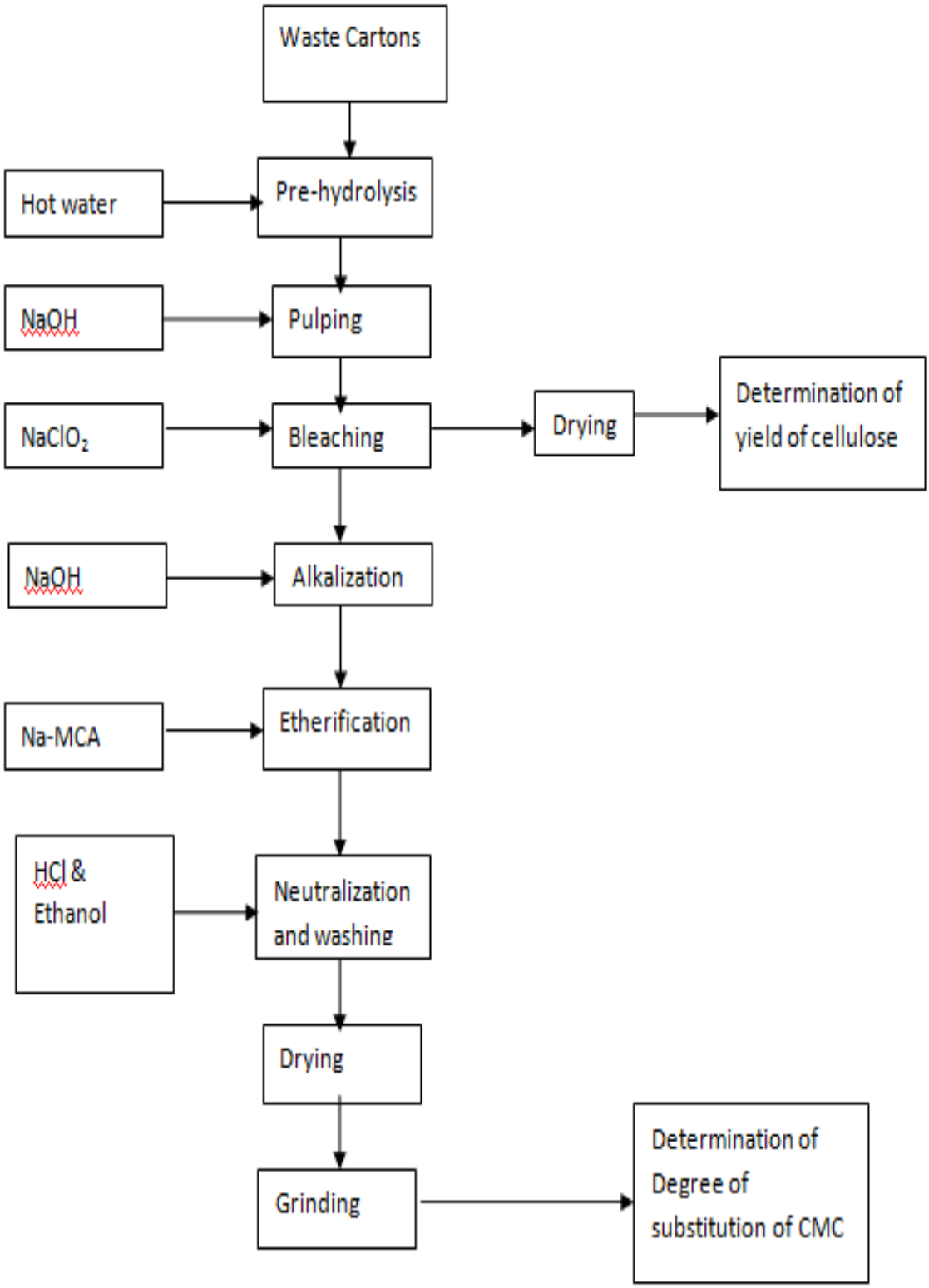


Figure 3.1 Overall experimental frame work

3.3.2 Sample collection and preparation:

Waste cartons were collected from National Tobacco Enterprise (NTE), Addis Ababa.

Sample preparation process include: manual size reduction (Knife cutting), drying, grinding and sieving. Grinding of carton boxes into powder form gives the surface area of the sample increased which enhance the contact between hemicelluloses and lignin with water and NaOH solution to facilitate the dissolution of hemicelluloses and lignin.

Steps involved in sample preparation were:

- After collection, waste carton boxes were manually cut in to pieces of about 3-5 cm for easy drying and grinding.
- Samples were dried using oven to remove all the moisture present in it and to get easily crushable material.
- After drying, the samples were ground in cutting mill to 2 mm size.
- Then samples greater than 2 mm were separated using sieve and ground until all sample size became 2 mm or less.

3.3.3 Cellulose Extraction

The extraction of cellulose was done according to the method of preparing dissolving pulp (alpha-cellulose) from corn stalker by kraft process, (Behin et al, 2008). The sequence of experimental work was: water pre-hydrolysis, followed by kraft pulping and bleached by the HEH sequence.

Pre-hydrolysis

The primary objective of pre-hydrolysis was to efficiently remove the hemicelluloses polymers from the carton chips by water or dilute mineral acid hydrolysis. It also plays beneficial role in the reduction of ash by dissolving minerals. Both of which in a dissolving pulp are considered contaminants in the preparation of cellulose derivatives.

Water pre-hydrolysis was carried out in a stainless steel mini-digester (batch reactor) that was heated by an outer jacket containing electrical wires. The temperature was measured with a thermometric probe accommodated inside the reactor.

The carton chips were placed in the reactor together with the liqour. The conditions employed were:

- 100 g of dry matter sample was used for extraction
- Liquor to dry material ratio: 5:1 to ensure a homogeneous mixture;
- Operation temperature:160˚C

- Operation pressure: 5.5 atm
- Rise to operation (maximum) temperature: 30 minutes
- Residence temperature at operation temperature: 30 minutes
- At the end of pre-hydrolysis stage the pulp was washed, neutralised, disintegrated in a laboratory blender, oven dried at 60˚c temperature and stored in a plastic bag for further use.

Pulping

Kraft pulping (cooking) of pre-hydrolysed carton chips was conducted with the same pre-hydrolysis mini-digester as mentioned above.

- The liquor to dry fiber ratio:5:1
- Cooking temperature: 170˚C
- Rise time to operation temperature: 30 min
- Residence time at the operation temperature:90min
- Operation pressure: 7.5 atm
- Active alkali: 14-20% optimum (20%) based on oven dried pulp
- Sulphidity level: 10-25% optimum (25%) based on oven dried pulp
- At the end of cooking the pulps were mechanically disintegrated in a 3-bleded mixer for 2minutes, followed by thorough washing with tap water.

Bleaching

Bleaching of kraft pulp was performed in two bleaching sequences: HEH and HEHP. The HEH sequence, pioneered by MacMillen Bloedel, was developed to reduce the bleach plant effluent colour of semi-bleached kraft pulp for news print. Conditions for each bleaching stage were as follows:

- H (hypochlorite , 1st stage) : the pulp (10% consistency) was treated with a NaClO solution (charge of 2.5% based on pulp weight), pH=10 for 60min at 60˚C and the product was filtered ,then washed with water till free of chlorine ions.
- E (sodium hydroxide extraction,2nd stage): the product of the 1st stage was suspended in an aqueous solution (10% consistency) which contained NaOH (5% based on pulp weight) the suspension was agitated for 90 minutes at 60˚C ,filtered and the product was washed with water until reaching neutral condition.

- H (hypochlorite, 3rd stage) : the product of the 2nd stage (10% consistency) was agitated with a NaClO solution (5% based pulp weight) , pH=10 for 70 min at 70˚C and the product was filtered then washed with water until reaching neutral condition and then oven dried.

- Yield was determined on oven dried fiber basis.

3.3.4. Synthesis of carboxymethyl cellulose :

The experiment was performed in such a way that preparation of carboxymethylcellulose was followed by subsequently performing the two main reactions.

Firstly, alkalization reaction initiate after introduction of:

- 5 g of waste carton cellulose powder was weighed and added to 250 ml Schott bottle followed by 100ml of iso-propanol.

- 10ml sodium hydroxide solution with various concentration of 10% to 50% aqueous sodium hydroxide was added drop-wise while it is stirred for an hour at 30˚C. (Pushpamalar et al., 2006).

Here alkaline condition was created and the hydroxyl functional groups were ready to be substituted by other functional groups. And also the alcohol is usually either ethanol or isopropanol and serve as inert solvent, which act both as swelling agent and as dilutant and thus facilitate good penetration of NaOH in to the cellulose structure.

After alkali treatment, etherification reaction was continued by adding 2 to 10 g of sodium monochloroacetate (SMCA) per 5 g of cellulose at a reaction temperature of 30 to 70ºC in reaction mixture and placed in a water bath (Pushpamalar et al., 2006).

The reaction was then allowed to proceed under mechanical stirrer for 90 minutes. 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 degree substitution (Bhattacharyya et al., 1995; Heinze and Pfeiffer, 1999).

3.3.5. Purification of Carboxymethyl Cellulose:

The end product, carboxymethyl cellulose, was neutralized with 1 N HCl to remove the excess sodium hydroxide and washed with excess of ethanol (70%) after the reaction to

remove the by-products, sodium glycolate and sodium chloride (Pushpamalar et al., 2006). The use of isopropanol in carboxymethyl cellulose synthesis is reported to generate less sodium glycolate, as the less polar solvent provides an environment for chloroacetic acid. Lastly, the sample was dried in the oven at 60°C temperature for one day.

3.3.6. Characterisation of CMC synthesized:

Degree of Substitution

Most properties of the CMCs in actual applications, are dependent on a large extent, on three key parameters – molecular weight of the polymer, the average number of carboxymethyl substituents per anhydroglucose unit (degree of substitution, DS), and the distribution of the carboxymethyl substituents along the polymer chain (Schult and Moe, 1997). The DS is a major factor in the water solubility of Na-CMC, below approximately 0.4 the polymer is swellable but insoluble; above this, the polymer is fully soluble with its hydro affinity increasing with increasing DS (Togrul and Arslan, 2003). In this work, the perception in the factors, which affect the carboxymethylation reaction and allow determination of the optimum operating condition using the RSM to achieve carboxymethylated cellulose with a high degree of substitution, was studied. This provides a valuable input for the development of kinetic models for the carboxymethylation process in future studies.

The degree of substitution (DS) of carboxymethyl cellulose is the average number of sodium carboxymethyl groups bound per anhydroglucose unit and varies between 0 and 3. Convenient methods for the determination of the DS have been developed, and the three well known methods are:-

- Direct titration
- Back titration
- Cu salt precipitation

In this work the degree of substitution was determined by back titration method (ASTM, 1994). The back titration method is very useful because no expensive equipment and chemicals are required and at the same time degree of substitution value is also very reproducible provided the procedure is carried out very carefully. So, this method is recommended as a standard procedure for the determination of DS of carboxymethyl cellulose.

The carboxylic content was determined by back titration using 6N and 0.05N HCl and 0.2N NaOH standard solutions and phenolphthalein indicator. Prior to titration the phenolphthalein indicator showed a pink colour and it was changed to colour less.

This method involves conversion of sodium salt of the carboxymethyl cellulose to the acid form by treating with methanol acidified with hydrochloric acid or nitric acid, removal of the excess acid by washing with a methanol water solution, and drying the material. Weighed sample of the free acid is dissolved in distilled water containing an excess of standard sodium hydroxide and the excess is back titrated with standard hydrochloric acid using phenolphthalein indicator.

Back Titration Method

The back titration method was performed in the following way:-

- The obtained dry powdery sodium carboxymethyl cellulose (Na-CMC) from the process was dispersed in acetone by stirring with a stirrer
- Then it was converted to the acid form (H-CMC) by adding an aqueous solution of 6 ml of 6 N HCl per 2 g of the sample, with continued stirring for 30 min.
- The dispersion was filtered in order to remove the excess acid
- The precipitate was washed with a methanol-water solution (80 mass% of methanol).
- Then the precipitate was again dispersed in acetone, filtered, dried under vacuum at 50^{o}C, and ground.
- The obtained H-CMC was used for the DS determination.

After the above H-CMC samples had been prepared, the back titration method was followed as the steps below:-

- About 0.5 g of the H-CMC sample was dissolved in 20 ml of 0.2 N NaOH and 50 ml of bi-distilled water was also added.
- The solution was transferred to a 100 ml volumetric flask, which was then filled up to the mark with bi-distilled water.
- 25 ml of the solution was transferred to an Erlenmeyer flask and diluted by addition of 50–100 ml of bi-distilled water.

- The excess of NaOH was back-titrated with standard 0.05 N HCl using phenolphthalein as the indicator.
- The titration was repeated three times and the average value of the HCl volume was used for the calculations.

The milli-equivalents of consumed acid per gram of the sample (A) were calculated equation (3.1):-

$$A = \frac{(BC - DE)}{F} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots.(3.1)$$

Where,

A = milli-equivalents of consumed acid per gram of specimen.

B = Millilitres of added Sodium hydroxide.

C = Normal sodium hydroxide.

D = Millilitres of consumed hydrochloric acid.

E = Normal hydrochloric acid.

F = Specimen grams used.

The DS was calculated using equation (3.2)

$$DS = \frac{(0.162) * A}{1 - (0.058 * A)} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots.(3.2)$$

Where:

- 162 g/mol is the molar mass of an anhydroglucose unit (AGU),
- 58 g/mol is the net increase in the mass of an AGU for each carboxymethyl group substituted.

3.4. Optimisation Parameters

The effect of sodium hydroxide concentration, concentration of monochloroacetic acid, and etherification reaction temperature on the DS of the synthesized CMC was studied.

3.5. Experimental Design

During the alkali cellulose formation (mercerisation) different concentrations of sodium hydroxide (10% to 50%) were employed. During the carboxymetylation reaction stage different concentrations of monochloroacetic acid (2 to 10 g) were employed between temeperature ranges of 30 to 70˚c. Therefore, the controllable factors were sodium hydroxide concentration, monochloroacetate concentration, and reaction temperature. The response variable was degree of substitution of CMC.

In this study, response surface methodology (RSM) was used for the optimization of process variable to enhance the degree of substitution of the carboxymethy cellulose combined with the factorial experimental design of CCD. Therefore, to reduce the experimental runs in reasonable limit, some variables were fixed according to the literature review (Togrul and Arslan, 2003; Adinugrada et al., 2005; Dapia et al., 2003; Pushpamalar et al., 2006).The central composite experimental design method using Design expert® 6 software was chosen to optimize the alkalisation and carboxymethylation reaction in carboxymethyl cellulose production from waste carton box biomass and to determine the effect of three operating variables of the alkalisation and carboxymethylation reaction, including NaOH concentration, amount of monochloroacetic acid and temperature (T). For the response surface methodology involving CCD, a total of 20 experiments were conducted for three factors at two levels with six replicates at center point. Table 3.1 provides a list of independent variables and coded factor levels. The number of experiments required (N) is given by the expression:

2^k (2^3 = 8; star points) + 2 k (2 × 3 = 6; axial points) + 6 (center points; 6 replications)=20.

Selection of the factors and range of the variables were based on the operating condition, which has a significant influence on the alkalisation and etherification process according to previous works, with 10- 50%(w/w) NaOH concentration, 2-10g SMCA/5g cellulose, and 30 -70°C temperature.

Table 3.1.Complete Experimental Design Matrix of CCD for alkalisation and carboxymethylation in carboxymethyl cellulose production from carton box cellulose

Actual Factors	Coded Factors	Unit	Levels		
			-1	0	1
NaOH	A	%(w/w)	10	30	50
SMCA	B	g	2	6	10
Temperature	C	˚C	30	50	70

Table 3.2: Complete Experimental Design Matrix of CCD

Run no.	Codified levels			Non-codified levels			Degree of Substitution
	A	B	C	NaOH	SMCA	Temperature	
1	1	-1	-1	50	2	30	
2	0	0	0	30	6	50	
3	0	1	0	30	10	50	
4	0	0	0	30	6	50	
5	0	0	0	30	6	50	
6	0	0	1	30	6	70	
7	-1	-1	-1	10	2	30	
8	1	1	-1	50	10	30	
9	0	0	0	30	6	50	
10	0	0	0	30	6	50	
11	1	-1	1	50	2	70	
12	1	1	1	50	10	70	
13	-1	1	-1	10	10	30	
14	-1	0	0	10	6	50	
15	-1	-1	1	10	2	70	
16	1	0	0	50	6	50	
17	0	-1	0	30	2	50	
18	-1	1	1	10	10	70	
19	0	0	-1	30	6	30	
20	0	0	0	30	6	50	

3.6. Sample Analysis

The yield of cellulose was determined. The synthesized samples of CMC from each experiment run were analysed with respect to the response variable: degree of substitution. The degree of substitution (DS) of the carboxymethyl cellulose was determined using the back titration method.

3.7. Data Analysis

The resulting data of degree of subsitution in CMC production from waste carton box cellulose and the effect of three operating variables of CMC synthesis were analyzed using Design expert® 6 software. Significance of the result was set from analysis of variance (ANOVA).

4. Result and Discussion

4.1 Yield of Cellulose from Waste Carton

From the delignification process performed above the final cellulose obtained was about 36.8 gm.

$$\%\text{yield of cellulose} = \left(\frac{\text{weight of obtained cellulose(g)}}{\text{weight of carton chip used(g)}}\right) \times 100$$

$$\%\ \text{yield of cellulose} = \frac{36.8}{100} \times 100$$

$$\%\text{yield of cellulose} = 36.78\%$$

4.2 Determination of Degree of Substitution

The volume of HCl required for the titration in each sample was obtained and listed in the table below:

Table 4.1: Volumes of HCl determined from titration

Run order	Obtained Result in ml	Average Volume of HCl
1	48,48.5,48.4	48.3
2	40.4,40,40.2	40.2
3	40,39.5,39.6	39.7
4	40.6,39.8,39.9	40.1
5	40.9,40.1,40.2	40.4
6	42,42.1,42.8	42.3
7	46.2,46.9,46.1	46.4
8	43.2,44,43.3	43.5
9	40.3,40.1,40.2	40.2
10	40,40.5,40.1	40.2
11	44.4,43.5,44.1	44
12	42.4,43.3,43	42.9
13	45.8,44.9,45.5	45.4
14	43,42.5,42.6	42.7
15	44.7,43.6,44.3	44.2
16	42.3,41.2,41.9	41.8
17	41.4,40.3,41	40.9
18	46.6,45.8,45.9	46.1
19	44,44.3,43.4	43.9

20	40.4,40.1,39.8	40.1

Then, as an example for the fifth experiment:

Normality of HCl used = E = 0.05

Normality of NaOH used = C = 0.2

Volume of NaOH used = B = 20 ml

Volume of HCl obtained = D = 15.3 ml

Grams of H-CMC used = F = 0.5 gm

Using equation (3.1):

$$A = \frac{(BC - DE)}{F}$$

$$A = \frac{(20 \times 0.2 - 40 \times 0.05)}{0.5}$$

$$A = 3.96$$

Substituting the above result in equation (3.2):

$$DS = \frac{(0.162) \times A}{1 - (0.058 \times A)}$$

$$DS = \frac{(0.162) \times 3.96}{1 - (0.058 \times 3.96)}$$

Then the degree of substitution will be

$$DS = 0.833$$

All the values of the degree of substitution of carboxymethyl cellulose samples were calculated in the above way. The results are tabulated below.

Table 4.2: Factors and determined response

Run no.	NaOH [g]	SMCA [w/w]	Temperature [˚C]	Degree of Substitution
1	50	2	30	0.629
2	30	6	50	0.838
3	30	10	50	0.852
4	30	6	50	0.841
5	30	6	50	0.833
6	30	6	70	0.782
7	10	2	30	0.676
8	50	10	30	0.750
9	30	6	50	0.838
10	30	6	50	0.838
11	50	2	70	0.737
12	50	10	70	0.766
13	10	10	30	0.701
14	10	6	50	0.771
15	10	2	70	0.732
16	50	6	50	0.795
17	30	2	50	0.819
18	10	10	70	0.684
19	30	6	30	0.740
20	30	6	50	0.841

4.3. Statstical Analysis of Experimental Result

In this study, statistical experimental design techniques were used to determine the effects of NaOH concentration, sodium monochloroacetic acid concentration, and temperature on CMC production from waste carton box cellulose. A total of 20 experiments were conducted for optimization of CMC synthesis purpose and the effect of each factor was analyzed by taking minimum, maximum and center values from operating conditions which has significant influence on CMC synthesis. All experiments were carried out in a randomized order to minimize the effect of unexpected variability in the observed response due to

extraneous factors. The degree of substitution (DS) obtained from experiments were used as a response parameter for optimization and Table 4.2 shows experimental results of each run.

The resulting data, Table 4.2, were analyzed using Design expert® 6 software to determine the effects of sodiumhydroxide concentration, monochloroacetic acid concentration, and temperature. The dependent variable used as a response parameter was the degree of substitution of CMC. All experiments were carried out in a randomized order to minimize the effect of unexpected variability in the observed response due to extraneous factors.

Table 4.3 Design Summary

Study type	Response surface
Initial design	Central composite
Center points	
Design model	Quadratic
Runs	20
Blocks	no blocks

Factors	Name	units	Low actual	High actual	Low coded	High coded	Mean	Std. Dev.
A	NaOH con.	w/w	10	50	-1	1	0	
B	SMCA	g	2	10	-1	1	0	
C	Temperature	˚C	30	70	-1	1	0	
Response	Name	units	Obs	Min	Max	Mean	Std. Dev.	Model
Y1	DS		20	0.63	0.85			Quadratic

Table 4.4 Analysis of Variance (ANOVA)

Source	Sum of Squares	DF	Mean Square	F -Value	Prob > F	
Model	0.082	9.000	0.009	860.829	< 0.0001	significant
A	0.001	1.000	0.001	127.622	< 0.0001	
B	0.002	1.000	0.002	227.863	< 0.0001	
C	0.004	1.000	0.004	390.842	< 0.0001	
A^2	0.008	1.000	0.008	722.627	< 0.0001	
B^2	0.000	1.000	0.000	0.005	0.946	
C^2	0.016	1.000	0.016	1472.457	< 0.0001	
AB	0.004	1.000	0.004	350.733	< 0.0001	
AC	0.001	1.000	0.001	87.683	< 0.0001	
BC	0.003	1.000	0.003	311.136	< 0.0001	
Residual	0.000	10.000	0.000			
Lack of Fit	0.000	5.000	0.000	3.055	0.123	not significant
Pure Error	0.000	5.000	0.000			
Cor Total	0.082	19.000				

F- Value is a test for comparing model variance with residual (error) variance. If the variances are close to the same, the ratio will be close to one and it is less likely that any of the factors have a significant effect on the response. It is calculated by Model Mean Square divided by Residual Mean Square.

The Model F-value of 860.83 implies the model is significant. There is only a 0.01% chance that a "Model F-Value" this large could occur due to noise.

Values of "prob >F" less than 0.0500 indicate model terms are significant. In this case A, B, C, A^2, C^2, AB, AC, BC are significant model terms. Values greater than 0.10000 indicate the model terms are not significant. If there are many insignificant model terms (not counting those required to support hierarchy), model reduction may improve your model.

The "Lack of Fit-value" of 3.06 implies the Lack of Fit is not significant relative to the pure error. There is a 12.29% chance that a "Lack of Fit-value" this large could occur due to noise. Non-significant lack of fit is good since we want the model to fit.

Table 4.5 Model adequacy measures

Std. Dev	3.25E-03
Mean	0.77
C.V.	0.42
PRESS	1.53E-03

R-Squared	0.9987
Adj. R-Squared	0.9976
Predicted R-Squared	0.9813
Adequate Precision	95.805

As in table 4.5 "Predicted R-Squared" of 0.9813 is in reasonable agreement with the "Adj. R-Squared" of 0.9976.

"Adeq Precision" measures the signal to noise ratio. A ratio greater than 4 is desireable. The ratio of 95.805 indicates an adequate signal. So, this model can be used to navigate the design space.

Table 4.6 Regression coefficients and the corresponding 95% CI low and high

Factor	Coefficient Estimate	95% CI Low	95% CI High
Intercept	*0.8371*	*0.8346*	*0.8395*
A-NaOH conc.	0.0116	0.0093	0.0139
B-SMCA	0.0155	0.0132	0.0178
C-Temperature	0.0203	0.0180	0.0226
A2	-0.0526	-0.0570	-0.0483
B2	-0.0001	-0.0045	0.0042
C2	-0.0751	-0.0795	-0.0708
AB	0.0215	0.0189	0.0241
AC	0.0108	0.0082	0.0133
BC	-0.0203	-0.0228	-0.0177

Final Equation in Terms of Coded Factors:

$$\mathrm{DS} = +0.84 + 0.012 * \mathrm{A} + 0.016 * \mathrm{B} + 0.02 * \mathrm{C} - 0.053 * \mathrm{A\hat{}2} - 1.364\mathrm{E} - 004 * \mathrm{B\hat{}2} - 0.075 * \mathrm{C\hat{}2} + 0.021 * \mathrm{A} * \mathrm{B} + 0.011 * \mathrm{A} * \mathrm{C} - 0.02 * \mathrm{B} * \mathrm{C}$$

Final Equation in Terms of Actual Factors:

$$DS = +0.17006 + 5.51920E - 003 * NaOHcon. + 8.57102E - 003 * SMCA + 0.020512 * Temperature - 1.31591E - 004 * NaOH\ con.^2 - 8.52273E - 006 * SMCA^2 - 1.87841E - 004 * Temperature^2 + 2.68750E - 004 * NaOH\ con. * SMCA + 2.68750E - 005 * NaOH\ con. * Temperature - 2.53125E - 004 * SMCA * Temperature$$

Table 4.7 Actual versus model Predicted of degree of substitution

Standard Order	Actual Value	Predicted Value	Residual	Leverage	Student Residual	Cook's Distance	Outlier	Run Order
1	0.677	0.674	0.003	0.793	2.204	1.863	2.916	7
2	0.630	0.632	-0.003	0.793	-1.656	1.052	-1.844	1
3	0.700	0.702	-0.002	0.793	-1.521	0.887	-1.645	13
4	0.750	0.747	0.003	0.793	2.069	1.641	2.594	8
5	0.731	0.733	-0.002	0.793	-1.588	0.968	-1.743	15
6	0.738	0.735	0.003	0.793	2.001	1.535	2.451	11
7	0.684	0.681	0.003	0.793	2.136	1.750	2.749	18
8	0.766	0.769	-0.003	0.793	-1.724	1.140	-1.951	12
9	0.771	0.773	-0.002	0.491	-0.785	0.059	-0.769	14
10	0.795	0.796	-0.001	0.491	-0.440	0.019	-0.421	16
11	0.820	0.821	-0.001	0.491	-0.612	0.036	-0.592	17
12	0.851	0.852	-0.001	0.491	-0.612	0.036	-0.592	3
13	0.740	0.742	-0.002	0.491	-0.698	0.047	-0.679	19
14	0.781	0.782	-0.001	0.491	-0.526	0.027	-0.506	6
15	0.840	0.837	0.003	0.118	0.966	0.013	0.962	20

16	0.837	0.837	-0.001	0.118	-0.018	0.000	-0.017	2
17	0.834	0.837	-0.003	0.118	-1.002	0.013	-1.002	5
18	0.839	0.837	0.002	0.118	0.638	0.005	0.618	9
19	0.840	0.837	0.003	0.118	0.966	0.013	0.962	4
20	0.838	0.837	0.001	0.118	0.310	0.001	0.296	10

To see how well the quadratic polynomial model satisfies the assumptions of the analysis of variance (ANOVA), the plots of residuals and residual versus predicted values (Table 4.7) were analyzed.

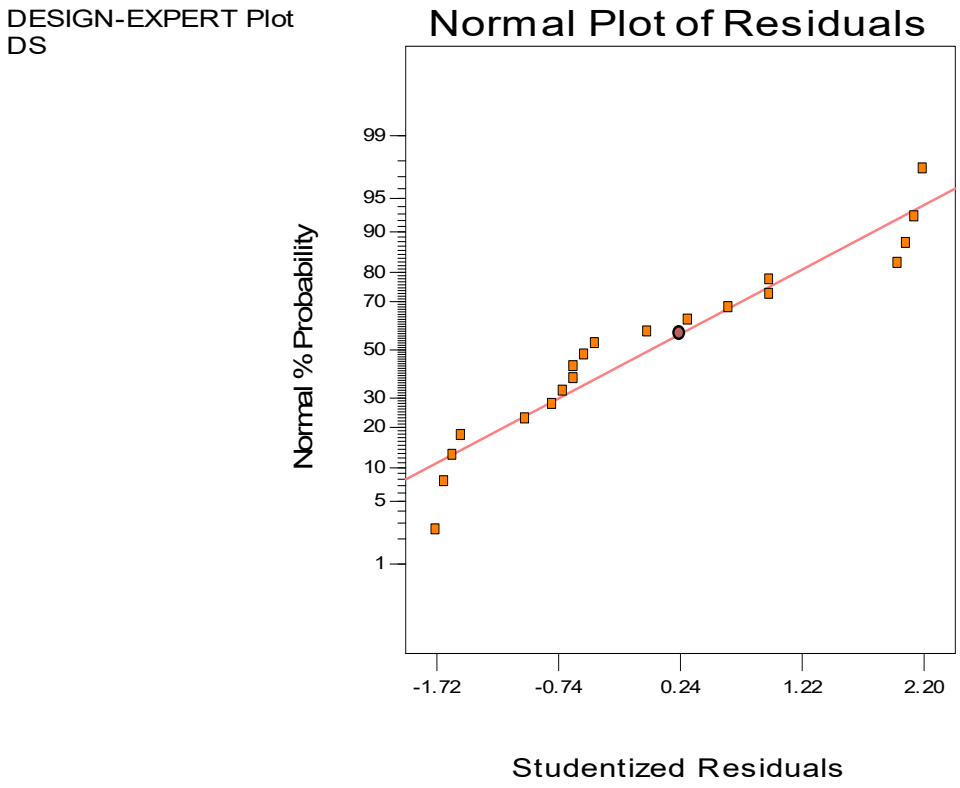


Figure 4.1Normal plot of residuals

The normal probability plot, (Fig. 4.1), indicates the residuals following a normal distribution, in which case the points follow a straight line. This indicates the model satisfies the assumption of ANOVA. i.e. the error distribution is approximately normal.

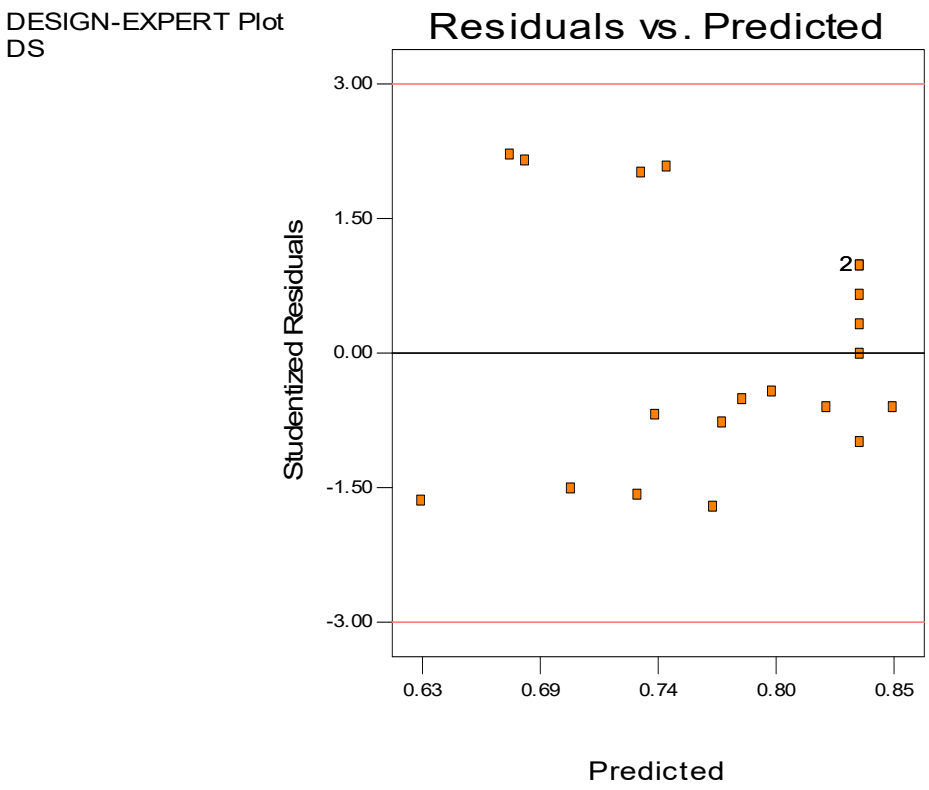


Figure4.2 Plot of residuals versus model predicted values

If the model is correct and the assumptions are satisfied, the residuals should be structure less; in particular, they should be unrelated to any other variable including the predicted response. A simple check is to plot the residuals versus the fitted (predicted) values. A plot of the residuals versus the rising predicted response values tests the assumption of constant variance. The plot shows random scatter which justifying no need for an alteration to minimize personal error.

4.4. Effects of Experimental Variables on CMC Synthesis

Effect of NaOH Concentration on DS

The effect of NaOH concentration on degree of substitution (DS) was shown in Fig. 4.3 The DS of CMC increased with increase in NaOH concentration and attained a highest DS of 0.84 at a NaOH concentration of 30 % (w/v). This is due to the crystalline region in cellulose was changed to amorphous and thus, atom at C2, C3 and C6 of anhydroglucopyranose unit (AGU) could be easily accessed by MCA (Olaru, Stoleriu and Timpu, 1997). However, the DS started declining at higher concentration of NaOH (>30 %)

which could be due to formation of sodium glycolate as a by-product in the synthesis of CMC and also degradation of cellulose polymer.

Besides, a similar result was also observed in CMC from the banana pseudo stem (Adinugraha, Marseno and Haryadi, 2005), sugar beet pulp (Togrul and Arslan 2003) and sago waste (Pushpamalar, Langford and Lim, 2006). Barai, Singhal and Kulkarni (1997) reported that at high concentration of NaOH, glycolate formation predominated, thus lowering the degree of substitution and CMC content as part of sodium monochloroacetic acid (Na-MCA) molecule tends to react with NaOH according to the following side or competing reaction.

$$NaOH + Cl\_CH2COONa \rightarrow HO - CH2COONa + NaCl$$

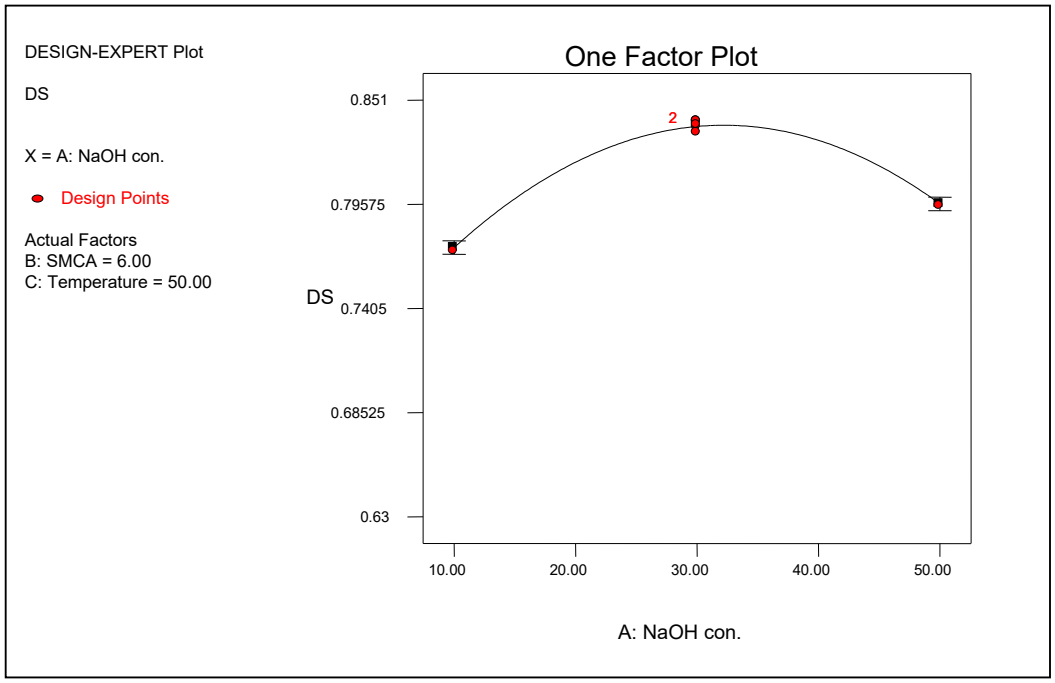


Figure 4.3: Effect of NaOH conc. on degree of substitution

Effect of Monochloroacetic Acid Concentration on DS

Increasing mono-chloroacetic acid concentration didn't have significant effect on the degree of substitution of the synthesized CMC, instead it slightly increased the degree of substitution. This is because increasing the chloroacetic acid concentration from 2gm to 10gm will most likely facilitate the side reaction (formation of sodium glycolate) to be dominated. In fact the chloroacetic acid concentration is impeded by other reaction condition such as NaOH concentration. This will further discussed in the interaction effect of MCAA and NaOH concentration part.

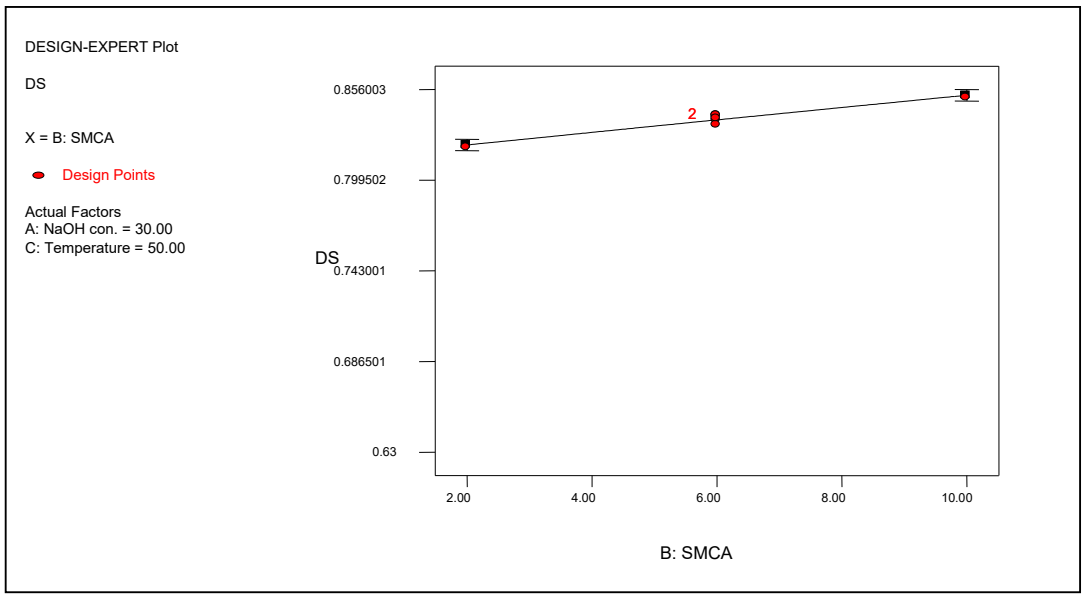


Figure 4.4: Effect of chloroacetic acid conc. on degree of substitution

Effect of Reaction Temperature on DS

As shown on the figures 4.5 the graphs indicate the effect of temperature on the degree of substitution.

Etherification temperature was the most important factor during synthesis of CMC in this study. Degree of substitution increases with an increasing etherification temperature. When the temperature was lower, it was difficult for the sodium hydroxide to seep into alkali cellulose and the DS could not achieve a high value. Increasing etherification temperature probably activates the functional groups to be substituted. The hydrogen atom easily removed and carboxymethyl group

replaced.

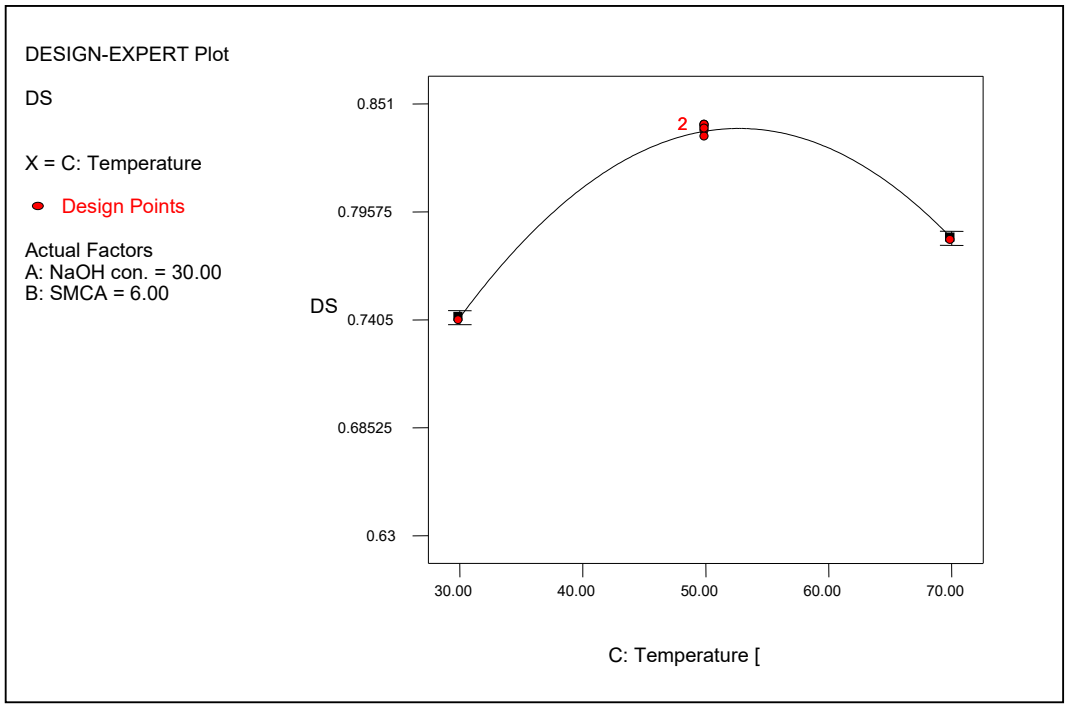
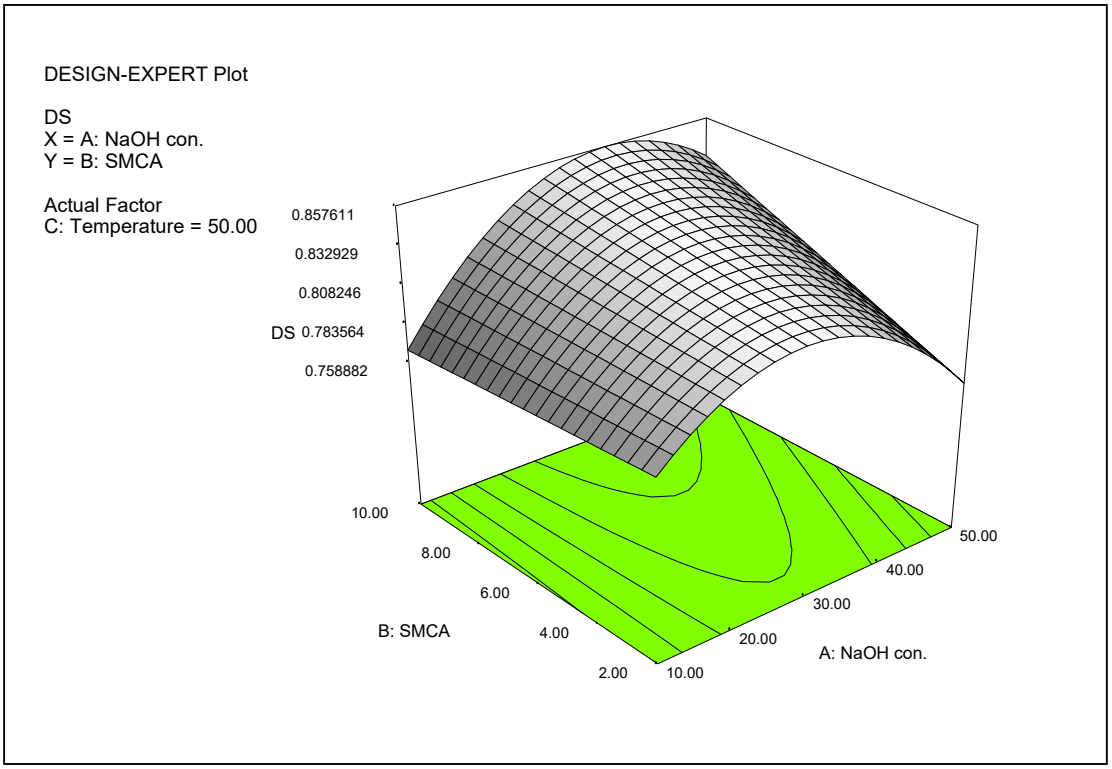


Figure 4.5: Effect of Temperature on degree of substitution

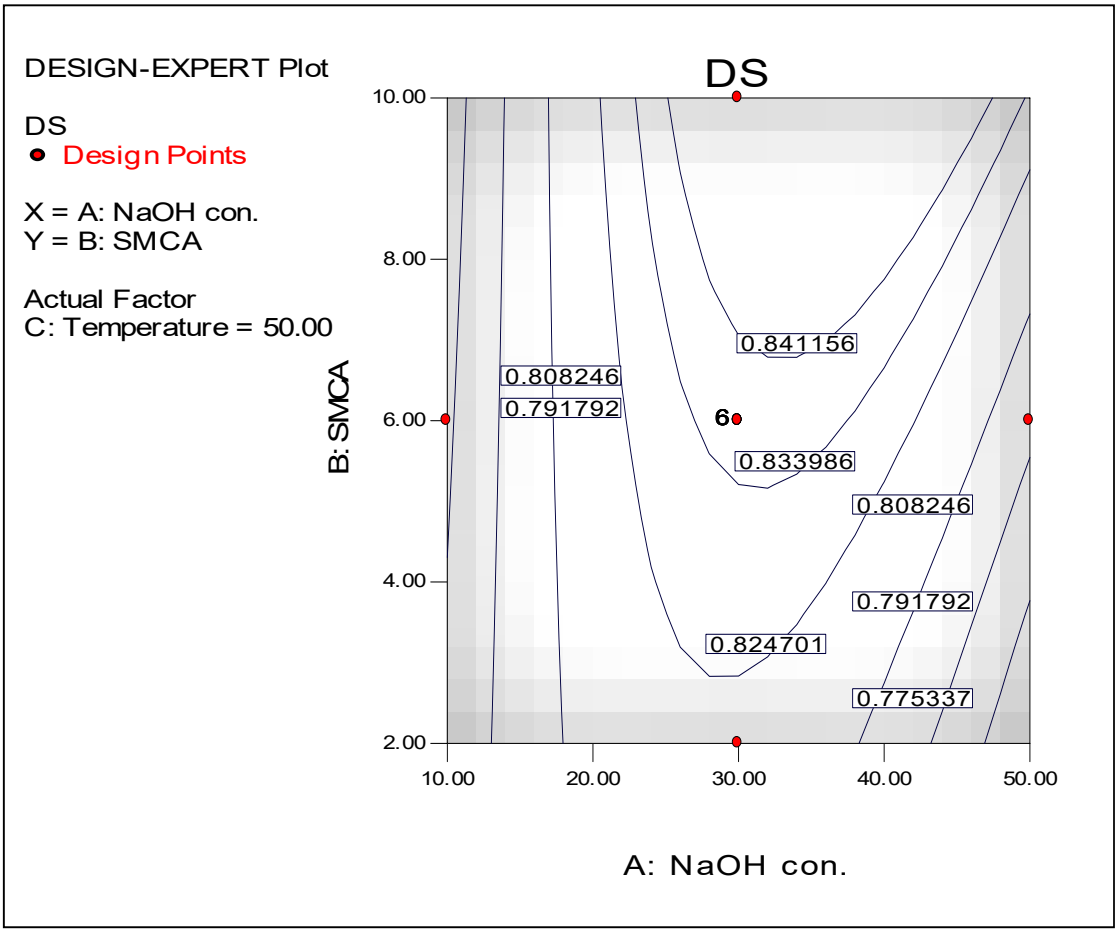
Interaction Effects

Etherification is influenced by different factors and the degree of substitution has a complex relationship with independent variables.

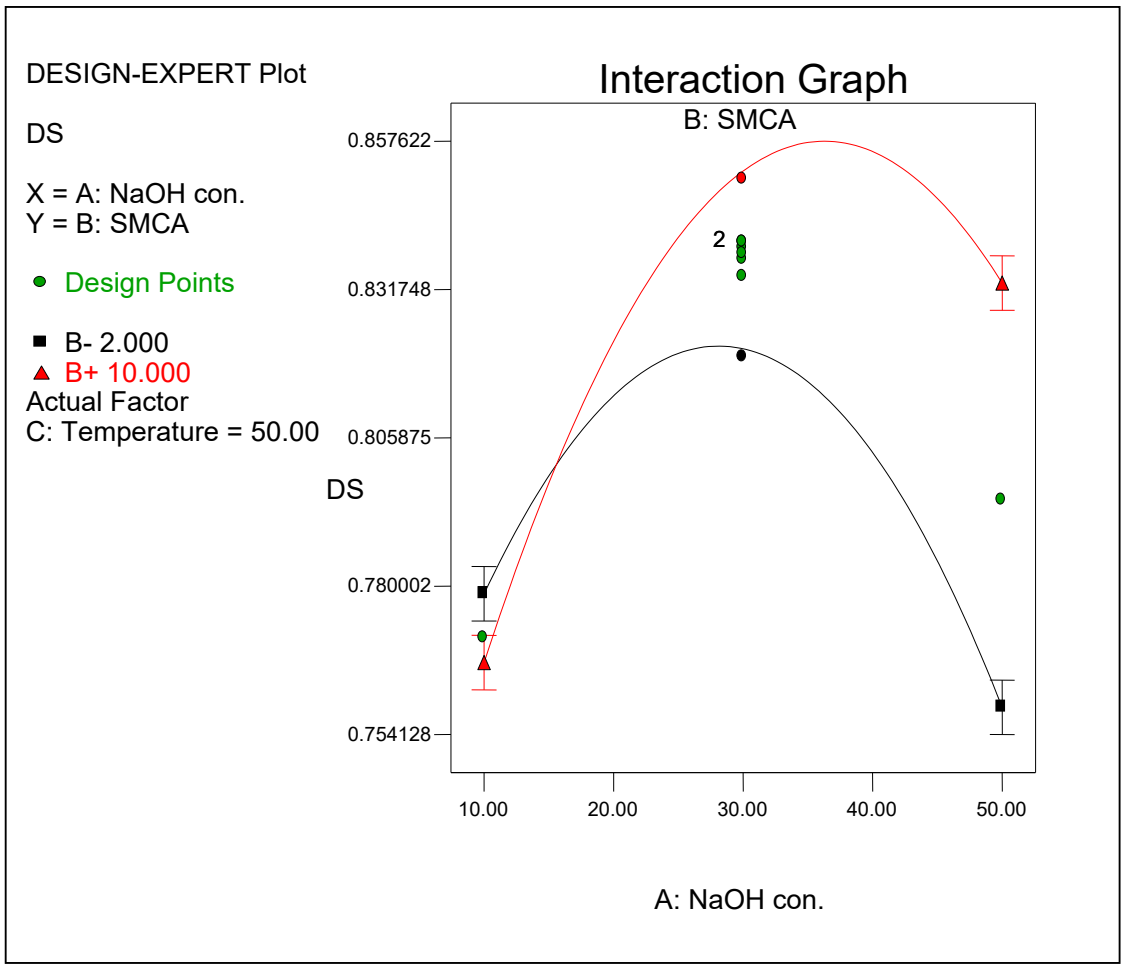
The best way of expressing the effect of any parameter on the degree of substitution within the experimental space under investigation was to generate response surface plots of the equation. The three dimensional response surfaces, contours and interactions were plotted in figures (4.6), (4.7), and (4.8) as a function of the interactions of any two of the factors by holding the other one at average value. In the interaction plots the black line represents low level of variables and the red line represents high level of variables.


DESIGN-EXPERT Plot
DS
X = A: NaOH con.
Y = B: SMCA
Actual Factor
C: Temperature = 50.00
0.857611
0.832929
0.808246
DS 0.783564
0.758882
10.00
8.00
6.00
4.00
2.00
B: SMCA
10.00
20.00
30.00
40.00
50.00
A: NaOH con.

(a)


DESIGN-EXPERT Plot
DS
Design Points
X = A: NaOH con.
Y = B: SMCA
Actual Factor
C: Temperature = 50.00
DS
10.00
8.00
6.00
4.00
2.00
B: SMCA
0.841156
0.808246
0.791792
6
0.833986
0.808246
0.791792
0.824701
0.775337
10.00
20.00
30.00
40.00
50.00
A: NaOH con.

(b)



(c)

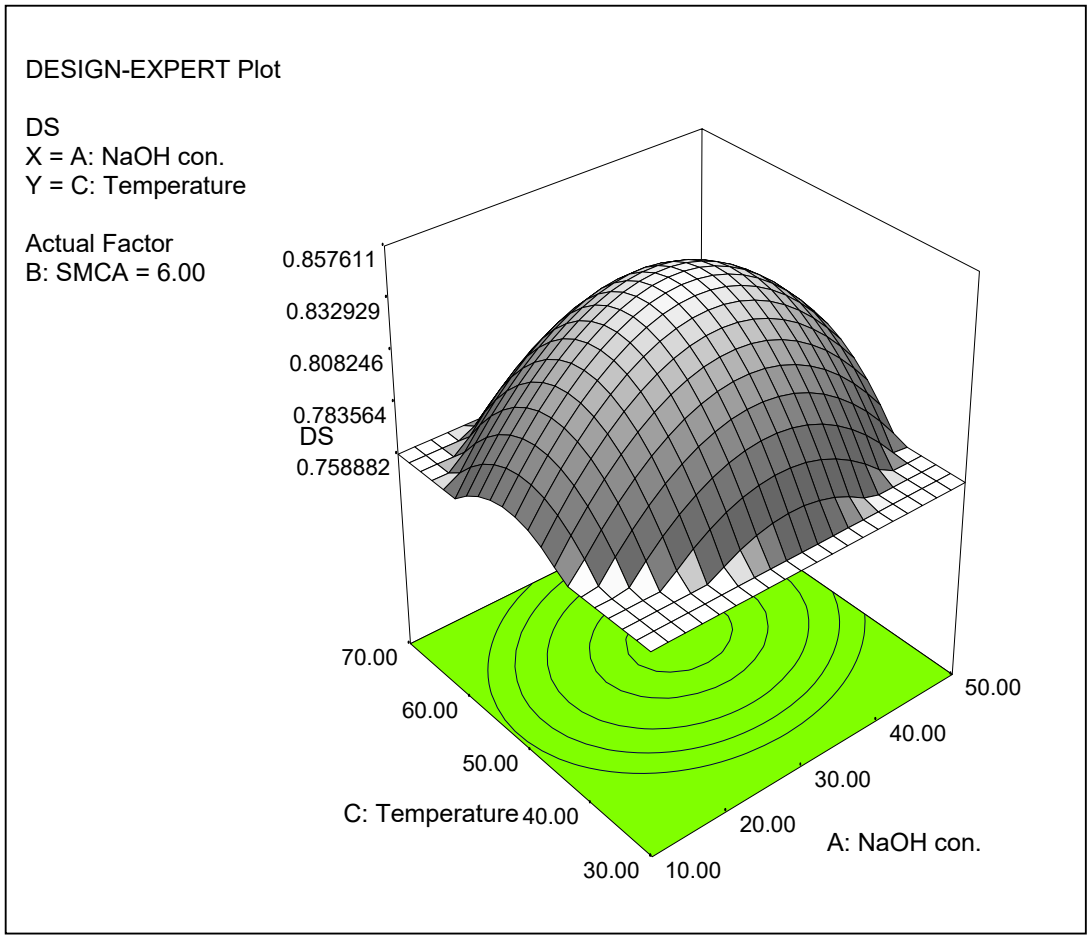
Figure 4.6 Response surface plot(a), contour plot (b) and interaction plot (c) of DS as a function of NaOH con. and SMCA

The response surface, figure 4.6 (a), obtained from sodiumhydroxide concentration and sodium monochloroacetic acid concentration was semi-cylinderical and which showed an increase of degree of substitution with increase in NaOH concentration up to 30% and then decreased with increasing NaOH. On the other hand the degree of substitution is not strongly affected by the sodium monochloroacetic acid concentration. It was suggested that synthesis of CMC from waste carton biomass cellulose affected by % NaOH due to the crystalline region in cellulose was changed to amorphous and thus, atom at C2, C3 and C6 of anhydroglucopyranose unit (AGU) could be easily accessed by MCA.

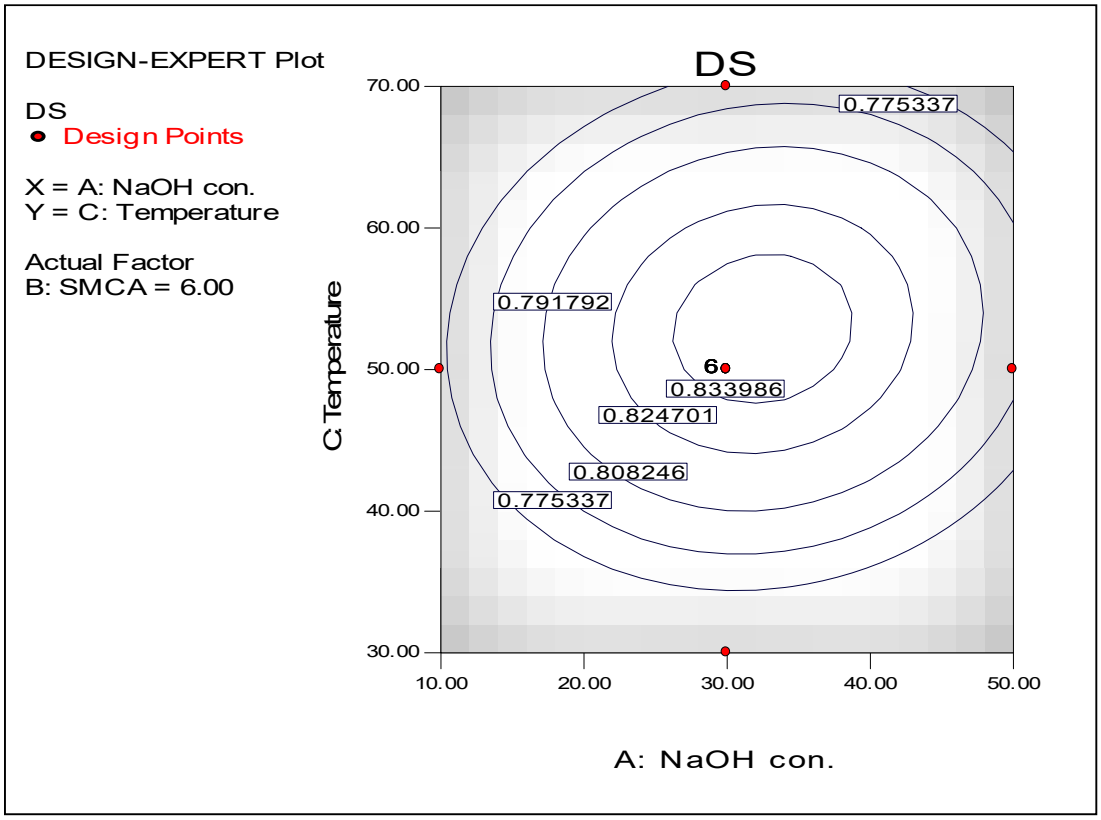
The contour plot profile, Figure 4.6(b), shows the interaction between sodiumhydroxide concentration and sodium monochloroacetic acid concentration and at higher level of sodiumhydroxide concentration and sodium monochloroacetic acid concentration maximum degree of substitution obtained. From contour plot, it was found that the predicted DS of

synthesized CMC was in the range of 0.775-0.841.Therefore synthesized CMC from waste carton biomass CMC can be used in many application such as in liquid detergent.

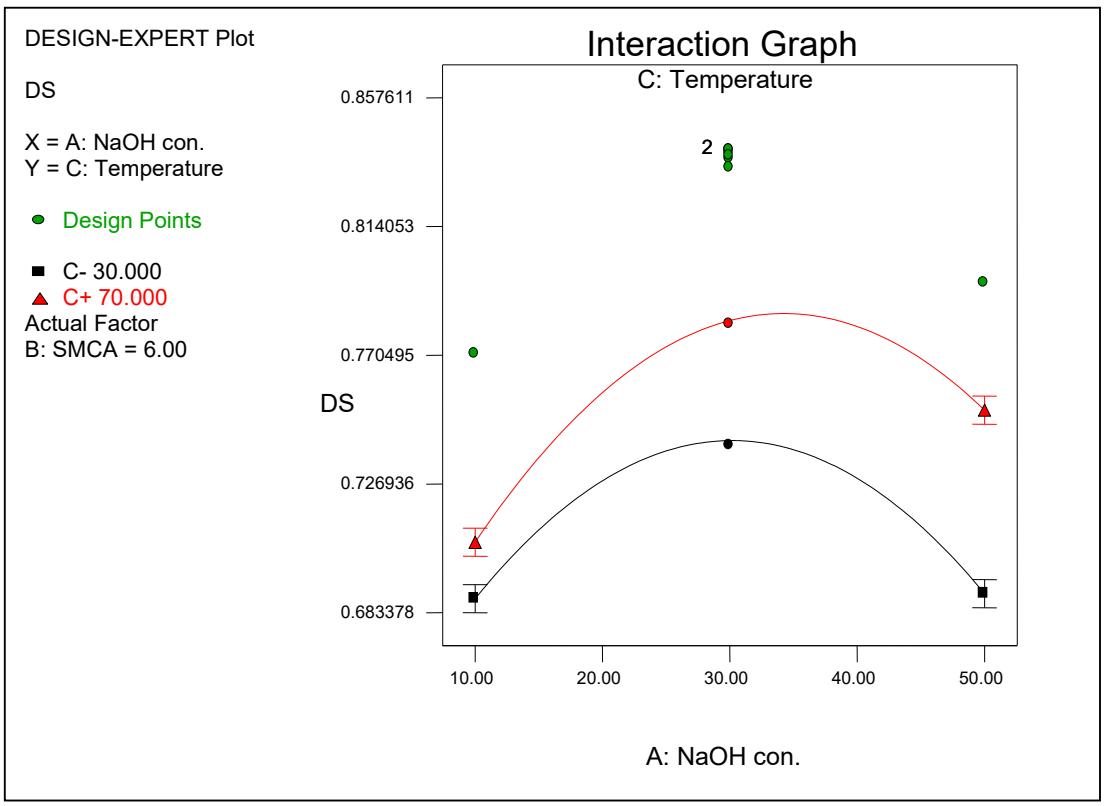
Interaction plot of sodiumhydroxide concentration and sodium monochloroacetic acid concentration on the degree of substitution is shown figures 4.6(c) above. Figure 4.6 (c) discloses that slight increase in degree of substitution was obtained with the increasing of sodiumhydroxide concentration.



(a)



(b)



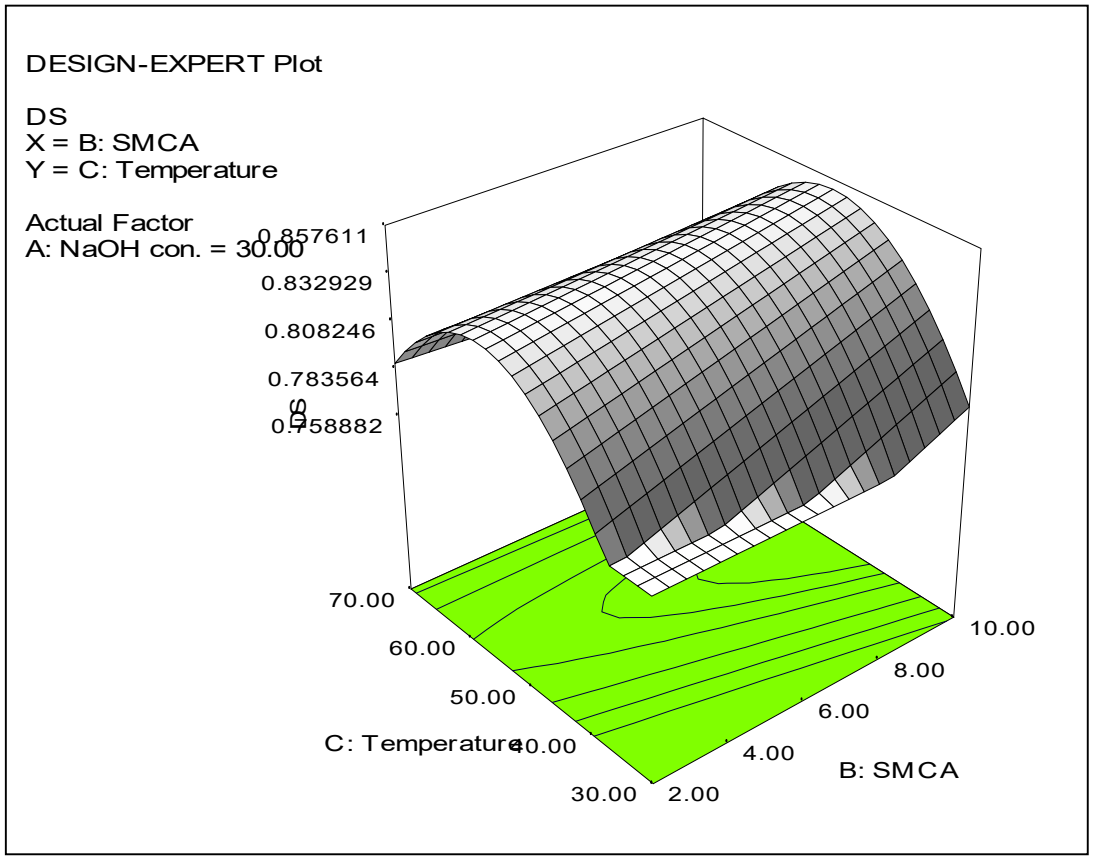
(c)

Figure 4.7 Response surface plot(a), contour plot (b) and interaction plot and (c) of DS as a function of NaOH con. and temperature

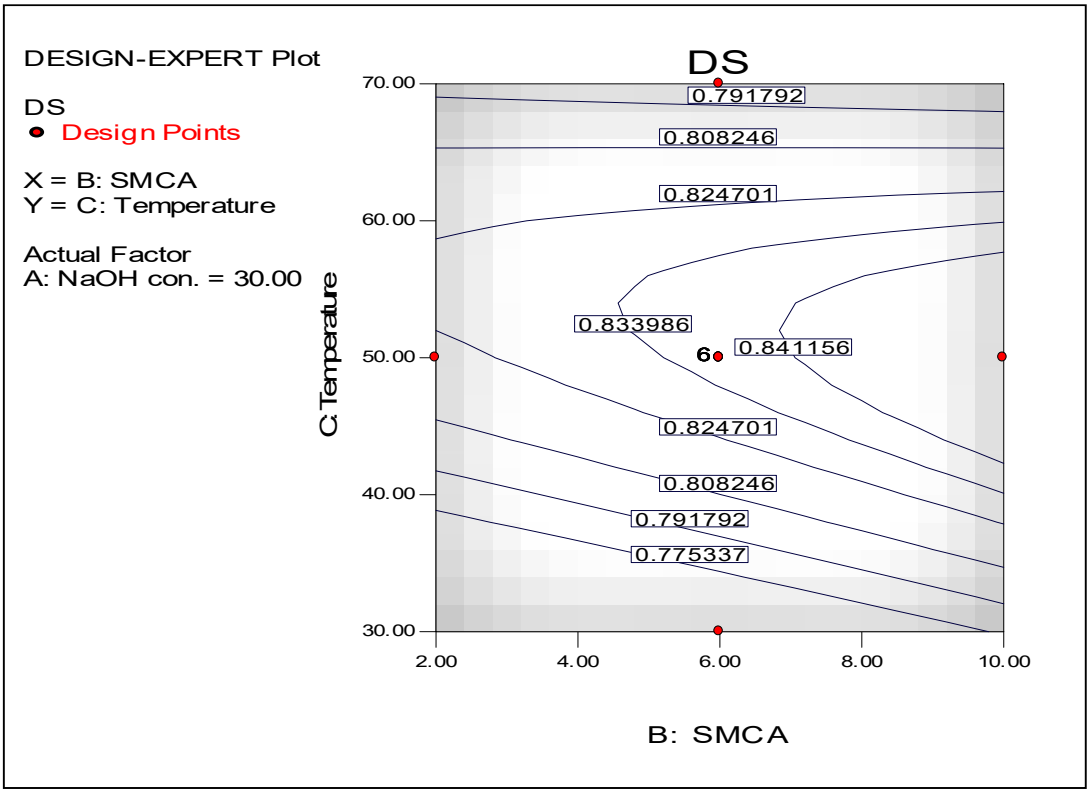
The response surface, figure 4.7 (a), obtained from sodium hydroxide concentration and temperature was semi-spherical and showed that the degree of substitution gradually increased with increasing NaOH concentration from 10% to 30% at any temperature and again gradually decreased above 30% NaOH. A similar trend was also observed for etherification reaction temperature.

The contour plot profile, Figure 4.7(b), shows the interaction between sodium hydroxide concentration and temperature and at low level of sodium hydroxide concentration and temperature maximum degree of substitution obtained.

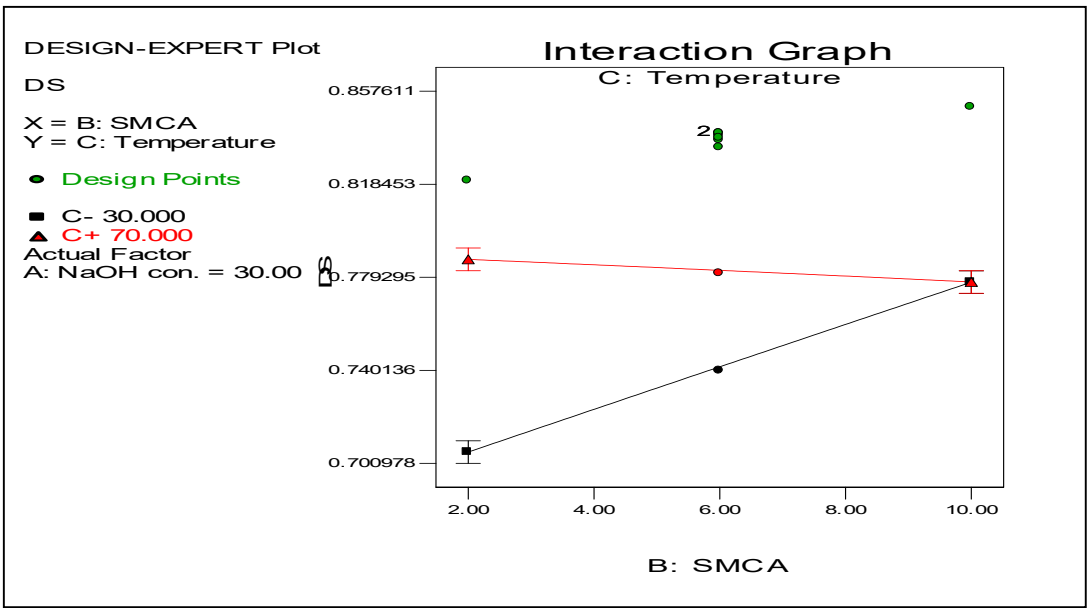
Interaction plot of sodiumhydroxide concentration and temperature on the degree of substitution is shown figures 4.7(c). Figure 4.7 (c) discloses that slight increase in degree of substitution was obtained with the increasing of temperature.



(a)



(b)



(c)

Figure 4.8 Response surface plot(a), contour plot (b) and interaction plot and (c) of DS as a function of SMCA con. and temperature

The response surface, fig. 4.8(a), obtained from sodium-monochloroacetic acid concentration and temperature is semi-cylinderical and symetrical which showed a gradual increase in degree of substitution with increase in temperature up to 55˚c and then gradually

decreased with increase in temperature beyond 55˚c. On the other hand the degree of substitution is not strongly affected by the sodium monochloroacetic acid concentration.

The contour plot, fig. 4.8(b), shows that the interaction between the monochloroacetic acid concentration and temperatuere is strong on the degree of substitution. As both monochloroacetic acid concentration and temperature increase, the degree of substitution increases.

The interaction of monochloroacetic acid concentration and temperature on the degree of substitution of CMC is shown in fig. 4.8(c). Fig 4.8 (c) shows at high level of temperature increasing monochloroacetic acid concentration resulted a slight increase in the degree of substitution of CMC ,while at low reaction temperature increase in acid concentration results in sharp increase in the degree of substitution of CMC.

4.5. Optimization

The optimum sodium hydroxide concentration, monochloroacetic acid concentration, and etherification temperature for maximum degree of substitution are 13.53%w/w,0.4w/w and 41.62^{o}C respectively with 0.76738 degree of substitution of CMC. The optimization criteria used are summarized in table below.

Table 4.8 Optimization criteria

Name	Goal	Lower limit	Upper limit
Sodium hydroxide	Minimise	10	50
Sodium monochloroacetic acid	Minimise	2	10
temperature	Minimise	30	70
Degree of substitution of CMC	Maximise	0.63	0.851

The optimum possible solutions for carboxymethyle cellulose synthesis in CMC production are shown below.

Table4.9. Optimum possible solutions

Solution number	Sodium hydroxide concentration	Sodium monochloroacetic acid concentration	Temperature	Degree of substitution	Desireability
1	13.24	2.00	41.49	0.765728	0.796
2	13.53	2.00	41.62	0.76738	0.796**
3	12.63	2.00	40.19	0.756957	0.795
4	10.00	2.00	44.69	0.765489	0.789
** selected as optimum conditions					

4.6. Model Validation

As determined by the central composite RSM design result using Design-Expert® v.6 software, an experiment with sodium hydroxide concentration, mono-chloroacetic acid concentration, and etherification temperature was conducted to carry out the effect of the design used. The optimal values test factors were 13 % w/w, 0.4 w/w, and 41°C (values near to that selected in table 4.9). The experiment was carried out at the optimized conditions. The degree of substitution of 0.767 (average) obtained and was in good agreement with the predicted one. Therefore the model is considered to be accurate and reliable for predicting the degree of substitution of CMC.

5. Economic Analysis

5.1 Process Description and Flow Diagram of CMC Production

CMC is produced from cellulose and monochloroacetic acid (MCA) and with sodium hydroxide (NaOH) as the third essential ingredient. The different steps in the CMC process are described in the flow sheet below.

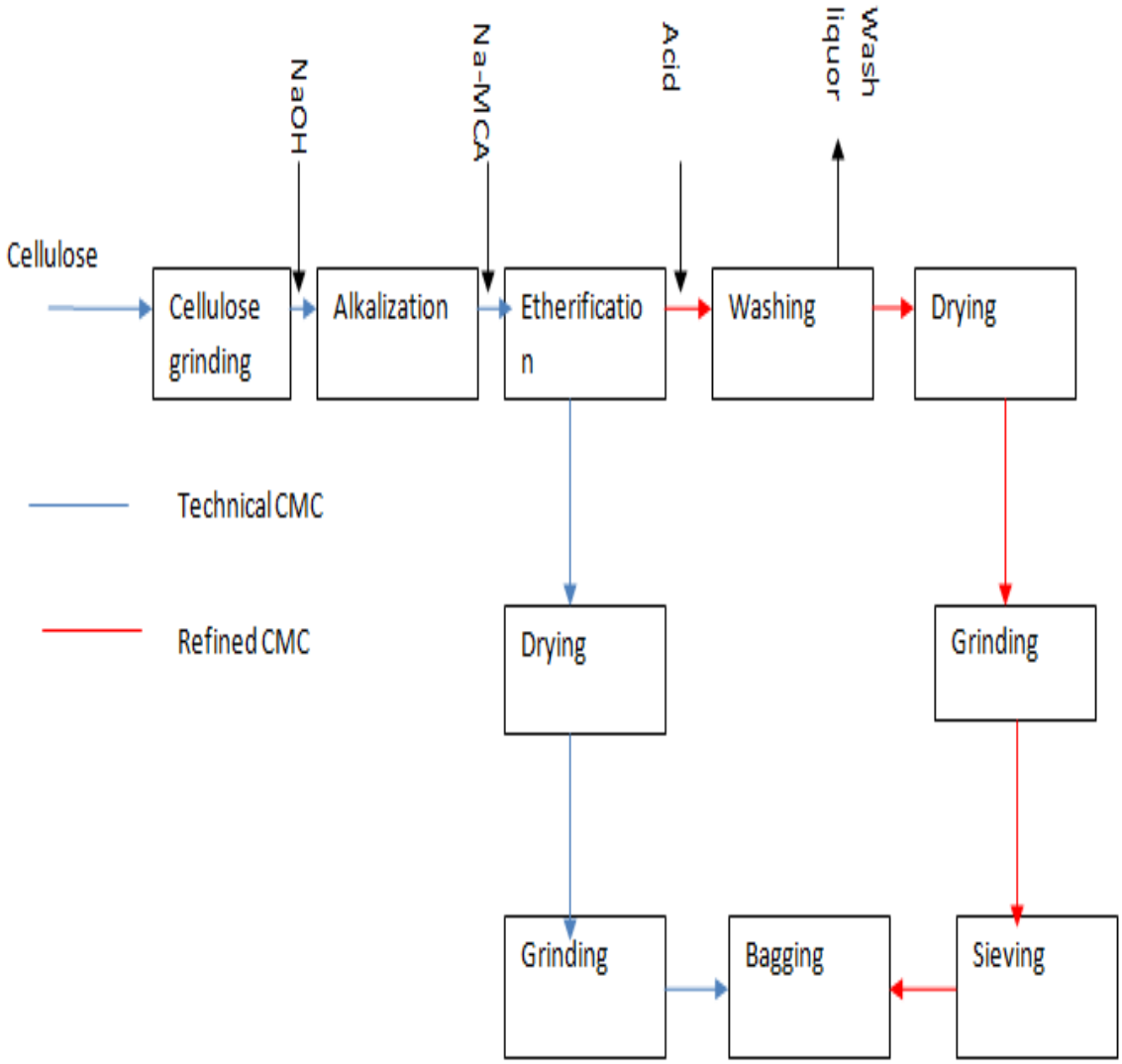


Figure 5.1 Process Flow Diagram for CMC Production

5.2 Material Balance

Material balances are the basis of process design. A material balance taken over the complete process will determine the quantities of raw materials required and products produced. Balances over individual process units set the process stream flows and compositions. They are also useful tools for the study of plant operation and trouble shooting. They can be used to check performance against design; to extend the often limited data available from the plant instrumentation; to check instrument calibrations; and to locate sources of material loss. On the other hand, in process design, energy balances are made to determine the energy requirements of the process: the heating, cooling and power required. In plant operation, an energy balance (energy audit) on the plant will show the pattern of energy usage, and suggest areas for conservation and savings (Coulson & Richardson's, 2005).

Even though, the projected demand indicated on table 2.4 was large enough to achieve scale of economies in the production operations, 90ton/year was assumed for this preliminary economic analysis.

$$\text{CMC} = \frac{(\frac{90\text{ton}}{\text{year}} * \frac{1000\text{kg}}{\text{ton}})}{(\frac{300\text{days}}{\text{year}} * \frac{8\text{h}}{\text{day}})}$$

$$\text{CMC} = 37.5\text{kg/h}$$

Averagely the reaction of cellulose to CMC yields about 1.3 g for each gram of cellulose reacted with monochloroacetic acid and sodium hydroxide (Penpun and Tasaso,2015).

Therefore,

$$\text{Cellulose used} = \frac{37.5}{1.3}\text{kg/h}$$

$$\text{cellulose used} = 28.8\text{kg/h}$$

During pulping, lignin, hemicelluloses and small amount of cellulose was dissolved and removed by filtration. The yield of the waste carton biomass was 35.5%. So the amount of waste carton biomass:

$$\text{waste carton biomass required} = \frac{28.8\text{kg/h}}{0.355}$$

$$\text{Waste carton biomass required} = 81.1\text{kg/h}$$

That is, for 300 working days a year and 8 working hours a day, the amount that is going to be treated annually is about 195 ton of waste carton biomass.

Inputs and outputs of each unit based on the laboratory report values were scaled up to the required amounts and are listed on table below.

Table 5.1: Amount of inputs and outputs

Units	Material	Inputs	Outputs
Delignifying Unit	Waste carton biomass	81.8kg/h	2012.6kg/h (2.3m^3/h)
	NaOH solution	69.8kg/h	
	Water	1861liter/h	
Washer	Delignified solution	2012.6kg/h (2.3m^3/h)	wet cellulose (79.82kg/h)....55% moist
	Wash water	1380kg/h (1.38m^3/h)	Removed solution (6079kg/h)
Dryer	Wet cellulose	79.82kg/h (70.51Lit/h)	Dried cellulose (35.92kg/h) Water (43.9kg/h)
Basification and Etherification Unit	Dried cellulose	35.92kg/h	710.92kg/h
	25% NaOH	156.16liter	
	Chloroacetic acid	19.52kg/h	
	Isopropanol	585liter/h	
Filtration	Reactor output	710.92kg/h	Isopropanol and unreacted (306.54kg/h) Wet mixtures (404.38kg/h)
Washing	Wet mixture	404.38kg/h	Wet CMC (89.8kg/h, 40%) Ethanol and by-products (437.79kg/h)
	Ethanol	123.21kg/h	
Drying	Wet CMC	89.8kg/h	Dried CMC 35.92 kg/h Ethanol 53.88kg/h

5.3. Cost Estimation

Cost estimation is a specialized subject and a profession in its own right. The design engineer, however, needs to be able to make quick, rough, cost estimates to decide between alternative designs and for project evaluation. Chemical plants are built to make a profit, and

an estimate of the investment required and the cost of production are needed before the profitability of a project can be assessed (Sinnott et al, 1999).

For the plant design to be acceptable, it must present a process that is capable of operating under conditions which will yield a profit. Since net profit equals total income minus all expenses, it is essential that the chemical engineer be aware of the many different types of costs involved in manufacturing processes (Max S. Peters et al, 1991).

A capital investment is required for any industrial process, and determination of the necessary investment is an important part of a plant-design project. The total investment for any process consists of fixed-capital investment for physical equipment and facilities in the plant plus working capital which must be available to pay salaries, keep raw materials and products on hand, and handle other special items requiring a direct cash outlay. Thus, in an analysis of costs in industrial processes, capital-investment costs, manufacturing costs, and general expenses including income taxes must be taken into consideration (Peters et al, 1991).

5.4. Plant Parameters

- Capacity, the plant is envisaged to produce 90 ton/year.
- Number of shifts /day is 1
- 300 working days/year
- Operating 8 hrs/shift

5.5. Cost of Raw Materials

In the chemical industry, one of the major costs in a production operation is for the raw materials involved in the process. The amount of the raw materials which must be supplied per unit of time or per unit of product can be determined from process material balances. In many cases, certain materials act only as an agent of production and may be recoverable to some extent. Therefore, the cost should be based on the amount of raw materials actually consumed as determined from the overall material balances. Direct price quotations from prospective suppliers are preferable to published market prices. For preliminary cost analyses, market prices are often used for estimating raw-material costs (Peters et al, 1991).

The annual material requirements and corresponding cost of the plant is shown on the table 5.2 below.

Table 5.2: Cost of raw materials

No	Raw material	Unit	Anual consumption	Cost (Birr)
1	carton biomass	Ton	195	48750
2	Sodium hydroxide	Ton	167.5	350000
3	sodium hypochlorite	Ton	84.8	310000
4	Mono chloroacetic acid	Ton	28	280000
5	Isopropanol	Ton	39	214500
			Total	1203250

Values for most raw materials were taken from local company and personal contact.

5.6. Machinery and Equipment Requirements

The cost of purchased equipment is the basis of several pre-design methods for estimating capital investment. Sources of equipment prices, methods of adjusting equipment prices for capacity, and methods of estimating auxiliary process equipment are therefore essential to the estimator in making reliable cost estimates. The most accurate method for determining process equipment costs is to obtain firm bids from fabricators or suppliers.

Table 5.3: Purchased equipment cost

Item	Quantity	Price, birr
Autoclave	1	325000
Jacketed & strirred reactor	1	225000
Vacuum drum filter	1	125000
Rotary Dryer	1	315000
Ball Mill	1	175000
Storage Tank	3	225000
Total		1390000

Values for most equipment were taken from local company and personal contact.

5.7. Total Capital Investment Estimation

Before an industrial plant can be put into operation, a large sum of money must be supplied to purchase and install the necessary machinery and equipment. Land and service facilities must be obtained, and the plant must be erected complete with all piping, controls, and services. In addition, it is necessary to have money available for the payment of expenses involved in the plant operation. The capital needed to supply the necessary manufacturing

and plant facilities is called the fixed-capital investment, while that necessary for the operation of the plant is termed the working capital. The sum of the fixed-capital investment and the working capital is known as the total capital investment (Peters et al, 1991).

Table 5.4: Total Capital Investment Estimation (according to Peters & Timmerhaus, 1991).

Items	**Cost(Birr)**
Direct costs (D)	**3,377,700.00**
Purchased equipment cost (PEC)	1,390,000.00
Purchased equipment installation = 39% PEC	542,100.00
Instrumentation and controls = 13% PEC	180,700.00
Piping(installed) = 31% PEC	430,900.00
Electrical equipment (installed) = 10% PEC	139,000.00
Buildings (including services) = 29% PEC	403,100.00
Yard improvements = 10% PEC	139,000.00
Service facilities (installed) = 50% PEC	69,500.00
Land(purchase not required) = 6% PEC	83,400.00
Indirect costs (I)	**3,377,700.00**
Engineering and supervision = 25% D	844,425.00
Construction expenses = 8% D	844,425.00
Contractor's fee = 15% D	844,425.00
Contingency = 10% D	844,425.00
Fixed Capital investment=FCI=(D+I)	**6,755,400.00**
Working capital = 15% FCI	**2,444,294.00**
Total capital investment=FCI+WORKING CAPITAL	**9,199,694.00**

5.8. Estimation of Total Product Cost

Table 5.5: Estimation of total product cost

Items	Cost(Birr)
A) Direct Production costs	**2,824,305.00**
1) Raw materials	1,203,250.00
2) Operating labour (OL)	918,000.00
3)Direct supervisory and clerical labour(15% OL)	137,700.00
4)Utilities (10% of total product cost)	396,470.00
5)Maintenance and repairs (2% FCI)	135,108.00
6) Operating supplies (0.5% FCI)	33,777.00
B) Fixed Charges	**770,115.00**
1)Depreciation(10%FCI)	675,540.00
2)Local taxes(1% FCI)	67,554.00
3)Insurance(0.4% FCI)	27,021.00
C)Plant overhead cost 50%(OL +maintenance + DS &CI	**153,292.00**
D)General expenses(GE)	**216,994.00**
Administration (15% OL)	137,700.00
Distribution and selling (2% of total product cost0	79,294
Annual total product cost(TPC)	**3,964,706.00**

5.9. Gross Earnings

The total income minus the total production cost gives the gross earnings made by the production operation, which can then be treated mathematically by any of several methods to measure the profitably of the proposed project. Because of income-tax demands, the final net profit is often much less than the gross earnings.

Whole selling price of 1kg of CMC=75 birr

Expecting all produced CMC will be sold

Sale revenue =75 birr/kg*90000kg

Total income = 6,750,000birr

Gross profit = Sales revenue-Total product cost

Gross profit = 6,750,000 – 3,964,706= 2,785,294 birr

Let the tax rate be 35% (income tax of Ethiopia)

Taxes = 0.35* 2,785,294 birr = 947,853birr

Net profit = Gross profit – tax

Net profit = 2,785,294 -947,853birr = 1,837,441birr

Rate of Return (ROR)

$$\text{ROR} = \frac{\text{net profit}}{\text{total capital investment}} * 100$$

$$\text{ROR} = \frac{1{,}837{,}441}{7{,}9199{,}694} * 100$$

$$\text{ROR} = 19.97\%$$

Payback period

$$\text{payback period} = \frac{\text{net investment}}{\text{annual cash returns}}$$

$$\text{payback period} = \frac{\text{fixed capital investment}}{\text{net profit} + \text{depreciation}}$$

$$\text{payback period} = \frac{6{,}755{,}400}{1{,}837{,}441 + 675{,}540}$$

$$\text{payback period} = 2.7 \text{ years}$$

6. Conclusion and Recommendation

6.1 Conclusion

Sustainability, industrial ecology, and green chemistry are new principles that are guiding the development of the next generation of materials, products and processes. Bio-based materials hold great promise for achieving the goals of sustainable development and implementing the principles of industrial ecology.

In this study, synthesis of CMC from cellulose extracted from waste cartons and effect of process parameters like etherification temperature, NaOH concentration and dosage of sodium monochloroacetic acid on the degree of substitution of the synthesized CMC was investigated. The result indicated that the CMC could be synthesized from cellulose of waste cartons by a sequence of alkalization and carboxymethylation reactions.

From optimization, best alternative conditions were obtained to achieve high degree of substitution by using design expert software version 6. The optimal synthesis conditions of CMC was etherification temperature of 41˚C, concentration of sodium hydroxide 13%w/w and dosage of sodium monochloroacetic acid 0.4w/w. Under these particular conditions, the obtained CMC with DS value of 0.767 was achieved.

The characterisation results of the synthesized CMC showed the technical feasibility of producing CMC from cellulose extracted from waste carton biomass and the possibility of valorisation of lignocellulosic waste into wealth was assured.

The economic evaluation also showed establishing investment project to produce CMC from waste carton biomass was feasible with return on investment of 19.97% and a payback period of 2.7 years.

Therefore, the thesis results confirmed, producing carboxymethyle cellulose from waste carton biomass answers the sustainability issues of economic, social and environment which are the three pillars of sustainability.

6.2 Recommendations

1. The bleaching method used was chlorine based which is environmentally not recommended. Therefore, for future work it will be better to work on suitable bleaching methods that are environmentally friendly and discharge less effluent.
2. The optimization of the dissolving pulp production (cellulose extraction step) has to be refined to maximise the yield of the extracted cellulose.
3. The reuse of the hydrolysate and the black liquor to bio-fuel generation is also another research area to tap the full potential of the waste cartons.
4. More practical research on the pilot scale production of the CMC from waste carton is recommended.

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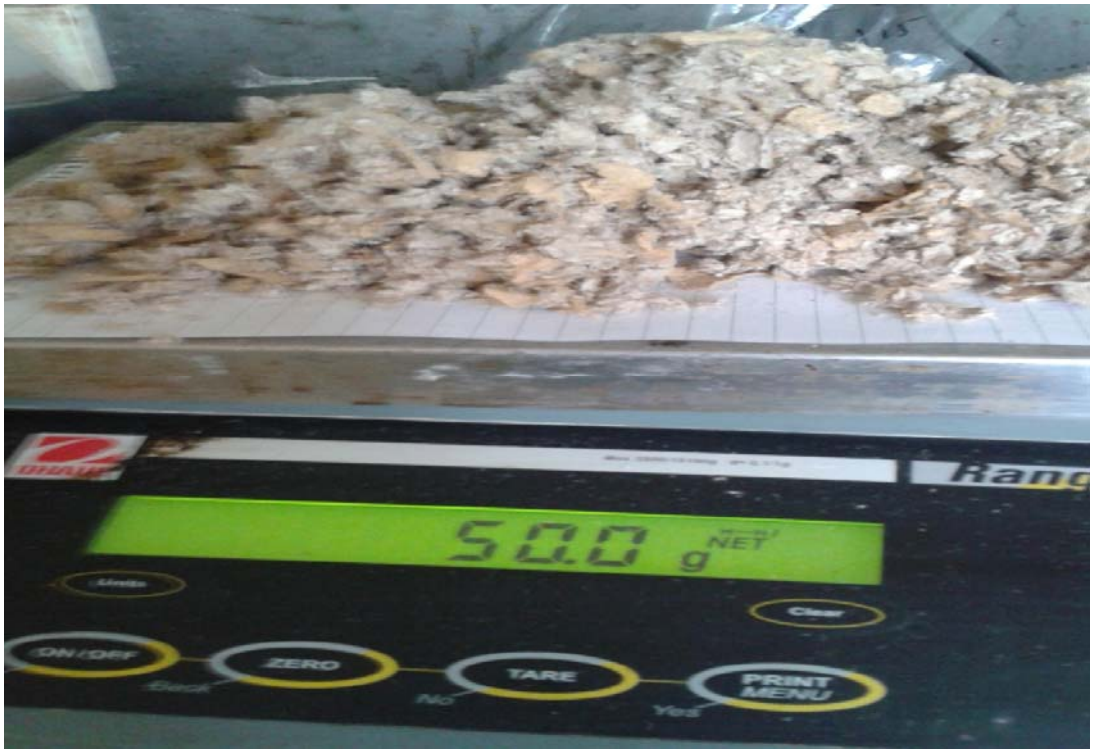
Appendix-A: Pictures taken during the experiment

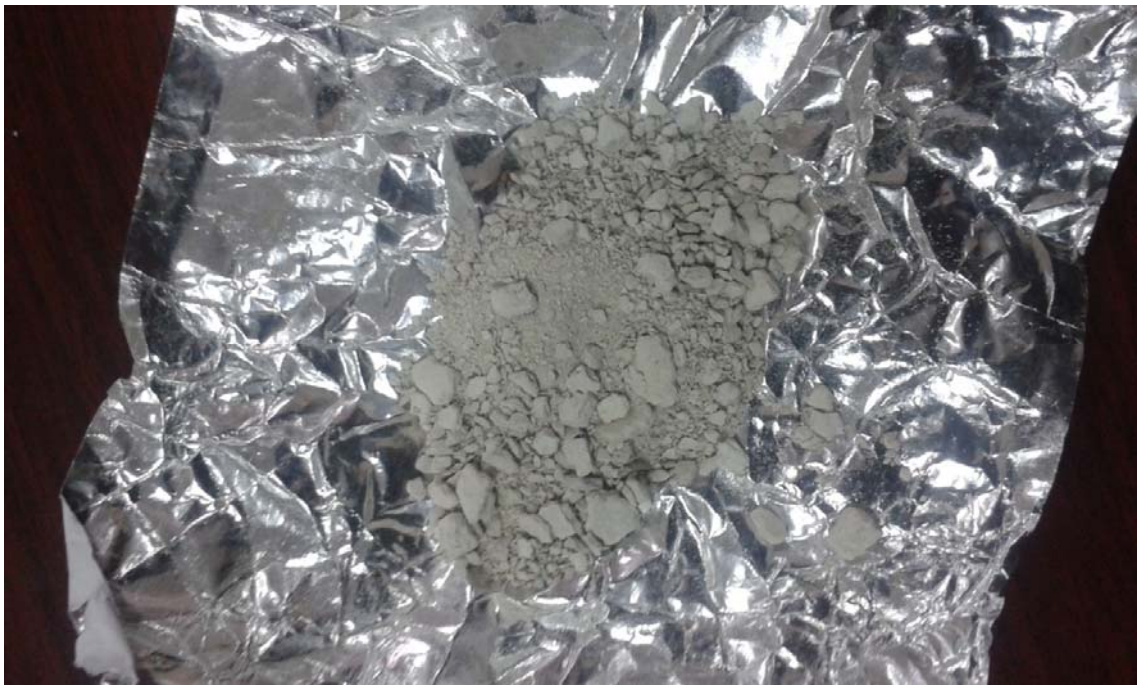
Waste cartons

Waste carton powder



Appendix-A: Pictures taken during the experiment

Synthesized CMC



Appendix-B Operating labor requirement and cost

Sr. No	Description	Req. No.	Monthly Salary	Annual Salary
A	**Administration**			
1	General Manager	1	10,500	126,000
2	Secretary	1	3,000	36,000
3	Finance and admin. Head	1	6,500	78,000
4	Sales person	1	4,000	48,000
5	Purchaser	1	4,000	48,000
6	Accountant	1	4,000	48,000
7	Cashier	1	3000	36,000
8	Store keeper	1	4000	48,000
9	Driver	3	9000	108,000
10	Guard	4	9600	115,200
11	Cleaning and messenger	1	1500	18,000
	Sub total	**16**	**42,200**	**709,200**
B	**Production and Quality**			
1	Production and technical head	1	7,500	90,000
2	Production supervisor	1	5,500	66,000
3	Quality head	1	6,500	78,000
4	Chemist	1	4,500	54,000
5	Operator	7	28,000	336,000
6	Electrician	1	5,000	60,000
7	Mechanic	1	5,000	60,000
8	Utility technician	1	5,000	60,000
9	Packing workers	15	22500	270,000
	Sub total	**29**	**123,900**	**1,074,000**
	total	**45**	**166,100**	1,993,200
	Employee benefits(10% of salary)		**16,610**	199,320
	Grand total	**45**	**182,710**	2,192,520

CERTIFICATE

This thesis has been read and approved as meeting the requirement of the School of Chemical and Bio-Engineering in the Addis Ababa Institute of Technology for the award of degree of masters of science in chemical engineering.

Advisor

signature

Date

DECLARATION

I, the under signed, declare that this thesis entitled "Production and Optimization of Carboxymethylcellulose from Waste Cartons" has not been submitted in any form for another degree, diploma or an award at any university or other institution of the tertiary education. Whenever contributions of others are involved, every effort is made to indicate this clearly, with due references to the literature review and discussions.

Information taken from the published and unpublished work of the others has been acknowledged in the text and a list of references were given.

The work was under the guidance of Dr. Ing. Abubeker Yimam (Chair of Process Engineering Stream), and instructor in Addis Ababa University, Addis Ababa Institute of Technology, School of Chemical and Bio-Engineering.

Abebe Hailu

Name

Signature

Place of Submission

Date of Submission