

**ADDIS ABABA UNIVERSITY  
SCHOOL OF GRADUATE STUDIES  
ADDIS ABABA INSTITUTE OF TECHNOLOGY  
DEPARTMENT OF CHEMICAL ENGINEERING  
(PROCESS ENGINEERING STREAM)**

**SYNTHESIS OF CARBOXYMETHYL CELLULOSE FROM  
SUGARCANE BAGASSE**

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By  
Yalew Woldeamanuel Sitotaw

JUNE, 2011  
ADDIS ABABA, ETHIOPIA

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*A thesis Submitted to the Research and Graduate School of Addis Ababa University, Addis Ababa Institute of Technology, Department of Chemical Engineering in partial fulfilment of the requirements for the attainment of the Degree of Masters of Science in chemical engineering (Process Engineering stream).*

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## **List of Acronyms**

3D – three dimensional

ANOVA – analysis of variance

CAA – chloroacetic acid

CMC – carboxymethyl cellulose

DS – degree of substitution

FCI – fixed capital investment

MCAA - monochloroacetic acid

OL – operating labor

ROI – return on investment

TPC – total product cost

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## ABSTRACT

*Sugar cane bagasse is a potential cellulose source, though usually used as a fuel source for the boiler. This work reports concisely on a method to utilize sugar cane bagasse for preparing sodium carboxymethylcellulose (CMC) and its characteristics. The desirable characteristics that are imparted on the cellulose were the solubility, viscosity and others which are responsible for many applications. Furthermore, in this work the carboxymethylation reaction was optimized against the reaction temperature, reaction time, monochloroacetate concentration and sodium hydroxide concentration. The sugar cane bagasse is obtained shortly after the juice is extracted in the roller mill. Sodium hydroxide, chloroacetic acid and isopropanol were used for the carboxymethylation process. Firstly, the sugarcane bagasse was dried, ground to pass 1mm screen. Then the cellulose was extracted using 4N NaOH at 100°C for 1 hour. Finally, cellulose was converted to carboxymethyl cellulose (CMC) by basification and etherification processes using sodium monochloroacetate and sodium hydroxide. Two reactions were taken place simultaneously during carboxymethylation that were the primary reaction which produces pure carboxymethyl cellulose and side reaction that produce undesired sodium glycolate. The degree of substitution and viscosity were determined and then analyzed with respect to the reaction conditions using design expert statistical software. From the analysis the maximum degree of substitution was 1.92, and the maximum viscosity 25.4 cp. But after optimization of reaction conditions had been carried out, the optimized degree of substitution was 1.79 and viscosity 14.63cp. These were obtained at a reaction temperature of 30°C, reaction time of 2.95 hours, NaOH concentration of 25% w/v and chloroacetic acid concentration of 0.5 w/w. It is concluded that the sugarcane bagasse is a good source of cellulose that can be modified by etherification reaction to carboxymethylcellulose with a medium degree of substitution of about 1.79.*

*Keywords: Degree of substitution, cellulose, carboxymethyl cellulose, sugar cane bagasse.*

# 1. INTRODUCTION

## 1.1. Background

Sustainable sources of materials to supply the needs of society in the coming decades are much needed at present as the world becomes increasingly aware of the limited nature of fossil fuels, especially petroleum resources. In response to this situation, lignocellulosic biomass from trees, grasses, cereals, and other plants, has become the main focus of the developing biorefining industry. Celluloses, the first most abundant class of polysaccharides found in nature, recently gain increasing importance as basis for new biopolymeric materials and functional polymers accessible by chemical modification reactions.

The chemical modification of polysaccharides is the most important route to modify the properties of the naturally occurring biopolymers and to use this renewable resource in the context of sustainable development. In general, all chemical reactions known from low molecular organic chemistry may be carried out. However, up to now only a limited number of products are produced commercially. Recent research and development is focused on the improvement of the known products and synthesis paths as well as on new derivatives and alternative synthesis concepts [1].

Cellulose which is the raw material of generating modified cellulose is a common natural polymer can be found vastly in plants. Thus, the resources can range from woods to even the agricultural waste. The availability of cellulose rich materials in Ethiopia is very wide with the abundant plantation of agricultural cereals and forests which have good potentials in producing modified cellulose from their by-product.

Carboxymethylation of cellulose is a widely studied conversion since it is simple and leads to products with a variety of promising properties [1]. In general, the polysaccharide is activated with aqueous alkali hydroxide mostly sodium hydroxide and converted with monochloroacetic acid or its sodium salt according to the Williamson ether synthesis yielding the carboxymethyl (CM) polysaccharide derivative. Not only cellulose but also various polysaccharides from different sources are applied as starting materials. Carboxymethyl cellulose (CMC, as it is usually called) was first prepared in 1918 and was produced commercially in the early 1920's. However, since then, significant improvements in process technology, in product quality, and in production efficiency have been made [21].

carboxymethylcellulose is important for its water soluble properties where vast applications are applied in food industry, cosmetics, pharmaceuticals, detergents, textiles, paper, drugs and as well as oil well drilling operation. The conversion of cellulose to carboxymethylcellulose provides variety of usage due to its excellent characteristics. Among categories of applications of carboxymethylcellulose that are in dissolved and dispersed forms are water binder, adhesives, film former, wet tact, binder, suspending aid and thickener.

The properties of cellulose derivatives are mainly signified by the degree of substitution. The selection of etherification condition is very essential in order to achieve high degree of substitution. Most of the researches are carried out and obtained degree of substitution ranges from 0.5-2.0. In commercial carboxymethylcellulose, the most common degree of substitution obtained is usually lower that is from 0.4 to 1.4.

## **1.2. Problem Statement**

Organic materials have many applications and are mainly derived from petroleum resource. But the petroleum resource is depleted and in the near future it all be used up. Moreover, new environmental regulations, societal concerns, and growing environmental awareness have raised many questions on petrochemical industries and resulted in triggering the search for new products and processes that are compatible with the environment.

As a result, biodegradable organic materials such as polymers and bio-based polymer products based on annually renewable agricultural and biomass feedstock can form the basis for a portfolio of sustainable, eco-efficient products that can capture markets currently dominated by products based exclusively on petroleum feedstock. Almost all products obtained from petrochemical processes can be obtained from biomass through direct, catalytic, or aggressive conversion of cellulose, hemicelluloses, and lignin [3].

However, the application of cellulose itself is limited due to its insolubility in water, but its water soluble derivatives, in particular carboxymethyl cellulose , play an important role in our daily life that we often are not aware of. The problem here is how we can modify the structure of cellulose so that it will be water soluble to be applicable in a wide range of areas.

## **1.3. Objectives**

### **1.3.1. General Objective**

The main objective of this thesis work was to modify the structure of cellulose, obtained from sugar cane bagasse, and produce the final product that is carboxymethyl cellulose and optimize the process conditions.

### **1.3.2. Specific Objectives**

The specific objectives were:-

- ✓ Extracting cellulose from the sugarcane bagasse.
- ✓ Carry out operations to produce carboxymethyl cellulose.
- ✓ Optimize the carboxymethylation reaction against the reaction temperature, reaction time, monochloroacetate concentration, NaOH concentration.
- ✓ Analyze the degree of substitution and viscosity with respect to the reaction conditions.

## **1.4. Significance of the Thesis**

This thesis work has shown that there are different directions through which waste materials generated from agricultural and industrial sites can be used to produce valuable products. The interest in the technology of the synthesis of sodium-carboxymethyl cellulose has been developed, as it has a wide range of applications in medicine, oil-extraction, construction and domestic products. This is related to the fact that sodium-carboxymethyl cellulose is water-soluble and a biodegradable polymer, which provides its ecological friendliness. These properties served as the basis for expansion of application fields of carboxymethyl cellulose.

Furthermore depletion of petroleum based products created interests in cellulose and cellulose derivatives as a renewable resource [8]. That is Carboxymethylated polysaccharides; in particular carboxymethyl cellulose is based on renewable resources. It is biodegradable and non-toxic products that are finding an increasing number of applications. Carboxymethyl cellulose is assumed to be applied in more than 200 applications today. From

the current conditions, the importance of carboxymethylation of polysaccharides will further increase in the context of increasing use of renewable resources, i.e., in the context of sustainable development, on one hand. On the other, polysaccharide possess unique structures synthesized by nature that are an excellent basis of the development of advanced and highly engineered products for present and future applications [21].

There have been quite numerous discoveries on the degree of substitution of carboxymethylcellulose of different sources such as sugar cane bagasse cellulose, saw dust and other cellulose sources. The idea of producing useful component out of waste is indeed environmental friendly which everyone has been trying to implement in most of the industries. This is a very good step in promoting the country as being creative, innovative as well as contributing to form an environmental friendly atmosphere.

The other benefits that can be acquired from this research are to achieve the optimum condition of the carboxymethyl cellulose production in the analyzed reaction conditions which can be used commercially.

## 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. 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 [13].

Mostly used waste materials that can be used as a cellulose sources are:-

- Fruit peels
- Rice husk
- Wheat straw
- Saw dust
- Sugarcane bagasse
- Bamboo and others.

The following table contains the chemical composition of some cellulosic materials.

Table 1: Chemical composition of some cellulosic materials

Source	Compositions %			
	Cellulose	Hemicelluloses	lignin	Extracts
Hard wood	43 - 47	25 - 35	16 – 24	2 – 8
Soft wood	40 – 44	25 – 29	20 – 31	1 – 5
Bagasse	40-45	25-30	20-25	5-10
Corn stalks	35	25	35	5
Cotton	95	2	1	0.4
Wheat straw	30	50	15	5

## 2.2. Sugar Cane Bagasse

The sugar cane stalk consists of two parts, an inner pith containing most of the sucrose and an outer rind with Lignocellulosic fibers. During sugar processing, the sugar cane stalk is crushed to extract the sucrose. This procedure produces a large volume of residue, the bagasse, which contains both crushed rind and pith fibres [15].



(a)



(b)

Figure 1: Sugar cane bagasse. (a) Raw bagasse, (b) Dried and grounded bagasse

The importance of systematic utilization of bagasse or sugar cane cellulosic residues has been noted in the past decade. Environmental concerns have fuelled this focus not only because of the quantity of bagasse produced annually but also because of the nature of the material. The

growth of the sugar cane plant is remarkably efficient photo synthetically. The sugar product from this plant represents only thirteen percent of the biomass. Bagasse from sugar production is twenty eight percent of the biomass. These numbers vary depending on the source of the sugar cane. Even though, huge amounts of bagasse are and will continue to be generated and the utilization of this material is of growing importance [3].

### **2.2.1. Components of sugar cane bagasse**

Bagasse is the solid, pulpy material remaining after extraction of the juice from sugar cane. It is dried and used mostly as fuel. It mainly contains cellulose and lignin. The lignin is the part that attaches the cellulose strands together and it must be removed to get the pure cellulose.

The composition of sugarcane bagasse is 43.7% cellulose, 24.4% hemicellulose, 28.0% lignin, and 0.75% ash. Spectroscopic techniques can be used for the characterization of this and other lignocellulosics [3]. The important components that need to be considered when characterizing this material are:

Carbohydrates: - The two major polysaccharides are:-

#### **Cellulose**

Cellulose is the most abundant constituent and is a homo-polysaccharide composed entirely of  $\beta$ -1, 4-glucosidic linked glucose monomers. It may have a degree of polymerization (number of glucose unite bound together) in excess of 10000. The linear structure of the cellulose chain enables the formation of inter and intra-molecule hydrogen bonds. Approximately 50-90% of the total cellulose is crystalline, depending on the biomass source. The combination of the structure and intermolecular hydrogen bonding gives cellulose a high tensile strength, a resistance against microbial attack and makes it insoluble in most solvents.

#### **Hemicelluloses**

Hemi-cellulose are any of a group of short-chain complex carbohydrates that, with other carbohydrates (e.g. pectins), surround the cellulose fibres of plant cells. In contrast to cellulose that is crystalline, strong, and resistant to hydrolysis, hemicellulose has a random, amorphous structure with little strength. It is easily hydrolyzed by dilute acid or base.

Hemicellulose contains many different sugar monomers (glucose, xylose, mannose, galactose, rhamnose, and arabinose). In contrast, cellulose contains only anhydrous glucose.

The specific composition varies among different plants. It has a low degree of polymerization (typically below 200), often contains side chains and is typically acetylated. Bagasse hemicellulose is composed of a backbone of xylose, branched with glucose and arabinose units.

### **Lignin**

Lignin is a three dimensional polymer of three different phenyl-propane precursor monomers: p-coumaryl, coniferyl and sinapyl alcohols. They are joined together by aryl-aryl, alkyl-aryl and alkyl-alkyl ether bonds. This polymer is imbedded in the cellulose/hemicelluloses structure acting as glue like material. It helps impart rigidity and offers further protection to the biomass against microbial and chemical attack.

### **Ash**

Ash is typically the inorganic components of the biomass.

### **Protein**

Protein is typically a combination of protein and nitrogen containing compounds.

### **Moisture**

Bagasse contains large amount of moisture as soon as produced from the mill.

## **2.3. Cellulose**

Cellulose is a linear, high molecular weight, could be a primary chemical resource in the future because it is renewable, biodegradable, biocompatible, and derivatizable. However, cellulose still has not reached its potential applications in many areas because it is difficult to process in normal solutions or in the melting state on account of its strong inter-molecular and intra-molecular hydrogen bonding. In other words due to its strong inter- and intra-

molecular hydrogen bonding, cellulose neither melts nor dissolves readily in common solvents. Chemical modification reactions continue to play a dominant role in improving the overall utilization of cellulose to produce water-soluble derivatives for various applications [12].

The existence of cellulose as the common material of plant cell walls was first recognised by Anselm Payen in 1838. It occurs in almost pure form in cotton fibre and in combination with other materials, such as lignin and hemicelluloses, in wood, plant leaves and stalks, etc. Although generally considered a plant material, cellulose is also produced by some bacteria. It has been accepted for many years that cellulose is a long chain polymer, made up of repeating units of glucose, a simple sugar. In the early 1900s, cellulose was further characterised by Cross and Bevan. They removed the related plant materials that occur in combination with cellulose by dissolving them in a concentrated sodium hydroxide solution. They designated the undissolved residue as  $\alpha$ -cellulose. The soluble materials (designated as  $\beta$ -cellulose and  $\gamma$ -cellulose) were later shown not to be celluloses, but rather, relatively simple sugars and other carbohydrates. The  $\alpha$ -cellulose of Cross and Bevan is what is usually meant when the term “cellulose” is used now.

### **2.3.1. Structure of cellulose**

Among the polysaccharides, the structure of cellulose is unique and simple. However, this influences its chemical reactions significantly. Cellulose being rigid, highly crystalline, and insoluble in common organic solvents is an ideal structural engineering material. Cellulose is a polydisperse, linear, syndiotactic polymer. Its basic monomeric unit is D-glucose (anhydroglucose unit, AGU), which links successively through a  $\beta$ -configuration between carbon 1 and carbon 4 of adjacent units to form a long chain. Two glucose molecules react to form a cellobiose which is the basic chemical unit of a cellulose molecule (Hon, 1996).

It is derived from D-glucose units, which condense through  $\beta(1\rightarrow4)$ -glycosidic bonds. This linkage motif contrasts with that for  $\alpha(1\rightarrow4)$ -glycosidic bonds present in starch, glycogen, and other carbohydrates. Cellulose is a straight chain polymer: unlike starch, no coiling or branching occurs, and the molecule adopts an extended and rather stiff rod-like conformation, aided by the equatorial conformation of the glucose residues. The multiple hydroxyl groups

on the glucose residues from one chain form hydrogen bonds with oxygen molecules on the same or on a neighbour chain, holding the chains firmly together side-by-side and forming micro fibrils with high tensile strength. This strength is important in cell walls, where the micro fibrils are meshed into a carbohydrate matrix, conferring rigidity to plant cells. The figure below is a diagrammatic representation of a cellulose molecule. Note that each glucose unit in the cellulose chain has three hydroxyl groups, each of which is capable of hydrogen bonding to an adjacent molecule.

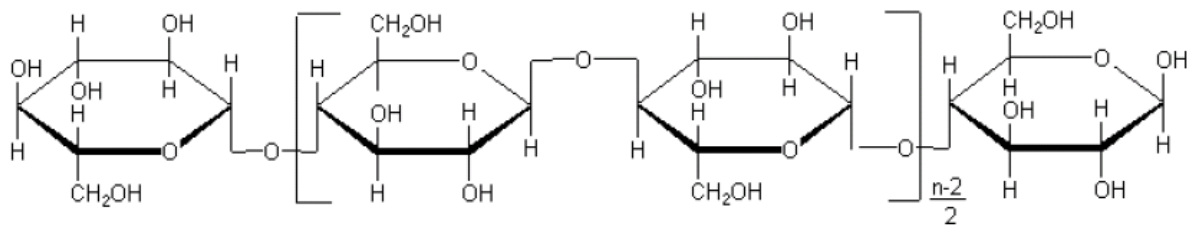


Figure 2: Structure of cellulose

As the following figure indicates, cellulose is viewed pictorially as a series of circles connected together in a long, linear chain. It shows a group of cellulose molecules in water. Because of the abundance of hydroxyl groups, and their ability to hydrogen bond to a neighbouring molecule, the chains are bound tightly together. Water molecules, at any temperature, cannot force their way in between the chains to hydrate them, thus cellulose is water insoluble [4].

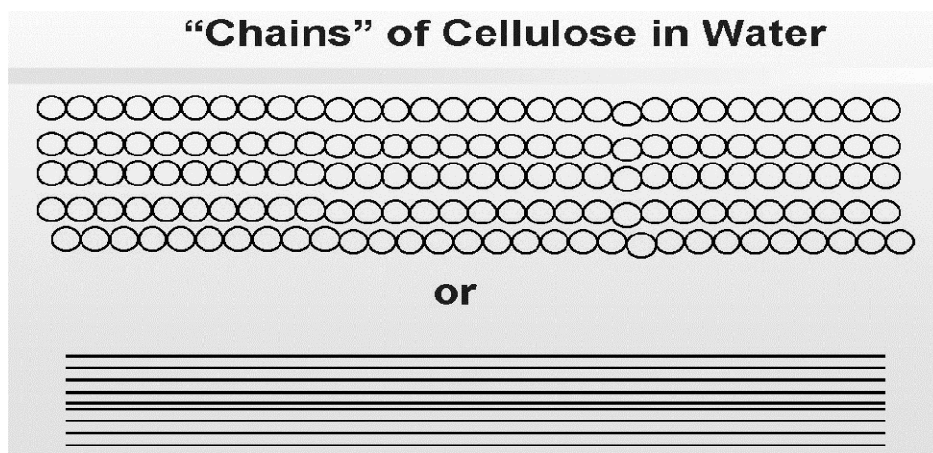


Figure 3: Cellulose in water

### **2.3.2. Derivatives of cellulose**

As a carbohydrate, the chemistry of cellulose is primarily the chemistry of alcohols; and it forms many of the common derivatives of alcohols, such as esters, ethers, etc. These derivatives form the basis for much of the industrial technology of cellulose in use today. Cellulose derivatives are used commercially in two ways, as transient intermediates or as permanent products. Because of the strong hydrogen bonds that occur between cellulose chains, cellulose does not melt or dissolve in common solvents. So, the need is obtaining the derivatives by modifying its structure to have some of the desirable properties like solubility.

Chemical modifications of cellulose include reactions of hydroxyl groups such as esterification, etherification, intermolecular cross linking reactions, and macro-cellulosic free radical reactions, particularly in the formation of graft cellulose copolymers to increase the usefulness of cellulose by altering its properties. These cellulose derivatives are grouped according to the processes and substituents, for instance, esters- cellulose acetate through esterification and ethers-methyl cellulose, carboxymethyl cellulose via etherification. Chemical modifications continue to play a dominant role in improving the overall utilization of cellulosic polymers. The accessibility to hydroxyl groups and their reactivity open prospects for preparation of specific molecular structures for future applications. Broader and more specialized applications of advanced and trend setting materials based on this unique and renewable macromolecule will increase the demand for more diverse synthesis paths and derivatives [9].

Table 2 summarises industrially and commercially important cellulose derivatives and their application sectors.

Table 2: Commercially important cellulose derivatives

Product	Global production (t/a)	FG	DS	Solubility	Application
Cellulose acetate	900,000	-OAc	0.6 - 0.9 1.2 – 1.8 2.2 – 2.7 2.8 – 3.0	Water 2-methoxy ethanol Acetone Chloroform	Coatings and membranes
Cellulose nitrate	200,000	-NO <sub>2</sub>	1.8 – 2.0 2.0 – 2.3 2.2 – 2.8	Ethanol Methanol, Acetone Acetone	Membranes and explosives
Cellulose xanthate	32,000,000	-C(S)SNa	0.5 – 0.6	NaOH/Water	Textiles
Carboxymethyl cellulose	300,000	-CH <sub>2</sub> COONa	0.5 - 2.9	Water	Coating, paints, adhesives, detergents & pharmaceuticals
Methyl cellulose	150,000	-CH <sub>3</sub>	0.4 – 0.6 1.3 – 2.6 2.5 – 3.0	4% aqu. NaOH Cold water Organic solvents	Films, textiles, food & tobacco industries
Ethyl cellulose	4,000	-CH <sub>2</sub> CH <sub>3</sub>	0.5 – 0.7 0.8 – 1.7 2.3 – 2.6	4% aqu. NaOH Cold water Organic solvents	Pharmaceuticals industry
Hydroxymethyl cellulose	50,000	-CH <sub>2</sub> CH <sub>2</sub> OH	0.1 – 0.5 0.6 – 1.7	4% aqu. NaOH Cold water	

### 2.3.3. Reactions of Cellulose

The cellulose molecule contains three different kinds of anhydroglucose units, the reducing end with a free hemi-acetal (or aldehyde) group at C-1, the non-reducing end with a free hydroxyl at C-4, and the internal rings joined at C-1 and C-4. But because of the long chain length, the chemistry of the alcohol groups of the internal units predominates, so long as the chains are not cleaved by the reaction conditions. Unlike simple alcohols, however, cellulose reactions are usually controlled more by steric factors than would be expected on the basis of

the inherent reactivity of the different hydroxyl groups. There are potentially three hydroxyl groups available on each anhydroglucose ring, so derivatives are usually characterised in terms of a “degree of substitution” (DS), which is an average for the whole chain and can range between 0 and 3. In most cases, partial reaction to  $DS < 3$  gives products that are essentially block copolymers, where virtually all of the hydroxyls occurring in the less ordered regions may be derivatised, while those in the crystalline regions remain unreacted. Higher degrees of substitution, or reaction conditions which disrupt the crystalline regions, can be used to reduce inter-chain hydrogen bonding and force the chains apart. This can result in a cellulose derivative that is soluble in common solvents, and thus capable of extrusion to form filaments, or other structures.

Of the most known reactions of cellulose, etherification reaction is the one which is responsible for carboxymethyl cellulose formation.

### **Etherification reaction**

Cellulose ethers can be made using a number of common alkylating agents. Many partially substituted types of ether (usually with  $DS\ 0.5 - 2.0$ ) are important commercially. These range from simple methyl and ethyl ethers, to more complex materials, such as carboxymethyl celluloses, which are made by reaction of cellulose with chloroacetic acid. Reaction of cellulose with ethylene oxide or other epoxides yields hydroxyethyl cellulose, or other hydroxyalkyl derivatives, which can have a number of useful properties, depending on DS and the length of the hydroxyalkyl side chains. Cellulose hydroxyls can also be made to add across activated double bonds, as in the formation of cyanoethyl cellulose from reaction with acrylonitrile.

Etherification process is mostly applied in industries due to its low toxicity, wide availability, easy handling and its economic efficiency. Carboxymethylcellulose is prepared by etherification of the hydroxyl groups with sodium monochloroacetate in the presence of aqueous alkali.

## **2.4. Carboxymethylcellulose (CMC)**

Despite the large variety of cellulose derivatives that have been made, there is continuous expansion in the worldwide market of cellulose ethers because of their availability, economic

efficiency, easy handling, low toxicity, and great variety of types. Combined effects of flow control, stabilization, water retention, film formation, etc. provided by cellulose ethers are not generally obtainable by the use of fully synthetic polymers. Cellulose ethers such as carboxymethyl cellulose, have gained their position in the market due to their multifunctional properties. The worldwide annual production of cellulose ethers is estimated to be over 300,000 metric ton [20].

Carboxymethylcellulose is a linear, long-chain, water-soluble, anionic polysaccharide. Purified carboxymethylcellulose is a white- to cream-colored, tasteless, odourless, free-flowing powder. Some papers have reported that the synthesis of carboxymethylcellulose is possible from various agricultural wastes such as from sugar beet pulp, banana pseudo stem, orange peel and papaya peel.

Carboxymethyl cellulose or cellulose gum is a cellulose derivative with carboxymethyl groups (-CH<sub>2</sub>-COOH) bound to some of the hydroxyl groups of the glucopyranose monomers that make up the cellulose backbone. It is often used as its sodium salt, sodium carboxymethyl cellulose.

#### 2.4.1. 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:-

Table 3: Imported quantity of carboxymethyl cellulose from 2000-2006

Year	Import quantity (tonnes)	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.

$$\text{average percent increment} = ((31.8 + (-21.67) + (-20.1) + 118.1))/4$$

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

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

$$\text{import average} = 23$$

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:

Table 4: Projected demand of CMC from the given data

year	Demand (tonnes)
2007	29.21
2008	37.1
2009	47.1
2010	59.8
2011	75.95
2012	96.46
2013	122.5
2014	155.6
2015	197.6

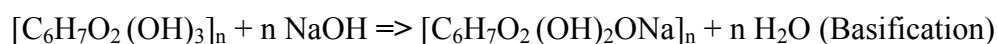
#### 2.4.2. Process Description

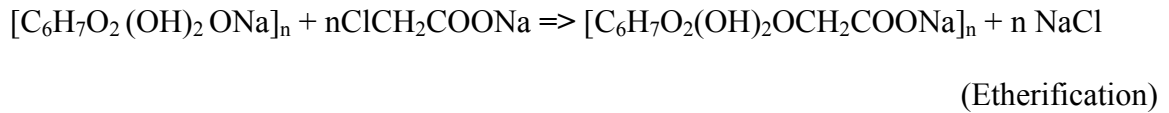
After sugarcane bagasse is obtained, it will be treated with NaOH to remove the lignin and make the cellulose free from it. The main step in carboxymethylation reaction is the formation of alkali cellulose, which has modified the crystalline structure of cellulose and increased the accessibility of fibers to chemicals by swelling. Cellulose fibers are swollen in concentrated NaOH [5].

Carboxymethylcellulose is ether in which the hydroxyl group of anhydrous glucose is replaced by the carboxymethyl group of monochloroacetate. Under alkaline conditions, the hydroxyl group of cellulose shows high activity. For production of carboxymethylcellulose, two consecutive steps of reactions are required. These reactions are known as basification and etherification. The reactions can be carried out with or without solvents. Isopropanol is used as a suitable solvent [17].

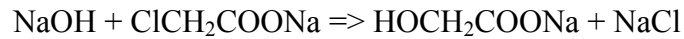
Generally the chemical modification process of cellulose with sodium hydroxide and chloroacetic acid involves two-step consecutive reactions, accompanied by an undesired side reaction [7].

The main reactions of the carboxymethylation sequence are given by:





The side reaction is the formation of sodium glycolate from chloroacetic acid and sodium hydroxide:



During carboxymethylation reaction the structure of cellulose is changed as an idealized unit structure of CMC depicts in the figure below. The CMC shown here has a degree of Substitution of 1.0. If the remaining two hydroxyl groups on this unit became substituted, the degree of substitution would be 3.0. a degree of substitution of 3.0 is the theoretical maximum one could attain.

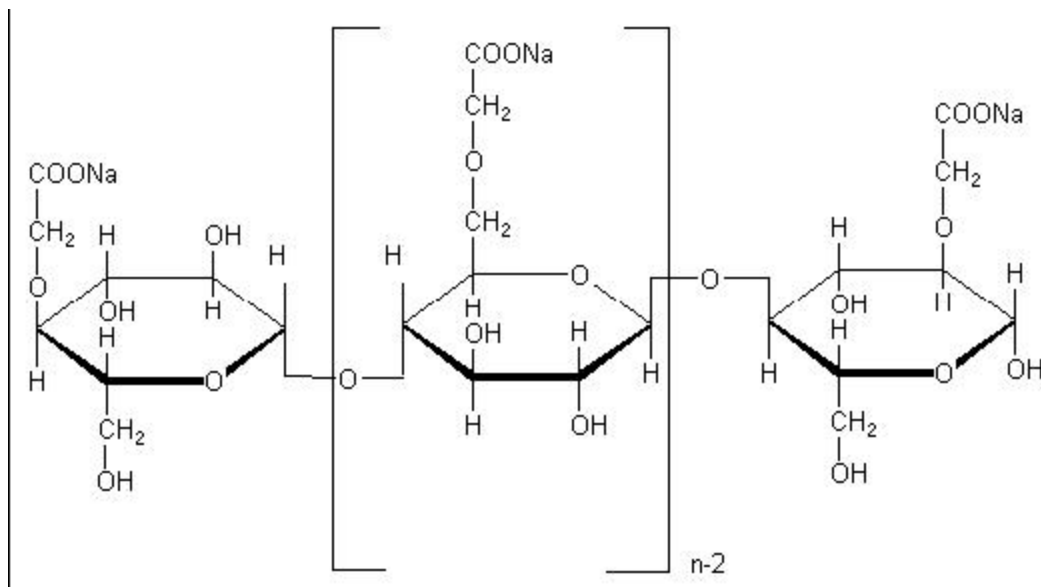


Figure 4: Structure of carboxymethyl cellulose

The figure below is also showing us a pictorial representation of CMC molecules. Note that, the carboxymethyl groups protrude from the cellulose backbone, such that the hydroxyl groups of the backbone cannot get close enough to hydrogen bond to each other. The result is that even in the dried state, water can slip in between the CMC molecules and hydrate them,

causing them to "peel apart" from each other and go into solution. This is what the most desirable property of carboxymethyl cellulose.[4]

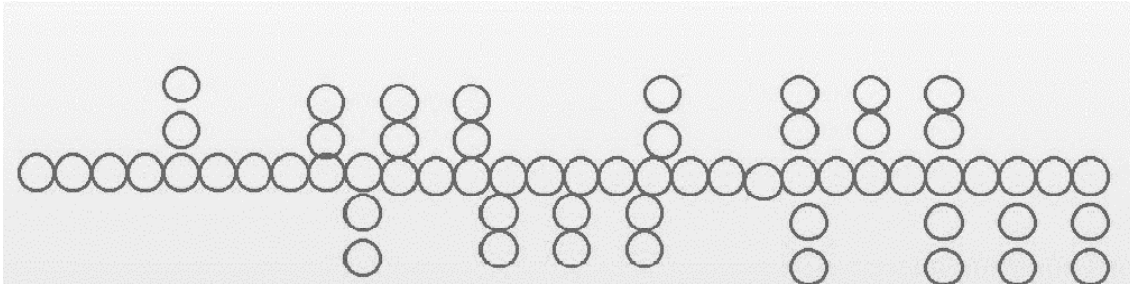


Figure 5: Carboxymethyl cellulose in water

### 2.4.3. Uses

Carboxymethyl cellulose is used in synthetic detergent formulations due to its ability to prevent re-deposition of dirt on clothing by creating a negatively charged barrier to soils in the wash solution. It is used as a warp size in textile manufacturing, because it has a good sizing action and it is easily removed by water. Carboxymethyl cellulose is also used in paper industry to size paper boxboard to permit printing, decrease wax penetration, and impart grease resistance. Since carboxymethyl cellulose is physiologically inert, it is used extensively for food, pharmaceuticals and cosmetics.

Carboxymethyl cellulose is used in food science as a viscosity modifier or thickener, and to stabilize emulsions in various products including ice cream. It is also a constituent of many non-food products, such as toothpaste, laxatives, diet pills, water-based paints and various paper products. It is used primarily because it has high viscosity, is non-toxic, and is non-allergenic. Carboxymethylcellulose is used as a lubricant in non-volatile eye drops (artificial tears). Other application of carboxymethyl cellulose includes its use in oil well drilling mud, in ceramics and refractories because of its suspending and binding properties and acts as a viscosity modifier and water retention agent.

In Ethiopia it is highly applied as warp sizing agent in textile industries and anti-redeposition agent in detergent industries. Since the mud drilling activities are not well developed, its consumption is insignificant and considered as nil.

#### **2.4.4. Identification**

##### **Solubility**

A known amount of carboxymethyl cellulose is dissolved in a known volume of distilled water and the undissolved portion is separated by centrifuge. It is then dried in an oven and weighed. The dissolved portion was then calculated.

##### **Foam test**

Vigorously shake a 0.1% solution of the sample. No layer of foam appears. This test distinguishes sodium carboxymethyl cellulose from other cellulose ethers and from alginates and natural gums.

##### **Precipitate formation**

To 5 ml of a 0.5% solution of the sample add 5 ml of a 5% solution of copper sulphate or of aluminium sulphate. A precipitate appears. (This test permits the distinction of sodium carboxymethyl cellulose from other cellulose ethers, and from gelatine, carob bean gum).

##### **Colour reaction**

Add 0.5 g of powdered carboxymethylcellulose sodium to 50 ml of water, while stirring to produce a uniform dispersion. Continue the stirring until a clear solution is produced. To 1 ml of the solution, diluted with an equal volume of water, in a small test tube, add 5 drops of 1-naphthol TS. Incline the test tube, and carefully introduce down the side of the tube 2 ml of sulphuric acid so that it forms a lower layer. A red-purple colour develops at the interface.

### 3. MATERIALS AND METHODS

Different materials and procedures or processing steps have been used to accomplish the experimental work.

#### 3.1. Materials

The raw materials used were:

- Sugarcane bagasse which were obtained from Wonji Shoa sugar factory.
- Reagent grade monochloroacetic acid and isopropanol solutions, which were purchased from faculty of science. Addis Ababa University.
- Reagent grades sodium hydroxide powder, HCl, ethanol, methanol and acetone were also obtained from local chemical importers.

Equipment and devices used in the lab were:-

- Pulverizer (FRITSCH)
- Sieve (Retsch, AS-200)
- Beakers
- Spatula
- Thermostat (GP-200)
- Metal Stand with clamps
- Motor stirrer (Ika)
- Flask with circular bottom
- P<sup>H</sup> meter
- Oven (memmert)
- Filter cloth
- Viscometer(sv-10)
- Conductivity meter
- Analytical balance (OHAUS)
- Moisture analyzer (MB-45)
- Hot plate (SH-3)

## **3.2. Methods**

### **3.2.1. Quantitative determination of cellulose and lignin**

#### **3.2.1.1. Determination of Lignin in Bagasse**

The lignin content of sugarcane bagasse was determined by dissolving the holocellulose component in sulfuric acid solution. The following procedure has been applied in the laboratory.

The wet bagasse that has been brought from Wonji shoa sugar factory was dried and ground to a size of 2mm. 2gm was weighed and transferred to a beaker. It was well mixed with 25 milliliters of 72 percent sulfuric acid at 20°C and maintained at that temperature for 2 hours. The resulting mixture was transferred to circular bottom flask and diluted with water to make a 3 percent acid solution and then boiled for 2 hours by using hot plate and condenser. The hydrolyzed residue was filtered with vacuum filtration unit, washed free of acid by means of hot water, dried, and weighed. The lignin content is calculated on the basis of the oven-dry sample [14].

#### **3.2.1.2. Determination of Holocellulose**

Holocellulose is the part that contains hemicelluloses and cellulose. It was determined by the following way.

A five gram sample of dry pulp was transferred to 250 ml Erlenmeyer flask with 160 ml of distilled water, 0.5 ml of acetic acid, and 1.5 gm of sodium chlorite. The sample were heated in water bath at 70 – 80°C with agitation every 10 min for 60 min. Then, 0.5 ml of acetic acid and 1.5 gm of sodium chlorite were added. This addition was repeated at 60 min intervals for four hours reaction time. The sample was then filtered. The residue was washed with 1.6 liter of hot distilled water. Subsequently, it was washed with acetone and dried at room temperature [6].

### **3.2.1.3. Determination of $\alpha$ -cellulose**

$\alpha$ -cellulose content was determined from above holocellulose content in the following way:

One gram sample of holocellulose (with known humidity) were transferred to 150 ml beaker. Then 11.8 ml of 17.5% NaOH solution were added with stirring for 5 minutes. 5ml being added in the first 1min, 3.4ml in the next 45sec and 3.4ml in the next 15 sec. the sample were left at rest by 3min. 13.6ml of 17.5% NaOH was added over 10min. 3.4ml with stirring initially, 3.4ml were added in the 2.5 min, 3.4ml in the 5<sup>th</sup> min, and 3.4ml in the 7.5<sup>th</sup> min. Sample were covered and left in for 30min. Afterwards, 33.4ml of distilled water was added, and the mixture was left for another 30min. The sample were filtered and washed with 8ml of 8.3% NaOH and washed with 400ml of distilled water. The volume was completed with acetic acid 2mol/L and left at rest for 3min. It was filtered to remove acetic acid, washed with 3L of distilled water and dried overnight [6].

### **3.2.2. Preparation of Bagasse**

The sugarcane bagasse obtained from Wonji Shoa Sugar factory was physically treated in the following way:

- ✓ The sugar cane bagasse was directly soaked in boiled water for 30 minutes, so that the soluble polysaccharides and much of the hemicelluloses were removed.
- ✓ Then the wet bagasse was allowed to dry by exposing it to sunlight for three days.
- ✓ After drying, it has been ground using a cutter mill (Retsch) to a size of 1mm.

### **3.2.3. Cellulose Extraction from Bagasse**

The sugarcane bagasse was first screened to remove the fine particles, pith cell, which is mainly lignin and then soaked in boiled water for 30 minutes to remove any soluble polysaccharide and hemicelluloses. The wet bagasse was sun-dried for 2 days. Dried bagasse was grounded with a cutter to screen into powder with size below 1 mm. 80gm of the powder bagasse was cooked with 4 molar NaOH (1 liters) for 1 hour. The obtained black solution was separated into black liquor and thick slurry which contains mainly cellulose. The thick

slurry was washed with cold water. 5liters of water was required to remove the black color of the pulp. The residue was dried in oven at 105°C overnight. Percent yield of cellulose pulp from bagasse powder delignified with NaOH concentration was obtained as 32.5%. The cellulose was grounded to pass through 250µm screen and kept in plastic bags to use for modification to CMC in the next process [19].

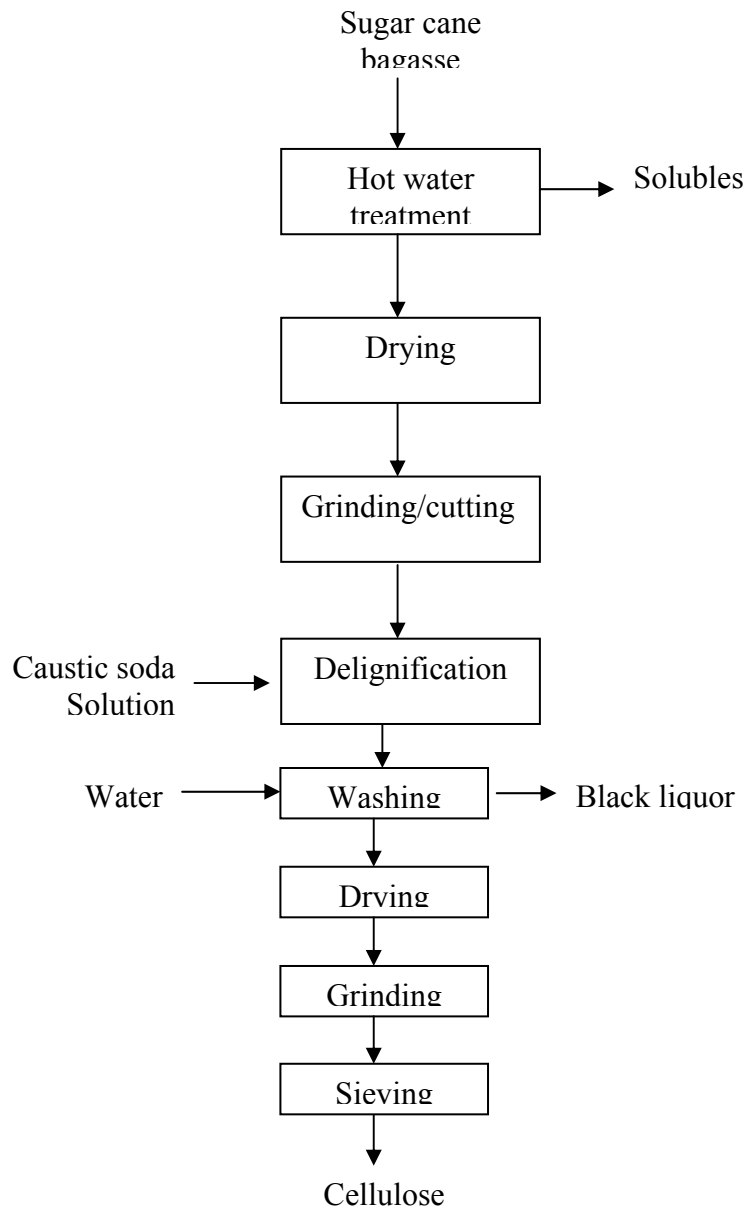


Figure 6: Flow sheet for cellulose extraction from sugar cane bagasse

Figure 7 below is the laboratory setup for cellulose extraction (delignification). It includes the hot plate to boil the mixture and the condenser at the top of the circular bottom flask to condense the water and return back to the solution.

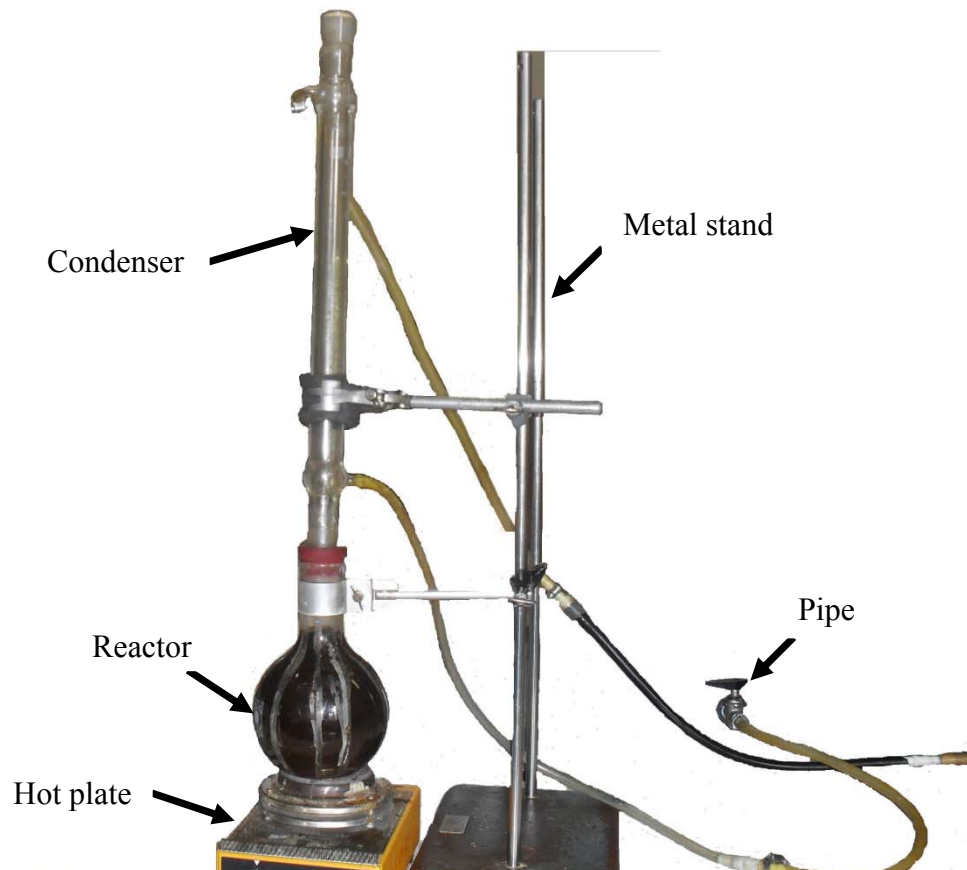


Figure 7: Laboratory set up for cellulose extraction from sugar cane bagasse

#### 3.2.4. Synthesis of carboxymethyl cellulose from sugar cane bagasse cellulose

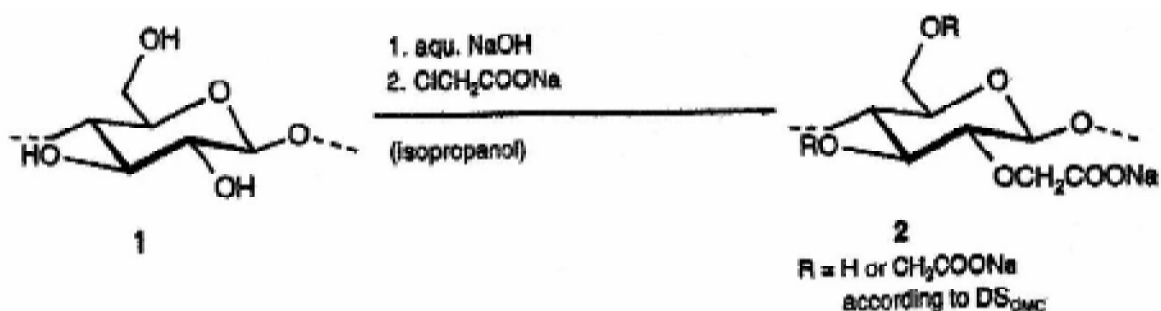
The experiment was performed in such a way that preparation of carboxymethylcellulose was followed by subsequently performing the two main reactions.

Preparation of carboxymethyl cellulose consists of two reactions which are:-

- ✓ alkalization and
- ✓ Carboxymethylation reaction.

Firstly, alkalization reaction was begun after introduction of sodium hydroxide solution with a concentration of 25% and 45%, into 5 g of pure sugarcane bagasse cellulose powder for a reaction time of 1 hr and reaction temperature of 25°C. Here alkaline condition was created and the hydroxyl functional groups were ready to be substituted by other functional groups [1].

Secondly, carboxymethylation reaction was started once 2.5gm and 7.5gm of monochloroacetic acid were mixed with a solvent of isopropanol (1:20 cellulose/isopropanol) at a reaction temperature of 30 and 70°C. The reaction was then allowed to proceed under mechanical stirrer (Ika) for 1 and 4 hrs. 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. 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 [1].



Lastly, the sample was dried in the oven (memmert) at 60°C temperature for two days. 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 color and it was changed to color less [1].

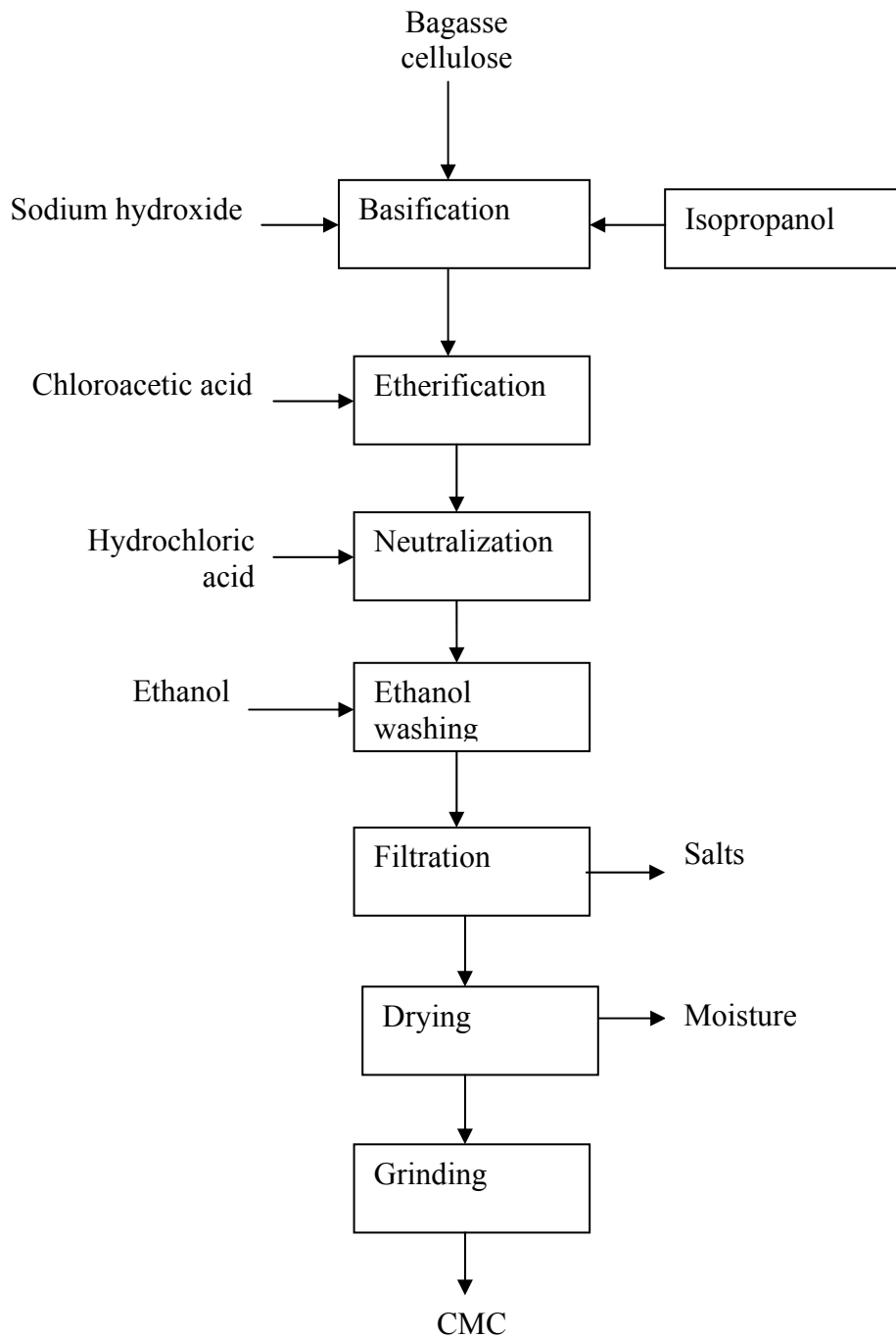


Figure 8: Flow sheet for carboxymethyl cellulose production

The laboratory setup for alkalization and carboxymethylation reactions is shown below,

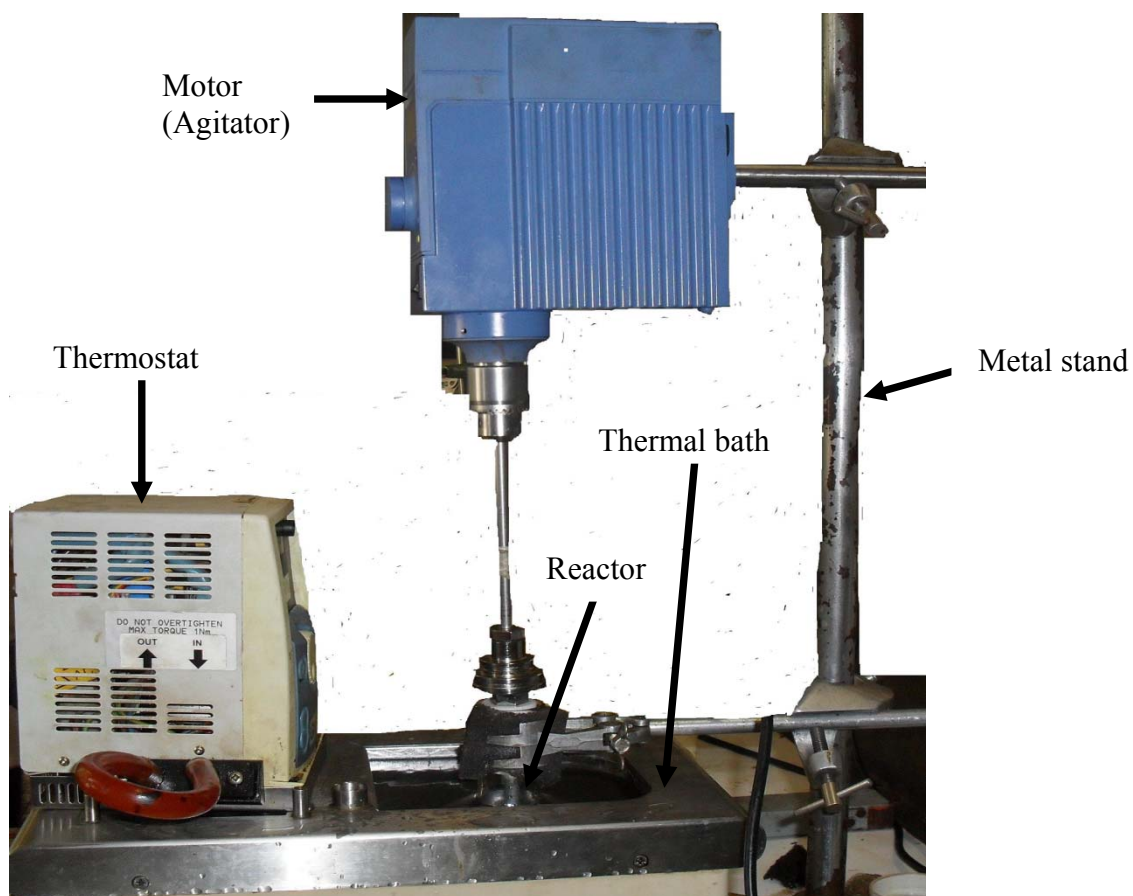


Figure 9: Laboratory setup for carboxymethyl cellulose synthesis

### 3.3. Experimental factors and responses

#### 3.3.1. Study factors

The effects of the factors listed below on the degree of substitution and viscosity were studied.

- Etherification reaction temperature
- Etherification reaction time
- Monochloroacetic acid concentration
- NaOH concentration

The four factors were analyzed against two levels (low [-] and high [+]), that is the 2<sup>4</sup> design. About (2\*2\*2\*2=16) runs were performed and analysis has been done to know the interaction effects between the factors and their effect on the degree of substitution and viscosity of the carboxymethyl cellulose, obtained as a final product.

### Factors and the Corresponding Ranges and levels

Table 5: Factors and the corresponding ranges and levels

Factors	Range	Levels	
		Low (-)	High (+)
Reaction temperature (°C)	30 – 70	30	70
Reaction time (min)	60 – 240	60	240
Monochloroacetic acid conc. (g of MCA/ g of cellulose)	0.5 – 1.5	0.5	1.5
NaOH conc. (w/v %)	25 - 45	25	45

Since only 16 runs were done with two levels, the lower and higher values from the above range had been taken. This is because significant response variations could be observed only if a significant gap between the lower and higher levels was kept. If the gap between the lower and higher levels was smaller, there would be a problem of identifying whether there is an increment or decrement of the response.

## Combination of factors and levels

Table 6: Combination of factors and levels

Run	Time(hrs) (A)	Temp. (°C) (B)	NaOH conc. (w/v %) (C)	MCAA conc. (w of MCAA/w of cellulose) (D)	Treatment combinations
1	4 (+)	70 (+)	25 (-)	1.5 (+)	abd
2	1 (-)	70 (+)	25 (-)	1.5 (+)	bd
3	4 (+)	30 (-)	25 (-)	1.5 (+)	ad
4	1 (-)	30 (-)	25 (-)	1.5 (+)	d
5	4 (+)	70 (+)	45 (+)	1.5 (+)	abcd
6	1 (-)	70 (+)	45 (+)	1.5 (+)	bcd
7	4 (+)	30 (-)	45 (+)	1.5 (+)	acd
8	1 (-)	30 (-)	45 (+)	1.5 (+)	cd
9	4 (+)	70 (+)	25 (-)	0.5 (-)	ab
10	1 (-)	70 (+)	25 (-)	0.5 (-)	b
11	4 (+)	30 (-)	25 (-)	0.5 (-)	A
12	1 (-)	30 (-)	25 (-)	0.5 (-)	1
13	4 (+)	70 (+)	45 (+)	0.5 (-)	Abc
14	1 (-)	70 (+)	45 (+)	0.5 (-)	Bc
15	4 (+)	30 (-)	45 (+)	0.5 (-)	Ac
16	1 (-)	30 (-)	45 (+)	0.5 (-)	C

### 3.3.2. Measured Responses

#### 3.3.2.1. Degree of substitution

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
- Cu salt precipitation and
- Back titration

The back titration method has been selected. It 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 [24].

Equipments used for the determination of degree of substitution were:-

- ✓ Magnetic stirrer (Ruhromag)
- ✓ Oven (memmert)
- ✓ Analytical balance (OHAUS)
- ✓ Filter cloth
- ✓ 250 ml beaker
- ✓ 250 ml Erlenmeyer flask
- ✓ 50 ml burette

The chemicals used during determination of degree of substitution were:-

- ✓ Acetone
- ✓ HCl
- ✓ Methanol
- ✓ NaOH
- ✓ Distilled water
- ✓ 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 magnetic stirrer
- ✓ Then it was converted to the acid form (H-CMC) by adding an aqueous solution of 6 ml of 6 M 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) until the conductivity of the filtrate was about 25  $\mu\text{S}/\text{cm}$ . Then the precipitate was again dispersed in acetone, filtered, dried under vacuum at 50°C, and ground.
- ✓ The obtained H-CMC was used for the DS determination.



Figure 10: H-CMC samples ready to be titrated

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 M NaOH and 50 ml of bidistilled water was also added.
- ✓ The solution was transferred to a 100 ml volumetric flask, which was then filled up to the mark with bidistilled water.
- ✓ 25 ml of the solution was transferred to an Erlenmeyer flask and diluted by addition of 50–100 ml of bidistilled water.
- ✓ The excess of NaOH was back-titrated with standard 0.05 M 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 as:-

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

Where,

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

B = Milliliters of added Sodium hydroxide.

C = Normal sodium hydroxide.

D = Milliliters of consumed hydrochloric acid.

E = Normal hydrochloric acid.

F = Specimen grams used.

The DS was calculated using equation below

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

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.

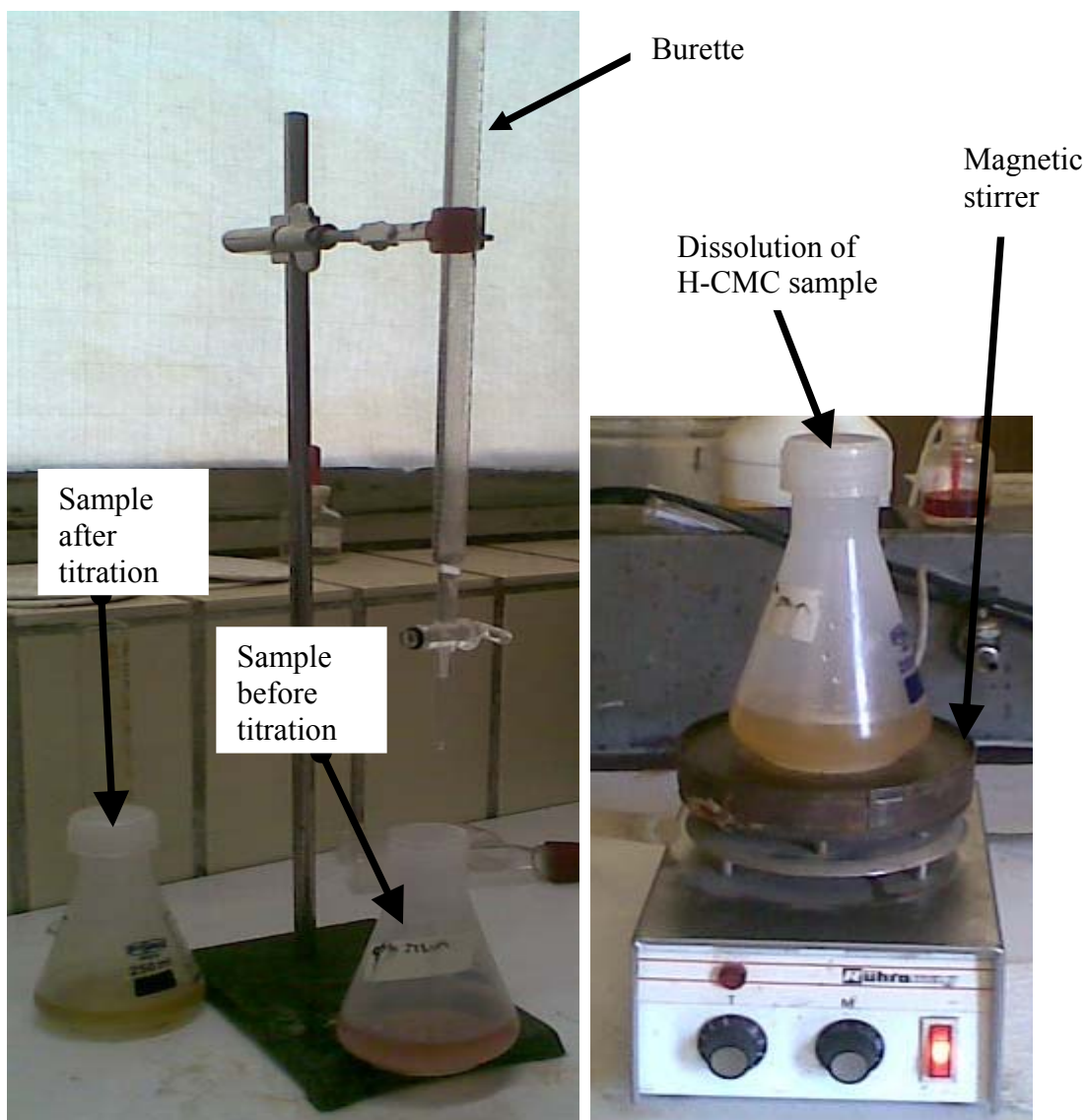


Figure 11: Laboratory setup for DS determination

### 3.3.2.2. Viscosity

To measure the viscosity of carboxymethyl cellulose solutions, 2% (w/w) solution of carboxymethyl cellulose were prepared in water. The viscosity was measured using viscometer. The temperature was maintained at 30<sup>0</sup>C along the reaction. The solution stirred with a magnetic stirrer to be sure that all the material soluble (usually 1 to 3hrs is required). When solution was completed, immediately the spindle was inserted (with the guard attached) into the solution. Three readings were taken and there average recorded as the viscosity of the material [17].

## 4. RESULTS AND DISCUSSION

### 4.1. Yield of cellulose from bagasse

From the delignification process performed above the final cellulose obtained was about 26 gm.

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

$$\% \text{ yield cellulose} = (26/80) * 100$$

$$\% \text{ yield cellulose} = \underline{32.5\%}$$

### 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 7: The volumes of HCl determined from titration

Run order	Obtained results in ml	Average volume of HCl
1 <sup>st</sup>	14, 15.5, 14.6	14.7
2 <sup>nd</sup>	15.5, 15, 13	14.5
3 <sup>rd</sup>	16.8, 17, 16.4	16.73
4 <sup>th</sup>	15.6, 15.2, 15	15.3
5 <sup>th</sup>	11.9, 11.8, 11.5	11.73
6 <sup>th</sup>	10.6, 10.7, 10.5	10.6
7 <sup>th</sup>	15.2, 15.4, 15.5	15.4
8 <sup>th</sup>	18.9, 18.6, 18.2	18.57
9 <sup>th</sup>	15.5, 15,0	15.25
10 <sup>th</sup>	14.7, 14, 14.35	14.35
11 <sup>th</sup>	10.7, 10.4, 10.3	10.47
12 <sup>th</sup>	16.8, 16.3, 17.2	16.77
13 <sup>th</sup>	9.5, 9.8, 9.9	9.73
14 <sup>th</sup>	13.7, 13.5, 13.6	13.6
15 <sup>th</sup>	19, 19.5, 18	18.8
16 <sup>th</sup>	18.5, 18.3, 18.7	18.5

Then, as an example for the **forth** 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

From the equation:

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

$$A = (20 * 0.2 - 15.3 * 0.05)/0.5$$

$$A = \underline{6.47}$$

Substitute the above result in the formula below:

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

$$DS = \frac{(0.162) \times 6.47}{1 - (0.058 \times 6.47)}$$

Then the degree of substitution will be

$$DS = \underline{1.68}$$

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

Table 8: Factors and determined responses

Run order	Time (hr)	Temp. (°C)	NaOH conc. (w/v)	MCA conc. (w/w)	Degree of substitution	Viscosity (cp)
1	4	70	25	1.5	1.7	3.34
2	1	70	25	1.5	1.71	5.17
3	4	30	25	1.5	1.62	0.94
4	1	30	25	1.5	1.68	2.06
5	4	70	45	1.5	1.83	14.27
6	1	70	45	1.5	1.88	19.8
7	4	30	45	1.5	1.67	1.19
8	1	30	45	1.5	1.55	0.87
9	4	70	25	0.5	1.68	2.11
10	1	70	25	0.5	1.72	10.8
11	4	30	25	0.5	1.89	22
12	1	30	25	0.5	1.62	0.88
13	4	70	45	0.5	1.92	25.4
14	1	70	45	0.5	1.75	14.3
15	4	30	45	0.5	1.54	2.08
16	1	30	45	0.5	1.55	0.78

### 4.3. Experimental Design

For the analysis of the data, Design Expert software (version 7.0.0, Stat-Ease Inc., Minneapolis, USA) was used. The design was chosen based on its capability to provide accurate regression analysis and less runs were needed for carboxymethylation reaction study [22].

At each combination of the process settings, the degree of substitution and viscosity of the samples were recorded.

This experimental design was made to:-

- ✓ Screen out insignificant factors and identify significant factors. Get some idea about the existence of interaction effects.
- ✓ Understand main effects and get complete information about 4 factor interactions.

- ✓ Characterize how the significant factors affect the responses (for optimization purposes.)

The number of runs, number of factors, name and units of factors and their levels, the response name and unit was entered and the following design summary table generated:

Table 9: Design summary

<b>Design Summary</b>									
<b>Study Type</b>	Factorial		<b>Runs</b>	16					
<b>Initial Design</b>	2 Level Factorial		<b>Blocks</b>	No Blocks					
<b>Center Points</b>	0								
<b>Design Model</b>	4FI								
<b>Factor</b>	<b>Name</b>	<b>Units</b>	<b>Type</b>	<b>Low Actual</b>	<b>High Actual</b>	<b>Low Coded</b>	<b>High Coded</b>	<b>Mean</b>	<b>Std. Dev.</b>
A	Time	hr	Numeric	1	4	-1	1	2.5	1.5
B	Temp.	celcius	Numeric	30	70	-1	1	50	20
C	NaOHconc.	w/v	Numeric	25	45	-1	1	35	10
D	MCAAc onc.	w/w	Numeric	0.5	1.5	-1	1	1	0.5
<b>Response</b>	<b>Name</b>	<b>Units</b>	<b>Obs</b>	<b>Analysis</b>	<b>Min</b>	<b>Max</b>	<b>Mean</b>	<b>Std. Dev.</b>	<b>Ratio</b>
Y1	DS	number	16	Factorial	1.54	1.92	1.706	0.117	1.246
Y2	Viscosity	mpa.s	16	Factorial	0.78	25.4	7.8743	8.326225	32.564

This design summary table indicates the report of the design, factors, and response information. New items are the factors and response mean and standard deviation.

### **4.3.1. Pre-Analysis of Main Effects through Simple Plots**

On the graph column of the following figures the variations of the factors with respect to the degree of substitution are shown.

#### **4.3.1.1. Effect of Reaction Temperature on DS and viscosity**

As shown on the figures 12 and 13, the graphs indicate the effect of temperature on the degree of substitution and viscosity.

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.

The graphs show that temperature has a large impact on the degree of substitution and slightly a lesser impact on viscosity. Generally, increasing the temperature increases the degree of substitution and viscosity.

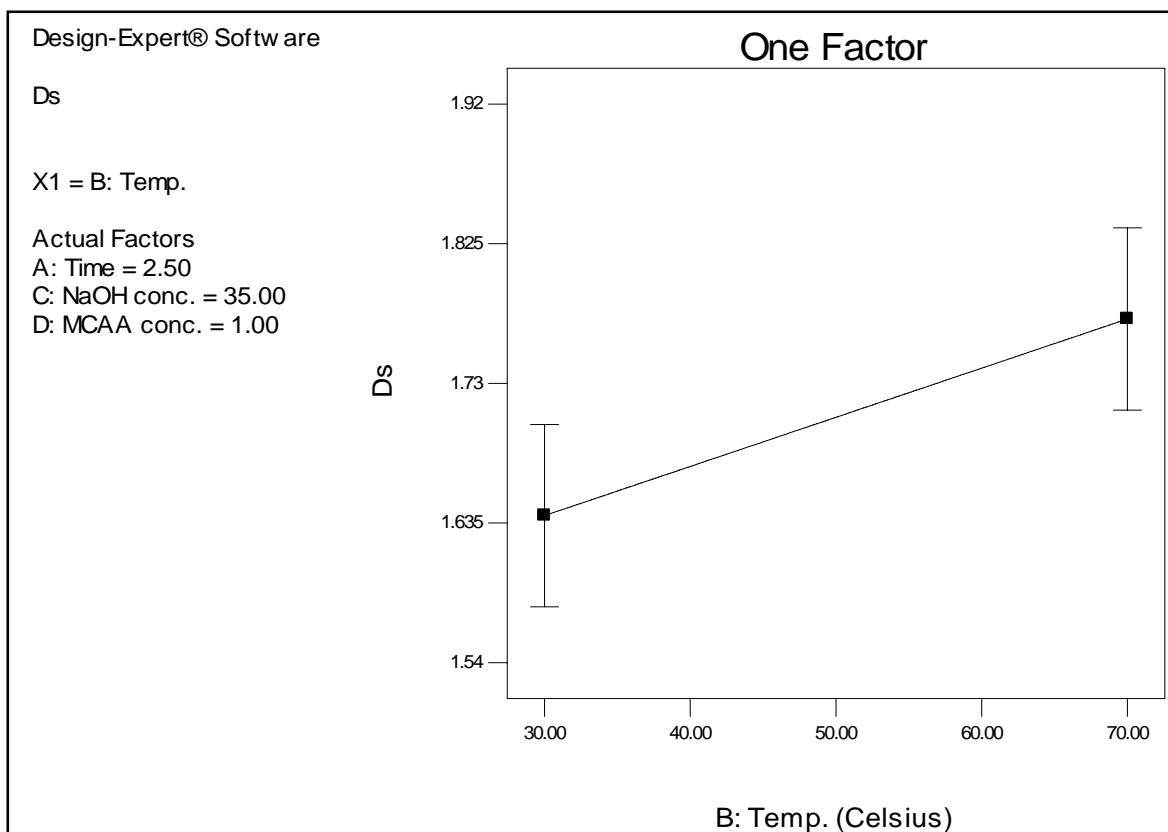


Figure 12: Effect of temperature on degree of substitution

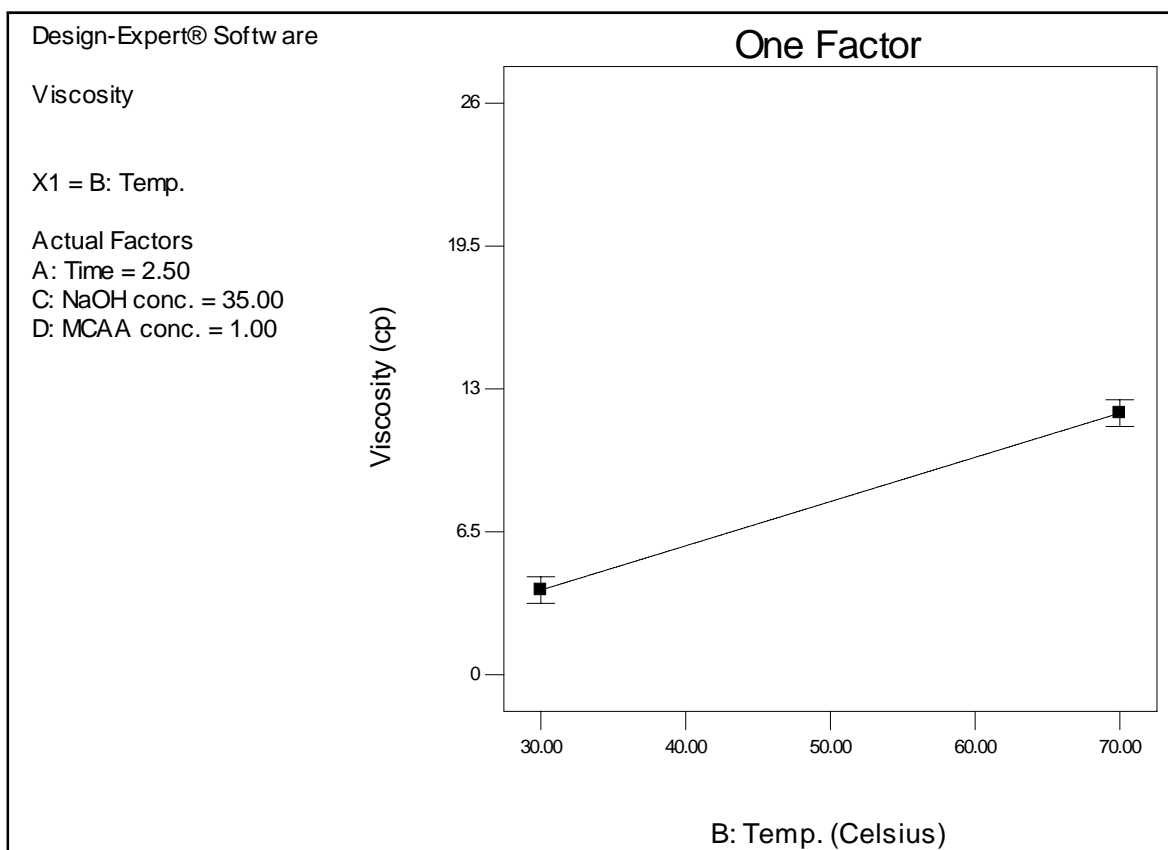


Figure 13: Effect of temperature on viscosity

Moreover, the effect of variation of temperature on the degree of substitution was observed by making the three factors constant (sodium hydroxide concentration = 25%, monochloroacetic acid concentration = 0.5 and time of carboxymethylation reaction = 1 hr) and the temperature was varied to 30°C, 40°C, 50°C, 60°C and 70°C. As a result, the final degree of substitution was calculated and tabulated below.

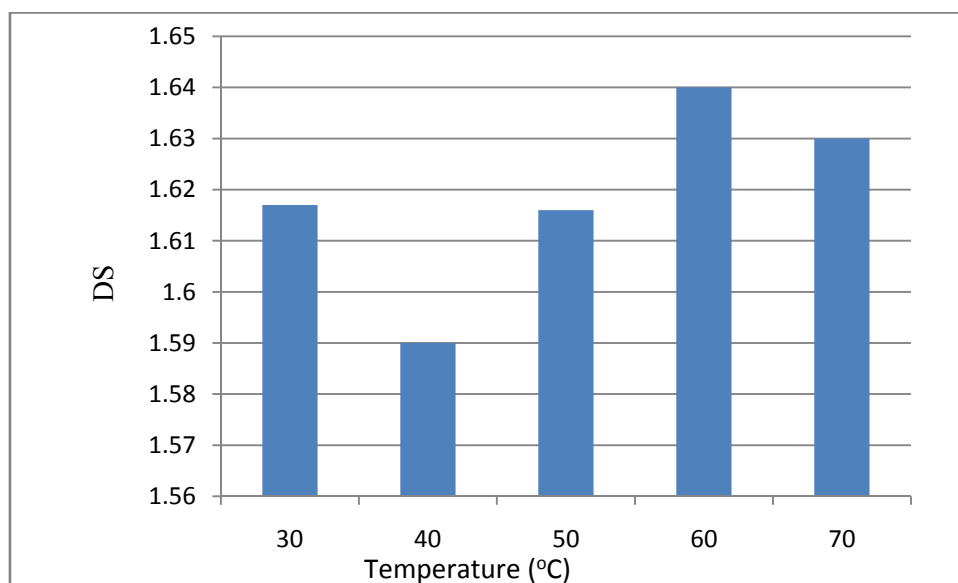


Figure 14: Effect of temperature variation on degree of substitution

Again the above figure indicates the degree of substitution is increased with an increasing of carboxymethylation reaction temperature. But, beyond 60°C the degree of substitution has reduced. This is because, when the temperature was higher, the reaction might have been so fast that not only local reaction occurred but also the CMC on the surface of cellulose would hinder diffusing, seeping and reaction of sodium hydroxide, which played a negative role in the DS of the product.

#### 4.3.1.2. Effect of Reaction Time on DS and Viscosity

The degree of substitution and viscosity are increasing with an increase in reaction time. This means the longer the reaction time, the longer the carboxymethylation process continues to substitute the functional groups of cellulose which will further increase the value of degree of substitution. In other words as etherification time increases the substitution reaction becomes

nearer to completion. But the viscosity is affected by the time increment to a lesser extent relative to degree of substitution.

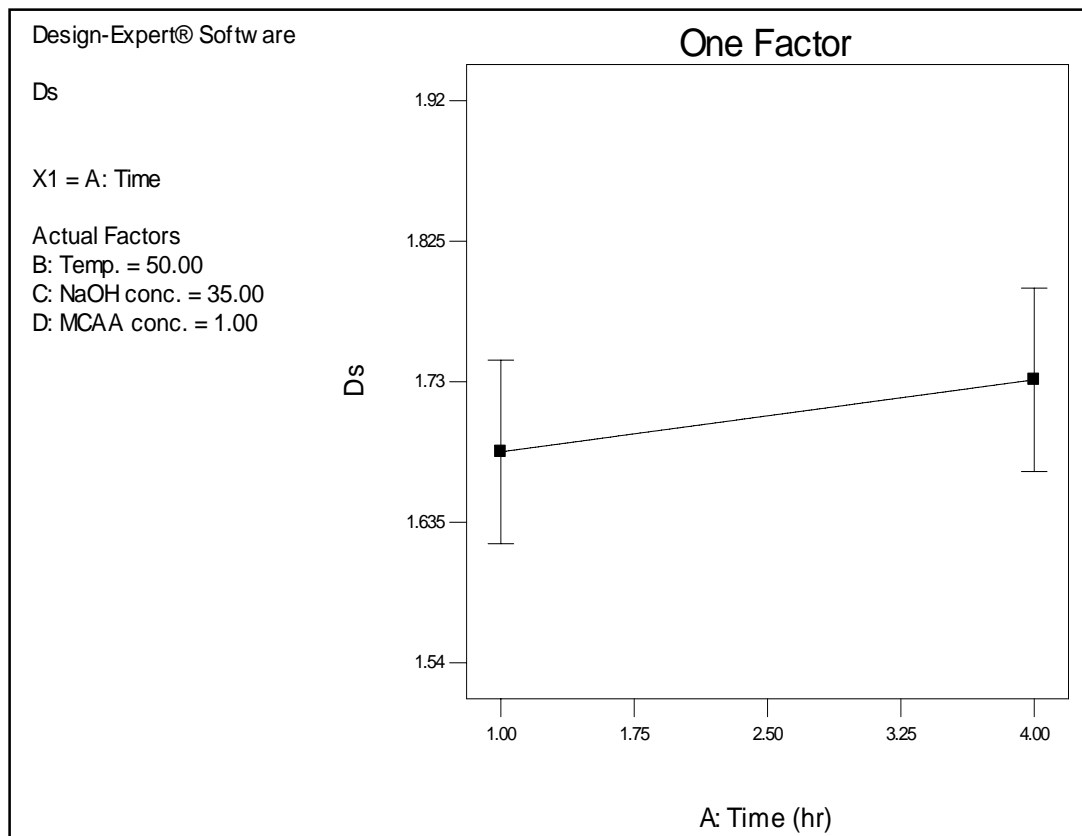


Figure 15: Effect of time on degree of substitution

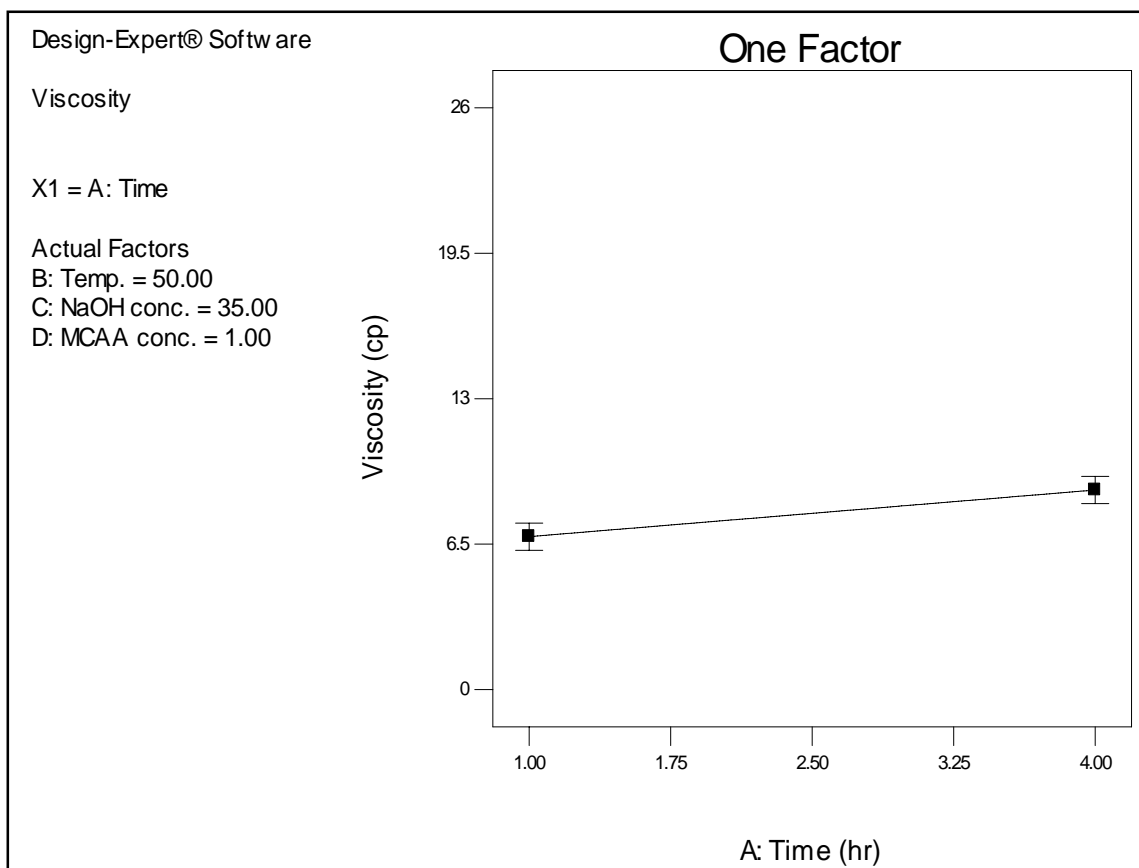


Figure 16: Effect of time on viscosity

#### 4.3.1.3. Effect of NaOH concentration on DS and Viscosity

The NaOH concentration plays great role in determining the production of CMC and the by-product. From the result obtained above, the degree of substitution and viscosity are increased slightly with the increment of NaOH concentration. The maximum degree of substitution attained is 1.92 at NaOH concentration of 45%w/v. Further increment of NaOH concentration will not yield the pure product of CMC instead the by-product, sodium glycolate.

The role of sodium hydroxide was to swell and alkalize the cellulose of bagasse, and to resume the reaction character of hydroxyl group of the cellulose chain. Cellulose cannot be effectively swelled and alkalized with a low dose but the cellulose chain will be broken at high doses. The presence of high amount of NaOH probably resulted in the formation of sodium glycolate by-product or the polymer being degraded owing to the high concentration. It is also observed that low NaOH resulted in low viscosity and low purity of CMC because the low concentration of NaOH hardly forms alkali cellulose and neutralized sodium chloroacetate. So sodium hydroxide dose was an important factor for CMC preparation.

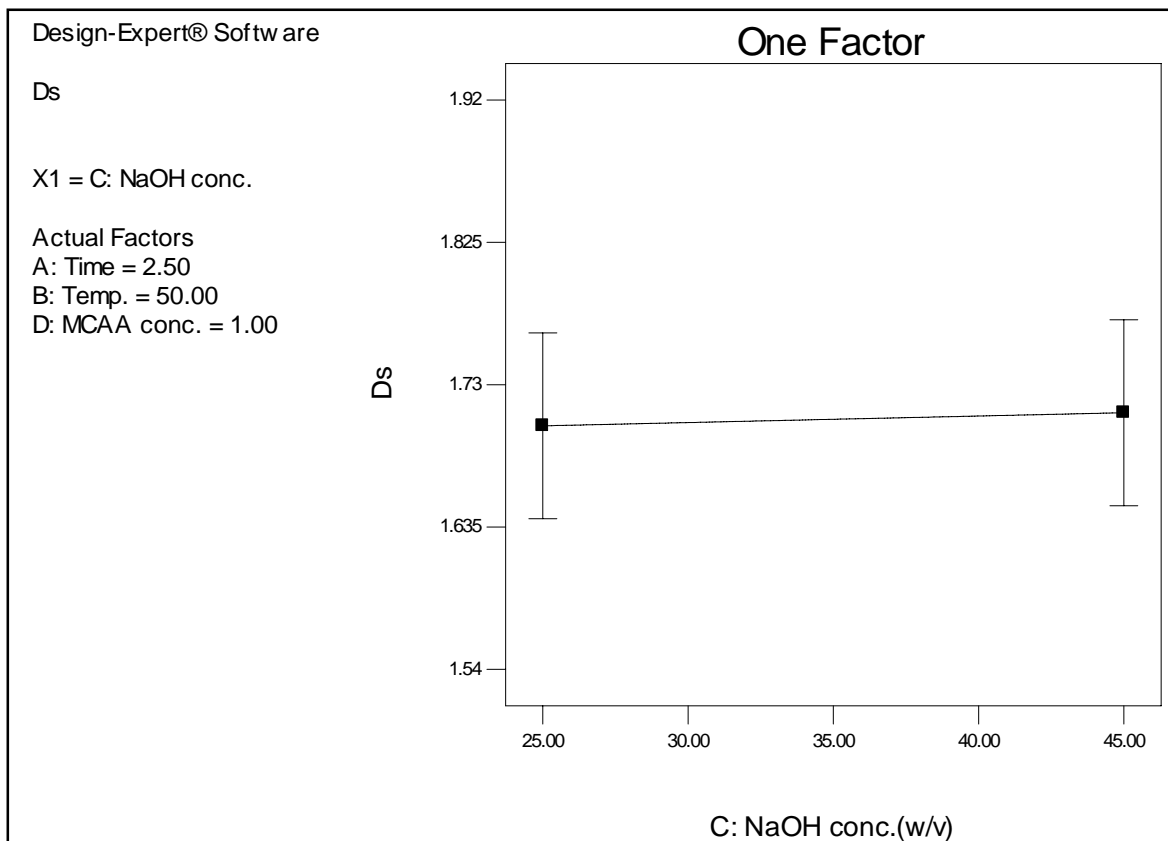


Figure 17: Effect of NaOH conc. On degree of substitution

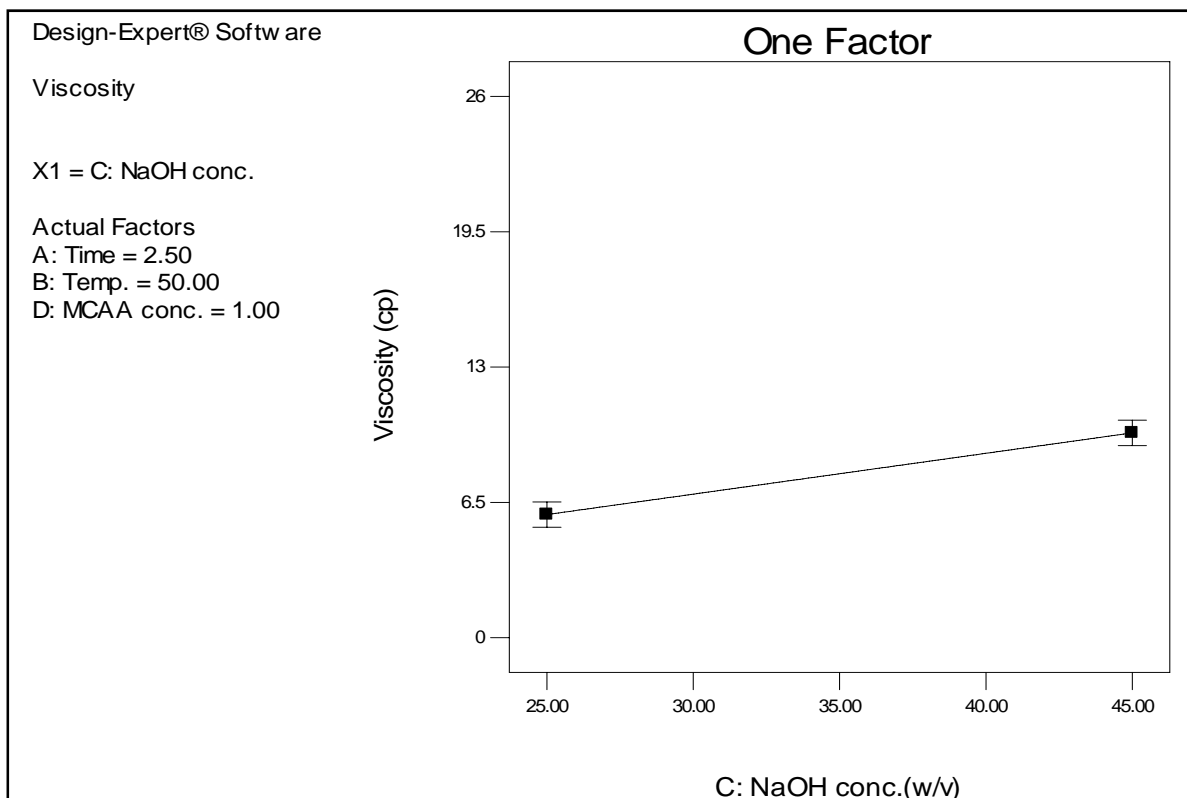


Figure 18: Effect of NaOH conc. On viscosity

#### 4.3.1.4. Effect of Monochloroacetic Acid Concentration on DS and viscosity

Increasing chloroacetic acid concentration doesn't have significant effect instead it slightly decreases the degree of substitution. This is because increasing the chloroacetic acid concentration from 2.5gm to 7.5gm 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.

The viscosity of carboxymethyl cellulose is also highly affected by chloroacetic acid concentration. It is decreasing with an increase of chloroacetic acid concentration.

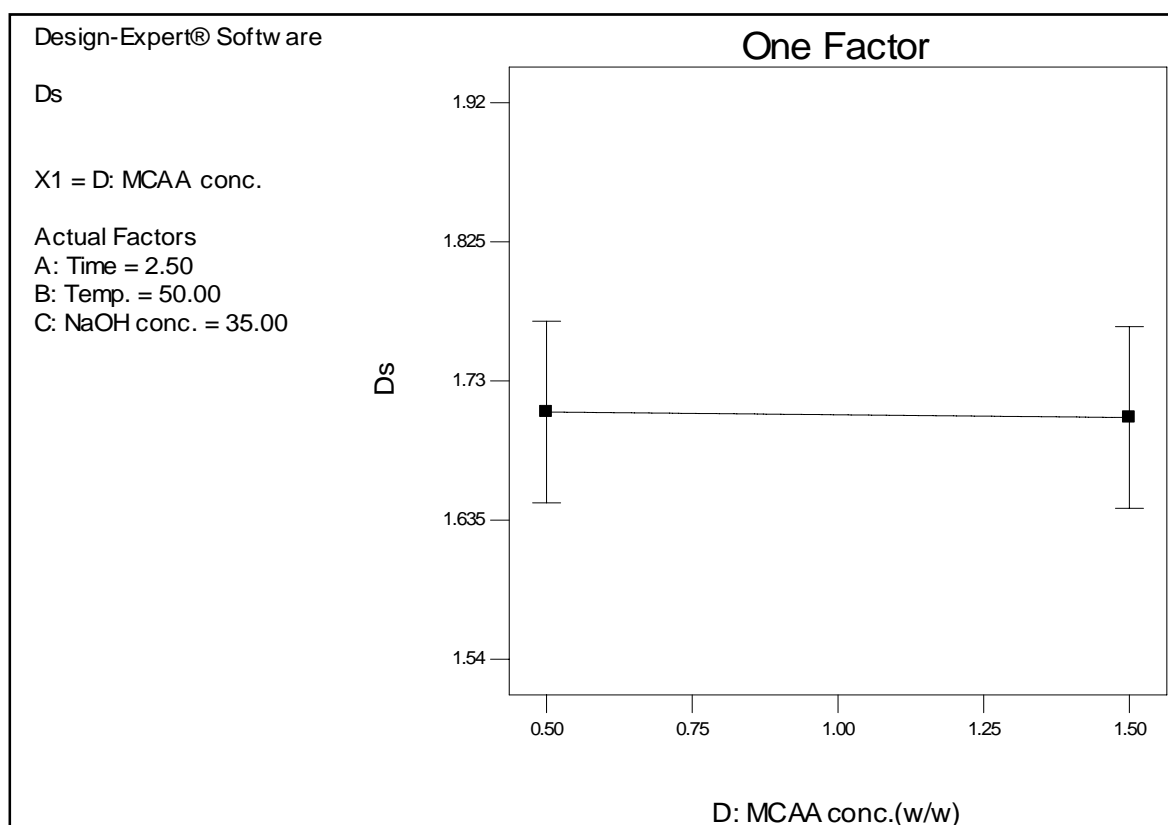


Figure 19: Effect of chloroacetic acid conc. on degree of substitution

Design-Expert® Software

Viscosity

X1 = D: MCAA conc.

Actual Factors

A: Time = 2.50

B: Temp. = 50.00

C: NaOH conc. = 35.00

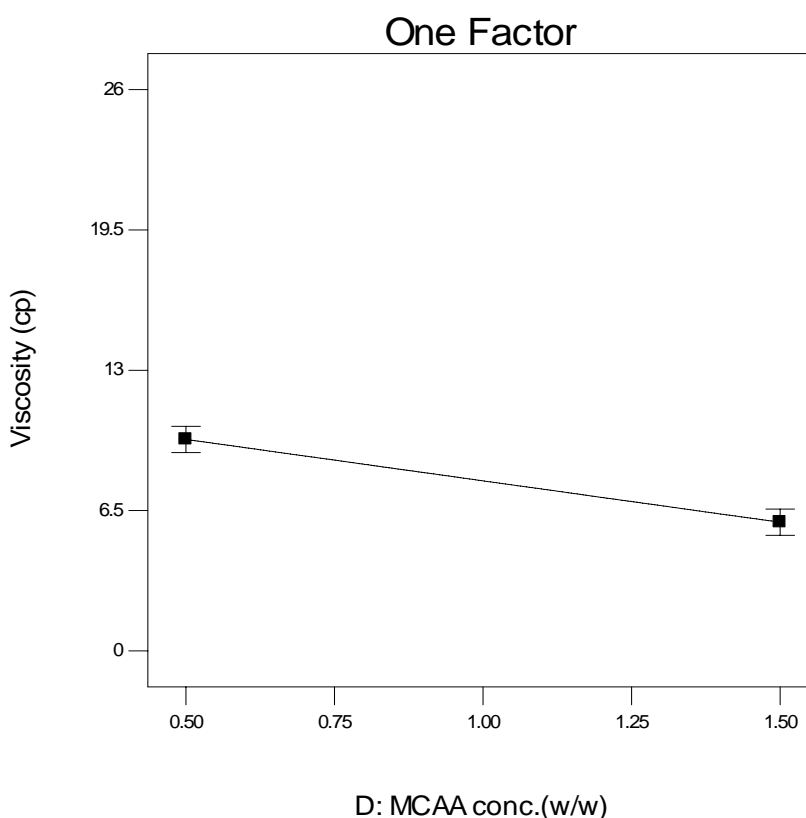


Figure 20: Effect of chloroacetic acid conc. on viscosity

#### 4.3.2. Pre-analysis of interaction effects through 3D-surfaces

The 3-D response surface curves were plotted to understand interaction between the variables and to determine the optimum levels of each variable for maximum response.

##### 4.3.2.1. Interaction effects of temperature and time

As shown on figure 21, the 3D surfaces show the interaction effects of temperature and time with respect to degree of substitution and viscosity.

The interaction graphs show that the degree of substitution and viscosity are increasing with reaction temperature and time. Higher reaction time and temperature will favor on the effect of having higher degree of substitutions. This is because the swellability of cellulose as well as diffusion and adsorption of reactants will be increasing. This condition may provide better environment for carboxymethylation reaction as well as a good substitution of functional groups. But on the viscosity graph, higher viscosity was obtained at higher temperature and lower time. This is because the longer reaction time may significantly cause the degradation of cellulose chain and CMC structure.

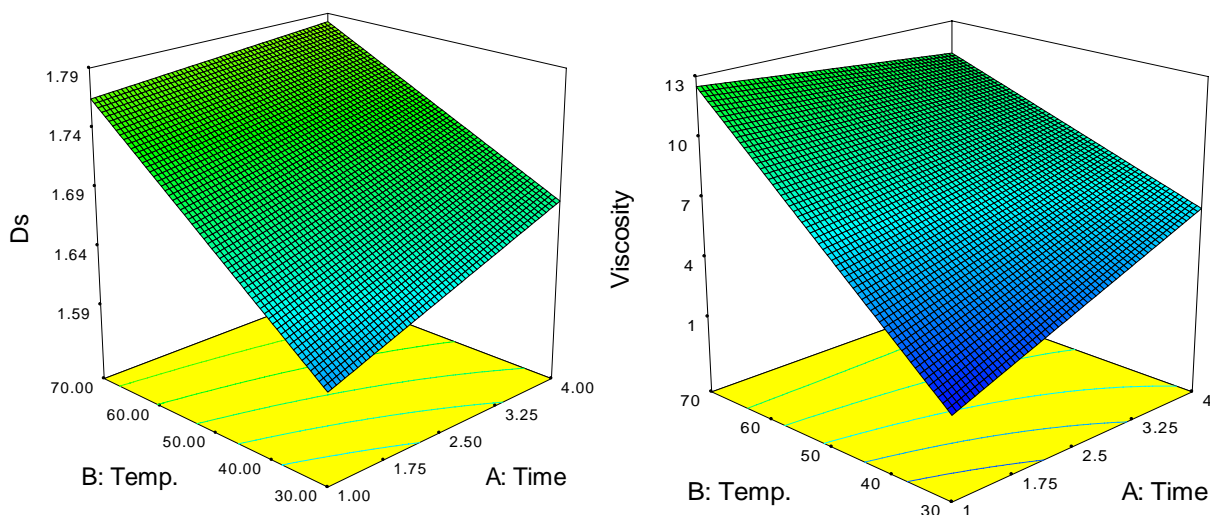


Figure 21:3D surface for temperature-time interaction

#### 4.3.2.2. Interaction effects of NaOH conc. And time

From figure 22, higher degree of substitution and viscosity are obtained at higher values of NaOH concentration and temperature. This is clearly due to the reason that at higher values of NaOH concentration more functional groups are activated and being ready to be substituted. So that, at etherification step the higher temperature will favor the H atom to be replaced by  $\text{CH}_2\text{COOH}$  group.

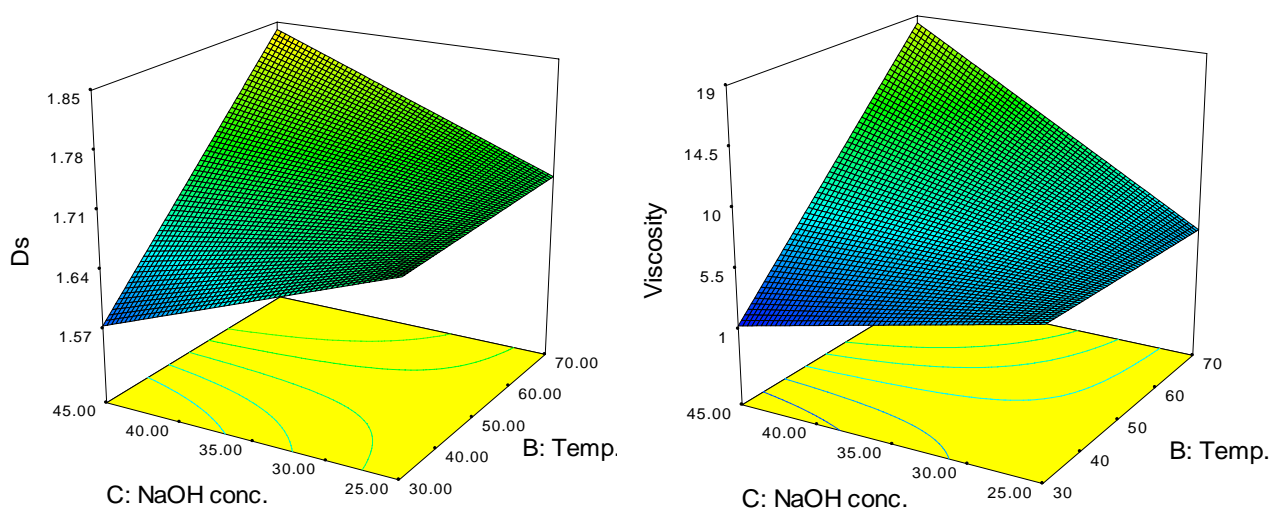


Figure 22: 3D surfaces for interaction of NaOH conc. and temp.

### 4.3.2.3. Interaction effects of MCAA and NaOH conc.

Higher MCAA and NaOH concentrations will increase the degree of substitution value. This is because the main reaction which leads to CMC production and the side reaction which leads to the by-product sodium glycolate are becoming competitive. This is to mean that although the side reaction exists the substitution of the hydroxyl groups are also high due to the presence of enough amounts of reactant molecules. The side reaction is resulted in the formation of sodium glycolate from SMCA and NaOH. A side reaction is a two competitive reaction in carboxymethylation process which converts the sodium chloroacetate to sodium glycolate. However, the concentration of sodium glycolate will increase if the concentration of NaOH is higher. It is because the chloroacetic acid molecules tend to react with NaOH which may lead to the destruction of cellulose chain or CMC polymer, becoming responsible for viscosity reduction. That is why the viscosity is higher at higher NaOH concentration and lower monochloroacetate.

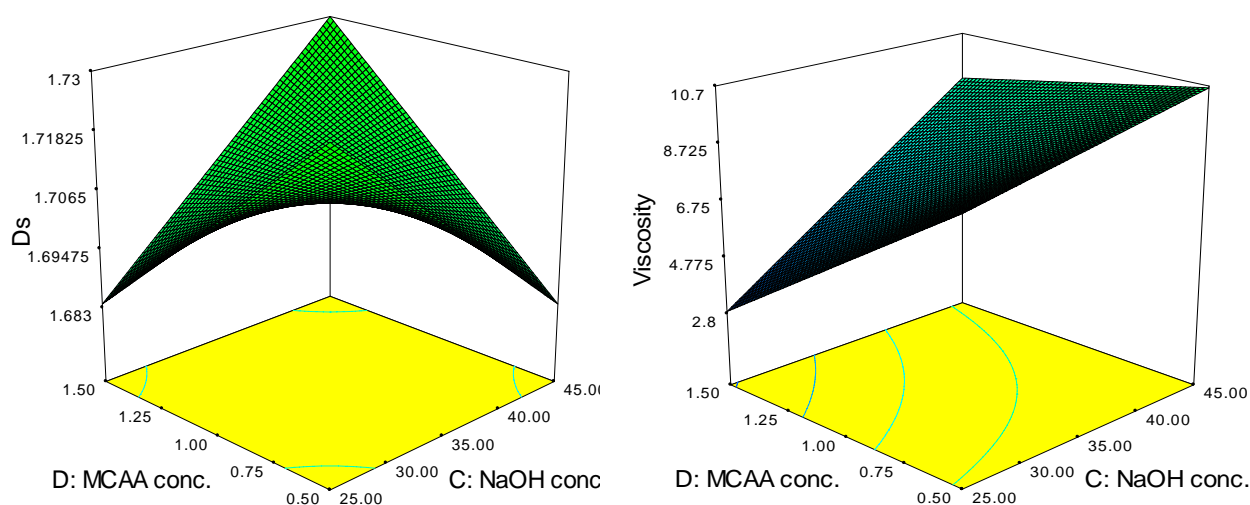


Figure 23:3D surfaces for the interaction of MCAA and NaOH conc.

### 4.3.3. Screening of Factors

Generally, the percent contribution of each combination was obtained by summing all the term sum of squares and then taking each individual SS and dividing by the total SS and

multiplying by 100. When all terms have the same degrees of freedom, the % Contributions can be used to determine which terms are larger contributors than others.

From the table in annex-1, the highlighted terms indicated the significant terms. That is we can conclude that the significant factors for the degree of substitution are A, B, AB, AD, BC, CD, ABC, ACD, BCD, and ABCD. They together account about 99.2 % of the variability. So, these significant factors have used for the analysis of variance.

Again the significant factors for viscosity as indicated in annex-1 are A, B, C, D, AB, AD, BC, BD, CD, ABC, ABD, BCD, and ABCD. They together account about 99.93% of the variability.

This is not the only way to know the significant effects. The half-normal probability versus standardized effect plots shown on annex-2 is also another alternative way to identify the significant effects. In this graph all the non significant points are close to the line except points with significant effects.

In addition, the percent contribution table in annex-1 confirms that the order of the factors influencing the degree of substitution is: etherification temperature (32.36%) > etherification time (4.3%) > dosage of sodium hydroxide (0.14%) > dosage of sodium chloroacetate (0.03%). That is etherification temperature has the highest effect on the reaction and on the degree of substitution as well.

The order of the factors influencing the viscosity is: etherification temperature (23.36%) > dosage of sodium hydroxide (5.55%) > dosage of monochloroacetic acid (5.31%) > etherification time (1.57%). Here also etherification temperature has the highest effect.

#### **4.3.4. Analysis of Variance for DS**

##### **4.3.4.1. Analysis of variance for the response degree of substitution**

<b>Response</b>	<b>1</b>	<b>Ds</b>
-----------------	----------	-----------

##### **Backward Elimination Regression with Alpha to Exit = 0.050**

Terms on the table below are automatically removed from the model. This is because there significance for the model is negligible.

Table 10: Non-significant terms for degree of substitution

<b>Removed</b>	<b>Coefficient Estimate</b>	<b>t for H0 Coeff=0</b>	<b>Prob &gt;  t </b>	<b>R-Squared</b>	<b>MSE</b>
ABD	0.00	0.00	0.05	1.00	
D-MCAA conc.	0.00	-3.00	0.20	1.00	0.00
AC	0.00	3.13	0.09	1.00	0.00
C-NaOH conc.	0.00	1.58	0.21	1.00	0.00
BD	0.01	2.50	0.07	1.00	0.00

Table 11: ANOVA for degree of substitution

**ANOVA for selected factorial model**

**Analysis of variance table [Partial sum of squares - Type III]**

<b>Source</b>	<b>Sum of Squares</b>	<b>df</b>	<b>Mean Square</b>	<b>F Value</b>	<b>p-value Prob &gt; F</b>	significant
Model	0.2194	10	0.0219	63.3682	0.0001	
A-Time	0.0095	1	0.0095	27.4549	0.0034	
B-Temp.	0.0716	1	0.0716	206.6606	< 0.0001	
AB	0.0039	1	0.0039	11.2816	0.0201	
AD	0.0095	1	0.0095	27.4549	0.0034	
BC	0.0716	1	0.0716	206.6606	< 0.0001	
CD	0.0086	1	0.0086	24.7112	0.0042	
ABC	0.0046	1	0.0046	13.1588	0.0151	
ACD	0.0028	1	0.0028	7.9603	0.0370	
BCD	0.0060	1	0.0060	17.3466	0.0088	
ABCD	0.0315	1	0.0315	90.9928	0.0002	
Residual	0.0017	5	0.0003			
Cor Total	0.2211	15				

The Model F-value of 63.37 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, AB, AD, BC, CD, ABC, ACD, BCD, ABCD are significant model terms. Values greater than 0.1000 indicate the model terms are not significant. If there are many insignificant model terms (not counting those required to support hierarchy), term reduction may improve the model.

As shown on annex-3, the "Pred R-Squared" of 0.92 is in reasonable agreement with the "Adj R-Squared" of 0.98. "Adeq Precision" measures the signal to noise ratio. A ratio greater than 4 is desirable. Here a ratio of 25.76 indicates an adequate signal. This model can be used to navigate the design space.

Based on the above significant factors, the coefficients for the model were estimated.

Table 12: Model coefficients for degree of substitution

Factor	Coefficient Estimate	df	Standard Error	95% CI Low	95% CI High	VIF
Intercept	1.707	1	0.005	1.695	1.719	
A-Time	0.024	1	0.005	0.012	0.036	1.000
B-Temp.	0.067	1	0.005	0.055	0.079	1.000
AB	-0.016	1	0.005	-0.028	-0.004	1.000
AD	-0.024	1	0.005	-0.036	-0.012	1.000
BC	0.067	1	0.005	0.055	0.079	1.000
CD	0.023	1	0.005	0.011	0.035	1.000
ABC	0.017	1	0.005	0.005	0.029	1.000
ACD	0.013	1	0.005	0.001	0.025	1.000
BCD	-0.019	1	0.005	-0.031	-0.007	1.000
ABCD	-0.044	1	0.005	-0.056	-0.032	1.000

**Final Equation in Terms of Coded Factors:**

$$DS = 1.71 + 0.024 * A + 0.067 * B - 0.016 * A * B - 0.024 * A * D + 0.067 * B * C + 0.23 * C * D + 0.017 * A * B * C + 0.013 * A * C * D - 0.019 * B * C * D - 0.044 * A * B * C *$$

**Final Equation in Terms of Actual Factors:**

$$DS = 0.79469 + 0.744 * ti + 0.01626 * te + 0.017 * cs + 0.98854 * ca - 0.012885 * ti * te - 0.019 * ti * cs - 0.61354 * ti * ca - 3.52 * 10^{-4} * te * cs - 0.018396 * te * ca - 0.027 * cs * ca + 3.52 * 10^{-4} * ti * te * cs + 0.01 * ti * te * ca + 0.016542 * ti * cs * ca + 5.45833 * 10^{-4} * te * cs * ca - 2.95833 * 10^{-4} * ti * te * cs * ca$$

Where,

ti = etherification time

te = etherification temperature

cs = caustic soda (NaOH conc.)

ca = chloroacetate (MCAA conc.)

#### 4.3.4.2. Analysis of Variance for Viscosity

**Response 2: Viscosity**

#### Backward Elimination Regression with Alpha to Exit = 0.050

Here again, the terms AC and ACD are removed due to their negligible effect to the model. That is its probability to satisfy the null hypothesis is true.

Table 13: Non significant terms for viscosity

<b>Removed</b>	<b>Coefficient Estimate</b>	<b>t for H0 Coeff=0</b>	<b>Prob &gt;  t </b>	<b>R-Squared</b>	<b>MSE</b>
ACD	-0.139	0.071	0.050	1.000	
AC	-0.143	-1.027	0.492	1.000	0.311

Terms on the table below are automatically selected for the model. This is because their significance for the model is important.

Table 14: ANOVA for viscosity

**ANOVA for selected factorial model**  
**Analysis of variance table [Partial sum of squares - Type III]**

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	
Model	1108.578	13	85.275	267.085	0.0037	significant
A-Time	17.368	1	17.368	54.397	0.0179	
B-Temp.	259.130	1	259.130	811.603	0.0012	
C-NaOH conc.	61.583	1	61.583	192.881	0.0051	
D-MCAA conc.	58.944	1	58.944	184.615	0.0054	
AB	44.123	1	44.123	138.194	0.0072	
AD	68.021	1	68.021	213.045	0.0047	
BC	335.897	1	335.897	1052.042	0.0009	
BD	7.089	1	7.089	22.203	0.0422	
CD	19.914	1	19.914	62.371	0.0157	
ABC	74.261	1	74.261	232.589	0.0043	
ABD	11.30640625	1	11.30641	35.412058	0.0271	
BCD	25.78100625	1	25.78101	80.74701	0.0122	
ABCD	125.1601563	1	125.1602	392.00597	0.0025	
Residual	0.6385625	2	0.319281			
Cor Total	1109.216394	15				

Therefore, we can easily understand that the Model F-value of 267.08 implies the model is significant. There is only a 0.37% 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, D, AB, AD, BC, BD, CD, ABC, ABD, BCD, ABCD are significant model terms. Values greater than 0.1000 indicate the model terms are not significant. If there are many insignificant model terms (not counting those required to support hierarchy), term reduction may improve the model.

Here also as indicated on annex-3, the "Pred R-Squared" of 0.9632 is in reasonable agreement with the "Adj R-Squared" of 0.9957. "Adeq Precision" measures the signal to noise ratio. A ratio greater than 4 is desirable. The ratio of 46.951 indicates an adequate signal.

Table 15: Model coefficients for viscosity

Factor	Coefficient Estimate	df	Standard Error	95% CI Low	95% CI High	VIF
Intercept	7.874	1.000	0.141	7.267	8.482	
A-Time	1.042	1.000	0.141	0.434	1.650	1.000
B-Temp.	4.024	1.000	0.141	3.417	4.632	1.000
C-NaOH conc.	1.962	1.000	0.141	1.354	2.570	1.000
D-MCAA conc.	-1.919	1.000	0.141	-2.527	-1.312	1.000
AB	-1.661	1.000	0.141	-2.268	-1.053	1.000
AD	-2.062	1.000	0.141	-2.670	-1.454	1.000
BC	4.582	1.000	0.141	3.974	5.190	1.000
BD	0.666	1.000	0.141	0.058	1.273	1.000
CD	1.116	1.000	0.141	0.508	1.723	1.000
ABC	2.154	1.000	0.141	1.547	2.762	1.000
ABD	0.841	1.000	0.141	0.233	1.448	1.000
BCD	-1.269	1.000	0.141	-1.877	-0.662	1.000
ABCD	-2.797	1.000	0.141	-3.405	-2.189	1.000

Based on the above model coefficients, the following equation is developed.

**Final Equation in Terms of Coded Factors:**

$$\begin{aligned} \text{Viscosity} = & 7.87 + 1.04 * A + 4.02 * B + 1.96 * C - 1.92 * D - 1.66 * A * B - 2.06 * A \\ & * D + 4.58 * B * C + 0.67 * B * D + 1.12 * C * D + 2.15 * A * B * C + 0.84 \\ & * A * B * D - 1.27 * B * C * D - 2.8 * A * B * C * D \end{aligned}$$

**Final Equation in Terms of Actual Factors:**

$$\begin{aligned} \text{Viscosity} = & -66.5 + 53.89 * ti + 1.143 * te + 1.4 * cs + 56.637 * ca - 1.01534 * ti * te \\ & - 1.2823 * ti * cs - 37.53 * ti * ca - 0.0289 * te * cs - 1.26 * te * ca \\ & - 1.42646 * cs * ca + 0.0258 * ti * te * cs + 0.71 * ti * te * ca + 0.9137 * ti \\ & * cs * ca + 0.0339 * te * cs * ca - 0.0186 * ti * te * cs * ca \end{aligned}$$

Where,

$t_i$  = etherification time

$t_e$  = etherification temperature

cs = caustic soda (NaOH conc.)

ca = chloroacetate (MCAA conc.)

#### 4.3.5. Diagnostics

Parity plots were prepared to investigate the agreement between experimental (actual) values and model predictions.

On the parity plots below (figure 24 and 25) the actual values and the predicted values were compared. The actual value was the measured response data for this particular run,  $y_i$ , and the predicted value was also the value predicted from the model, generated by using the prediction equation. These plots show that the agreement between experiments and models is satisfactory. The experimental and the predicted values fall on the 45 degree line, this indicates that the predicted values are agreed with the experimental one.

Design-Expert® Software  
Ds

Color points by value of  
Ds:

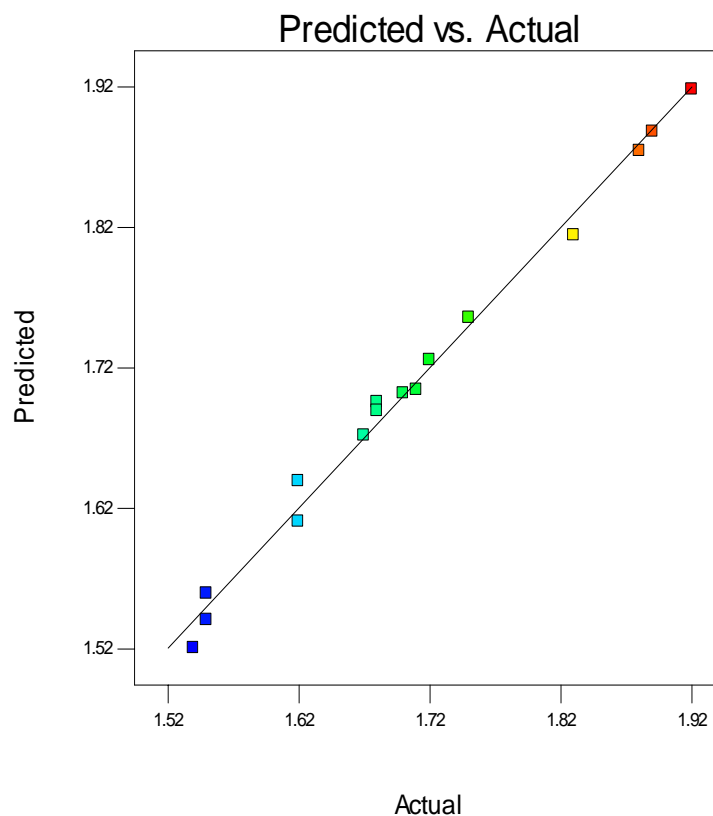
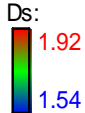
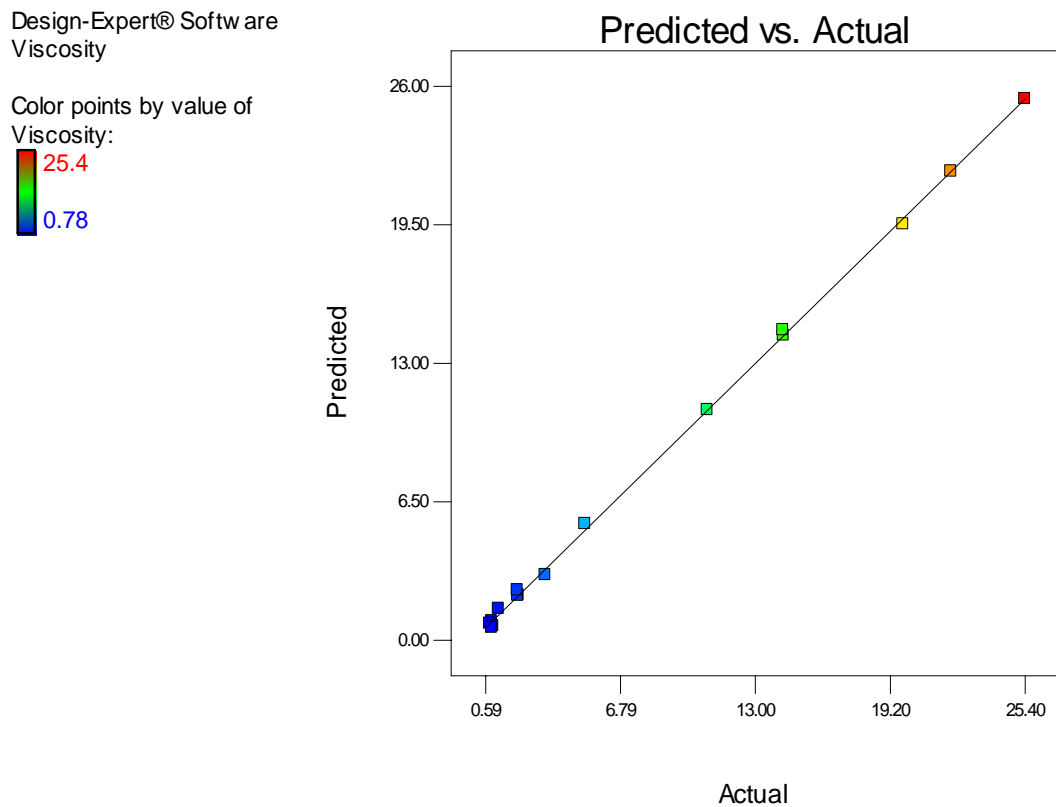


Figure 24: Predicted versus actual values for DS



## Constraints

Table 16: Constraints for optimization

Name	Goal	Lower Limit	Upper Limit	Lower Weight	Upper Weight	Importance
Time	minimize	1	4	1	1	3
Temp.	minimize	30	70	1	1	3
NaOH conc.	minimize	25	45	1	1	3
MCAA conc.	minimize	0.5	1.5	1	1	3
Ds	maximize	0.4	3	1	1	5
Viscosity	maximize	0.78	25.4	1	1	5

Below was the output from the design expert statistical software. It analyzed the input data from the experimental work, predicts 29 possible solutions and suggested one of them as an optimum value. The solutions are arranged based on their desirability for the target. So, the first one is an optimum value for our condition. The optimum degree of substitution and viscosity were 1.79 and 14.63, respectively. These values are obtained at a temperature of 30°C, NaOH concentration of 25%w/v, chloroacetic acid concentration of 0.5w/w (2.5gm) and a reaction time of 2.95 hrs.

Table 17: Possible optimized solutions

Number	Time	Temp.	NaOHconc.	MCAAconc.	Ds	Viscosity	Desirability	
1	2.95	30.00	25.00	0.50	1.79	14.63	0.66	<b>Selected</b>
2	2.94	30.00	25.00	0.50	1.79	14.48	0.66	
3	2.69	30.04	25.00	0.50	1.77	12.80	0.66	
4	3.00	30.02	25.16	0.51	1.79	14.74	0.65	
5	3.02	30.00	25.34	0.50	1.79	14.87	0.65	
6	2.86	30.15	25.46	0.50	1.78	13.63	0.65	
7	2.79	30.00	25.00	0.53	1.77	13.08	0.65	
8	2.81	30.00	25.00	0.56	1.77	12.96	0.64	
9	2.82	30.00	25.01	0.57	1.77	12.82	0.64	
1	3.11	30.00	26.31	0.50	1.79	14.84	0.64	
11	2.65	31.14	25.00	0.54	1.76	11.93	0.64	
12	2.36	30.10	25.02	0.50	1.74	10.45	0.64	
13	2.84	30.01	25.00	0.59	1.77	12.75	0.64	
14	2.81	30.25	25.00	0.61	1.76	12.22	0.63	
15	2.36	33.49	25.00	0.50	1.73	10.15	0.63	
16	2.83	30.00	27.47	0.50	1.75	12.24	0.63	
17	2.77	30.00	25.11	0.64	1.76	11.65	0.62	
18	1.82	30.00	25.01	0.50	1.69	6.62	0.59	
19	2.01	43.27	25.00	0.50	1.71	7.97	0.58	
20	1.71	43.94	25.00	0.50	1.69	6.88	0.56	
21	1.51	50.63	25.00	0.50	1.69	6.98	0.55	
22	1.38	52.14	25.00	0.50	1.69	6.96	0.55	
23	1.00	55.37	25.00	0.50	1.68	7.17	0.55	
24	1.00	55.13	25.00	0.50	1.68	7.12	0.55	
25	1.21	52.75	25.00	0.50	1.68	6.81	0.55	
26	1.07	54.53	25.00	0.50	1.68	7.04	0.55	
27	1.20	53.35	25.00	0.50	1.68	6.92	0.55	
28	1.08	54.99	25.00	0.50	1.68	7.15	0.55	
29	1.00	57.51	29.21	0.50	1.69	8.20	0.54	

## 5. MATERIAL BALANCE

Taking the annual requirement of the plant from table 4, the average of the years 2011 and 2012, equal to 86.2 ton/yr. It is:

$$\begin{aligned}\text{CMC} &= (86.2\text{ton/yr} * 1000\text{kg/ton}) / (300\text{days/yr} * 8\text{hrs/day}) \\ &= \underline{35.92\text{kg/hr}}\end{aligned}$$

Averagely the yield of cellulose to CMC is 100%

Therefore,

$$\begin{aligned}\text{Cellulose used} &= 35.92/1 \\ &= \underline{35.92\text{kg/hr}}\end{aligned}$$

During pulping, lignin, hemicelluloses and small amount of cellulose was dissolved and removed by filtration. The yield of the depithed sugarcane bagasse was 32.5%. So the amount of depithed sugar cane bagasse is:

$$\begin{aligned}\text{Depithed sugar cane bagasse used} &= (35.92 \text{ kg/hr})/0.322 \\ &= \underline{110.5 \text{ kg/hr}}\end{aligned}$$

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 265.23 ton of depithed sugar cane bagasse.

Ideally about 80% of the total pith (which contains small amount of trace cellulose) was removed by screening with 1mm screen.

From 100gm sample the following sieve analysis has been done:

Table 18: Sieve analysis values for the pith removal amount

Amount	Passed	Retained on
46 gm	-----	4.5 mm
12 gm	4.5	2.5 mm
8 gm	2.5 mm	1.8 mm
8.7 gm	1.8 mm	1.4 mm
9 gm	1.4 mm	1 mm
13.3 gm	1 mm	500 $\mu$ m
3.3 gm	500 $\mu$ m	pan

This is to mean that about 16.6% of the material is removed before pulping. This is a pith cell, mainly contains lignin.

$$\begin{aligned} \text{Raw bagasse used} &= (110.5\text{kg/hr})/0.834 \\ &= \underline{132.5\text{kg/hr}} \end{aligned}$$

Annually, 318 ton/yr raw bagasse will be used.

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 19: Amount of inputs and outputs

Unit	Material	Inputs	Outputs
Delignify unit	Depithed bagasse	110.5 kg/hr	4699.123 kg/hr (4.754 m <sup>3</sup> /hr)
	NaOH solution	339.898 kg/hr	
	Water	4248.725 liter/hr	
Washer	Delignified solution	4699.123 kg/hr (4.754m <sup>3</sup> /hr)	Wet cellulose (79.82 kg/hr)...55% moist
	Wash water	1380 kg/hr (1.38 m <sup>3</sup> /hr)	Removed solution (5999.3 kg/hr)
Dryer	Wet cellulose	79.82 kg/hr	Dried cellulose (35.92kg/hr) Water (43.9 kg/hr)
		70.51 Lit/hr	
Basification and Etherification unit	Dried cellulose	35.92 kg/hr	710.92 kg/hr
	25% NaOH	156.160 liter	
	Chloroacetic acid	19.52 kg/hr	
	Isopropanol	585 liter/hr	
Filtration	Reactor outputs	710.92 kg/hr	Isopropanol and unreacteds (306.54kg/hr)
			Wet mixtures (404.38 kg/hr)
Washing	Wet mixture	404.38 kg/hr	Wet CMC (89.8kg/hr, 40%)
	Ethanol	123.21 kg/hr	Ethanol and by-products (437.79kg/hr)
Drying	Wet CMC	89.8 kg/hr	Dried CMC 35.92 kg/hr
			Ethanol 53.88 kg/hr

## 6. 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 [18].

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 [16].

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 [16].

### 6.1. Plant Parameters

- ✓ Capacity, the plant is envisaged to produce 86.2 ton/year.
- ✓ Number of shifts /day is 3
- ✓ 300 working days/year
- ✓ Operating 8 hrs/shift

## 6.1. 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 [16].

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

Table 20: Cost of raw materials

No	Raw material	Unit	Annual consumption	Cost (Birr)
1	Depithed Sugarcane bagasse	Ton	265.23	
2	Cellulose	Ton	86.2	
3	Sodium hydroxide	Ton	351.35	4,918,900
4	Mono chloroacetic acid	Ton	43.1	23,791,200
5	Isopropanol	Ton	135.5	39,650,000
6	Ethanol	Ton	163	6,197,720
7	Hydrochloric acid	Ton	102.6	6,897,000
			<b>Total</b>	<b>81,454,820</b>

## 6.2. 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 21: Cost of equipment

Items	Quantity	Price, birr
Vibratory screen	1	299200
Reactor (delignifier)	1	255000
Washing tank	2	323000
Filter press	1	691900
Dryer	2	1094800
Pulveriser-1	1	319600
Pulveriser -2	1	202000
Reactor	1	499800
Mixing tank (neutralizer)	1	367200
<b>Total</b>		<b>4052500</b>

## 6.3. Estimation of Fixed Capital Investment

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 [16].

Table 22: Estimation of fixed capital investment

Item		Assu- med % of FCI	Description/ factor	Total cost, birr
I. Direct costs	A. Material + labor			
	a. Purchased Equipment	23*FCI	0.23*FCI	4052500
	b. Installation	8.3*FCI	0.083*FCI	1462000
	c. Instrumentation	6.4*FCI	0.064*FCI	1127600
	d. Piping	7.3*FCI	0.073*FCI	1286000
	e. Electrical	4.6*FCI	0.046*FCI	810500
	B. Building + auxiliary	4.6*FCI	0.046*FCI	810500
	C. Yard improvements	1.8*FCI	0.018*FCI	317000
	D. Service facilities	13.8*FCI	0.138*FCI	2431500
	E. Land	0.9*FCI	0.009*FCI	158500
	Total direct cost			<b>12456100</b>
II. Indirect cost	A. Engineering & supervision	9.2*FCI	0.092*FCI	1621000
	B. Construction	11*FCI	0.11*FCI	1938000
	C. contractors fee	1.8*FCI	0.018*FCI	317000
	D. Contingency	7.3*FCI	0.073*FCI	1286000
	Total indirect cost			<b>3876000</b>
III. Fixed capital investment	Direct + Indirect			<b>16332100</b>
IV. Working capital	0.15 * fixed capital investment			<b>2449800</b>
Total capital investment	Fixed capital investment + Working capital			<b>18781900</b>

## 6.4. Estimation of Total Product Cost

Table 23: Estimation of total product cost

Item	Description/factor	Total cost, birr	
I. Manufacturing cost	A. Fixed charges		
	a. Depreciation	0.1*machinery +0.02*building.	421460
	b. Local taxes	0.02*FCI	326600
	c. Insurance	0.006* FCI	98000
	Total fixed charges	a + b + c	<b>846060</b>
	B. Direct production cost		
	Total product cost	fixed charge/0.15	5640400
	a. Raw materials	Already estimated	81,454,820
	b. Utilities	0.15*TPC	846060
	c. Operating labor	0.1*TPC	564040
	d. Supervisory	0.1*OL	56404
	e. Maintenance	0.05*FCI	816600
	f. Operating supplies	0.005*FCI	81660
	g. Lab charges	0.12*OL	67680
	Total of B		<b>83,887,264</b>
	C. Plant overheads	0.1*TPC	564040
	Total manufacturing cost	A+B+C	<b>85297364</b>
II. General expenses	a. Administrative cost	0.04* TPC	225616
	b. Distribution	0.1*TPC	564040
	c. R & D	0.05*TPC	282020
	d. Interest	0.05*TCI	939000
	Total general expenses	a + b + c + d	<b>2010676</b>
Total product cost	I + II	<b>87308040</b>	
Total product cost/kg CMC	$\frac{87308040}{86200} = 1013 \text{ birr/kg}$		

## 6.5. 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 profitability 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=1200 birr

Expecting all produced CMC will be sold

Total income =1200 birr/kg\*86200kg

Total income = 103440000 birr

Gross income = total income-total product cost

Gross income = 103440000 - 87308040= 16131960 birr

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

Taxes = 0.35\* 16131960 birr = 5646186birr

Net profit = gross income – tax

Net profit = 16131960 -5646186birr = 10485774birr

Rate of return:

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

$$\text{ROR} = \frac{10485774}{18781900} * 100$$

$$\text{ROR} = \underline{\underline{55.8\%}}$$

Payout period:

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

$$\text{Pay out period} = \frac{16332100}{10485774 + 421460}$$

$$\text{Payout period} = \underline{\underline{1.5 \text{ years}}}$$

## 6. CONCLUSION

In this work, from optimization, best alternative conditions were obtained to achieve high DS and viscosity by using design expert software. About 29 optimized results obtained from the raw data and one particular result was selected to be carried out. The optimal preparation conditions of CMC was etherification temperature of 30°C, etherification time of 2.95 hours, dosage of sodium hydroxide 25%w/v and dosage of sodium chloroacetate 0.5w/w. Under these particular conditions the obtained CMC with viscosity about 14.63 cp and DS value of 1.79 was achieved.

Moreover, in the process of preparation of CMC, what was observed is that, the order of factors influencing the reaction was: etherification temperature >etherification time> dosage of sodium hydroxide > dosage of chloroacetate.

In addition, regarding the effect of operating conditions on the final product the following two points are concluded.

- ✓ The values of degree of substitution and viscosity were slightly increasing by increasing the etherifying agents (etherification temperature, etherification time, dosage of sodium hydroxide and dosage of sodium chloroacetate) within the range studied.
- ✓ The apparent viscosity increase with increasing degree of substitution.

Beside the experimental design, the cost analysis has been done to know its profitability. The rate of return and payback period are 55.8% and 1.5 years, respectively. This is to mean that 55.8 % of the total capital investment will be returned within one year and it will take only 1.5 years to return the whole capital investment cost.

Generally, from the results, it is concluded that cellulose from sugar cane bagasse in the process of organic solvent system can be used for the preparation of carboxymethyl cellulose of medium degree of substitution, with a good profitability.

## 7. RECOMMENDATION

In the laboratory experiments, I identified many ideas which need consideration for the result to be very refined.

1. In delignification of sugar cane bagasse, the final cellulose obtained was affected by many parameters. It would be better if all the parameters are studied carefully and the conditions at which a good cellulose yield obtained is determined. At higher values of sodium hydroxide concentration the cellulose itself will be degraded and at a low value the efficiency of the process to remove the lignin will be reduced. Again the maximum and minimum temperature values have a similar effect on the cellulose yield. So that, an optimum value is required.
2. In the basification reaction of carboxymethyl cellulose production process, the parameters, basification time and its temperature shall be varied and the optimum result should be selected to have a better degree of substitution value. In this thesis work the time for the basification reaction and its temperature were fixed at specific values (basification time and temperature of 1hr and 25°C, respectively). This was because studying more than four parameters is very difficult task, especially on the laboratory work. But, they can be investigated separately.
3. The production of carboxymethyl cellulose needs a medium under which the reaction is taking place. The medium may be an aqueous solvent or organic solvents. These solvents have an effect on the reaction. The best solvent should be selected on the basis of its activity towards the reaction, its cost and so on. It would be better if various solvents are tested and each other are compared from different angles.

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## Annex-1 Percent Contributions

Table: Percent contribution of the factors and their interaction to degree of substitution

Require	Term	Stdized. effect	Sum of squares	% contribution
Model	A-Time	0.0488	0.0095	4.2987
Model	B-Temp.	0.1338	0.0716	32.3573
Model	C-NaOH conc.	0.0088	0.0003	0.1385
Model	D-MCAA conc.	-0.0038	0.0001	0.0254
Model	AB	-0.0313	0.0039	1.7664
Model	AC	0.0088	0.0003	0.1385
Model	AD	-0.0488	0.0095	4.2987
Model	BC	0.1338	0.0716	32.3573
Model	BD	0.0163	0.0011	0.4776
Model	CD	0.0463	0.0086	3.8691
Model	ABC	0.0338	0.0046	2.0603
Model	ABD	0.0013	0.0000	0.0028
Model	ACD	0.0263	0.0028	1.2464
Model	BCD	-0.0388	0.0060	2.7160
Model	ABCD	-0.0888	0.0315	14.2470

Table: Percent contribution of the factors and their interaction to viscosity

Require	Term	Stdized. effect	Sum of squares	% contribution
Model	A-Time	2.08	17.37	1.57
Model	B-Temp.	8.05	259.13	23.36
Model	C-NaOH conc.	3.92	61.58	5.55
Model	D-MCAA conc.	-3.84	58.94	5.31
Model	AB	-3.32	44.12	3.98
Model	AC	-0.29	0.33	0.03
Model	AD	-4.12	68.02	6.13
Model	BC	9.16	335.90	30.28
Model	BD	1.33	7.09	0.64
Model	CD	2.23	19.91	1.80
Model	ABC	4.31	74.26	6.69
Model	ABD	1.68	11.31	1.02
Model	ACD	-0.28	0.31	0.03
Model	BCD	-2.54	25.78	2.32
Model	ABCD	-5.59	125.16	11.28

## Annex-2 Half Normal Probability Plots

Design-Expert® Software  
Ds

Shapiro-Wilk test  
W-value = 0.960  
p-value = 0.811

A: Time  
B: Temp.  
C: NaOH conc.  
D: MCAA conc.

■ Positive Effects  
■ Negative Effects

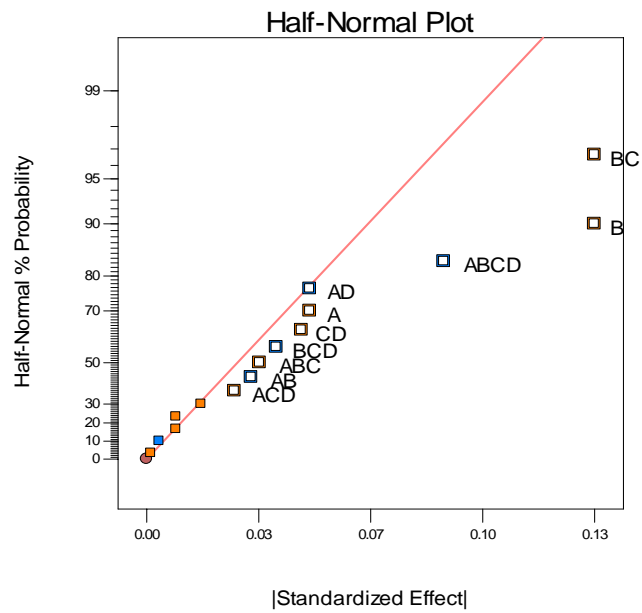


Figure: Half-normal probability versus effect for DS

Design-Expert® Software  
Viscosity

A: Time  
B: Temp.  
C: NaOH conc.  
D: MCAA conc.

■ Positive Effects  
■ Negative Effects

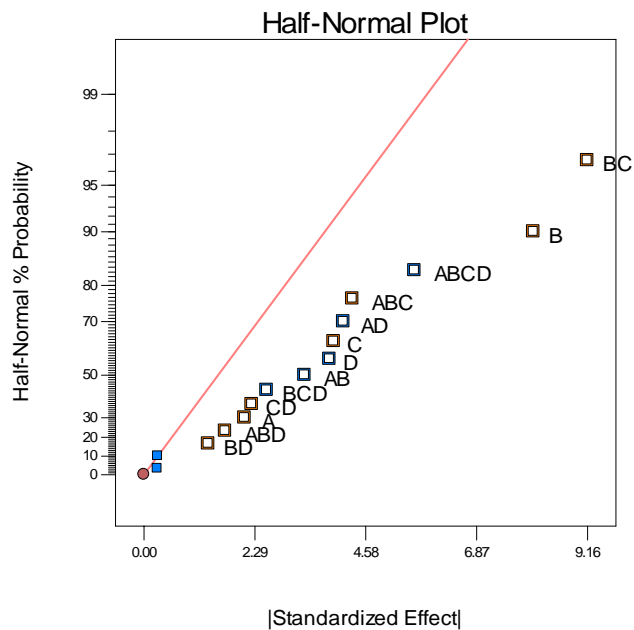


Figure: Half-normal probability versus effect for viscosity

### Annex-3 Statistical Information

Table: Statistical information for the DS

Std. Dev.	0.02		R-Squared	0.99
Mean	1.71		Adj R-Squared	0.98
C.V. %	1.09		Pred R-Squared	0.92
PRESS	0.02		Adeq Precision	25.76

Table: Statistical information for the viscosity

Std. Dev.	0.565		R-Squared	0.999
Mean	7.874		Adj R-Squared	0.996
C.V. %	7.176		Pred R-Squared	0.963
PRESS	40.868		Adeq Precision	46.951

