

**IZMIR KATIP CELEBI UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE AND  
ENGINEERING**

**USING ALCOHOL AS A CARRIER IN PRODUCING POLYANIONIC  
CELLULOSE (PAC) POLYMER FROM SOLID TEXTILE WASTE**

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**TEKSTİL ATIKLARINDAN, TAŞIYICI OLARAK ALKOL KULLANILARAK  
SAF TİP POLİANYONİK SELÜLOZ POLİMERİNİN ÜRETİMİ**

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*To my family,*



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I would like to thank my advisor, Assoc. Prof. Dr. Şerafettin Demić, for his healthy degree of optimisms. He answered all my questions in detail with patience and he never hesitated to spend his valuable time to help me.

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## ABBREVIATIONS

<b>AGU</b>	: D-anhydroglucopyranose unit
<b>API</b>	: American Petroleum Institute
<b>CMC</b>	: Carboxymethyl cellulose
<b>DP</b>	: Degree of polymerization
<b>DS</b>	: Degree of Substitution
<b>MCA</b>	: Monochloroacetic acid
<b>MW</b>	: Molecular Weight
<b>NaCl</b>	: Sodium chloride
<b>NaMCA</b>	: Sodium salt of monochloroacetic acid
<b>NaOH</b>	: Sodium hydroxide
<b>PAC</b>	: Polyanionic cellulose
<b>PAC LV</b>	: Low viscosity grade polyanionic cellulose
<b>PAC HV</b>	: High viscosity grade polyanionic cellulose
<b>SEKA</b>	: Turkish Cellulose and Paper Factories
<b>TP</b>	: Turkish Petroleum
<b>TÜBİTAK</b>	: The Scientific and Technological Research Council of Turkey



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## **USING ALCOHOL AS A CARRIER IN PRODUCING POLYANIONIC CELLULOSE (PAC) POLYMER FROM SOLID TEXTILE WASTE**

### **SUMMARY**

Cellulose is the most abundant organic polymer on earth. It is naturally regenerated by forests and cotton plantations with a speed of 10 billion metric tons per year regularly. Not only its natural reproduction makes it ecologically beneficial but also its biological degradability makes cellulose an ‘eco-friendly material’. Applications of cellulose is limited due to its insolubility in water. Contrarily, its water-soluble derivatives, especially cellulose ethers, are found in nearly all the products we are using in our daily life.

Although cellulose is the main raw material for producing cellulose ethers, its commercial production stopped with the shutdown of ‘Turkish Cellulose and Paper Factories’ (SEKA) in 2006. Turkish cellulose ether producers are forced to import all the cellulose they are using in their production. In 2009, 425 thousand tons of household textiles waste and 458.5 thousand tons of industrial textile waste was generated in Turkey. Most of these wastes are made of cotton yarn which has 90% cellulose content.

This study aimed to use this type of textile waste as raw material for the production of polyanionic cellulose polymer (PAC), so that they would be returned back to the economy with higher values. This study is carried out as a project by The Scientific and Technological Research Council of Turkey (TÜBİTAK) and Ugur Seluloz Kimya A.S. under the 1507 - SME RDI (Research, Development & Innovation) Grant Programme. In this waste recovery process, solid textile waste is used as raw material and the alcoholic (ethyl alcohol) medium is used to increase the quality of the PAC products in order to meet the criteria of PAC LV (low viscosity) and PAC HV (high viscosity) standards introduced by American Petroleum Institute (API).

The most important outcome of this study was to produce PAC-LV and PAC-HV polymers in API standards from textile waste without using any imported cellulose. This production method not only prevents the import but also enables the use of natural wastes so that the added value of the product increases. Quality of synthesized products (PAC-LV and PAC-HV) are verified by Turkish Petroleum (TP) Research Laboratories.



## TEKSTİL ATIKLARINDAN, TAŞIYICI OLARAK ALKOL KULLANILARAK SAF TİP POLİANYONİK SELÜLOZ POLİMERİNİN ÜRETİMİ

### ÖZET

Dünya üzerindeki en yaygın organik polimer olan selüloz, bitkiler ve ağaçlar tarafından her yıl düzenli olarak yenilenmektedir. Selülozun ekolojik bir ürün olmasının sağlayan sadece doğal yöntemlerle yenilenebilmesi değil, aynı zamanda doğal olarak çözünebilmesidir de. Her ne kadar selüloz uygulamaları suda çözünemediğinden dolayı sınırlı olsa da, selüloz türevleri, özellikle de selüloz eterleri nitelik ve nicelik bakımından geniş bir kullanım alanına sahiptir.

Selüloz, her ne kadar selüloz türevlerinin üretilmesi için ana hammadde olsa da, Türkiye Selüloz ve Kağıt Fabrikaları A.Ş.'nin (SEKA) 2006'da faaliyetlerine son vermesiyle ülkemizde linter selüloz üretimi durmuştur. Yerli selüloz eteri üreticileri bu tarihten sonra ancak selüloz ithal ederek üretimlerine devam etmek zorunda kalmışlardır. 2009 yılında ülkemizde 425 bin ton evsel tekstil atığı, 458 bin 500 ton da üretime dayalı tekstil atığı ortaya çıkmıştır. Dünyanın 7. büyük pamuk üreticisi konumundaki ülkemizde oluşan bu atıkların çoğu %90 oranında selüloz ihtiva eden pamuklu atıklardan oluşmaktadır.

Bu çalışmada geri dönüştürülemeyen tekstil atıklarının, taşıyıcı olarak alkol (etil alkol, izopropil alkol) kullanılarak saf tip polianyonik selüloz (PAC) polimerine dönüştürülmesi, bu sayede ekonomiye geri kazandırılması ve aynı zamanda ithal selülozla üretilen polianyonik selüloz (PAC) polimerine göre daha düşük maliyetle elde edilmesi amaçlanmıştır. Bu araştırma Türkiye Bilimsel ve Teknolojik Araştırma Kurumu, TÜBİTAK'tan alınan destek ile Uğur Selüloz Kimya A.Ş. tarafından 1507 - KOBİ Ar-Ge Başlangıç Destek Programı kapsamında gerçekleştirilmiştir. İthal selüloz yerine tekstil atığının kullanıldığı bu geri kazanım işleminde, eterleşme kalitesi reaksiyonda alkol (etil alkol) kullanılarak artırılmıştır. Böylece mevcut yöntemlerle ithal selüloz kullanılarak üretilen polianyonik selüloz (PAC) polimerinin hem düşük hem de yüksek viskoziteli tipleri Amerikan Petrol Enstitüsü'nün (API) belirlediği standartlarda üretilmiştir.

Bu çalışmanın en önemli çıktısı polianyonik selüloz (PAC) polimerinin hem düşük hem de yüksek viskoziteli tipleri olan PAC-LV ve PAC-HV polimerlerinin, ithal selüloz kullanılmadan, tekstil atıklarından üretilmesine olanak sağlayan bir üretim yönteminin geliştirilmesidir. Bu yöntemin uygulanmasıyla hem cari açık azalacak hem de ürünün katma değeri artacaktır. Araştırma kapsamında elde edilen PAC-LV ve PAC-HV numuneleri, Türkiye Petrolleri Anonim Ortaklığı (TPAO) Araştırma Laboratuvarı'na gönderilerek API standartlarına uygunluğu bağımsız laboratuvar tarafından test edilerek onaylanmıştır.



## 1. INTRODUCTION

Cellulose, the most abundant organic polymer on earth, is an important structural component of the primary cell wall of green plants. Long before its discovery in 1838 by the French chemist Payen, it started to serve mankind as an indispensable material for clothing and housing. Cellulose has been a very special industrial raw material due to two reasons. It is naturally regenerated by forests and cotton plantations with a speed of  $10^{12}$  metric tons per year regularly. Plants contain approximately 33% cellulose whereas wood contains around 50 per cent and cotton contains 90%. Not only its natural reproduction makes it ecologically beneficial but also its biological degradability makes cellulose an 'eco-friendly material'. As we consider the fact that  $10^{11}$  to  $10^{12}$  tons of cellulose-based materials are produced annually, its ability to decompose in the open gains vital importance in protection and sustainability of our environment and, thus, mother earth (Adden, 2010; Krässig et al., 2012).

Humankind is familiar to this glucose polymer not only through textiles and paper, but also through an increasing variety of applications. Although the application of cellulose is limited due to its insolubility in water, its water-soluble derivatives, especially cellulose ethers, are found in nearly all the products we are using in our daily life. They are used as anti-redeposition agent in detergents, as thickening agent in toothpaste, yoghurt and paints, as adhesive and retardant in glues, as stabilizer in ice-cream, as strengthener in paper and textile industry, as binder in drilling fluids, as film formers, and drug delivery pharmaceuticals, to name just a few. Its amount never exceeds 2 %, but this small level is vital for the properties of the product (Adden, 2010; Thielking & Schmidt, 2006)

Renewable and biodegradable modified cellulose, meeting environmental requirements, is a great substitute for petroleum-based polymers, which fails to meet these requirements in today's world. The diversity and variety of modified cellulose applications are based on the easiness of controlling its physiochemical properties, such as the water solubility, thickening ability or gelation behavior. These properties

are determined by the modification process of the cellulose. Since cellulose is a natural product, correlation between its modification and properties of the final product is an important area of interest in order to analyze and increase the applications of this ‘eco-friendly material’ (Adden, 2010; D Klemm, Philipp, Heinze, Heinze, & Wagenknecht, 1998b).

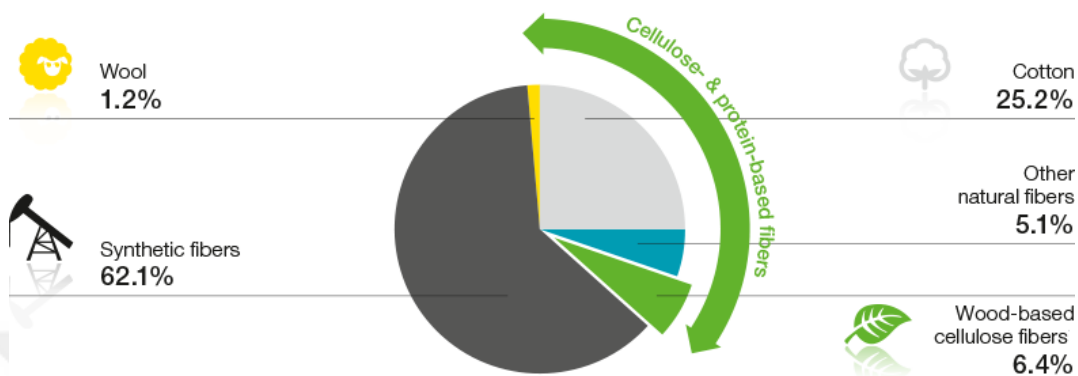
McGraw-Hill Dictionary of Scientific & Technical Terms defines ‘cellulose fiber’ as “any fiber based on esters or ethers of cellulose” (“cellulose fiber. (n.d.),” 2003). Fibers are classified into two groups; natural and man-made (Table 1.1). Among the natural fibers, natural cellulose fibers are the ones derived from the original source of plant (vegetable and wood) without chemical modification. On the other hand, man-made cellulose fibers are regenerated from natural cellulose by chemical modification (semi-synthetic) (“Cellulose fiber,” n.d.).

**Table 1.1:** Types of fibers

Natural			Man-Made			
Plant*	Animal	Mineral	Regenerated	Semi-synthetic*	Synthetic	
					Mineral	Polymer
Abacá	Alpaca	Asbestos	Artificial silk	Acetate	Glass	Acrylic
Bagasse	Angora			Diacetate	Carbon (Tenax)	Aramid (Twaron, Kevlar, Technora, Nomex)
Bamboo	Byssus			Lyocell		
Coir	Camel			Modal	Basalt	
Cotton	Cashmere			Rayon	Metallic	
Fique	Catgut			Triacetate		
Flax	Chiengora					Microfiber
Linen	Guanaco					Modacrylic
Hemp	Human					Nylon
Jute	Llama					Olefin
Kapok	Mohair					Polyester
Kenaf	Pashmina					Polyethylene (Dyneema, Spectra)
Piña	Qiviut					
Pine	Rabbit					
Raffia	Silk					Spandex
Ramie	Sinew					Vinylon
Rattan	Spider					Vinyon
Sisal	Wool					Zylon
Wood	Vicuña					
	Yak					

\*Cellulose fibers

Global fiber market consumption was at about 94.0 million tons in 2015. Oil-based synthetic fibers had the biggest share with 62.1%. Cellulosic and protein-based fibers consist of cotton (around 25.2%), wood-based cellulose fibers (around 6.4%), other natural fibers (around 1.5%) and wool (around 1.2%) (“Lenzing Group Annual Report,” 2015).



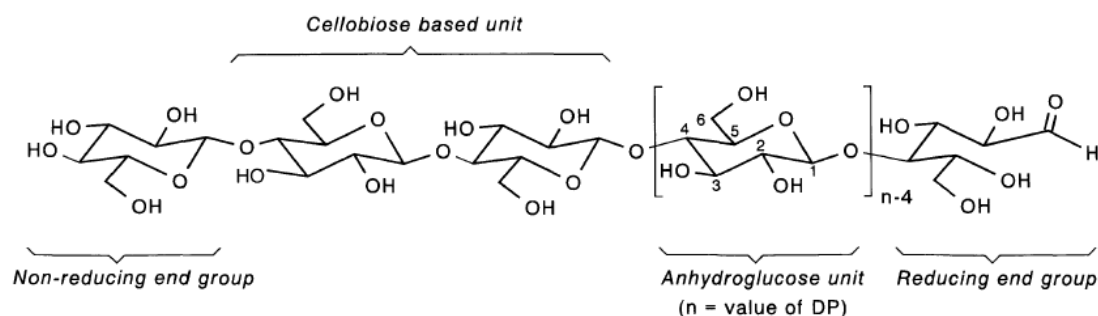
**Figure 1.1:** Global fiber consumption in 2015

Cellulose structure, modification opportunities and economical aspects of the cellulose ethers are briefly described in the following chapters 1.1 to 1.4.

## 1.1 Cellulose Structure

### 1.1.1 Molecular Structure of Cellulose

Cellulose is an organic compound with the formula  $(C_6H_{10}O_5)_n$ , a polysaccharide consisting of a linear chain of several hundred to over ten thousand  $\beta(1\rightarrow4)$  linked D-glucose units. Cellulose is the combination of “cellobios” units, side by side. Every “cellobiose” unit is made of two “D-anhydroglucopyranose” units (AGU) those bonded to each other with  $\beta(1\rightarrow4)$  glycosidic bond. This linkage motif contrasts with that for  $\alpha(1\rightarrow4)$ -glycosidic bonds present in starch, glycogen, and other carbohydrates (D Klemm, Philipp, Heinze, Heinze, & Wagenknecht, 1998a).



**Figure 1.2:** Molecular structure of cellulose

Cellulose has no taste, is odorless, is hydrophilic, is insoluble in water and most organic solvents, is chiral and is biodegradable. It can be broken down chemically into its glucose units by treating it with concentrated acids at high temperature. In the solid state, AGU units are rotated by 180° with respect to each other due to the constraints of  $\beta$ -linkage (Granström, 2009).

The chain length of the cellulose polymer depends on its origin and the method of isolation. Degree of polymerization (DP) of various cellulose types are shown in Table 1.2 (Krässig et al., 2012).

**Table 1.2:** Degree of polymerization of celluloses of different origins

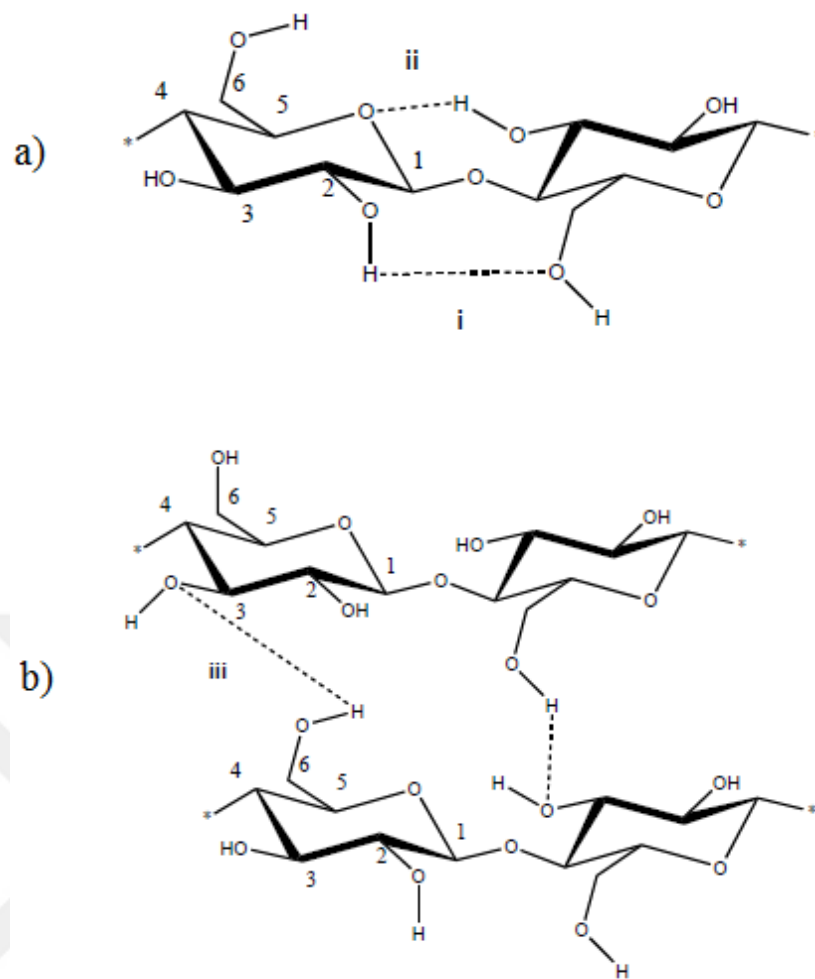
Type of cellulose	DP
Cotton, raw	7,000
Cotton, raw (according to Russian work)	14,000
Cotton, purified	1,500 - 300
Cotton linters	6,500
Flax	8,000
Ramie	6,500
$\alpha$ -Cellulose (isolated from wood fibers)	1,100 - 800
Spruce, pulped	3,300
Beech, pulped	3,050
Aspen	2,500
Fir	2,500
Bacterial cellulose	2,700
Acetobacter cellulose	600

### 1.1.2 Supramolecular structure of cellulose

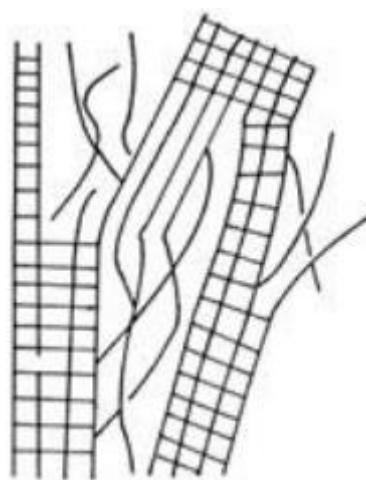
Cellulose chains tend to aggregate and form ordered structures. This behavior originates from the OH groups by forming hydrogen bonds in the cellulose molecule. This bonding interaction both occurs between suitably positioned OH groups in the same molecule (intermolecular, Figure 1.3a, i and ii) and between neighboring cellulose chains (intermolecular) via their C3-OH and C6-OH groups (Figure 1.3b, iii) (Granström, 2009).

The crystalline order of cellulose supramolecular structure suggests the uniform distribution of cellulose chains parallel to each other. On the contrary, there are ‘less ordered’ regions of cellulose polymer called “amorphous regions”. This two phase model, known as ‘fringed fibril model’, describes the heterogeneous accessibility of the cellulose. Figure 1.4 exhibits this model, in which the strains illustrates the amorphous regions and the squares crystalline (Kihlman, 2012).





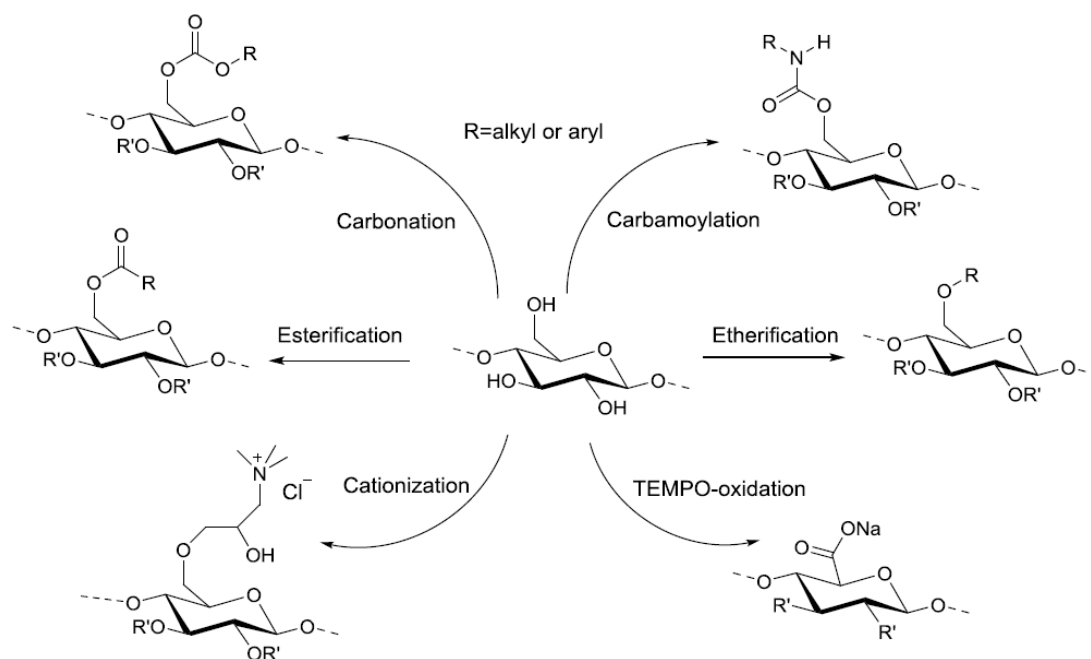
**Figure 1.3:** Cellulose structures showing a) the intramolecular hydrogen bonding between C2-OH and C6-OH (i), and C3-OH with endocyclic oxygen (ii); and b) the intermolecular hydrogen bonding between C3-OH and C6-OH (iii).



**Figure 1.4:** Schematic representation of the fringed fibril model of cellulose supramolecule

## 1.2 Cellulose Modification

The idea of chemical modification of cellulose is to introduce functional groups in the cellulose backbone. It is usually achieved by substituting the protons in the hydroxyl groups of cellulose (O-2, O-3, and O-6 (Fig. 1.3)) to a varying extent. This substitution can actualize in the forms of esterification, etherification, carbamoylation, carbonation, cationization, oxidation, intermolecular crosslinking reactions, or macrocellulosic free radical reactions (Labafzadeh, 2015; Varshney & Naithani, 2011).



**Figure 1.5:** Various types of cellulose modification

Modification takes place either homogeneously or heterogeneously. Homogeneous modification can only be achieved after complete dissolution of cellulose in order to modify individualized cellulose chains uniformly. On the contrary, heterogeneous modification can be achieved where cellulose stays in solid or swollen state during the reaction. Since we are going to focus on carboxymethyl cellulose, a cellulose ether, in this study it is important to understand the reasons lying behind the preference of heterogeneous modification over homogeneous reaction in the synthesis of this cellulose derivative.

Poor solubility property of cellulose polymer requires the use of complicated, expensive, and toxic solvents for uniform and complete dissolution. Commercial production of cellulose derivatives generally involves heterogeneous reaction unless

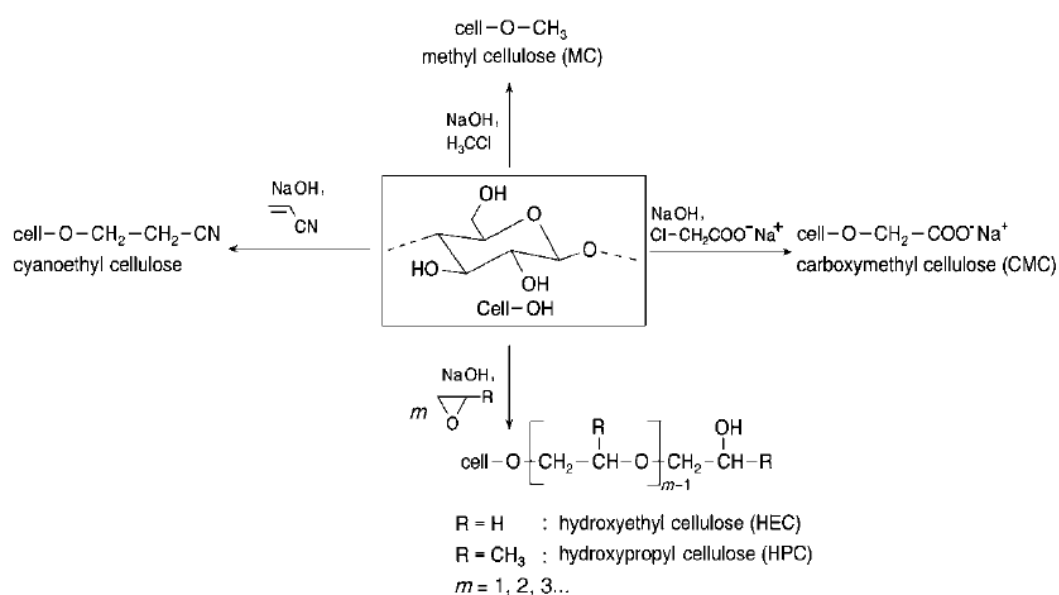
higher degrees of substitution is desired. The choice of homogeneous modification eases the purification, limits the depolymerization and most importantly prevents from using expensive and toxic solvents (Labafzadeh, 2015). Thus, heterogeneous reaction condition is highly preferred in the commercial production of cellulose esters and ethers due to the cost lowering reasons stated above.

### 1.3 Cellulose Ethers

Cellulose ethers are nontoxic, water soluble and chemically stable organic polymers. They are the most common chemical compound in organic nature. Their extensive utilization in the worldwide market originates from their availability, cost efficiency, easy handling and numerous variety of types. Among the various synthesis routes of cellulose ethers, two types of reactions are used commercially (Granström, 2009; D Klemm, Philipp, Heinze, Heinze, & Wagenknecht, 1998c; Labafzadeh, 2015; Thielking & Schmidt, 2006);

- a) reactions that consume sodium hydroxide solution (Williamson ether synthesis)
- b) alkali (sodium hydroxide) catalyzed additions of epoxide (alkoxylation)

The synthesis and examples of most common cellulose ethers are illustrated in Figure 1.6 (Dieter Klemm, Heublein, Fink, & Bohn, 2005).



**Figure 1.6:** The synthesis and examples of cellulose ethers

More than half million tons of cellulose ether is commercially produced each year for various applications (Granström, 2009). Table 1.3 summarizes industrially and commercially important cellulose ethers and their application sectors (Adden, 2010).

**Table 1.3:** Major fields of application for common industrial cellulose ethers

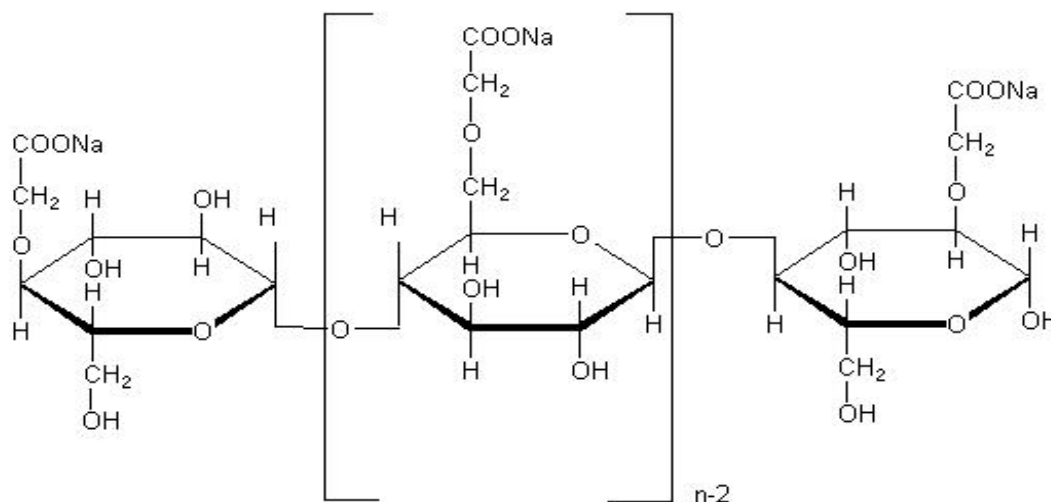
Carboxymethyl cellulose	methyl cellulose, hydroxyalkyl methyl cellulose	hydroxyethyl cellulose	hydroxypropyl cellulose
paper	tile adhesives	latex paints	adhesives
detergents	plasters/ renders	adhesives	Ceramics
oil and gas drilling	pharma/ cosmetics	building materials	cosmetics
pharma	joint compounds	cosmetics	encapsulation
cosmetics	wallpaper paste	oil and gas drilling	Food
textile industry	polymerization	agriculture	household goods
food	food	paper	printing inks
coatings	latex paints	synthetic resins	polymerization
encapsulation	cement extrusion	textile industry	Films

Cellulose ethers can be sorted according to their economic significance, thus global production. In terms of sales volume carboxymethyl cellulose (CMC) is the largest product group (approx. 300,000 tons per annum) among cellulose ethers. Methyl cellulose (approx. 150,000 t/a), hydroxyethyl cellulose (approx. 60,000 t/a) and hydroxypropyl cellulose (less than 10,000 t/a) are the other cellulose ethers following CMC respectively (Granström, 2009; Thielking & Schmidt, 2006).

## 1.4 Carboxymethyl cellulose (CMC)

### 1.4.1 Structure

Carboxymethyl cellulose (CMC) 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. Carboxymethyl cellulose (CMC) was initially synthesized in 1918, and was produced commercially in 1920 at the IG Farbenindustrie AG in Germany. It is produced in a Williamson ether synthesis from alkali cellulose with sodium chloroacetate or with chloroacetic acid itself, which reacts in-situ with caustic soda to form the salts. The polar (organic acid) carboxyl groups render the cellulose soluble and chemically reactive (Heinze & Koschella, 2005a).



**Figure 1.7:** Idealized unit structure of CMC, with Degree of Polymerization= $n$  and Degree of Substitution = 1.0

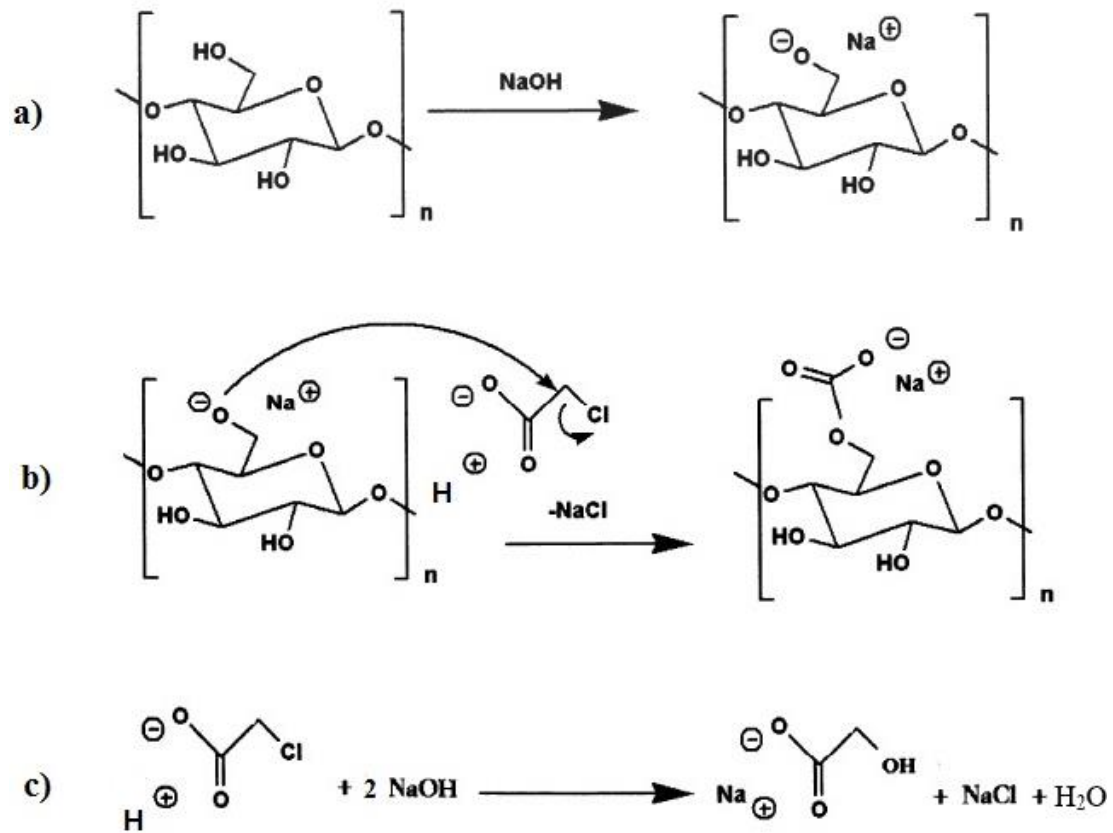
### 1.4.2 Synthesis and Manufacture

The synthesis of carboxymethyl cellulose (CMC) is a two-step process. In the first step CMC is treated with sodium hydroxide (NaOH) at room temperature for alkalization. This activation reaction, in which cellulose becomes accessible and reactive, is generally called ‘mercerization’ (Fig. 1.8a). The second step of carboxymethylation involves addition of monochloroacetic acid (MCA) or its sodium salt (NaMCA) to the reactive and accessible alkali cellulose at 70 °C (Fig. 1.8b). In the meantime, excess NaOH, introduced in the alkalization step, reacts with MCA or NaMCA in a side reaction to give sodium glycolate (sodium hydroxyacetate (HOCH<sub>2</sub>COONa)) and sodium chloride (NaCl) (Fig 1.8c).

The presence of an organic solvent in both alkalization and etherification steps promotes a uniform distribution of NaOH and MCA during the reaction, thus favors more uniform and higher etherification. Short-chain alcohols are used for this promotion as transfer and exchanging agent. Ethanol is the most common organic solvent, used as slurry medium in the processes with high mass fraction of cellulose (Adden, 2010; D Klemm et al., 1998c; Stigsson, Kloow, & Germgård, 2006; Thielking & Schmidt, 2006).

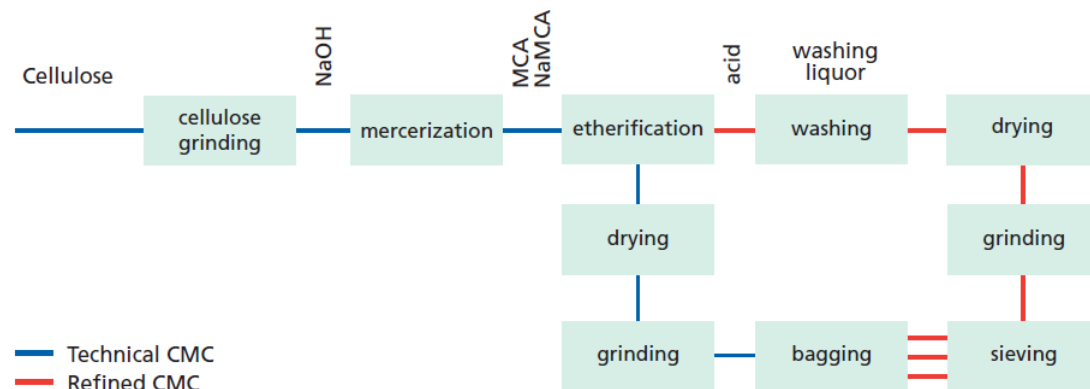
Depending on the required purity, product mixture is washed with alcohol-water mixture, usually with the same alcohol used in the reaction. Since CMC and other salts are soluble in water, washing with alcohol is an unavoidable process to get rid of the by-products. The suspended solid state material, CMC, is separated from the

suspension with various methods such as screening and sieving. Alcohol, used in washing should be regained as much as possible for economic reasons (Majewicz, Erazo-Majewicz, & Podlas, 2002; Thielking & Schmidt, 2006).



**Figure 1.8:** Synthesis of CMC a) alkalization reaction of cellulose b) etherification reaction of alkali cellulose c) side reaction between NaOH and MCA (or NaMCA)

Operational steps in the manufacture of CMC is illustrated in Figure 1.9 (Majewicz et al., 2002).



**Figure 1.9:** Operational steps in the manufacture of CMC

### **1.4.3 Physical Properties**

#### **1.4.3.1 Degree of Substitution (DS)**

The degree of substitution (DS), also known as ‘degree of etherification’, is defined as the average number of carboxymethyl groups introduced per anhydroglucose unit in the cellulose. For example, if 10 anhydroglucose units have 7 carboxymethyl groups; DS of the polymer chain is 0.7. The maximum DS for a CMC polymer chain would be 3.0, since each anhydroglucose unit has 3 functional hydroxide groups available for carboxymethylation, but this is not possible to achieve. DS should be chosen carefully for industrial applications. DS determines some of properties such as solubility, chemical and bacterial resistance, film strength and rheology. Average DS values are between 0.40 - 0.90 for CMC. The water solubility of CMC as the most relevant applicational property depends primarily on the DS due to the fact that DS represents the water soluble carboxymethyl character of CMC apart from its cellulose character which is insoluble in water. Contrarily, the CMCs with lower levels of DS are soluble in aqueous or alkali solutions; the intermediate ranges are soluble in cold water, and the higher DS values indicate increasing solubility in organic solvents. Previous research has shown that products with a lower degree of substitution ( $DS < 0.6$ ) can exhibit good solubility, due to their different substituent distribution along their backbones (Granström, 2009; Heinze & Koschella, 2005a; D Klemm et al., 1998c; Labafzadeh, 2015; Thielking & Schmidt, 2006).

#### **1.4.3.2 Degree of Polymerization (DP)**

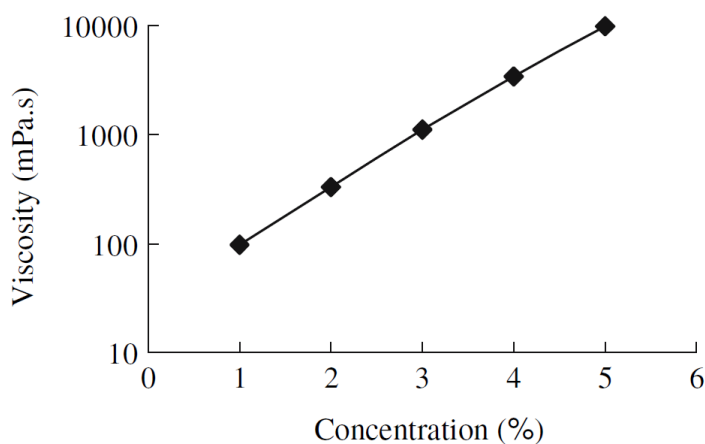
The degree of polymerization (DP) or chain length of CMC is the number of anhydroglucose units, bonded each other by oxygen. Average chain length (DP) and DS determine molecular weight (MW) of the polymer. Generally, cellulose products of high averaged DP have better film strength properties than those of lower averaged DP. Also as DP increases, the viscosity of CMC solution increases. Approximate values (weight averages) for the DP and MW of several viscosity types of CMC are given in Table 1.4 (D Klemm et al., 1998c).

**Table 1.4:** Typical molecular weights for representative viscosity types of CMC (DS = 0.7 in all cases)

Viscosity Type	Degree of Polymerization	Molecular Weight
High	3,200	700,000
Medium	1,100	250,000
Low	400	90,000

### 1.4.3.3 Viscosity

The most important and useful property of CMC is its ability to impart viscosity to its aqueous solutions. It can easily absorb water and has favorable water solubility. Indeed, it is soluble in cold or hot water to become colloidal solution, but insoluble in organic solvents such as methanol, ethanol, acetone, chloroform and benzene. The viscosity of CMC aqueous solution firmly depends on the average DP of cellulose raw material, degradation degree of cellulose during alkalization and etherification process, as well as homogeneity of reaction. Apart from DP of cellulose and the distribution, the solution viscosity is also affected by the solution concentration, pH value, temperature, velocity gradient and substitution degree. The viscosity of a CMC solution increases rapidly with concentration. A fairly good rule of thumb is that viscosity increases eight to ten fold when the concentration is doubled. The viscosity of CMC solutions is both concentration and temperature dependent. As the temperature increases, the viscosity decreases. As the concentration increases, the viscosity increases (Kařstner, Hoffmann, Dořnges, & Hilbig, 1997; Stigsson, Wilson, & Germgärrd, 2004). Figure 1.10 shows the relationship between viscosity and concentration of a CMC solution (Yang & Zhu, 2007).



**Figure 1.10:** Viscosity of CMC solution against concentration in weight percent



#### 1.4.4 Grades and Applications

CMC, main product of carboxymethylation reaction, is acquired with the by-products; sodium glycolate ( $\text{HOCH}_2\text{COONa}$ ) and sodium chloride ( $\text{NaCl}$ ). This unpurified mixture, called ‘technical CMC’, is commercially available. The grades of CMC depending on its purity and typical applications of these grades are exhibited in Table 1.5 (Adden, 2010; Thielking & Schmidt, 2006).

CMC, used in the oil and gas drilling industry as an ingredient of drilling mud, is called polyanionic cellulose (PAC). PAC has the same structure, properties and usage in drilling fluids to CMC. It is considered to be a premium product because it specifically has high degree of carboxymethyl substitution and high purity ( $> 98\%$ ), although some PACs have less purity (Safi, Zarouri, Chabane-Chaouache, Saidi, & Benmounah, 2015).

**Table 1.5:** Carboxymethyl cellulose (CMC) grades and typical applications

Quality	Examples of application areas	Content of CMC [%]	Content of salts [%]
unpurified (technical)	detergents, mining, floating	$< 75$	$> 25$
semi-purified	oil and gas drilling muds	75 - 85	15 - 25
purified	paper coating, textile sizing and printing, ceramic glazing	$> 98$	$< 2$
highly purified (cellulose gum)	food, toothpaste, pharmaceuticals	$> 99.5$	$< 0.5$

CMC is physiologically inert, chemically stable, odorless and tasteless substance which safe for health and environment. The other properties of CMC include high viscosity, non-toxic nature, and hypoallergenic. These unique features enable the use of CMC in many fields as stabilizer, thickener and moisture retention aid in foods, thickener, emulsifier and viscosity control agent in pharmaceuticals and personal care products, viscosity modifier and water retention agent in oil and gas drilling, sizing agent in textile manufacture, strengthener and stabilizer in paper manufacture, binder in adhesives, temporary binder in refractories, stabilizer, thickener and binder in glazes, viscosifier in latex paints, and anti-redeposition agent in detergents (Adden, 2010; Heinze & Koschella, 2005a; D Klemm et al., 1998c; Majewicz et al., 2002; Thielking

& Schmidt, 2006). The detailed lists of specific applications of highly purified CMC and other grades are exhibited in Table 1.6 and Table 1.7 respectively (Hercules Incorporated, 1999).

**Table 1.6:** Applications for purified CMC

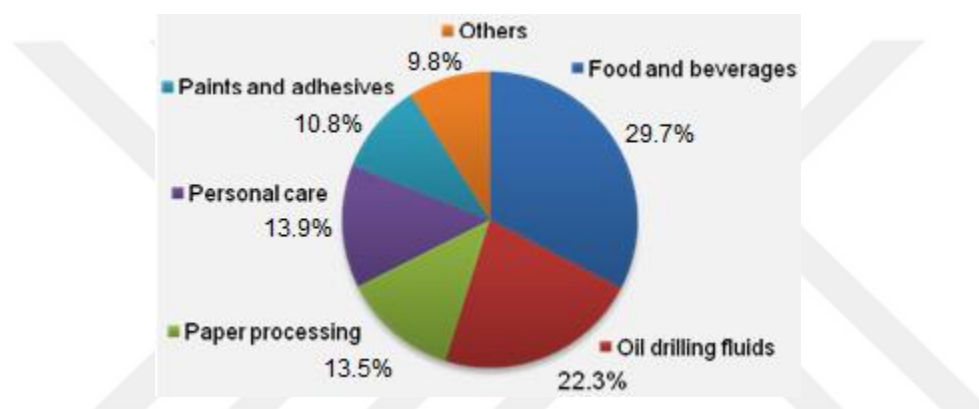
<b>Types of Uses</b>	<b>Specific Applications</b>	<b>Properties Utilized</b>
Cosmetics	Toothpaste	Thickener; flavor stabilizer; suspending aid; binder
	Shampoos; foamed products	Suspending aid; thickener; foam stabilizer; high water-binding
	Creams; lotions	Emulsion stabilizer; film-former; thickener
	Gelled products	Thickener; gelling agent; film-former
	Denture adhesives	Wet tack; long-lasting adhesion
Foods	Frozen desserts; soft-serve	Controls ice crystal growth; improves mouthfeel, body, and texture
	Pet food	Water binder; gravy thickener; extrusion aid; binder of fines
	Protein foods	Retains water; improves mouthfeel
	Baked goods	Batter viscosifier; improves moisture retention and texture
	Beverages	Suspending aid; rapid viscosifier; improves mouthfeel and body; protein stabilizer in acidified drinks
	Desserts; icings; toppings	Odorless and tasteless; thickens; controls sugar crystal size; improves texture; inhibits syneresis
	Low-calorie foods	No caloric value; thickens; imparts body and mouthfeel
	Syrups	Clear; thickens; imparts favorable mouthfeel and body
	Dressings; sauces	Thickener and suspending aid; imparts mouthfeel
	Animal feed; extrusion products	Lubricant; binder; film-former
Pharmaceuticals	Ointments; creams; lotions	Stabilizer; thickener; film-former
	Jellies; salves	Thickener; gelling agent; protective colloid, film-former
	Tablet binder; granulation aid	High-strength binder
	Bulk laxatives	Physiologically inert; high water-binding capacity
	Syrups	Thickener
	Suspensions	Thickener; suspending aid

**Table 1.7:** Applications for unpurified, semi,purified and purified CMC (< 99.5%)

<b>Types of Uses</b>	<b>Specific Applications</b>	<b>Properties Utilized</b>
Adhesives	Wallpaper paste	Water-binding aid; adhesion; good open time; nonstaining
	Starch-corrugating adhesive	Thickener; water-binding and -suspending aid
	Latex adhesives	Thickener; water-binding aid
Aerial-drop fluids	Insecticides	Thickener; binder; suspending aid
	Drift-control agent	Thickener
Ceramics	Glazes	Binder for green strength; thickener; suspending aid
	Porcelain slips	
	Vitreous enamels	
	Refractory mortars	Binder; thickener; lubricant
Welding rod coatings		
Coatings	Foundry core wash	Binder; thickener; suspending aid
	Latex paints; paper coatings	Rheology control; suspending aid; protective colloid
Detergents	Laundry	Whiteness retention through soil suspension
Drilling	Completion/Workover Fluids	Rheology modifier
	Drilling Fluids	Improves filtercake lubricity, stabilizes fluid rheology, inhibits shales swelling and disintegration
Lithography	Fountain and gumming solutions	Hydrophilic protective film
	Water-based inks	Binder; rheology control; suspending aid
Paper and paper products	Internal addition	High-strength binder; improves dry strength of paper
	Surface addition	High-strength binder; oil-resistant film-former; provides control of curl and porosity and resistance to oils and greases
	Pigmented coatings	Thickener; rheology control; water-retention aid
Textiles	Laundry and fabric sizes	Film-former
	Latex adhesives; backing compounds	Rheology control; thickener; water binding and holdout
	Printing pastes and dyes	
	Warp sizing	High film strength; good adhesion to fiber; low BOD value
Tobacco	Cigar and cigarette adhesive	Good wet tack; high film strength
	Reconstituted sheet	High-strength binder and suspending aid

### 1.4.5 Market

The global CMC market was estimated at \$1.152 billion in 2014 and is projected to register a compound annual growth rate of 4.2% between 2015 and 2020 (“Carboxymethyl Cellulose Market by Application - Trends & Forecasts to 2020,” 2015). CMC is widely used as thickener, stabilizer, binder and dispersant in variety of applications such as food and beverages, pharmaceutical and cosmetics, detergents, oil and gas, paper processing and others. The global carboxymethyl cellulose market share, by end-user segment is illustrated in Figure 1.11 (“Carboxymethyl Cellulose Market - Global Industry Analysis, Size, Share, Growth, Trends and Forecast, 2013 - 2019,” 2014).



**Figure 1.11:** Global CMC market share, by end-user segment, 2012

The leading producers in the global CMC market are Akzo Nobel N.V., CP Kelco U.S. Inc., (A Subsidiary of J.M. Huber Corporation Company), Ugur Seluloz Kimya A.S., Química Amtex S.A. De C.V., The Dow Chemical Company, DKS Co. Ltd., Nippon Paper Industries Co. Ltd., Daicel Corporation, Ashland Inc., and Lamberti S.P.A. (“Carboxymethyl Cellulose Market by Application - Trends & Forecasts to 2020,” 2015).

Among these producers, a Turkish company, Ugur Seluloz Kimya A.S. is the only pure CMC producer of Turkey. All the Turkish CMC producers excluding Ugur produce only technical CMC, which does not require high technology. This creates a difference between the values of exported and imported CMC products from and to Turkey respectively (Table 1.8) (“Foreign trade statistics for carboxymethyl cellulose,” n.d.).

**Table 1.8:** CMC foreign trade statistics of Turkey

Year	Total Value of Exports (\$)	Amount of Export (kg)	Unit value of export (\$/kg)	Total Value of Imports (\$)	Amount of Import (kg)	Unit value of Import (\$/kg)
2011	35,434,059	33,805,247	<b>1.05</b>	11,750,888	2,605,548	<b>4.51</b>
2012	40,527,534	38,899,514	<b>1.04</b>	9,976,289	2,206,239	<b>4.52</b>
2013	47,180,058	42,912,171	<b>1.10</b>	9,745,518	2,054,953	<b>4.74</b>
2014	47,424,064	41,738,436	<b>1.14</b>	12,801,559	2,980,750	<b>4.29</b>
2015	42,978,297	42,511,867	<b>1.01</b>	11,542,886	3,104,293	<b>3.72</b>

### 1.5 Objective and Aims of Study

Although cellulose is the main raw material for producing CMC, its commercial production stopped with the shutdown of ‘Turkish Cellulose and Paper Factories’ (SEKA) in 2006 (“Report on Paper, Paper Products and Printing Industry,” n.d.). Turkish CMC producers are forced to import all the cellulose they are using in their production. This decreases the added value of the production and increases the foreign dependency of the industry. Under these circumstances, textile waste is an important and cheap alternative in the production of CMC.

According to Altun’s research 425 thousand tons of household textile waste and 458.5 thousand tons of industrial textile waste was generated in 2009 in Turkey (Altun, 2012). More than 95% of textile waste is recyclable. In the textile industry; cloth pieces, yarn waste, mattress pieces, fiber waste, cotton dust, oakum and velvet powder consist industrial solid waste. 16% of this waste is dropped to landfills each year. Since Turkey is the 7<sup>th</sup> cotton producer in the world most of these wastes are made of cotton yarn which has 90% cellulose content (Büyükaslan, Jevsnik, & Kalaoğlu, 2015; Lüy, Varınca, & Rtlek, 2007).

The wastes gathered from production of textile and clothing woven fabrics, embroidery and other textile products can be evaluated since their pieces are large. However, the wastes acquired from the production of yarn is burned without evaluation (Ağdağ & Kırımhan, 1999). For these reasons, this type of textile waste can be recycled by using in the production of CMC. By using this type of textile waste as raw material for the production of CMC polymer they would be returned back to the economy with higher values (Kalin, 2005).

This study is carried out as a project by The Scientific and Technological Research Council of Turkey (TÜBİTAK) and Ugur Seluloz Kimya A.S. under the 1507 - SME RDI (Research, Development & Innovation) Grant Programme. This study aims to produce polyanionic cellulose (PAC), the most premium grade of CMC, by using textile waste as main raw material in alcoholic medium. In this waste recovery process, solid textile waste will be used as raw material and the alcoholic (ethyl alcohol and isopropyl alcohol) medium will be used to increase the quality of the PAC products in order to meet the criteria of PAC LV (low viscosity) and PAC HV (high viscosity) standards introduced by American Petroleum Institute (API) (API, 2006).



## 2. EXPERIMENTAL PROCEDURE

### 2.1 Materials

Textile wastes, cotton cut waste (Fig. 2.1a) and cotton clips (Fig. 2.1b) are provided from the textile manufacturers. While cotton cut waste is used without shredding, cotton clips are used after shredding (2 mm filter).



**Figure 2.1:** Textile wastes; a) cotton cut waste (used without shredding), b) cotton clips (unshredded (left) and shredded (right))

Sodium hydroxide caustic soda, (47.98 % w/w, aqueous solution) was provided from PETKİM Petrokimya Holding A.Ş. (Turkey).

Monochloroacetic acid (MCA) flakes (98.0 % purity) was provided from Akzo Nobel N.V. (Netherlands).

Denatured ethyl alcohol, (96.0 % w/w, aqueous solution) was provided from Dewan Sugar Mills Ltd. (Pakistan).

2-propanol (isopropyl alcohol), (99.8 % purity) was provided from Merck KGaA (Germany).

Hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>), (50.0 % w/w, aqueous solution) was provided from Akkim Kimya San ve Tic A.Ş. (Turkey).

Refined Sodium Bicarbonate (Na<sub>2</sub>CO<sub>3</sub>), (99.3 % purity) was provided from Şişecam Chemicals Group Soda Sanayii A.Ş. (Turkey).

## 2.2 Materials Processing

A custom-made laboratory-scale research mixer/reactor, which is built with the support of TÜBİTAK, is used for the etherification reaction. This mixer/reactor is designed and built with a heating/cooling system and a temperature probe to control and measure the temperature of the reaction respectively.

40 different experiments were performed with textile wastes for the synthesis/manufacture of PAC LV and PAC HV during the study and they were labeled from **1** to **40**. While 17 of these experiments were conducted by using cotton cut waste (Experiments **1** to **16** and **40**), rest 23 of them (Experiments **17** to **39**) were held by using cotton clips, which are used after shredding.

## 2.3 Characterization

### 2.3.1 Moisture

The moisture content of the PAC samples was determined by using an oven, regulated to 105 °C ± 3 °C, a balance with an accuracy of ± 0.01 g, an evaporating dish up to 150 ml capacity and a desiccator, with calcium sulfate (CaSO<sub>4</sub>) desiccant. Initially, 10 g ± 0,1 g of the PAC sample was weighed into a tared evaporating dish and its mass is recorded as *m*. After drying the sample in the oven for 4 h, it was cooled down to room temperature in the desiccator. Then, the dried PAC sample was reweighed, and its mass is recorded as *m*<sub>2</sub>. Moisture content of the PAC sample, in percent, is calculated with Equation 2.1 below (API, 2006).

$$\%Moisture = 100 \frac{(m - m_2)}{m} \quad (2.1)$$

*m* = the mass of sample (g)



$m_2$  = the mass of residue (g)

### 2.3.2 Purity (Active Content)

The purity of PAC samples was determined by washing the product several times with ethanol to remove the reaction by-products (sodium glycolate and sodium chloride). A 3 g sample was stirred mechanically in a beaker for 15 min with each of two 150 mL portions of ethanol (80 % by volume) at a temperature of 60 to 65 °C initially. The supernatant liquid was decanted through a tared filtering crucible after each treatment. The undissolved residue was transferred quantitatively to the crucible, dried in the oven at 105 °C for 2 h and weighed at room temperature respectively. The purity (active content) of the PAC sample, in percent, is calculated with Equation 2.2 below (ASTM, 2008).

$$\%Purity = \frac{(A \times 10000)}{(B(100 - C))} \quad (2.2)$$

$A$  = the mass of dried residue (g)

$B$  = the mass of sample (g)

$C$  = the moisture content of the sample (%)

### 2.3.3 Degree of Substitution (DS)

A 4 g of PAC sample was weighed into a 250 mL beaker before adding 75 mL of ethyl alcohol (95 %). The mixture was stirred with an air-driven stirrer until a good slurry is obtained. 5 mL of concentrated nitric acid ( $\text{HNO}_3$ , 1.42 g/cm<sup>3</sup>) was added to the mixture while agitating for 1 to 2 min. The resulting slurry was heated and boiled for 5 min. The supernatant liquid was decanted through the filter and the precipitate was transferred to the filter with 50 to 100 mL of ethyl alcohol (95 %). The precipitate was washed with ethyl alcohol (80 %) that has been heated to 60°C, until all of the acid is removed (approx. 4-6 washings). The precipitate was finally washed with a small amount of anhydrous methanol and was dried by passing air through it until the alcohol is completely removed. The precipitate was transferred to an aluminum weighing dish provided with a cover. The uncovered dish was heated on a steam bath until the odor of alcohol can no longer be detected (in order to avoid fires due to methanol fumes in the oven), then the uncovered dish and its contents was dried for 3 h at 105 °C. The

dish was covered and was cooled down to room temperature in a desiccator. A 1-1.5 g  $\pm$  0.01 g of the dried acid PAC (depending on the normality of the acid and base to be used) was weighed into a 500-mL Erlenmeyer flask. 100 mL of water and 25.00 mL of 0.3 to 0.5 N NaOH solution were added while stirring. The resulting solution was heated and boiled for 15 to 30 min. While the solution is hot, the excess NaOH was titrated with 0.3 to 0.5 N hydrochloric acid (HCl) solution to a phenolphthalein end point. The DS of the PAC sample, is calculated with Equation 2.3 and 2.4 below (ASTM, 2008).

$$A = \frac{(BC - DE)}{(F)} \quad (2.3)$$

$$DS = \frac{0.162A}{(1 - 0.0584A)} \quad (2.4)$$

*A* = milliequivalents of acid consumed per gram of sample

*B* = NaOH solution added, mL

*C* = normality of the NaOH solution

*D* = HCl solution required for titration of the excess NaOH, mL

*E* = normality of the HCl solution

*F* = dried acid PAC used, g

162 = gram molecular mass of the anhydroglucose unit of cellulose

58 = net increase in molecular mass of anhydroglucose unit for each carboxymethyl group substituted

## 2.3.4 Viscosity

### 2.3.4.1 Viscosity of cellulose

The intrinsic viscosity of textile wastes is determined with the standard test method of American Society of the International Association for Testing and Materials (ASTM) by using Cannon-Fenske type viscometer (ASTM, 2012).

A weighed cellulose sample was dissolved in a 0.5 M cupriethylenediamine hydroxide solution. 7.0 mL of resulting solution was transferred to viscometer, which was previously placed in the bath at 25°C and was flushed with nitrogen. After 5 min the solution was drawn into the lower bulb of the viscometer until the top meniscus is a little above the mark between the two bulbs. The time, required for the meniscus to

pass from this mark to the mark below the lower bulb, was measured and noted three times in a row. Same measurement was performed with 0.5 M cupriethylenediamine hydroxide solution to determine the viscosity of the solvent. The relative viscosity of cellulose sample is calculated with Equation 2.5 and the corresponding intrinsic viscosity is read from a specific table (ASTM, 2012).

$$\eta_{rel} = \frac{t}{t_0} \quad (2.5)$$

$t$  = outflow time of cellulose solution, s

$t_0$  = outflow time of solvent, s

By means of interested table,  $[\eta]c$ , the product of intrinsic viscosity and concentration (g/dL) was determined corresponding to the value of the relative viscosity. From this value and the concentration, the intrinsic viscosity was calculated in deciliters per gram (ASTM, 2012).

#### **2.3.4.2 Brookfield viscosity of PAC**

Brookfield Viscometer DV-E was used for determining the viscosity of aqueous solutions of PAC LV and HV samples in the viscosity range from 10 to 10 000 centipoises (cP) at 25 °C (ASTM, 2008).

#### **2.3.4.3 Apparent viscosity of PAC**

42 g ± 0.01 g of sea salt (commercially available) and 35.0 g ± 0.01 g of potassium chloride (KCl) were dissolved in 1 L ± 2 mL of deionized water. 5.0 g ± 0.01 g of PAC LV (3.0 g ± 0.01 g of PAC HV) was added to the prepared solution gradually while stirring on the Hamilton mixer. After stirring for 20 min ± 1 min, resulting suspension was aged at room temperature for 16 h ± 0.5 h. sealed. After stirring the aged suspension for 5 min ± 0.1 min, it was poured into the viscometer cup provided with the Fann Viscometer (Model 35). Half of the dial reading at 600 rpm and at 25 °C ± 1 °C gives the apparent viscosity of corresponding PAC sample (API, 2006).

#### **2.3.5 Filtrate volume**

42 g ± 0.01 g of sea salt (commercially available) and 35.0 g ± 0.01 g of potassium chloride (KCl) were dissolved in 1 L ± 2 mL of deionized water. After stirring for 3

min  $\pm$  0.1 min on the Hamilton mixer, 1.0 g  $\pm$  0.01 g of sodium bicarbonate was added to the solution. After stirring for 3 min  $\pm$  0.1 min on the mixer, 28.0 g  $\pm$  0.01 g of API standard evaluation base clay was added to the solution. After stirring for 5 min  $\pm$  0.1 min on the mixer, 2.0 g  $\pm$  0.01 g of PAC LV (1.0 g  $\pm$  0.01 g of PAC HV) was added to the prepared solution gradually while stirring on the mixer. After stirring for 20 min  $\pm$  1 min, resulting suspension was aged at room temperature for 16 h  $\pm$  0.5 h. sealed. After stirring the aged suspension for 5 min  $\pm$  0.1 min, it was poured into a Fann filter press cell. The filter press cell was assembled to filter press and a container was placed under the drain tube. After applying 690 kPa  $\pm$  35 kPa pressure with nitrogen for 7.5 min  $\pm$  0.1 min, the container below the drain tube was replaced by a dry 10 mL graduated cylinder. After 22.5 min  $\pm$  0.1 min, the graduated cylinder was removed and volume of the collected filtrate was recorded. Twice the recorded volume gives the filtrate volume of corresponding PAC sample (API, 2006).

### **2.3.6 Color**

Konica Minolta CM-2600d portable spectrophotometer was used to measure the color values of textile wastes and PAC products. The measurement is performed according to International Commission on Illumination (French Commission internationale de l'éclairage, hence its CIE initialism). It measures the lightness of the color ( $L^* = 0$  yields black and  $L^* = 100$  indicates diffuse white), its position between red/magenta and green ( $a^*$ , negative values indicate green while positive values indicate magenta), and its position between yellow and blue ( $b^*$ , negative values indicate blue and positive values indicate yellow). All measurements were performed in three replicates (HunterLab, 2007).

### **2.3.7 pH**

WTW Inolab 720 pH meter was used for determining the pH values of aqueous solutions of PAC LV and HV samples at 25 °C.

### **2.3.8 Water insoluble matter**

A 2 g of PAC sample (on dry basis) was weighed into a 250 mL beaker. A mechanical stirrer was placed about 2-5 cm above the powder and 200 ml of carbon dioxide free water was added before stirring for 30 min. The solution was aged at room temperature for 16 h sealed. 100 ml of the aged solution was centrifuged at 3000 rpm for 15

minutes. The supernatant liquid was decanted, was replaced with an equal volume of water and was centrifuged under the same conditions. This procedure was repeated until all the gelatinous material had dispersed. The supernatant liquid was replaced with an equal volume of 0.01 N HCl solution, was stirred and was centrifuged under the same conditions. The acid was replaced with an equal volume of acetone, was stirred and was centrifuged under the same conditions. The supernatant liquid was filtered through a tared sintered glass crucible. The residue was washed with acetone before drying in the oven at 105 °C for 2 h and was weighed at room temperature respectively. 100 times of the recorded weight gives the water insoluble matter of corresponding PAC sample, in percent (IS, 1992).

### 2.3.9 Physical requirements of PAC LV and PAC HV

The physical requirements to meet the minimum standards of American Petroleum Institute (API) are illustrated in Table 2.1 (API, 2006).

**Table 2.1:** Physical requirements of PAC LV and PAC HV

Requirement	Standard	
	PAC-LV	PAC-HV
Presence of starch	Absent	Absent
Moisture content	Maximum 10%	Maximum 10%
Apparent viscosity	Maximum 40 cP	Minimum 50 cP
Filtrate volume	Maximum 16 mL	Maximum 23 mL

### 3. RESULTS AND DISCUSSION

#### 3.1 Color Measurement Results

Color values of textile wastes used as cellulose in the etherification reaction and the PAC products synthesized from corresponding these textile wastes are measured with Konica Minolta CM-2600d portable spectrophotometer. While the color values of dried PAC products manufactured from cotton cut wastes (**8** and **16**) were measured to be lighter than those of corresponding textile wastes, the color values of dried PAC product manufactured from cotton clips (**25**) was measured to be darker than those of corresponding textile waste (Table 3.1).

**Table 3.1:** Color values of various PAC products and their main raw materials

Experiment No	Textile Waste			PAC Product		
	L*	a*	b*	L*	a*	b*
<b>8</b>	84.16	1.28	11.57	88.31	1.07	15.78
<b>16</b>	83.16	2.42	12.27	87.13	1.14	16.05
<b>25</b>	94.25	2.22	-10.12	88.10	0.50	7.89

In order to explain this phenomenon, it is important to realize the relatively much whiter color of cotton clips used in the synthesis of PAC product **25** with respect to the cotton cut wastes used in the synthesis of PAC products **8** and **16** as it is exhibited in both Figure 2.1 and Table 3.1.

Alkalization process, which involves NaOH treatment, might have increased the whiteness of the cotton cut wastes, which are less white than cotton clips. The effect of etherification step should be the same on both type of textile wastes since it is performed at 70 °C (Ghanbarzadeh, Almasi, & Entezami, 2010).

### 3.2 Viscosity Measurement Results

Intrinsic cellulose viscosity values of textile wastes and Brookfield (2.0%, dry basis, 25 °C) and apparent viscosities of corresponding PAC products are shown in Table 3.2.

**Table 3.2:** Viscosity values of textile wastes and corresponding PAC products

Experiment No	Textile Waste Viscosity (dL/g)	Purity (%)	Product		
			Brookfield V <sub>2</sub> (cP)	PAC LV Apparent (cP)	PAC HV Apparent (cP)
1	3.121	68	45	11	
2	2.987	71	52	10	
3	3.001	67	35	8	
4	3.298	72	63	28	
5	3.133	71	55	19	
6	3.060	63	31	22	
7	2.993	65	29	19	
8	5.087	72	28	19	7
8	5.087	98	269	52	11
9	4.406	68	8	12	
9	4.406	98.7	74	33	
10	3.118	62	23	13	
11	4.956	60	33	19	
12	3.806	61	27	15	
13	5.559	65	42	22	
14	4.442	60	43	25	
15	3.928	63	35	23	
15	3.928	98.5	298	43	
16	5.673	65	8	21	
16	5.673	98.8	73	37	9
17	7.379	70.6	4300		17
17	7.379	98	18500		39
18	6.339	98	18500		44
19	7.262	98.7	16900		46
20	6.455	99	22000		50
21	5.968	96	3500		17
22	5.703	98.5	7000		39
23	12.703	97.2	28000		63
24	10.357	98	38000		65
25	10.858	97.5	32500		55
26	7.623	96.5	11000		32
27	8.055	98.5	13700		35
28	7.322	98.5	9000		29
29	7.853	98.8	7500		35
30	7.874	99	5000		21
31	7.437	98	18000		41
32	8.404	98.5	19500		48
33	8.911	99	32000		52
34	8.146	99	26000		48
35	12.957	98	35000		58
36	11.705	98.5	32000		49
37	12.130	98.5	48000		62
38	11.763	98	45000		59
39	13.211	98	48000		65
40	3.123	45	3	3	7

Although there is not much difference between the intrinsic viscosities of cotton cut waste and cotton clips, Brookfield viscosities of PAC products manufactured from the cotton clips are much higher than the viscosities of those manufactured from the cotton cut waste. The ratio between the intrinsic viscosities of cotton cut waste and Brookfield viscosities of corresponding unpurified products (**1** to **16**) is in single digits. The proportion between the intrinsic viscosities of cotton cut waste and Brookfield viscosities of corresponding purified products (**8**, **15** and **16**) is in double digits.

The ratio between the intrinsic viscosity of cotton clips and Brookfield viscosity of corresponding unpurified product (**17**) is in double digits. The proportion between the intrinsic viscosities of cotton clips and Brookfield viscosities of corresponding purified products (**17** to **39**) is in triple digits.

Apart from these data, both Brookfield and apparent viscosities are largely dependent on the purity of the PAC product. This is an expected result due to the viscosity increasing behavior of CMC with respect to the by-products sodium glycolate and sodium chloride (Holmgren, 2010).

### **3.3 Filtrate Volume Measurement Results**

The filtrate volume of the purified products is measured to be higher than those of unpurified products as expected. This is due to the water absorbing property of CMC. The filtrate volume values of both unpurified and purified products largely depend on the DS values of these products. This is due to the carboxymethyl character of these products introduced by etherification. Higher DS value of these products indicate higher carboxymethyl cellulose character. Higher carboxymethyl cellulose character of these products indicate higher water absorption capacity. Higher water absorption capacity of these products indicate higher filtrate volume values. The filtrate volume values of PAC products are exhibited in Table 3.3.



**Table 3.3:** Filtrate volume values of PAC products

Experiment No	Purity (%)	Product		
		DS	PAC LV Filtrate Volume (mL)	PAC HV Filtrate Volume (mL)
1	68	0.45	42.0	
2	71	0.51	38.0	
3	67	0.44	58.0	
4	72	0.65	25.0	
5	71	0.63	27.0	
6	63	0.91	18.0	
7	65	0.79	23.0	
8	72	0.95	13.6	85.0
8	98	0.93	9.0	110.0
9	68	0.89	14.8	
9	98.7	0.91	12.8	
10	62	0.52	35.0	
11	60	0.64	28.0	
12	61	0.68	25.0	
13	65	0.75	23.0	
14	60	0.81	18.0	
15	63	0.94	16.0	
15	98.5	0.97	14.6	
16	65	0.95	18.0	
16	98.8	0.95	15.4	95.0
17	70.6	0.63		31.6
17	98	0.63		20.8
18	98	0.90		20.0
19	98.7	0.84		20.8
20	99	0.81		21.0
21	96	0.71		50.0
22	98.5	1.04		22.0
23	97.2	0.83		19.8
24	98	0.87		16.8
25	97.5	0.91		14.8
26	96.5	0.83		24.6
27	98.5	0.88		18.8
28	98.5	0.91		20.0
29	98.8	0.98		19.2
30	99	1.05		25.0
31	98	0.83		20.0
32	98.5	0.82		20.0
33	99	0.90		18.0
34	99	0.96		18.4
35	98	0.92		17.2
36	98.5	0.88		18.6
37	98.5	0.91		18.8
38	98	0.90		18.4
39	98	0.95		16.4
40	45	0.31	139	

### **3.4 Effect of textile waste type on physical properties of PAC products**

Between the two types of textile wastes used in the experiments, intrinsic viscosity values of cotton cut wastes are measured to be lower than those of cotton clips. This phenomenon automatically made the cotton cut wastes a preferred raw material for producing low viscosity polyanionic cellulose (PAC-LV). Thus, cotton clips became a preferred raw material for producing high viscosity polyanionic cellulose (PAC-HV).

### **3.5 Effect of alcohol type on physical properties of PAC products**

Ethyl alcohol (ethanol) and isopropyl alcohol (2-propanol) are used in the experiments as it is stated in the project proposal. The first three experiments (**1-3**) are performed with isopropyl alcohol. Although isopropyl alcohol is defined as a better carrier with respect to ethyl alcohol in various studies, water insoluble matter values of products **1-3** are measured as 2-3 times higher than those of other products. Since this result directly decreases the active content of the product, rest of the experiments were carried out by using ethyl alcohol (Heinze & Koschella, 2005b; Olaru, Olaru, Stoleriu, & Țîmpu, 1998; Pushpamalar, Langford, Ahmad, & Lim, 2006; Stigsson et al., 2006; Yokota, 1985; Zhang, Li, Zhang, & Shi, 1993).

This phenomenon can be explained by the insufficiency of relatively less polar organic solvent isopropyl alcohol in breaking the intermolecular hydrogen bonds (Fig. 1.3b) between the parallel polymer chains with respect to more polar organic solvent ethyl alcohol.

### **3.6 Effect of alcohol amount on physical properties of PAC products**

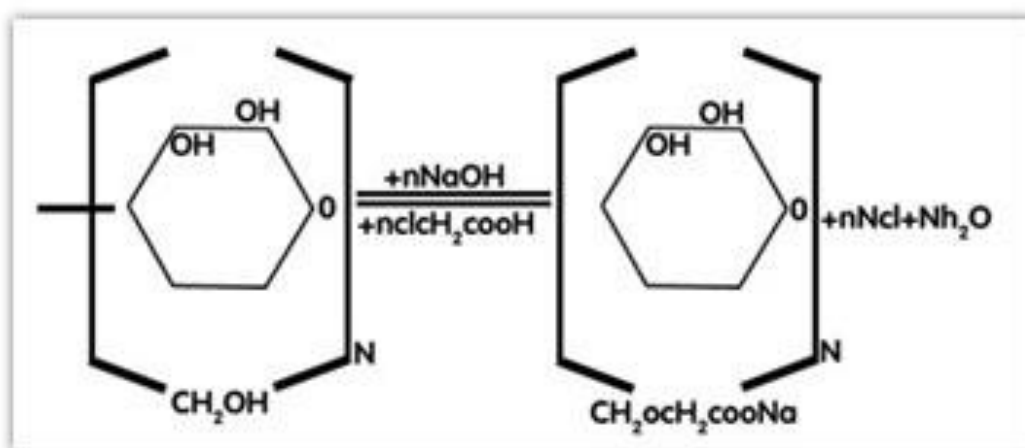
The amount of ethyl alcohol used during alkalization and etherification was gradually increased until the physical requirements PAC-LV and PAC-HV are met by using cotton cut wastes and cotton clip respectively. 2.21 equivalent (with respect to cellulose) of ethyl alcohol is used to meet the physical requirements of the PAC-LV in the synthesis of product **8**. 3.81 equivalent (with respect to cellulose) of ethyl alcohol is used to meet the physical requirements of the PAC-HV in the synthesis of product **8**.

The difference between the amounts of alcohol comes from the higher viscosity requirement of the PAC-HV product. This requirement can only be met by increasing

the carboxymethyl cellulose character of the product, hence increasing the DS value, which indicates the etherification.

### 3.7 Effect of NaOH concentration on physical properties of PAC products

The concentration of the NaOH solution used in all of the experiments was 48% except one. In experiment **40**, NaOH solution with 21% concentration has been used for alkalization. As you can check from Tables 3.2 and 3.3, degree of etherification was recorded as the lowest of all experiments 0.31 and hence the purity 45%. This is an expected result because of the water molecules. Water is produced at the end of both etherification (Fig. 3.1) and side (Fig. 1.8c) reactions.



**Figure 3.1:** Chemically balanced etherification equation of cellulose

Since 21% NaOH means more water in the reaction medium with respect to the 48% NaOH, chemical equilibrium is shifted towards the reactants side by decreasing the etherification.

### 3.8 Effect of etherifying agent type on physical properties of PAC products

Monochloroacetic acid (MCA) and sodium monochloroacetate (NaMCA) are used for the etherification of alkali textile wastes in the experiments. Experiments **10** to **16** and **18** were performed with NaMCA, and the rest were done with MCA. While using the MCA as etherifying agent, the reaction temperature was elevated to 70 °C faster than the experiments in which NaMCA was used as etherifying agent. In the 8 experiments (**10-16, 18**) performed with NaMCA, viscosity and filtrate volume values of the synthesized products were comparably lower than those of products gathered from the

other experiments. This is mainly due to the lower purity achieved by the reactions. Since the reaction temperature takes more time to reach etherification temperature (70 °C) while using NaMCA, under the same time conditions with the rest of the experiments, alkali cellulose would have less time for carboxymethylation with respect to the other experiments performed with MCA.

### 3.9 Effect of using alcohol on physical properties of PAC products

As stated before, due to the inconvenience of isopropyl alcohol, ethyl alcohol was used as a carrier in all of the experiments but three of them. Before performing this study, none of the CMC producers in Turkey was able to produce PAC polymers from textile waste. They were able to produce PAC-LV from imported linter cellulose, but not from textile waste. The effect of using alcohol on physical properties of PAC products is illustrated in Table 3.4 by comparing the PAC production methods with and without ethyl alcohol.

**Table 3.4:** The effect of using alcohol on physical properties of PAC products

			Without alcohol	With ethyl alcohol	
		Requirements		PAC-LV	PAC-HV
	Type of textile waste			Cotton cut waste	Cotton clips
	Purity (%)		~60	72.0	97.5
	Degree of Substitution (DS)		~0.7	0.91	0.95
	Brookfield Viscosity (cP) (25 °C, dry basis, % 2 conc.)			28	32,500
	Water Insoluble Matter %		~10	0.9	0.8
PAC-LV	Apparent Viscosity (cP):	Max 40	~80	19	
	Filtrate Volume (mL):	Max 16.0	~35	13.6	
PAC-HV	Apparent Viscosity (cP):	Min 50	~20		55
	Filtrate Volume (mL):	Max 23.0	~40		14.8

#### 4. CONCLUSIONS

The aim of this study was to produce polyanionic cellulose polymers (PAC-LV and PAC-HV) from solid textile waste by using alcohol as carrier. Cellulose ethers have surrounded us like mosquitos in every aspect of the life. Their water-soluble, non-toxic and viscosifier/binder properties are pushing us to prevent the import of these products and find new ways to increase the added value of the domestic products. Textile wastes are very big and important opportunity to catch in this matter, given that the only domestic cellulose producer of Turkey (SEKA) ran out of business in 2006.

This study had three parts. In the first and most comprehensive part, PAC polymers were synthesized in a laboratory-scale reactor/mixer by using different organic solvents (ethyl alcohol and isopropyl alcohol). In the second part, synthesized products were purified and characterized simultaneously in order to determine the way of research. In the last step, two samples, PAC-LV and PAC-HV, among the synthesized products were sent to accredited Turkish Petroleum (TP) Research Laboratories for verification (Fig. 4.1 – 4.2).

The most important outcome of this study was to produce PAC-LV and PAC-HV polymer in API standards from textile waste without using any imported cellulose. This production method not only prevents the import but also enables the use of natural wastes so that the added value of the product increases.

For further work, this method can be applied to manufacture of highly pure grade CMC polymers, used in pharmacy and food industry. High cellulose content of these textile wastes promises the manufacture of many other types of CMC products with added value. The textile wastes, used in this project are chosen from white wastes. The whitening of colored textile wastes without breaking the cellulose chains can enable the use of colored wastes in CMC and PAC production. This is also a very efficient future work to focus on.



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ANALİZ RAPORU

AB-0072-T  
5029  
12-15

Numune Kodu : 15-03-2518-01  
Numune Geliş T. : 16.12.2015  
Yapılan Analiz(ler) : PAC  
Test Tarih Ara. : 22.12.2015 - 23.12.2015

PAC ANALİZ SONUCU

API Spec. 13/A Section 17 PAC-LV Standardı				
Özellikler	Birim	En Az	En Çok	Test Sonucu
* Görünür Viskozite	cp		40	19
* Süzüntü Hacmi	ml		16	13
Nem içeriği	%		10	5
Nişasta veya nişasta türevleri varlığı*				0

\* İşaretili deneyler akreditasyon kapsamı dahilindedir.


\* Nişasta miktar sonuçları, nişasta ölçülmesi durumunda 1, ölçülmemesi durumunda 0 girilecektir.

**Açıklamalar:** Pac-LV numunesi API Spec. 13/A Section 17 Pac-LV standardına uygundur.  
Ölçümler API Spec 13/A esas alınarak yapılmıştır.

Analizi Yapan Laboratuvar	Yazan	Onaylayan
Kalite Kontrol Laboratuvarı	 Mehmet EROL Mühendis	 Selçuk ERKEKOL Ünite Müdürü

Bu raporda yer alan deney sonuçları sadece deneyi yapılan numuneye aittir.  
Bu rapor, laboratuvarın yazılı izni olmadan kısmen veya tamamen kopyalanıp çoğaltılamaz.  
İmzasız ve mühürsüz raporlar geçersizdir.  
Deney sonuçlarına 1 ay boyunca itiraz edilebilir.

**Figure 4.1:** Test result of PAC-LV sample given by TP

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	<b>Numune Kodu</b> : 15-03-2517-01	
	<b>Numune Geliş T.</b> : 16.12.2015 <b>Yapılan Analiz(ler)</b> : PAC <b>Test Tarih Ara.</b> : 22.12.2015 - 23.12.2015	



### PAC ANALİZ SONUCU

TS EN ISO 13500 Kısım 18 Yüksek Viskoziteli Polianyonik Selüloz (PAC-HV) Şartnamesi				
Özellikler	Birim	En Az	En Çok	Test Sonucu
* Görünür Viskozite	cp	50		68
* API Süzüntü Hacmi	mL		23	17
Nem İçeriği	%		10	8
Nişasta veya nişasta türevleri varlığı <sup>a</sup>				0

\* İşaretti deneyler akreditasyon kapsamı dahilindedir.

<sup>a</sup> Nişasta miktarı sonuçları, nişasta ölçülmesi durumunda 1, ölçülmemesi durumunda 0 girecektir.

**Açıklamalar:** Pac-HV numunesi TS EN ISO 13500 PAC-HV şartnamesine uygundur.  
Ölçümler API Spec 13A esas alınarak yapılmıştır.

Analizi Yapan Laboratuvar	Yazan	Onaylayan
Kalite Kontrol Laboratuvarı	 Mehmet EROL Mühendis	 Selçuk ERKEKOL Ünite Müdürü

Bu raporda yer alan deney sonuçları sadece deneyi yapılan numuneye aittir.  
Bu rapor, laboratuvarın yazılı izni olmadan kısmen veya tamamen kopyalanıp çoğaltılamaz.  
İmzasız ve mühürsüz raporlar geçersizdir.  
Deney sonuçlarına 1 ay boyunca itiraz edilebilir.

**Figure 4.2:** Test result of PAC-HV sample given by TP

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