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CELLULOSE BASED BIOCHEMICALS AND THEIR APPLICATIONS
ABSTRACT

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The basic objective of this Bachelor’s thesis was to make a research on the application of cellulose and its derivatives in the field other than paper. Since the beginning cellulose has been used widely as a main source of paper, today there is the requirement to find out its alternative applications. This thesis work shows its possible applications on other fields. Mainly, the task was more concerned on production of bioethanol from forest biomass, nanocellulose, its different applications, cellulose based biochemicals and their applications.

Mainly two variants were chosen to accomplish this thesis work. Discussion about the topic with the teacher and collection of the materials throughout the resource areas were opted. It includes the study of those materials, good arrangement of the sources and in optimization.

The cellulose and its derivatives such as methyl cellulose, ethyl cellulose and many more have been included here and their different properties with various utilities. The method used for this work was using the different books and the sources from the internet. The production of ethanol from the forest biomass has been more focused. Nanocellulose, their derivatives were researched, categorized and sorted.

Keywords: Cellulose, Cellulose Derivatives, Nanocellulose, Hydrolysis, Bioethanol, Methyl Cellulose, Ethyl cellulose, Nanofibres, Cellulose Acetate, Cellulose Propanoate.
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INTRODUCTION

Cellulose is the most abundant biopolymer in the world. It has been widely used as a main source of paper since the beginning. Besides, this work is mainly concerned on expanding the use of it in other different fields. Especially when dealing with cellulose and its derivatives and their utilities, the main objective is focused on the present demand for its utility in the production of bioethanol.

New field of research is going on to find out the possible application of the cellulose from the forest wood, mainly in the areas of bio fuels - the success of which leads to the great benefit for both to the environment and energy requirement. Cellulosic ethanol is a great possibility since cellulose fibers which are actually a major and universal component in plant cells' walls it is possible to produce ethanol.

Another area is nanocellulose. The nano structure of the cellulose has provided great advantages for its application in different fields in which the cellulose fibers are used. It is a material composed of nano sized cellulose fibrils that has a high aspect ratio i.e. length to width ratio. Typical dimensions of it are 5–20 nanometers width, and length can be up to 2000 nanometers. Besides, it is a pseudo-plastic compound i.e. it exhibits the property of plastic-like substance but is not really a plastic.

The derivatives of cellulose include methyl cellulose, ethyl cellulose, propyl cellulose, ethyl methyl cellulose and so on. The basic purpose was to extract all these biochemicals and find out their applications. The used methods were studying the material, searching the source from the Internet and getting ideas from the instructor.
2 CELLULOSE

The general concept and its structure give an overall ideas about cellulose.

2.1 General

Cellulose is the fundamental constituent of fiber wall, the share of which is 40-50% of the wood’s dry mass. It is a long chain of linked sugar molecules that provides the wood its prominent strength. It is the basic building block for all fiber based papers and many textiles. Cotton is an example of the purest natural form of cellulose. In the laboratory, ashless filter paper is a source of almost 100% pure cellulose. Cellulose is a natural polymer. It consists of long chain which is made up of linking of smaller molecules. For industrial purposes, it is mostly obtained from wood pulp and cotton. The principal use of it is the production of paperboard and paper and it is also used to convert into different derivative products like cellophane, rayon etc. The conversion of cellulose from energy crops into biofuels like cellulosic ethanol is the matter of investigation. At present the research is going on to find out its alternative source of fuel. [1]

2.2 Structure

Cellulose is composed of linear chains of D-glucose which is linked by β-1,4-glycosidic bonds with the degree of polymerization from 10,000 in native wood to 1,000 in bleached kraft pulps. Every D-anhydroglucopyranose unit bears hydroxyl groups at C2, C3, and C6 positions that can undergo the typical reactions known for primary and secondary alcohols. The molecular structure exposes cellulose with its characteristic properties: hydrophylicity, chirality, degradability, and broad chemical variability. Figure 1 shows the general structure of cellulose. The cellulose chain bristles with polar -OH groups. These groups form many hydrogen bonds with OH groups on adjacent chains, bundling the chains together. The chains also pack regularly in places to form hard, stable crystalline regions that give the bundled chains even more stability and strength. Cellulose has a strong tendency to form intra- and inter-molecular hydrogen bonds by the hydroxyl groups on these linear cellulose chains, which stiffen the straight chain and promote aggregation into a crystalline structure.
and give cellulose a multitude of partially crystalline fiber structures and morphologies. [2]

![Figure 1 Structure of Cellulose](image)

**3 CELLULOSE BASED BIOFUEL**

Bioethanol is focused as cellulose based biofuel.

**3.1 Bioethanol in general**

Bioethanol is the most widely used liquid biofuel. In 2008 worldwide production of bioethanol was over 41 billion liters. The largest producers in the world are Brazil (37%), the United States (33%), and Asia (14%). Production of bioethanol from sugarcane in Brazil reached over 16.4 billion liters (2008) that accounts for nearly 18% of the country’s automotive fuel needs. In Brazil, ethanol-powered and flexible-fuel vehicles are manufactured for operation with hydrated ethanol, an azeotrope of ethanol (around 93% v/v) and water (7%). As a result of this, coupled to the development of domestic deep-water oil sources, Brazil has achieved complete self-sufficiency in oil. Recently the United States (US) came over Brazil as the world’s largest producer of bioethanol. [3]

The demand for bioethanol has increased dramatically in recent years. So the ethanol from forest biomass is a huge source for that. In 1999 the US signed an executive order specifying a tripling in the production of bio based products and bio energy by the year 2015. As a result, US oil imports will be reduced by nearly 4 billion barrels over that time. With this effort to decrease GHG (green
house gas) emissions, it is targeted the increase in the production of renewable energy source by 6% within European Union. In France, the approval of a clean air act could increase ethanol production to 500 million liters. Similar projects in Spain, Sweden and the Netherlands are expected to increase the utilization of ethanol to account for over 30 % of transportation fuels by 2015. [3]

Fuel ethanol can be used in a variety of ways. It is commonly used as an oxygenated fuel additive in order to reduce emissions of carbon monoxide; nitrous oxides and hydrocarbons. Numerous common ethanolic motor-fuel formulations are being used with increasing frequency. Ethanol has a higher octane rating than petroleum fuels that enables combustion engines to run at higher compression ratios resulting higher net performance. Moreover, ethanol exhibits higher vapor pressure and heat of vaporization than gasoline and therefore increased power outputs are observed while using ethanol. [3]

3.2 Cellulosic ethanol production processes

The production of bio ethanol from the cellulose is a noble process. There have been developed many ways for its production. Some of the common methods are cellulolysis, gasification and consolidated bio processing. Cellulolysis involves hydrolysis on pretreated lignocellulosic materials; enzymes break down complex cellulose into simple sugars like glucose. Gasification converts biomass into gaseous carbon monoxide and hydrogen, these can be turned into ethanol through fermentation or chemical catalysis. Consolidated bioprocessing (CBP) is a system in which cellulase production, substrate hydrolysis, and fermentation are accomplished in a single process step by cellulolytic microorganisms. CBP offers the potential for lower biofuel production costs due to simpler feedstock processing, lower energy inputs, and higher conversion efficiencies than separate hydrolysis and fermentation processes. Moreover, it is an economically attractive near-term goal for “third generation” biofuel production. [3]
Figure 2 Cellulosic ethanol production process[4]

Figure 2 above shows the schematic diagram of the production of cellulosic ethanol. The first step is that the biomass is harvested thereby delivering to the bio refinery. Thereafter the biomass is cut into shreds and then pretreated with heat and chemicals to make cellulose accessible to enzymes. Then the enzymes breakdown cellulose chains into sugars. The process then follows as microbes ferment sugar into ethanol. Finally the produced ethanol is purified through distillation and prepared for distribution. [4]

3.2.1 Cellulolysis
This process can be studied under pretreatment and cellulolytic process.

3.2.1.1 Pretreatment

Pretreatment is usually done through chemical or physical means, this is done to make the biomass susceptible to the enzymes that break it down or to reduce the physical size of the biomass. This biomass can be anything from wood chips to sorghum, or corn husks to rice straw. Different types of pretreatment
techniques include acid hydrolysis, organosolve, steam explosion, and many more techniques. The setback of these pretreatments are that some are toxic; some more than others. For example hydroxymethyl furfural (HMF) is the most toxic one.\[4\]

3.2.1.2 Cellulolytic Process

Cellulose is made of long sugar molecule chains, during hydrolysis these chains are broken down into simple sugars. There are two different ways of doing this, the first is through chemical reactions using acid and the other is through an enzymatic reaction. Hydrolysis is performed breaking down the cellulose with acid. Dilute acid can be used under high heat and high pressure. Alternatively more concentrated acid can be used at lower temperatures and atmospheric pressure. During the process a decrystalized cellulosic mixture of acid and sugars reacts in the presence of water to complete individual sugar molecules. This process is hydrolysis. The following equation 3.1 shows the hydrolysis of cellulose,

\[
(C_{6}H_{10}O_{5})_{n} + H_{2}SO_{4} + H_{2}O \rightarrow C_{12}H_{22}O_{11} \quad (3.1)
\]

\(\text{cellulose} \quad \text{acid} \quad \text{water} \quad \text{sugar molecule}\)

The product from this hydrolysis is then neutralized and yeast fermentation is used for the production of ethanol. Moreover, the significant obstacle to the dilute acid process is that the hydrolysis is so harsh that toxic degradation products are produced and it can interfere with fermentation. So to avoid this concentrated acid must be separated from the sugar stream for recycle (simulated moving bed (SMB) chromatographic separation for example) to be commercially attractive. Cellulose can be broken down into glucose by cellulose enzymes. Lignocellulosic materials can be enzymatically hydrolyzed, this enables effective cellulose breakdown without formation of byproducts. The following equation 3.2 shows the enzymatic hydrolysis of cellulose,

\[
(C_{6}H_{10}O_{5})_{n} + (C_{6}H_{10}O_{5})n \rightarrow C_{6}H_{12}O_{6} \quad (3.2)
\]

\(\text{Cellulose} \quad \text{Cellulase} \quad \text{glucose}\)
The gasification phenomena include the conversion of the carbon in the biomass into gas instead of breaking cellulose into sugars. The carbon monoxide, carbon dioxide, and hydrogen made will then be fed into a special fermenter. In the fermenter microorganisms will consume all these gases as a result of which the production of ethanol and water occurs. Instead of sugar fermentation with yeast, this process uses a microorganism named Clostridium ljungdahlii. The gasification process itself thus can be accomplished in three steps,

1. Gasification — Complex carbon based molecules are broken apart to access the carbon as carbon monoxide, carbon dioxide and hydrogen are produced
2. Fermentation — Convert the carbon monoxide, carbon dioxide and hydrogen into ethanol using the Clostridium ljungdahlii organism
3. Distillation — Ethanol is separated from water

A recent study has found another Clostridium bacterium that is to be twice as efficient in producing ethanol from carbon monoxide as the one mentioned above. [4]

3.3 Fermentation
Fermentation process can be studied in the following topics.

3.3.1 Fermentation general
Fermentation process is concerned on extracting energy from the oxidation of organic compounds such as carbohydrates. The process uses an endogenous acceptor. The electron acceptor is usually an organic compound. Whereas, respiration is the process where electrons are donated to an exogenous electron acceptor, such as oxygen. It happens via an electron transport chain. The process is important in anaerobic conditions when there is no oxidative phosphorylation to maintain the production of ATP (Adenosine triphosphate). This happens by the process called glycolysis. During fermentation, pyruvate is metabolized to various other compounds. Moreover homolactic fermentation is the process where the production of lactic acid from pyruvate occurs. Alcoholic fermentation converts pyruvate into ethanol and carbon dioxide. In other hand
heterolactic fermentation is the production of lactic acid, other acids and alcohols. Fermentation can be carried out without an anaerobic environment too. For example, even in the presence of plenteous oxygen, yeast cells prefer fermentation to oxidative phosphorylation. It continues as long as sugars are readily available for consumption.[6]

Current strategies to produce fuel ethanol from cellulose, referred to as “second-generation” biofuels, utilize simultaneous sacharification and fermentation (SSF) or simultaneous sacharification and co-fermentation (SSCF). The following equation 3.3 and 3.4 shows the fermentation equation of glucose to ethanol,

\[
C_{12}H_{22}O_{11} + H_2O + \text{invertase} \rightarrow 2 C_6H_{12}O_6 \tag{3.3}
\]

(Sugar) (Water) (Glucose)

\[
C_6H_{12}O_6 + \text{Zymase} \rightarrow 2C_2H_5OH + 2 \text{CO}_2 \tag{3.4}
\]

(Glucose) (Ethanol) (Carbondioxide)

The process involves firstly that the sugar molecule gets converted into glucose in presence of the enzyme invertase and then the glucose in presence of enzyme zymase is converted into ethanol with carbondioxide biproduct.

Both SSF and SSCF require extensive pre-treatment of the cellulosic feedstock by steam-explosion and/or acid treatment, followed by addition of exogenously produced cocktails of cellulolytic enzymes to hydrolyze cellulose chains and release the glucose monomers that is needed for fermentation. Figure 2 shows the fermentation process in the fourth step where the microbes ferment sugar into ethanol[6].

### 3.3.2 Consolidated bioprocessing (CBP)

Consolidated bioprocessing (CBP) is an alternative processing strategy in which cellulase production, substrate hydrolysis, and fermentation are accomplished in a single process step by microorganisms that express cellullolytic (and hemicellulolytic) enzymes. CBP offers the potential for lower biofuel production
costs due to simpler feedstock processing, lower energy inputs (and therefore better energy balance), and higher conversion efficiencies than SSF based processes. Consolidated bioprocessing is not a new technology. It involves collapsing two steps in the ethanol production system: breaking down cellulose, and converting sugars into ethanol. CBP is an economically attractive near-term goal for process for “third generation” biofuel production. Successful development of “third generation” biofuels depends heavily on a detailed understanding of the metabolism of cellulolytic bacteria[7].

3.3.3 Cellulose feedstocks

Biofuels may be produced from the sugars of a variety of different feedstocks, including food crops and cellulosic substrates. Food crops such as sugarcane and sugar beets contribute to 60% of the world’s bioethanol production and contain large amounts of sucrose. Other crops, including corn and cereal crops like wheat, contain starch that is then converted into glucose during fermentation. The expansion of biofuels production, particularly in the United States, together with increased world-wide demand for grains and increased energy costs, has led to drastically higher grain prices. In the US, competition for land and other resources used to produce corn for fuel ethanol already has led to restrictions in land use for oilseed production and consequently higher prices associated with lower production levels. The pursuit of lower biofuels production costs and competition with traditional food crops has led many to consider cellulosic substrates as a potential feedstock.

3.4 Biohydrogen from cellulose

The production of biohydrogen from cellulose is a very noble process.

3.4.1 General

The production of hydrogen from forest biomass is a noble process to solve the energy problem. Biohydrogen from biomass resources could be used in bitumen upgrading for synthetic crude oil (SCO) production. Moreover, there is some use of the agricultural residues but in contrary most of it is left to rot in the field, although it is possible to use them for biohydrogen production. Normally, natural gas and coal are used for producing hydrogen that is consumed in
chemical and oil industries. In 2005, Western Canada had a production capacity of about 3 million tonnes of hydrogen and 31% of this was used for upgrading 527 thousand barrels of bitumen/day. The capacity of upgrading bitumen is expected to be about 2045 thousand barrels of bitumen/day in 2020 and. That is why it seems that the demand for hydrogen fuel for bitumen upgrading will increase\textsuperscript{[8]}.

Consumption of hydrogen fuel in bitumen upgrading varies with primary upgrading technology and quality of synthetic crude oil (SCO); typical value is 1000 standard cubic feet (scf) of hydrogen/barrel of bitumen (i.e. about 2.41 kg of H\textsubscript{2}/barrel of bitumen) upgraded. Additionally, about 2.86 kg of natural gas is consumed as fuel and feed, emitting 11.88 kg of CO\textsubscript{2} equivalent for producing 1 kg of H\textsubscript{2} by steam methane reforming (SMR) process; this rate may change with plant size and efficiency though. The use of biomass for producing hydrogen will reduce the intensity of CO\textsubscript{2} emission from oil sands industries\textsuperscript{[8]}.

Many experiments were performed before to produce the hydrogen using gasification process but it did not turn to work out. Some studies have dealt with techno-economic assessment of hydrogen fuel production from gasification of biomass especially from wood. This could be possibly the great idea of the utilization of the forest biomass for hydrogen production. Furthermore, Most of these studies have considered a certain-value for delivered-biomass cost (approximately $30–$60/dry tonne), and estimated production cost of H\textsubscript{2} is in the range of $1–$2/kg of H\textsubscript{2} for plants processing 360–5000 dry tonnes biomass/day. Contrarily some of the studies have estimated production cost of $2–$5/kg of H\textsubscript{2}. In an earlier study by the researchers; the cost of producing biohydrogen from whole-forest was estimated along with the cost of transportation\textsuperscript{[8]}.

3.4.2 Gasification technologies

The gasification of biomass can be carried out in an atmospheric pressure gasifier or a pressurized gasifier. There are two gasifiers commonly used; Battelle Columbus Laboratory (BCL) gasifier and Gas Technology Institute (GTI) gasifier. The key difference between these two gasifiers is in their
operating pressure. BCL gasification is an atmospheric pressure (\(\sim 0.16 \text{ MPa}\)) and involves feedstock drying with flue gases from char combustion, a wet gas cleaning process, a water-gas shift reaction, and a purification process. GTI gasification operates at high pressure (\(\sim 3.45 \text{ MPa}\)) and includes a high temperature syngas (\(\sim 982 \, ^\circ\text{C}\)) cleaning process, a shift reaction, and a purification process. In fact, pure oxygen is obtained from an oxygen production plant for the process in the GTI gasifier. This adds to the capital cost of the GTI process. The oxygen flow rate for GTI gasification process is 0.3 kg/kg of dry biomass, meanwhile 0.4 kg and 0.3 kg steam are supplied for each kg of dry biomass feed rate in BCL and GTI gasifiers, respectively.\(^8\)

Figure 3 BCL Gasifier\(^8\)
Figure 3 and Figure 4 shows the gasification process of biomass in a BCL and in a GTI gasifier, respectively. Syngas clean up, compression, water-gas shift reaction, and pressure swing adsorption (PSA) are the remaining steps in the BCL gasification process; hot gas clean up, water-gas shift reaction, and PSA are the remaining steps in the GTI gasification process. The basic operating principle of fluidized bed reactors is the same for gasification, combustion, or pyrolysis of biomass or coal. Some studies have considered fluidized bed gasifiers for the biomass gasification process. Biomass is fed into a bubbling fluidized bed (BFB) reactor, meanwhile oxidant and steam flow at the bottom of the reactor to create the fluidized medium, and product gases leave at the top of the reactor. Solid-particle-removal units like cyclone, baghouse filter, and/or electrostatic precipitator separate ash. The circulating fluidized bed (CFB) gasifier (i.e. the BCL gasifier) has similar operating feature, except that heat is transferred to the reactor by hot sand which leaves through the top of the reactor with product gases and char.\cite{8}

### 3.4.3 Estimating the cost of biohydrogen production

In the base case, the size of the biohydrogen plant is expected to be 2000 dry tonnes of biomass/day. The cost of biohydrogen production involves the cost of all upstream and downstream processes. The key components of the cost of biohydrogen production involving forest residues and straw include: cost of feedstock delivery with harvesting cost, transportation cost, and premium payment to the producer, the capital cost of the plant, the cost of plant operation and maintenance, the cost of ash disposal, and the cost of site reclamation.
Once all the economic and technical parameters are determined, a data intensive discounted cash flow techno-economic model using spreadsheet program was developed to estimate the cost and optimum plant size [9].

4 CELLULOSE DERIVATIVES

The cellulose derivatives are categorized in this section.

4.1 Methyl cellulose

Methylcellulose is a chemical compound derived from cellulose. It is a hydrophilic white powder in pure form and dissolves in cold (but not in hot) water, when dissolved it forms a clear viscous solution or something that looks like gel. It is used as a thickener and emulsifier in various food and cosmetic products, and also as a treatment of constipation. It is non-digestible, non toxic, and non allergenic [10].

\[
\begin{array}{c}
\text{\textbf{R}} = \text{H or CH}_3 \\
\end{array}
\]

Figure 5 Methyl Cellulose [10]

4.1.1 Properties

Methylcellulose has a lower critical solution temperature (LCST) between 40°C and 50°C. At temperatures below the LCST, it is readily soluble in water; above the LCST, it is not soluble, which has a paradoxical effect that heating a saturated solution of methylcellulose will turn it to solid, because methylcellulose will precipitate out. The temperature at which this occurs depends on degree of substitution (DS) value, with higher DS-values giving lower solubility and lower precipitation temperatures because the polar hydroxyl groups are masked [10].
Preparing a solution of methylcellulose with cold water is difficult though: as the powder comes into contact with water, a gluey layer forms around it, and the inside remains dry. A better way is to first mix the powder with hot water, so that the methyl cellulose particles are well dispersed in the water, and cool down this dispersion while stirring, leading to the dissolution of those particles \( ^{[10]} \).

4.1.2 Uses

Methylcellulose has been used in many fields.

4.1.2.1 Thickener and emulsifier

Methyl cellulose is often added to hair shampoos, tooth pastes and liquid soaps, to generate their characteristic thick consistency. This is also done for foods, for example ice cream or croquette. Methylcellulose is also an important emulsifier, preventing the separation of two mixed liquids. Methylcellulose is also used as paint rheological modifier to prevent paint sagging problem \( ^{[10]} \).

4.1.2.2 Medical application

Methylcellulose is not absorbed by the intestines but passes through the digestive tract undisturbed when it is eaten. It attracts large amounts of water into the colon, producing a softer and bulkier stool. It is widely used to treat constipation, diverticulosis, hemorrhoids and irritable bowel syndrome. It should be taken with sufficient amounts of fluid to prevent dehydration. Because it absorbs water and potentially toxic materials and increases viscosity, it can also be used to treat diarrhea. A well-known trade name of methylcellulose when used as a drug is Citrucel by GlaxoSmithKline. Methylcellulose is used as a variable viscosity personal lubricant; it is the main ingredient in Jelly. The lubricating property of methyl cellulose is of particular benefit in the treatment of dry eyes. Dry eyes are common in the elderly and are often associated with rheumatoid arthritis. The lachrymal gland and the accessory conjunctival glands produce fewer tears. It can be used as a tear substitute. \( ^{[11]} \)
4.1.2.3 Construction materials

Methylcellulose is used as a performance additive in construction materials. It is added to mortar dry mixes to improve the mortar's properties like workability, open and adjustment time, water retention, viscosity, adhesion etc. The construction materials can be cement based or gypsum based. Notable examples of dry mixture mortars which utilize methyl cellulose include: tile adhesives, insulating plasters, hand-towed and machine sprayed plaster, self-leveling flooring, extruded cement panels, joint and crack fillers, and tile grouts. Usual usage is about 0.2% ~ 0.5% of total dry powder weight for dry mixture. Derivatives of methyl cellulose, which improve upon the performance characteristics, include hydroxypropyl methyl cellulose (HPMC) and hydroxyethyl methylcellulose (HEMC). These derivatives help to enhance the characteristics like water retention, vertical surface slip-resistance, open time, etc \[11\].

4.1.2.4 Glue and binder

Methylcellulose can be utilized as mild glue. Later it can be washed away with water. This may be used in the fixation of delicate pieces of art as well as in book conservation to loosen and clean off old glue from spines and book boards. Methylcellulose is the main ingredient in many wallpaper pastes. It is also used as a binder in pastel crayons and also as a binder in medications \[11\].

4.1.2.5 Cell culture/virology

Methylcellulose is also used in cell culture to study viral replication. It is dissolved in the same nutrient containing medium in which cells are normally grown. A single layer of cells are grown on a flat surface, and then infected with a virus for a short time. The strength of the viral sample used can determine how many cells get infected during that period. The thick methyl cellulose medium is then added on top of the cells in place of normal liquid medium. As the viruses replicate in the infected cells, they are able to spread between cells whose membranes touch each other, but are trapped when they enter the methyl cellulose. Only cells closely neighboring an infected cell will become
infected and die. This leaves small regions of dead cells called plaques in a larger background of living uninfected cells. The number of plaques formed is determined by the strength of the original sample \cite{11}.

4.1.2.6 Stem cell differentiation

Methyl cellulose is used to quantify multiple or single lineage-committed hematopoietic progenitors, called colony-forming cells (CFCs). This works in combination with culture supplements that promote their proliferation and differentiation, and allow the clonal progeny of a single progenitor cell to stay together and thus form a colony of more mature cells. MethoCult and Colonygel are examples of that methylcellulose-based media \cite{11}.

4.1.2.7 Special effects

The slimy, nontoxic, non allergenic, and edible properties, makes methylcellulose popular for use in special effects for motion pictures and television. In the film Ghostbusters, for example, the gooey substance the supernatural entities used to slime the Ghostbusters was mostly a thick water solution of methyl cellulose. Methyl cellulose is used to safely simulate molten materials. In several of the terminator films, it was back-lit with colored gels and films to reproduce the heated glow of iron in the large pouring ladles used to transport the metal from the smelting ovens to the various molds \cite{11}.

4.1.2.8 Other uses

Methylcellulose is used in the manufacture of capsules in nutritional supplements; its edible and nontoxic properties provide a vegetarian alternative to the use of gelatin. It is used as sizing in the production of papers and textiles as it protects the fibers from absorbing water or oil. It is also used as a buffer additive in capillary electrophoresis to control electro osmotic flow for improved separations. Aqueous methylcellulose solutions have been used to slow bacterial cell motility for closer inspection. Changing the amount of methylcellulose in solution allows one to adjust the solution's viscosity. \cite{11}
4.2 Ethyl cellulose

Ethyl cellulose is a derivative of cellulose in which some of the hydroxyl groups on the repeating glucose units are converted into ethyl ether groups. The number of ethyl groups can vary depending on the manufacture. It is mainly used as a thin-film coating material. Ethyl cellulose is used as a food additive as an emulsifier \(^{[12]}\).

\[
R = H \text{ or } CH_2CH_3
\]

Figure 6 Ethyl Cellulose \(^{[12]}\)

4.3 Cellulose acetate

Cellulose acetate is the acetate ester of cellulose. It is used as a film base in photography, as a component in some adhesives, and as a frame material for eyeglasses. It is also used as a synthetic fiber and in the manufacture of cigarette filters and playing cards \(^{[13]}\).

Figure 7 Cellulose acetate \(^{[13]}\)
4.3.1 Production

The Federal Trade Commission definition for acetate fiber is that it is manufactured fiber in which the fiber-forming substance is cellulose acetate. Where not less than 92 percent of the hydroxyl groups are acetylated, the term triacetate may be used as a generic description of the fiber.

Figure 8 The production of cellulose acetate\cite{13}

Acetate is derived from cellulose by deconstructing wood pulp into a purified fluffy white cellulose. In order to get a good product special qualities of pulps dissolving pulps are used. A common problem with these is that the reactivity of the cellulose is uneven. Figure 8 shows the schematic method of cellulose acetate production. The cellulose is reacted with acetic acid and acetic anhydride in the presence of sulfuric acid. It is then put through a controlled, partial hydrolysis to remove the sulfate and a sufficient number of acetate groups to give the product the desired properties. The anhydroglucose unit is the fundamental repeating structure of cellulose and has three hydroxyl groups which can react to form acetate esters. The most common form of cellulose
acetate fiber has an acetate group on approximately two of every three hydroxyls. This cellulose diacetate is known as secondary acetate, or simply as acetate. After it is formed, cellulose acetate is dissolved in acetone into a viscous resin for extrusion through spinnerets. As the filaments emerge, the solvent is evaporated in warm air via dry spinning, producing fine cellulose acetate fibers.

### 4.3.2 Properties

Cellulose acetate is cellulosic and thermoplastic. It shows the properties of selective absorption and removal of low levels of certain organic chemicals. Cellulose acetate can be easily bonded with plasticizers, heat, and pressure. It is soluble in many common solvents including acetone and other organic solvents and can be modified to be soluble in alternative solvents like water. It is hydrophilic with good liquid transport and excellent absorption. In textile applications, it provides comfort and absorbency, but also loses strength when wet. Acetate fibers are hypoallergenic. It can be easily composted or incinerated. It can be dyed, however special dyes and pigments are required since acetate does not accept dyes ordinarily used for cotton and rayon. Acetate fibers are resistant to mold and mildew. It is easily weakened by strong alkaline solutions and strong oxidizing agents.

### 4.3.3 Major uses

Cellulose acetate is widely used to make buttons, sunglasses, linings, blouses, dresses, wedding and party attire, home furnishings, draperies, upholstery and slip covers. Industrially, it is used to make cigarette and other filters, ink reservoirs for fiber tip pens. It is used to make high absorbency products like diapers and surgical products. The original Lego bricks were manufactured from cellulose acetate from 1949 to 1963. Its use is common in Award Ribbon: Rosettes for equestrian events, dog/cat shows, corporate awards, and advertising and identification products all use cellulose acetate ribbon. KEM brand playing cards are made of cellulose acetate. It is used at the World Series of Poker and in many poker rooms at major casinos.
4.4 Nitrocellulose

Nitrocellulose is a highly flammable compound formed by nitrating cellulose through exposure to nitric acid or another powerful nitrating agent. When used as a propellant or low-order explosive, it is also known as guncotton. Nitrocellulose plasticized by camphor was used by Kodak, and other suppliers, from the late 1880s as a film base in photograph, X-ray films and motion picture films; and was known as "Nitrate film" [14].

![Figure 9 Nitro Cellulose](image)

4.4.1 Production

Nitrocellulose is produced by causing cellulose to react with nitrating acid (a mixture of nitric acid and sulfuric acid) as shown in figure 10. Following complex washing and stabilizing stages, damping agents (alcohols or water) or plasticizers are added to the nitrocellulose which is then marketed as Walsroder Nitrocellulose or Walsroder NC-Chips.
Figure 10 shows the schematic flow chart of an outline of its production. The raw material used for producing Walsroder Nitrocellulose and Walsroder NC-Chips is carefully selected and well-characterized types of cellulose, the exact specifications having been agreed with the cellulose suppliers. Compliance with these specifications is regularly checked during incoming goods inspections. This also applies to all other raw materials. This helps to maintain the consistent quality of Walsroder Nitrocellulose and Walsroder NC-Chips. The cellulose is caused to react with the nitrating acid in the nitrating process. After nitrination, centrifuges separate the nitrocellulose from the spent nitrating acid used in excess quantity. Nitrating acid is separated into nitric acid, sulfuric acid and water, and completely recycled back into the process. The next stage is the pre-stabilization stage where the nitrocellulose is washed with water. This process separates off any acid left on the fibers. After that, the viscosity of the
Nitrocellulose is adjusted by pressure boiling i.e. heating under pressure to temperatures above 100°C. This is followed by the post-stabilization stage where the nitrocellulose is washed with water and heated to temperatures below 100°C. The water is subsequently separated off to leave water content of 35%. This water-wet nitrocellulose can then be packaged. To produce alcohol-damped Walsroder Nitrocellulose, the water is replaced with the appropriate damping alcohol. To produce Walsroder NC-Chips, the appropriate plasticizer is added to water-wet nitrocellulose which is then dried. In the course of the entire production process all relevant properties of the nitrocellulose and of the process are constantly monitored to ensure the consistent high quality of Walsroder Nitrocellulose and Walsroder NC-Chips.\textsuperscript{14}

### 4.4.2 Uses

A nitrocellulose membrane or nitrocellulose paper is a sticky membrane used for immobilizing nucleic acid. It is also used for immobilization of proteins in Western blots and Atomic Force Microscopy for its non-specific affinity for amino acids. Nitrocellulose is widely used as support in diagnostic tests where antigen-antibody binding occur such as pregnancy tests, U-Albumin tests. Glycine and chloride ions make protein transfer more efficient. When the solution is dissolved in ether, alcohol or other organic solvents it produces collodion, discovered in 1846 and introduced as a wound dressing during the crimean war. It is in use today in topical skin applications, such as liquid skin and in the application of salicylic acid, the active ingredient in Compound wart remove. Magician's flash paper, sheets of paper or cloth are made from nitrocellulose, which burn almost instantly with a bright flash leaving no ash. Nitrocellulose lacquer is also used as an aircraft dope, painted onto fabric-covered aircraft to tauten and provide protection to the material.\textsuperscript{14}

### 4.5 Carboxymethyl cellulose

Carboxymethyl cellulose (CMC) is a cellulose derivative with carboxymethyl groups (-CH₂-COOH). It is often used as its sodium salt, sodium carboxymethyl cellulose.\textsuperscript{15}
4.5.1 Production

Carboxymethyl cellulose is produced by the alkali-catalyzed reaction of cellulose with chloroacetic acid. The polar carboxyl groups render the cellulose soluble and chemically reactive. The functional properties of CMC depend on the degree of substitution of the cellulose structure, also the chain length of the cellulose backbone structure and the degree of clustering of the carboxymethyl substituent.\textsuperscript{[15]}

4.5.2 Uses

It is used in food science as a viscosity modifier or thickener. In addition, it stabilizes emulsions in various products including ice cream. It is also a constituent of many non-food products, such as K-Y Jelly, toothpaste, laxatives, diet pills, water-based paints, detergents, textile sizing and various paper products. It is used primarily because it has high viscosity, is non-toxic, and is hypoallergenic. In laundry detergents it is used as a soil suspension polymer designed to deposit onto cotton and other cellulosic fabrics creating a negatively charged barrier to soils in the wash solution. It is also used as a lubricant in non-volatile eye drops. It has wide application food sector, pharmaceutical and dentifrice (toothpaste). An intermediate semi-purified grade is also produced, typically used in paper applications. It is used in the oil drilling industry as an ingredient of drilling mud, where it acts as a viscosity modifier and water retention agent. Insoluble micro granular carboxymethyl cellulose is used as a
cation-exchange resin in ion-exchange chromatography for purification of proteins. CMC is also used in ice packs to form a eutectic mixture resulting in a lower freezing point and therefore more cooling capacity than ice. Aqueous solutions CMC have also been used to disperse carbon nanotubes \cite{15}.

4.6 Hydroxypropyl cellulose

Hydroxypropyl cellulose (HPC) is a derivative of cellulose with both water solubility and organic solubility. It is an ether of cellulose in which some of the hydroxyl groups in the repeating glucose units have been hydroxypropylated forming -OCH₂CH(OH)CH₃ groups using propylene oxide. The average number of substituted hydroxyl groups per glucose unit is referred to as the degree of substitution. Because the hydroxypropyl group added contains a hydroxyl group, this can also be etherified during preparation of HPC. It has a combination of hydrophobic and hydrophilic groups, so it has a lower critical solution temperature (LCST) at 45 °C. At temperatures below the LCST, it is readily soluble in water; above the LCST, it is not soluble. It forms liquid crystals and many mesophases according to its concentration in water. Such mesophases include isotropic, anisotropic, nematic and cholesteric \cite{16}.

\[
\text{R} = \text{H or CH₂CH(OH)CH₃}
\]

Figure 12 Hydroxypropyl cellulose \cite{16}.

4.6.1 Uses

Hydroxypropyl cellulose is used to prepare artificial tears. It is used to treat medical conditions characterized by insufficient tear production such as keratoconjunctivitis sicca, recurrent corneal erosions, decreased corneal sensitivity, and exposure and neuroparalytic keratitis. It is also used as a lubricant for artificial eyes. As a food additive, it is used as a thickener, a low
level binder and as an emulsion stabilizer. In pharmaceuticals it is used as a disintegrant, and a binder, in tablets. It is used as a sieving matrix for DNA separations by capillary and microchip electrophoresis [16].

5 NANOCELLULOSE

Nanocellulose is a new field of research at the moment.

5.1 General

Nanocellulose also called as microfibrillated cellulose (MFC), is a material, which is composed of nanosized cellulose fibrils that have got high aspect ratio (length to width ratio). Most typical dimensions ranges from 5–20 nanometers width and length can range up to 2000 nanometers. It is pseudo-plastic and poses the property of certain gels that are viscous under normal conditions. Its flow becomes thin, less viscous over the time when it is shaken, agitated, or pressurized. This kind of property of nanocellulose is called as thixotropy. When the shearing forces are removed the gel regains much of its original state. The fibrils are isolated from any cellulose. The most common source of nanocellulose includes wood-based fibers (through high-pressure, high temperature and high velocity impact homogenization). Nanocellulose can also be obtained from native fibers by an acid hydrolysis, that results to highly crystalline and rigid nanoparticles and they are shorter from 100s to 1000 nanometers than the nanofibrils obtained through the homogenization route [17].

Figure 13 Nanocellulose [17]
5.2 Production

Nanocellulose can be prepared from any cellulose source material. Wood pulp is mostly used for its production. Its fibrils are isolated from the wood-based fibers using high-pressure homogenizers. The homogenizers are used to delaminate the cell walls of the fibers. This helps to liberate the nanosized fibrils. This production route is normally connected to high-energy consumptions that are associated with the fiber delamination. Cellulose nanowhiskers are more crystalline form of nanocellulose. It is formed by the acid hydrolysis of native cellulose fibers in which the concentrated inorganic salt, sulfuric or hydrochloric acid are used. The amorphous part of native cellulose is hydrolyzed and after careful timing, the crystalline sections can be retrieved from the acid solution by centrifugation followed by washing. Cellulose nanowhiskers are rodlike highly crystalline particles with a rectangular cross section. Its dimensions depend on the native cellulose source material, and hydrolysis time and temperature [18].

5.3 Properties

The properties of nanocellulose have given it a unique feature. The following properties describe the nature of nanocellulose.

5.3.1 Nanocellulose dimensions and crystallinity

The ultrastructure of cellulose derived from various sources has been extensively studied. Techniques such as transmission electron microscopy (TEM), scanning electron microscopy (SEM), atomic force microscopy (AFM), wide angle X-ray scattering (WAXS), small incidence angle X-ray diffraction and solid state $^{13}$C cross-polarization magic angle spinning (CP/MAS) nuclear magnetic resonance (NMR) spectroscopy have been used to characterize nanocellulose morphology. These methods have been applied to the investigation of dried nanocellulose morphology. The combination of microscopic techniques with image analysis can provide information on nanocellulose fibril widths, but it is more difficult to determine nanocellulose fibril lengths. It is due to entanglements and difficulties in identifying both ends of individual nanofibrils. It is reported that nanocellulose suspensions are not homogeneous and that they consist of cellulose nanofibers and nanofiber
bundles. Most methods have been applied to investigation of dried nanocellulose dimensions, although a study was conducted where the size and size-distribution of enzymatically pre-treated nanocellulose fibrils in a suspension were studied using cryo-TEM. The fibrils were found to be mono-disperse. The lower end of the thickness dimension is around 0.4 nm, which is believed to be the thickness of a cellulose monolayer sheet \cite{18}.

Figure 5.2 AFM height image of carboxymethylated nanocellulose Adsorbed on a silica surface. The scanned surface area is 1 µm\(^2\)\cite{18}

The influence of cellulose pulp chemistry on the nanocellulose microstructure has been investigated using AFM to compare the microstructure of two types of nanocellulose prepared at Innventia AB (enzymatically pre-treated nanocellulose and carboxymethylated nanocellulose). Due to the chemistry involved in producing carboxymethylated nanocellulose, it differs significantly from the enzymatically pre-treated one. The number of charged groups on the fibril surfaces is very different. The carboxymethylation pre-treatment makes the fibrils highly charged. This makes it easier to liberate, which results in smaller and more uniform fibril widths (5–15 nm) compared to the enzymatically pre-treated nanocellulose, where the fibril widths were 10–30 nm. The degree of crystallinity and the cellulose crystal structure of nanocellulose were also studied at the same time. The results clearly showed the nanocellulose exhibited cellulose crystal I organization and that the degree of crystallinity was
unchanged by the preparation of the nanocellulose. Typical values for the degree of crystalline were around 63% [18].

5.3.2 Viscosity

The unique rheology of nanocellulose dispersions was recognized by the early investigators. The high viscosity at low nanocellulose concentrations makes nanocellulose very interesting as a non-calorie stabilizer and gellant in food application. The dynamic rheological properties have been investigated in great detail and it has been found that the storage and loss modulus were independent of the angular frequency at all nanocellulose concentrations between 0.125% to 5.9%. The storage modulus values are particularly high (104 Pa at 3% concentration). Nanocellulose gels are highly sheared thinning. The shear-thinning behavior is specifically useful in a range of different coating applications [18].

5.3.3 Mechanical properties

The crystalline cellulose has quite interesting mechanical properties especially in its material applications. The stiffness of crystalline cellulose is in the order of 140–220 GPa, which is in the same size order as for instance Kevlar and is better than, for example, glass fibers, both of the fibers are used commercially to reinforce plastics. Films made from nanocellulose have been shown to have high strength (over 200 MPa), high stiffness (around 20 GPa) and high strain (12 %) [18].

5.3.4 Barrier properties

The crystalline regions of nanocellulose are gas impermeable in semi-crystalline polymers. Due to relatively high crystalline, in combination with the ability of the nanofibers to form a dense network held together by strong inter-fibrillar bonds (high cohesive energy density), it has been suggested that nanocellulose might act as a barrier material. Although the number of reported oxygen permeability values is limited, reports attribute high oxygen barrier properties to nanocellulose films. Changing the surface functionality of the cellulose nanoparticle can also affect the permeability of nanocellulose films. Films
constituted of negatively charged cellulose nanowhiskers could effectively reduce permeation of negatively charged ions, while leaving neutral ions virtually unaffected. Positively charged ions were found to accumulate in the membrane \[^{18}\].

**5.3.5 Surface modification**

The surface modification of nanocellulose is recently receiving a great attention. Nanocellulose exhibits a large amount of hydroxyl groups at the surface, which can be reached. However, hydrogen bonding strongly affects the reactivity of the surface hydroxyl groups. Moreover, impurities at the surface of nanocellulose such as glucosidic and lignin fragments need to be removed before surface modification in order to obtain acceptable reproducibility between different batches \[^{18}\].

**5.4 Uses**

Nanocellulose can be used in different fields. Some of the fields are mentioned below.

**5.4.1 Paper and paperboard**

The potential of nanocellulose applications in the area of paper and paperboard manufacture is obvious. Nanocelluloses are expected to enhance the fiber-fiber bond strength. So it has a strong reinforcement effect on paper materials. Nanocellulose may be useful as a barrier in grease-proof type of papers and as a wet-end additive to enhance retention, dry and wet strength in commodity type of paper and board products \[^{18}\].

**5.4.2 Food**

Nanocellulose can be used as a low calorie replacement for today’s carbohydrate additives used as thickeners, flavor carriers and suspension stabilizers in a wide variety of food products. It is also useful for producing fillings, crushes, chips, wafers, soups, gravies, puddings etc. The food applications were early recognized as a highly interesting application field for nanocellulose due to the rheological behavior of the nanocellulose gel.
Hydrocarbon fracturing of oil-bearing formations is a potentially interesting and large-scale application. Nanocellulose has been suggested for use in oil recovery applications as a fracturing fluid. Drilling mud based on nanocellulose has also been suggested [18].

5.4.3 Medical, cosmetic and pharmaceutical uses

The use of nanocellulose in cosmetics and pharmaceuticals was also early recognized. Freeze-dried nanocellulose aerogels is used in sanitary napkins, tampons, diapers or as wound dressing. The use of nanocellulose as a composite coating agent in cosmetics e.g. for hair, eyelashes, eyebrows or nails is also practiced. A dry solid nanocellulose composition in the form of tablets for treating intestinal orders is widely used. Nanocellulose films for screening of biological compounds and nucleic acids encoding a biological compound are of great use. Filter medium partly based on nanocellulose for leukocyte free blood transfusion is also used widely. A buccodental formulation, that consists of nanocellulose and a polyhydroxylated organic compound has been practiced. Powdered nanocellulose has also been used as an excipient in pharmaceutical compositions [18].

5.4.4 Other applications

Nanocellulose is used to activate the dissolution of cellulose in different solvents, Regenerated cellulose products, such as fibers films. It has a wide application in making tobacco filter additive. It is also used in organ metallic modified nanocellulose in battery separators. The use of nanocellulose in loud-speaker membranes is common. It can be used as super water absorbent (e.g. for incontinence pads material). Nanocellulose is also used together with super absorbent polymers. Use of nanocellulose in tissue, non-woven products or absorbent structures is also practiced. Moreover it is often used as antimicrobial films. Oil in water applications was early recognized. The area of non-settling suspensions for pumping sand, coal as well as paints and drilling mud was also explored by the early investigators. Hydrocarbon fracturing of oil-bearing formations is a potentially interesting and large-scale application. Nanocellulose
has been suggested for use in oil recovery applications as a fracturing fluid. Drilling mud based on nanocellulose has also been suggested[18].

6 CONCLUSION

The utility of cellulose and its derivatives is enormously increasing in various fields. Cellulose from forest biomass has got much possibility at present. The extraction of it gives great hopes for the present world. The bioethanol from forest biomass is of big interest at present too. Also hydrogen can be produced at $1.15/kg of H\textsubscript{2} ($9.58/GJ of H\textsubscript{2}) through BCL gasification by a plant able to process 3000 dry tonnes of forest residues/day. This is the optimum size for the plant, i.e. the size at which the cost of producing biohydrogen from forest residues is lowest. GTI gasifiers have a scale factor which results in a rapid reduction of capital cost per unit of output as capacity increases. Moreover the nanocellulose is of great importance and it has got the wide range of application in various fields.
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