

Higher School Certificate Chemistry

RESEARCH ASSIGNMENT

Cellulose, Biopolymers and the Future

Cameron Korb-Wells

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Fossil Fuels

Throughout human history, especially during the 20th century, society has come to rely enormously on fossil fuels—formed from long-buried plants and microorganisms. This dependence has become spread across all industries, with each requiring the natural resources that coal, natural gas and petroleum offer. There is cause for concern though, for the rate at which these natural resources currently being consumed is much greater than the rate at which they are being replaced in nature. This is due to the extensive time period needed for the fuels to form.

Petroleum

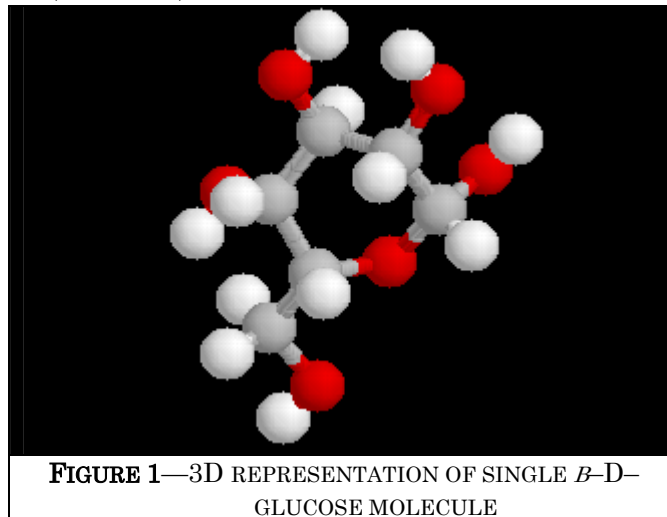
Petroleum, or crude oil, is a naturally occurring fossil fuel composed of various organic compounds, and is used as a fuel as well as a raw material for products of the petrochemical industry. This industry, through various processes, uses the organic compounds found in petroleum to produce products such as medicines, fertilisers, food products, plastic materials, building materials, paints and cloths, as well as to produce electricity. It is this versatility of petroleum to be able to be developed into other products, as well as its extensive and inexpensive supply, which have led the petrochemical industry and the petroleum that supply it to become essential cornerstones of the continued viability of the modern and industrialised world.

Petroleum however, like other fossil fuels, is not limitless in its supply, and recently its worldwide availability has begun to decline, with its cost increasing. It is expected that the natural supply of petroleum will extend into the early decades of the 21st century, when it is predicted that technological discoveries and advancements will no longer be capable of extending the availability of low-cost petroleum. In light of these predictions, it is apparent that alternative, and ideally renewable, sources must be found to provide raw materials currently utilised by the petrochemical industry.

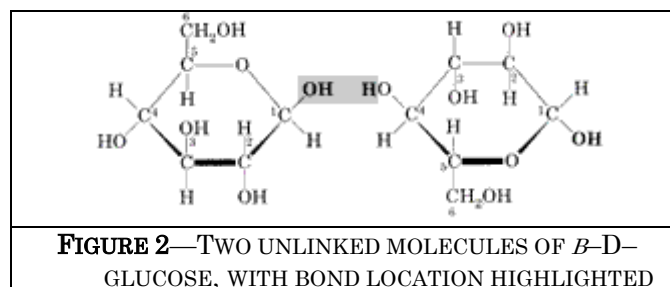
Cellulose

Cellulose is a complex carbohydrate consisting of a chain of linked sugar molecules. It is unquestionably the most abundant organic compound on Earth, comprising 50% or more of all carbon found in vegetation.

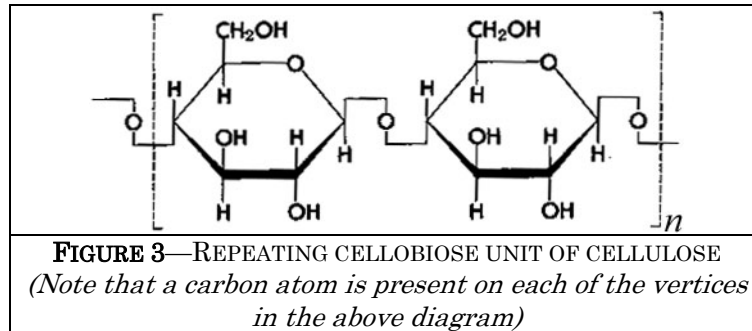
At its most basic level, cellulose is comprised of the sugar molecule β -D-glucose, which is a structural variation of the traditional straight-chain glucose molecule ($C_6H_{12}O_6$).



The polymerisation of cellulose begins with two of these β -D-glucose molecules combining a hydroxyl group from one with a hydrogen atom from the other (from the 1st and 4th carbon atom in the molecule), commonly called a β -1,4-glycosidic bond. The result of this reaction is the expulsion of one water molecule. This expulsion of a minor molecule in the formation of a polymer defines cellulose as a condensation polymer.



The disaccharide formed by the combination of the two β -D-glucose molecules is cellobiose. There are conflicting views as to whether it is this cellobiose disaccharide or β -D-glucose that acts as the monomer for cellulose, as both are repeating subunits. It is argued, however, that the positioning of the glucose molecules in cellobiose is important to the straight chain cellulose structure, and therefore cellobiose should be considered the monomer.



Cellulose as a resource

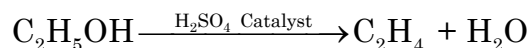
The basic carbon chain structures which cellulose contains means that it has come to be considered as a prime alternative source of some of the starting molecules of the petrochemical industry—compounds such as ethene, propene and butene. The process of decomposing cellulose into its constituent glucose molecules, which is required to produce these other compounds, is not a simple process however. Cellulose is therefore not currently an economically viable alternative when compared with relatively cheap petroleum resources.

There are presently three processes under development by industry to break down cellulose into usable products. These include the processes of acid cellulose conversion, enzymic cellulose hydrolysis and Syngas fermentation.

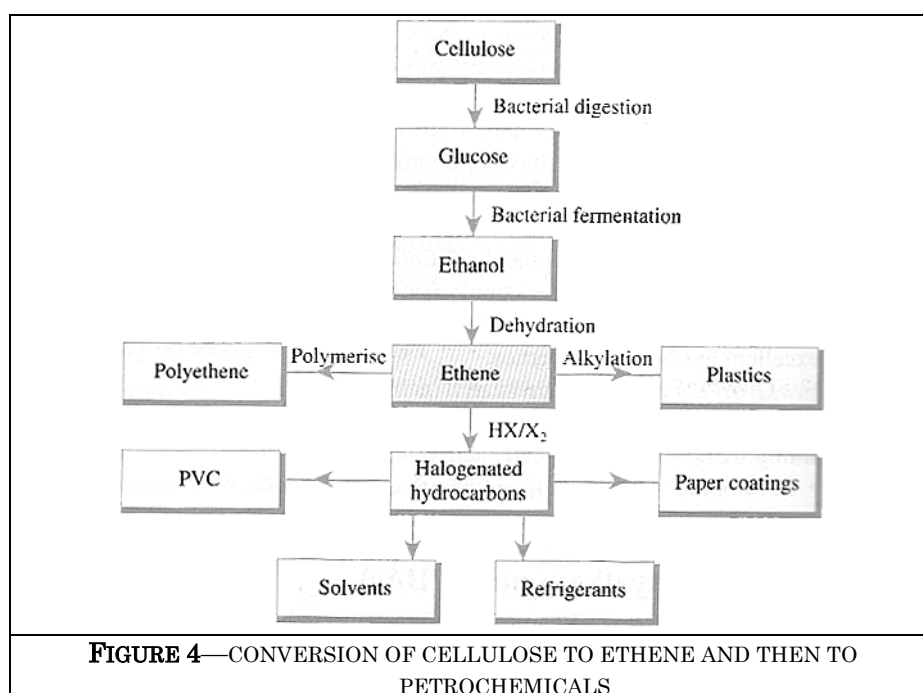
- The acid process involves using acids to disrupt the cellulose bonds, making them susceptible to hydrolysis, with the resulting mixture treated with bacteria to separate the acids and sugars.
- The enzymic process uses various enzymes to separate the glucose molecules from the cellulose chain.
- Syngas fermentation converts cellulose into a variety of gases which are then treated with bacteria to convert the gases into ethanol.

When a molecule such as glucose can be extracted from cellulose, it can then be treated to produce a molecule that can be utilised. For example, the glucose may be fermented into ethanol, a fuel alternative to petrol. Apart from being able to be utilised as a fuel source, the ethanol can also be treated to produce other chemicals such as ethene, considered an essential raw material in the petrochemical industry.

The process of producing ethene from ethanol is dehydration. This involves the use of a concentrated sulfuric or phosphoric acid which acts as a catalyst, as in the equation below:



From ethene, a wide variety of petrochemicals, such as polyethylene and other plastics, as well as halogenated hydrocarbons, can be manufactured. The process of converting cellulose to ethene and then into other petrochemicals is shown in the flow chart below.



Cellulose as a monomer

One property of the cellulose polymer, which has enabled it to be modified and manufactured by industry, is the high reactivity of the many hydroxyl groups on the polymer chain. Examples of substances whose production process exploits this reactivity are plentiful, but one specific material is cellulose acetate, formed by treating cellulose with acetic anhydride, causing each of the three hydroxyl groups on the cellulose chain to be converted into acetates. Of course, the cellulose chain can be treated with other chemicals, leading to the creation of a wide range of materials that are extensively utilised.

Cellulose can also be broken down into its repeating monomers, which can then be fermented into substances such as ethanol and then developed into other compounds, as discussed above.

Cellulose can, however, also be broken down in order to produce other polymers with altered physical and chemical properties. After the cellulose has been broken down into its cellobiose or β -D-glucose monomers, the monomer can then be treated and reproduced into a polymerised form. The new polymer is constructed in part by the initial monomer, but also of one or more other repeating sub-unit compounds. Materials such as this are classified as copolymers, and include a wide range of products from film media to explosives.

Biomass

The term biomass refers to all of the Earth's vegetation, and the many products derived from it. Biomass is, however, most commonly associated with biomass energy, which consists of varied and versatile fuels derived from biological sources, capable of matching and replacing any fossil fuel. This capability of biomass to be used as a fuel comes from the fact that all plant material contains energy captured by the sun through photosynthesis, giving it a high energy content. Biomass energy is also an essentially renewable resource, as long as vegetation is managed appropriately.

As previously mentioned, cellulose constitutes at least 50% of all carbon found in vegetation, due to its importance in the cell walls of plant cells, and is thus a hugely significant component of the Earth's biomass. Accordingly, it has great potential to be utilised as an alternative and renewable fuel source for the future when Earth's supplies of fossil fuels noticeably decline and prices are forced upwards. Apart from these economic motivations, other benefits of biomass fuels include the fact that biomass is composed of carbohydrate polymers, consisting mainly of carbon, hydrogen, oxygen and nitrogen. There is thus very little pollution produced if the fuel is fully combusted (the products of combustion are carbon dioxide and water). Biomass fuels would therefore greatly reduce the current adverse environmental impacts resulting from the use of fossil fuels.

One potential feedstock of biomass fuels are the many materials which contain cellulose, such as wood, straw, crop stalks and waste paper—all of which are in plentiful supply. If these cheap and widely available feedstocks could be broken down economically into their component sugars, cellulose-based materials could replace the fossil fuels currently used to meet our energy requirements (processes to break down these materials are outlined in *Cellulose as a resource*, above). In fact, several countries are currently developing or actively participating in programs such as these to produce fuels (primarily ethanol) through this process.

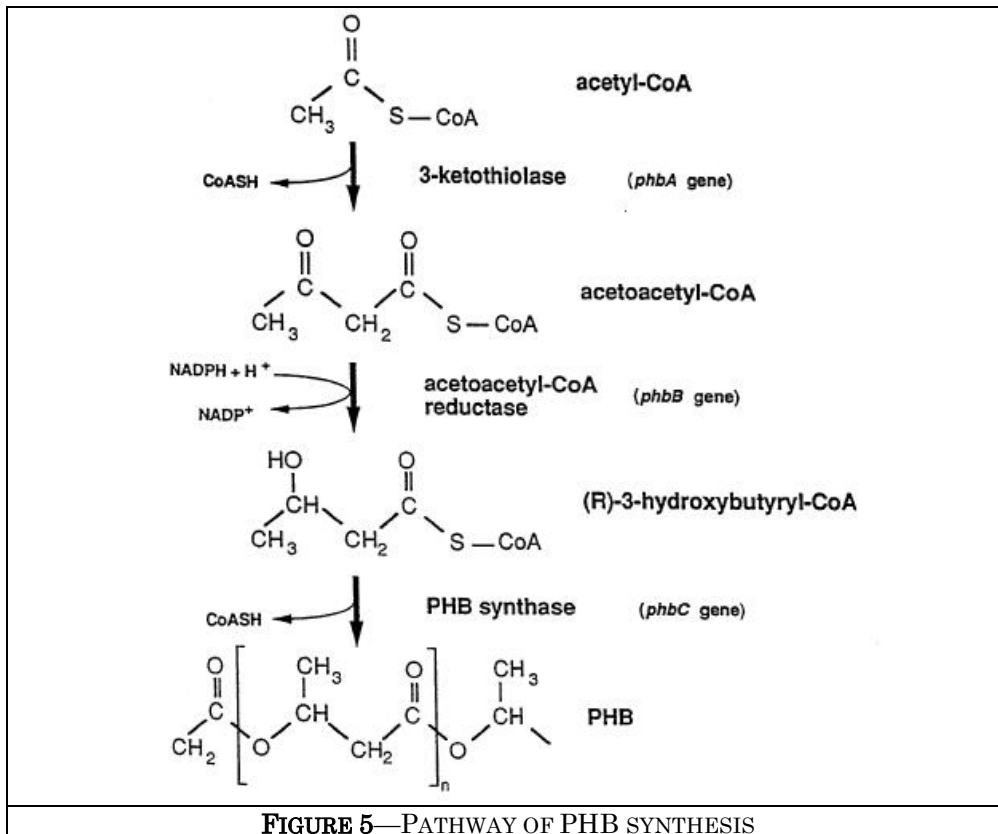
Biopolymers

Poly[β-hydroxybutanoate] (PHB)

Production

To produce the biopolymer PHB (also known as polyhydroxybutyrate), a culture of bacteria such as *Alcaligenes Eutrophus* is placed in a suitable growth medium and fed high levels of nutrients such as glucose, causing it to multiply rapidly and into a large population. Nitrogen is then restricted from the nutrient supply, making the bacteria unable to reproduce further. The bacteria store their excess energy in the biopolymer PHB, much as humans do with fatty tissue. Of course, thermal conditions must be suitable for the bacteria to act as desired, with optimum PHB levels occurring within the temperature range of 20°C to 30°C. Under these conditions, the levels of PHB extracted can reach a maximum of 80% of the bacterium's dry body weight, with the organism being harvested and the polymer separated out. The PHB is then milled to a powder or a pellet that can be used in molds.

The chemistry behind the production of PHB involves the consecutive action of 3 enzymes, those being 3-ketothiolase, acetoacetyl-CoA reductase and PHB synthase. The pathway of synthesis from acetyl-CoA to PHB and the actions of the enzymes are shown in the diagram below.

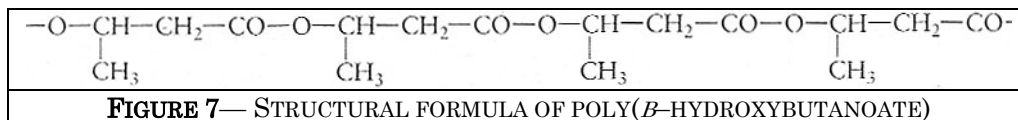
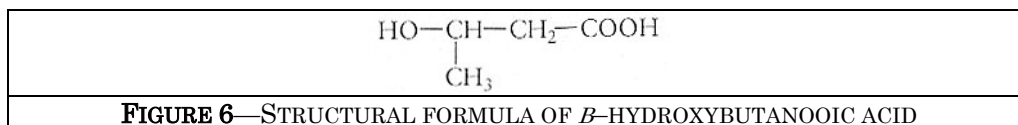


As can be seen from Figure 5, the production of the enzymes involved in PHB synthesis are reliant on specific genes, and thus the advent of genetic engineering has allowed the bacteria to be modified so as to increase the quantities of enzymes produced, and thus the productivity of the synthesis process.

Genetic technology has also allowed scientists to begin producing PHB in non-bacterial organisms. The transferal of the *phbA*, *phbB* and *phbC* genes—those responsible for the PHB enzyme synthesis—from bacteria into the plastids of higher plants have made it possible for those plants to produce the biopolymer as well. Scientists have also been able to clone these genes into populations of *Escherichia coli* bacteria, which have been much more extensively studied, and thus their behavior in producing the biopolymer can be more effectively controlled.

Properties

The PHB polymer contains ester linkages and is thus classified as a polyester, with β -hydroxybutanoic acid as its monomer. PHB has thermoplastic properties, meaning that it either melts or is softened when heated and solidifies when cooled, and can do so any number of times. The structures of both the monomer and polymer are shown below:



Pure PHB is a stiff and brittle material, and a research program conducted in the 1970s by Imperial Chemical Industries (ICI) discovered that the melting points, crystallinity, molecular weights, and tensile strengths of PHB and polypropylene were very similar (see Table 1 on the following page). However, the brittleness of the material limited its potential use and led ICI to begin developing PHB into a copolymer.

By altering the media on which the bacteria grow, chemists were able to control the chemical and physical properties of the PHB produced. When ICI grew the bacteria on a medium containing valeric acid, a copolymer of PHB and poly(β -valerate) was formed. This copolymer is stronger and more flexible than pure PHB, and is currently manufactured by ICI as Biopol®.

Apart from its properties being similar to other useful polymers, PHB is a biocompatible and biodegradable substance, readily degraded in soil,

sludge and seawater—a sheet of pure PHB polymer placed in soil at 30°C decomposed within 10 weeks.

<i>Chemical Resistance</i>	Acids—dilute	Fair
	Alcohols	Fair
	Alkalis	Poor
	Greases and oils	Good
<i>Electrical Properties</i>	Dielectric constant @1MHZ	3.0
	Volume resistivity	10 ¹⁶ ohm.cm
<i>Mechanical Properties</i>	Izod impact strength	35–60 J.m ⁻¹
	Tensile modulus	3.5 GPa
	Tensile strength	40 Mpa
<i>Physical Properties</i>	Density	1.25 g.cm ⁻³
	Resistance to UV	Fair
<i>Thermal Properties</i>	Melting point	181°C–185°C
	Upper working temperature	95°C

TABLE 1—PROPERTIES OF PHB

Uses

The biodegradability of PHB has given it extraordinary appeal as a potential replacement for the widely used polymers derived from petrochemicals. These petrochemical products, such as polypropylene and polyethylene, are often used for packaging, but are a hazard to the environment because of the fact that when discarded they do not decompose and can cause injury to plants and animals. PHB could thus be used as a replacement—in disposable nappies and packaging in the form of bottles, bags and wrapping, particularly for medical and hospital supplies—without fear of pollution, for PHB can be completely broken down by bacteria into only carbon dioxide and water.

PHB's biocompatibility and biodegradability also open it up to other uses, currently not possible with petrochemical products. The natural degradability of PHB plastics can be, and is being, utilized in the medical industry, where plates made from PHB can be left in place to heal fractured bones. Once the bone is healed, the PHB is slowly broken down within the body without any adverse effects.

Despite its appeal over petrochemical products, high production costs mean that the current cost of PHB-based plastics are 5 to 7 times that of petrochemical based products. Although there are these present economic disadvantages, there is much research devoted to the production of biopolymers. Much research will be required if society is going to be able to relieve its dependence on petrochemical derived products before they run out.

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