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TITLE **: "NON BACTERIAL WAY OF SYNTHESIS OF BIPFUEL FROM CELLULOSE AND OTHER POLYSACCARIDES"**

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ABSTRACT:

Cellulosic or starch feedstock is the main reactant polysaccharide carbohydrate in the natural fermentation process. Out of the many products obtained, ethanol is aimed at during fermentation. So bacterium is exposed to strain that optimizes this product. Complete chemical process totally takes place in few steps. The feedstock is meant for catalytic hydrolysis which is done by treating the feedstock in acidic conditions at a high temperature and pressure. This can be done by acidulous conditions and vigorous stirring at ambient pressure. The presence of coordinate compounds with chloride on ionic sphere of complex accelerates the reaction. The obtained products take a shape of carbohydrate which can be further synthesized to smaller alcohols which is desired bio-fuel is normally meant through yeast fermentation. Some have been discovered that directly converts cellulose/starch into ethanol. However to obtain a mono product at a high purity, the hydrolyzed feedstock is meant for catalytic reduction with HI in presence of heat. This reaction converts all sugars into long chain alcohols which can be converted into smaller alcohols and hydrocarbons through anaerobic pyrolysis. Since it is recently found that butanol is a best substitute (Refer to Chart1.) for gasoline than ethanol, we can alter our pyrolysis so as to obtain butanol as main product. The other products would be a 2carbon hydrocarbon at maximum. These smaller HCs can be removed as they are gasses and they find their application as biogas. This facility of obtaining variety of products as requires is only possible by an extreme controllable reaction like this artificial synthesis. So the availability of this technology irrespective of economics is at its absolute requirement.

INRODUCTION:

Fossil fuels are generally composed as a mixture of crude oil which is typical compound containing many hydro carbons that can be combusted and water. The composition of this mixture of crude oil and water varies with ambience temperature and many other environmental parameters. The extant of crude oil availability is also lessening gradually. Moreover the market demand for fuels is rising day by day with increasing population and automobile usage. Use of fuel in fuel cell to overcome energy crisis in countries like India and Pakistan is also a reason for excess demand for the fuel. This scenario is forcing a hike in the fuel costs. Moreover the war features and other international politics abmolish fuel rates. This hike in fuel rates reached an abnormal value of 143$/barrel (1barrel~=117.34Lts.) in July 2008. All these scenario forces people to find out an alternate fuel for automobiles. Though automobiles can get another fuel, the matter of fact is that all the vehicle engines throughout the world cannot be replaced at a stroke. This at least requires a 30-50 year time for complete change. Thus there arose an absolute need for raise in interest for biofuels. Biofuels resemble the normal petrochemicals and function similar to them in automobile engines that are using petrochemical now in the market. However there arises a change in octane/cetane number and efficiency of fuel per liter. However out of these biofuels that can be synthesized we look for probable fuel that best suit as petrochemicals.

Obtaining of biofuels can be done by fermentation of the biomass (containing good amount of starch/cellulose/sugar content) like cane, corn/maize which can be generalized as the mass that is obtaining from a biological source. The process involved in getting the biofuel from biomass takes part in several unit processes which are already in practice. Out of the available techniques, the most prevailing method now is biological fermentation of the biomass using yeasts. Yeasts are a growth form of eukaryotic microorganisms classified in the kingdom fungi. Even the alcohoic beverages are also obtained through fermentation of grapes which are indeed a form of biomass in anaerobic atmosphere for a long time. Indeed, alcoholic beverages contain smaller alcohols that also substitute as petrochemical for combustion. Biofuels can also be prepared from plants with higher amount of oil content like jathropa, oil palm, soy bean, algae, etc.,. Its oil can directly be used as biodiesel after reducing its viscosity. Both the ways are benevolent. However there is an interesting competition between these two ways of extractions. Fuel from seed oil involves a time taking and a very market risk as there is every possibility for spoilage of crop in that long time. For example if we take the crop of jathropha, an ingenious plant to southern asia, takes a long time of 3-4 years to grow. Though it resist for the drought conditions, its existence is at doubt for such a long time. Its seeds have to be cared a lot for their existence as there is every possibility for it to be lost from the plant, especially in rural parts of India. So, obtaining them through another slow but effective process i.e., by yeast fermentation of biomass is opted by many industries. However, this is also catalyzed by biocatalyst and other strains are established on bacterium races meant for this reaction to increase the desired product in greater extent. To have a rapid production of biofuel an artificial fermentation reaction is needed that creates absolute production in accordance with the demand. It however also depends on availability of feedstock.

Normal production plants are now able to deliver the fuel by 3-4 weeks time. But the urgency may cause a low concentrated alcoholic product. This effects combustion of fuel and at a long run effects the engine too. So, obtaining of purity and rapidity in biofuel production is only possible through artificial synthesis of biofuel from selective feedstock.

Let us get through the various unit processes involved in this non bacterial biofuel production plant in detailed. For renting quality in understanding, let us first stay away from economical calculations and let us do the price estimation at last.

On an over look, we can just say that the feedstock is processed through the following chemical unit process step wise. Though it cannot be taken as a mere chemical flow chart, but can be compared with it.

a) The feedstock is selected so as to obtain maximum biomass from a unit raw stock.
b) The feedstock is subjected for crystallization and then is processed for catalytic hydrolysis. This reaction is called as catalysis of cellulose or cellulolysis. If the feedstock contains greater extent of cellulose composition in it, it is likely profitable to use and exploit that nature of the feedstock and thus producing cellulosic ethanol or any other cellulosic fuel. If once we are prepared with hydrolysis of cellulose, it is a known fact that the reactor takes up even hydrolysis of the few more polysaccharides like hemicelluloses, etc. However, we can understand that the hydrolysis of some compounds such as lignin is not possible.
c) After obtaining the hydrolyzed lignocelluloses, the unhydrolysed part of feedstock which mainly contains lignin and other similar carbohydrates are meant for separation to separate lignin from the hydrolysed sugars. Depending upon the case, a unit process that converts polysaccharide cellulose to disaccharide can be installed. The expected product would be sugar of different carbon number.
d) The purified sugars can then be processed to a catalytic reduction using a hydrogen iodide (HI) solution. Once, the sugar gets reduced and alcohols of various carbon numbers are obtained.
e) The obtained high carbon alcohols can then be subjected for anaerobic pyrolysis stimulating the parameters for an adjustable product yield. Product can start from a single carbon methane gas to butanol, which is now being called as biobutanol representing the source which is found as a best substitute for gasoline.

f) The obtained mixture of hydrocarbons is then subjected for distillation where we can obtain almost pure forms of different hydrocarbons and then transferring them to use them in their respective utilizing equipments.

Let us evaluate the ideas/claims of this paper in detail

Selection of the ideal feedstock for evaluation:

Selection of an ideal feedstock is at its absolute necessity. Selection is done by means of the biomass percentage the source gives which can be converted by processing through this chemical plant to biofuel. We generally select a plant that has this sort of high biomass content and also we look for the indigenous plants for their ability to resist local infections and their rapid growth at the local temperature.

If we have a look at the plants we are using as sources for biomass, the majority of indigenous biofuel sources are opted for their ingredient carbohydrate content of starch/cellulose/hemicelluloses. They are also desired to have low amount of non hydrolysable carbohydrates such as lignin. If these are the characteristics depicted by any plant, then obviously it stands in the race of plants that stays as a source for biofuel. The main idea beyond this is that there are already discovered bacterium races that release yeasts for fermentation of this feedstock for a complete conversion of hydrolysable carbohydrates to smaller alcohols which suit as petrochemicals. To increase the production of a specific compound, the parameters are set up extremely favorable for the desired compound production.

If we look at the biological sources we are currently aware of for biofuel production, we find that sugars, starch, vegetable oils, animal oils, seeds/grains such as wheat, sunflower seeds served their purpose in first generation biofuels through a natural fermentation process after hydrolysis. The microbes that convert feedstock directly into biofuel through internal hydrolysis and fermentation were not in reputation at that time. An overview on vegetable oil as biofuel can be summered to state that the vegetable oil can directly be used in diesel engine after reducing their viscosity. In fact, diesel is meant as a dilute vegetable oil. However it is only meant at higher (warm) temperatures, i.e., summer season as solidification of oils is possible in engines that effect the engine prospects. The obtained diesel is termed as biodiesel depicting the source through its name. Biodiesel is the most common biofuel in Europe. It is produced from oils or fats using transersterification and is a liquid similar in composition to mineral diesel. Its chemical name is fatty acid methyl (or ethyl) ester (FAME). Oils are mixed with sodium hydroxide and methanol (or ethanol) and the chemical reaction produces biodiesel (FAME) and glycerol. One part glycerol is produced for every 10 parts biodiesel. Feed stocks for biodiesel include animal fats, vegetable oils, soy, rapeseed, jatropha, mahua, mustard, flax, sunflower, palm oil, hemp, field pennycress, and algae. Bio alcohols are also assumed as biofuels as they suit as substitute for gasoline. Biologically produced alcohols, most commonly ethanol, and less commonly propanol and butanol, are produced by the action of microorganisms and enzymes through the fermentation of sugars or starches (easiest), or cellulose (which is more difficult). Biobutanol (also called biogasoline) is often claimed to provide a direct replacement for gasoline, because it can be used directly in a gasoline engine (in a similar way to biodiesel in diesel engines). Out of all the bioalcohols, the predominant alcohol as a biofuel is bioethanol. Ethanol fuel is the most common biofuel worldwide, particularly in Brazil. Alcohol fuels are produced by fermentation of sugars derived from wheat, corn, sugar beets, sugar cane, molasses and any sugar or starch that alcoholic beverages can be made from (like potato and fruit waste, etc.). The ethanol production methods used are enzyme digestion (to release sugars from stored starches, fermentation of the sugars, distillation and drying. Second generation biofuel utilizes non food crops as their source for biomass. It is a solution for increasing inflation due to the migration of food crops to biofuel production in first generation biofuel plants. Cellulosic biofuels are a part of second generation biofuels. These, as the name itself suggests, are obtained from cellulose which is the most abundant carbohydrate in world.

The above given discussion shows the nature of market demand and requirement for both food crops and biofuel. So, obtaining the biofuel from a non food crop or an energy crop is ideal choice of the biomass source. Let us have a look a various energy crops and their status for use as a good source for a biofuel feedstock.

Switchgrass- indigenous plant of North America:

We observe that switch grass is the most used biological source in northern parts of America. It is a native crop of the continent. Similarly when it is the case with southern Asia, jathropa seed oil is prominent as biodiesel. But there are few practical problems to establish a biodiesel plant in south Asia. Switch grass is an ideal source but extending it to a humid environment that prevails in south Asia through cultivation in artificial environment obstructs the expected output. If we look at the profile of switch grass we find some interesting aspects.

Switchgrass (*Panicum virgatum*) is a summer perennial grass that is native to North America. It is a natural component of the tall-grass prairie which covered must of the great Plains, but which also was also found on the prairie soils in the Black Belt of Alabama and Mississippi. Many people do not realize that the natural vegetation of the Black belt was grassland, and not frost like most other parts of the southeastern USA. Need for agricultural chemicals to grow switchgrass is relatively low. Switchgrass is also very tolerant of poor soils, flooding and drought, which are widespread agricultural problems in the southeast. There are two main types of switchgrass: upland types, which usually grow 5 to 6 feet tall and are adapted to well drain soils, and low land types, that grow up to 12 feet tall and which are typically found on heavy soils in bottomland sites. Although switchgrass is native, plant breeders have developed a fairly large number of improved varieties for use as forage.

'Alamo' switchgrass is a robust lowland variety of switchgrass most suited to the southern US. In Auburn University test plots, it has frequently produced over 10 tons per acre per year, but on a commercial scale, it is more reasonable to expect 6 to 8 tons per acre. This is because test plots usually have perfect establishment, but commercial plantings almost always have weak spots in the field. However, for comparison, the average annual hay yield for Alabama is about 2.5 tons per acre, and the productivity of forests is only about half that of switchgrass. Despite poorer soils than in the Midwest, switchgrass yields are higher in the Southeast because of the adaptation of more productive switchgrass varieties in our region, and because we have a longer growing season. The seed of switchgrass is very small, and much of it is dormant (will not germinate) right after it is harvested. However, aging, treating it with water and chilling temperatures (stratification) or storing it in warm conditions will break dormancy. Partly because of the small size of the seed, switchgrass seedlings tend to be slow to develop, and are susceptible to weed competition. Unfortunately, there are no herbicides approved by government for weed control during establishment of switchgrass. However, it can still be successfully established by no-till planting and other strategic approaches.

Switchgrass reaches full yield only in the third year after planting; it produces a quarter to a third of full yield in the first year, and about two thirds of full yield in the second year. When managed for energy production it can be cut once or twice a year with regular hay or silage equipment. At maturity, widely spaced switchgrass plants can measure 20 inches in diameter at ground level. Switchgrass has a huge, permanent root system that penetrates over 10 feet into the soil, and weighs as much (6-8 tons/acres) as the above-ground growth from one year. It also has many fine, temporary roots. All these roots improve the soil by adding organic matter, and by increasing soil water infiltration and nutrient-holding capacity. Switchgrass fields provide habitat and a home for many species of wildlife, including cover for deer and rabbits, and a nesting place for wild turkey and especially quail.

Switchgrass has several other environmental benefits. If it is used to produce energy, it will reduce the risk of global warming by replacing fossil fuels (coal, natural gas and oil). When fossil fuels are burnt, carbon is removed from below ground (gas and oil wells and coal mines) and release into the atmosphere as carbon dioxide (CO_2). This is a greenhouse gas that increases the risk of global warming. In contrast, switchgrass (like all other plants) removes CO_2 from the atmosphere and incorporates it into plant tissue, both above and below the ground.

The accumulation of carbon, especially below the ground, is known as carbon sequestration, and is considered to be a very important strategy for reducing atmospheric CO_2. Switchgrass is unquestionably one of the best crops for doing this. when above-ground switchgrass is harvested and burned for energy, CO_2 is once again returned to the atmosphere from where it was originally obtained by the plant, but it will have reduced the need for some fossil fuel. Therefore, CO_2 is obviously just being recycled by use of switchgrass for energy, making this process CO_2-neutral (or actually CO_2-

negative if soil carbon sequestration is considered), compare to fossil fuels that add CO_2 to the atmosphere. when compared to low grade coal, burning switchgrass for energy will probably result also in less toxic emissions, such as the oxides of sulphur and nitrogen.

Together with its energy benefits, swicthgrass offers great opportunity for farmers. Because of its perenniality, compared to annual crops switchgrass is a true conservation crop which will substantially reduce soil erosion and release of soil carbon which are related to annual tillage, and it will reduce the use of toxic chemicals.

Perhaps most important, we must recognize that fossil fuels will be our main energy base for many years, and bioenergy from switchgrass is not intended to compete with these valuable resources, but rather, to complement them by softening their environmental impact.

Artificial cultivation of the switchgrass in India and other southern asia countries is possible by extending artificial envionment to the harvesting plant. However, the practice of waiting for 3-4 years for total yield is not amicable in such an expensive environment.

Jatropha a native crop of south Asia and central America (II generation biofuel crop):

Currently the oil from Jatropha curcas seeds is used for making biodiesel fuel in Philippines, promoted by a law authored by Philippine senators Miriam Defensor-Santiago and Miguel Zubiri. Likewise, jatropha oil is being promoted as an easily grown biofuel crop in hundreds of projects throughout India and other developing countries. The rail line between Mumbai and Delhi is planted with Jatropha and the train itself runs on 15-20% biodiesel. In Africa, cultivation of Jatropha is being promoted and is grown successfully in countries such as Mali.

Estimates of Jatropha seed yield vary widely, due to a lack of research data, the genetic diversity of the crop, the range of environments in which it is grown, and Jatropha's perennial life cycle. Seed yields under cultivation can range from 1,500 to 2,000 kilograms per hectare, corresponding to extractable oil yields of 540 to 680 liters per hectare.

Jatropha can also be intercropped with other cash crops such as coffee, sugar, fruits and vegetables. Large plots of waste land have been selected for Jatropha cultivation and will provide much needed employment to the rural poor of India. Businesses are also seeing the planting of Jatropha as a good business opportunity. The Government of India has identified 400,000 square kilometres (98 million acres) of land where Jatropha can be grown, hoping it will replace 20% of India's diesel consumption by 2011.

Jatropha is also similar to switch grass in its growth rate. However unlike switchgrass, jathropa produces seeds that are utilized for biodiesel production after reduction in their viscosity. But, harvesting a crop for 3-4 years without expecting a bet gain from land is not merely possible for establishing a heavy production plant. Even if it is subsidized by government, the care that has to be initiated inorder to save the seed and ascertain its perfect growth is very high as there is every possibility in irregularity in climatic conditions. So we are in an need for a crop that gives maximum cellulose (as in II generation crop) that requires least care and be able to yield even with the case of spoiled crop. Even, complete utilization of plant is not desirable since recultivation is again a time taking process. So a crop like cotton comes into picture with the desired qualities.

Cotton crop for biodiesel production:

Cotton is a soft, staple fiber that grows around the seeds of the cotton plant (*Gossypium* sp.), a shrub native to tropical and subtropical regions around the world, including the Americas, India and Africa. The fiber most often is spun into yarn or thread and used to make a soft, breathable textile, which is the most widely used natural-fiber cloth in clothing today. Successful cultivation of cotton requires a long frost-free period, plenty of sunshine, and a moderate rainfall, usually from 600 to 1200mm (24 to 48 inches). Soils usually need to be fairly heavy, although the level of nutrients does not need to be exceptional. In general, these conditions are met within the seasonally dry tropics and subtropics in the Northern and Southern hemispheres, but a large proportion of the cotton grown today is cultivated in areas with less rainfall that obtain the water from irrigation. Production of the crop for a given year usually starts soon after harvesting the preceding autumn. Planting time in spring in the Northern hemisphere varies from the beginning of February to the beginning of June. The area of the United States known as the South Plains is the largest contiguous cotton-growing region in the world. It is heavily dependent on irrigation water drawn from the Ogallala Aquifer. Out of different varieties of cotton organic cotton is notable cotton. Organic cotton is cotton that is grown without insecticide or pesticide. Worldwide, cotton is a pesticide-intensive crop, using approximately 25% of the world's insecticides and 10% of the world's pesticides. According to the World Health Organisation (WHO), 20,000 deaths occur each year from pesticide poisoning in developing countries, many of these from cotton farming. Organic agriculture uses methods that are ecological, economical, and socially sustainable and denies the use of agrochemicals and artificial fertilizers. Instead, organic agriculture uses crop rotation, the growing of different crops than cotton in alternative years. The use of insecticides is prohibited; organic agriculture uses natural enemies to suppress harmful insects. The production of organic cotton is more expensive than the production of conventional cotton. Although toxic pollution from synthetic chemicals is eliminated, other pollution-like problems may remain, particularly run-off. Organic cotton is produced in organic agricultural systems that produce food and fiber according to clearly established standards. Organic agriculture prohibits the use of toxic and persistent chemical pesticides and fertilizers, as well as genetically modified organisms. It seeks to build biologically diverse agricultural systems, replenish and maintain soil fertility, and promote a healthy environment.

Cotton fiber, once it has been processed to remove seeds (ginning) and traces of honeydew (a secretion from aphids), protein, vegetable matter, and other impurities, consists of nearly pure cellulose, a natural polymer. Cellulose content in cotton is nearly 90%. So cotton is treated as an excellent source of cellulose. Moreover, as cotton is an established crop and is being already under use, there is no need for awareness in cultivation of crop. The major feature is that spoiled or futile cotton can be used for biofuel synthesis.

Moreover equipments and processors for cotton management are well known and existing. So there is no absolute need for equipments arising. In india, Large amount of cotton farmers are under loss due to irregularity in precipitation. All of them come to a profitable edge is utility of cotton as a source of cotton instead of usage as a fabric materializes. Thus it can be stated that in a country like India, use of cotton for synthesis of biofuel is ideal than use of switchgrass or jatropha.

2. Hydrolysis of lignocelluloses that is obtained from cotton:

CELLULOSE HYDROLYSIS: Cellulose can get hydrolyzed by normal conventional acid hydrolysis as depicted in many abstracts before. However they show an interesting stimulated hydrolysis by using an acid catalyst under ionic liquid medium. This nature can be exploited for hydrolyzing cellulose to sugar. Cellulose in ionic liquid medium when heated with stirring at 100 °C, ambient pressure a clear solution is formed. To this cellulose solution then we add quickly H_2O (1.75 mole equiv. to cellulose) and appropriate amount of 98 wt % H_2SO_4. The reaction was then vigorously stirred. At different time intervals, samples were withdrawn, weighed, and quenched immediately with cold water for evaluation of product. The aqueous solutions were neutralized with NaOH, centrifuged at 10,000 rpm for 5 min, measured the volume and subjected to total reducing sugar (TRS) and glucose analysis. The reduced sugar yield can vary up to production of a 90-95%yield which is extremely preached as efficient.

This hydrolysis of cellulose in a ionic liquid with acid as a catalyst is the best way to obtain sugar from cellulose. Moreover, if you recall the prices of the reagents being used in the above cellulosis, it is obvious that it is a low expensive process. The obtaining can be manipulated over variety of ionic liquid solvents which is the future plan of this idea. There was an interesting paper presented by Dalian Institute of Chemical Physics and Graduate School of the Chinese Academy of Sciences in similar experiment where they have found and outstanding 95%sugar as output. Refer to fig 1.

Research was done by auburn university on dilute acid catalysis and the kinetics of normal cellulose hydrolysis using acid catalyst but in absence of ionic liquid solvent. They have stated a very interesting fact that the cellulosys is a single ordre kinetic reaction. They have extended their paper even through the probable reaction mechanism of cellulose hydrolysis.It was also shown that the crystallization ability of cellulose effects the hydrolyzation rate a lot.

HEMICELLULOSE HYDROLYSIS: When compared to cellulose both extraction and hydrolysis of hemicelluloses is very easy. In fact hemicelluloses get hydrolyzed to form xylase long before cellulose converts to sugars.

However there is another part of lignocelluloses called lignin which resists extremely to get hydrolysed for its aromatic behavior. Lignin hydrolysis is thus treated as impossible. So only cellulose and hemicelluloses gets hydrolysed to sugars and the obtained partially hydrolyzed solution is meant for separation where lignin is removed from the solution.

3. Catalytic reduction of the sugar solution to convert them to alcohols:
Though an endothermic reaction, it is not a difficult task to obtain a reduced mixture of hydrolyzed feedstock. In general, HI is employed for reducing the carbohydrates to sugars. It is ideal is we use HI in limited extent when compared with that of sugar so as to obtain varieties of partially hrdrolyses hydrocarbons. This conversion results into formation of iodine gas and a dilute solution of alcohol on product side.

4. Concentrating the alcohol and cracking:
The dilute alcohols can be then assumed to have a mixture of pentathol and hexanol as major products. The solution can be meant for distillation through various techniques that are already known to us and then the obtained product alcohols of higher concentrations are let for anaerobic pyrolysis. It is known that pyrolysis allows us to adjust the product by pressurizing reaction with varying parameters. Thus the required bioalcohol can be prepared and can be substituted for gasoline. A table containing the details on few products obtained after the chemical processing is done is as follows.

Depending on choice of fuel in accordance to the desire, parameters can be adjusted for a maximum yield of such a product.

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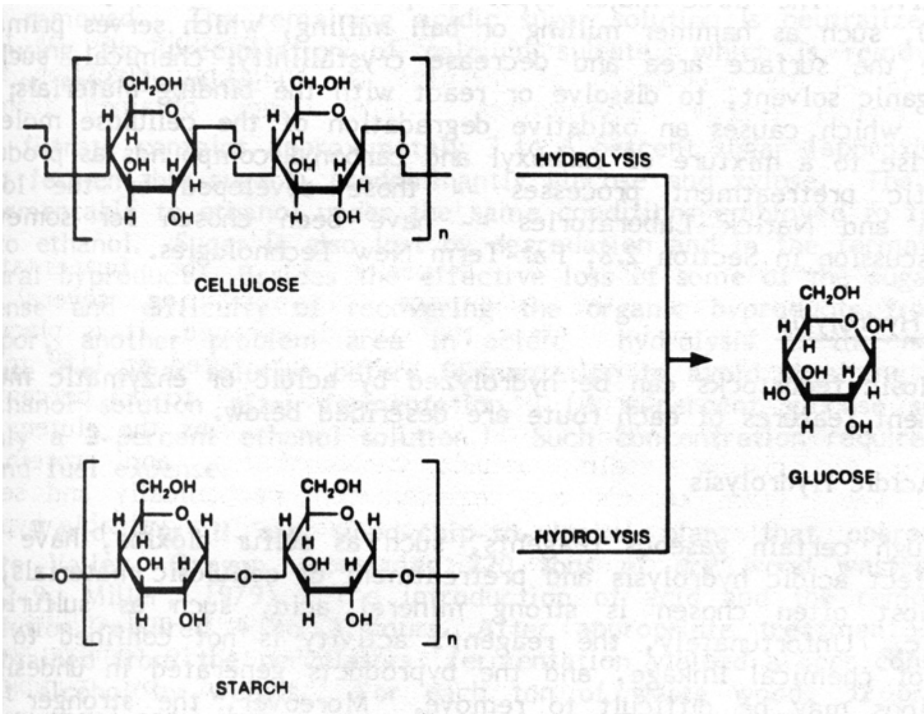

Figure1: STARCH/CELLULOSE HYDROLYSIS REACTION.

Fuel	Energy density	Air-fuel ratio	Specific energy	Heat of vaporization	RON **Octane rating**	MON
Gasoline and biogasoline	32 MJ/L	14.6	2.9 MJ/kg air	0.36 MJ/kg	91–99	81–89
Butanol fuel	29.2 MJ/L	11.2	3.2 MJ/kg air	0.43 MJ/kg	96	78
Ethanol fuel	19.6 MJ/L	9.0	3.0 MJ/kg air	0.92 MJ/kg	129	102
Methanol	16 MJ/L	6.5	3.1 MJ/kg air	1.2 MJ/kg	136	104

Chart1: CHART DEPICTING RELATIVE DETAILS OF ENERGY.