SGVU J CLIM CHANGE WATER
ISSN: 2347-7741 Volume 1, Issue 1, 2018, PP. 20-44

INNOVATION FOR PRODUCTION OF NEXT GENERATION BIOFUEL FROM LIGNOCELLULOSIC WASTES

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Abstract: The present communication highlights the evolution of biofuels while giving priority attention to next generation biofuel from lignocellulosic waste. Both biochemical (chemicals, enzymes, and fermentative microorganisms) and thermo-chemical (heat and chemical) processes, are addressed. For biochemical processes, topics related to the pre-treatment, hydrolysis, and fermentation steps as well as process integration, are also discussed. For the thermo-chemical processes, research topic such like process development and process analysis, will be dealt with. Important R&D technical aspects, economic assessment of available technologies, limitations of certain technological approaches, etc. will also be discussed in the present communication.

Keywords: Biofuel, Production, Biochemical, Next Generation

1. INTRODUCTION

With current global oil production approaching its peak, billions of tonnes of carbon emissions released into the atmosphere and threats of climatic change, it is obvious that clean energy is certainly an important scientific topic that needs special attention by the scientific community world-wide and, more so, in the context of the developing countries. It is in the above context that bioenergy has been recognized as a significant component in many future energy scenarios. Many developing countries rely primarily on biomass to satisfy their energy needs. Substitution of fossil fuels by biofuels, appears to be an effective strategy not only to avert an impending future energy crisis but also reducing carbon emissions from fossil fuels.

First generation biofuel are now exploited for nearly three decades. It is true that the technology applied for the production of bioethanol from sugar and starch crops (sugar cane, sugar beet, maize, etc.) is mature enough to permit to achieve liquid fuel competitive, both for price and performances, to gasoline and diesel but the fact remains that have proven grossly inadequate to augment rising global requirements. Also, their continued use has contributed towards global food for fuel crisis.

So, production of biofuels which do not compete with food and valorization of agro-waste from bio-based industry, is believed to be the main challenge for countries' building a sustainable bio-based industry of tomorrow. Hence, the priority is to make use of lignocellulosic biomass both forest (woody) and agricultural. Second-generation liquid biofuels are generally produced by two fundamentally different approaches i.e. biological or thermochemical processing, from agricultural lignocellulosic biomass, which are either non-edible residues of food crop production or non-edible whole plant biomass (e.g. grasses or trees specifically grown for production of energy).
Feedstock involved in the process can be bred specifically for energy purposes, enabling higher production per unit land area, and a greater amount of above-ground plant material can be converted and used to produce biofuels. Woodchips from slashes and tree tops, saw dust from saw mills and

waste paper pulp are common forest biomass feedstocks whereas switchgrass and miscanthus, etc., are agricultural feedstocks for cellulosic ethanol production.

Second generation biofuels production can be useful to entire world but it can benefit the large section of community in developing countries by providing energy security, business opportunities, employment generation and better environment conditions. Increasing awareness about power generation and bioethanol production from lignocellulosic materials is certainly creating a lot of interest worldwide. However, once again, the main argument against the second generation fuels is based on land availability and protection of global ecosystems.

Certainly, in context to developing countries, 2nd generation biofuel production is relevant. But it is also a fact that 2nd generation biofuel production is more dependent on resources available within the country. Therefore, in this paper, author tried to provide an overview of 2nd generation feedstock resource information for biofuel production in developing countries.

2. *Raw Materials*

This type of fuel is derived from non-food crops or inedible waste products, which have less impact on food, such as switchgrass, sawdust, rice hulls, paper pulp, wood chips, etc. Lignocellulose is the "woody" structural material of plants. The biomass resources that can be most favourable for second generation biofuels are lignocellulosic biomass.

2.1 Lignocellulosic biomass

Lignocellulosic biomass is term used for biomass from woody or fibrous plant material being a combination of lignin, cellulose and hemicellulose polymers interlinked in a heterogeneous matrix. The combined mass of cellulose and hemicellulose in the plant material varies with species but typically 50-75% of the total dry mass with the remainder consisting of lignin. The cellulose and hemicellulose can be converted to sugars through a series of thermochemical and biological processes and eventually fermented to bioethanol.

Lignocelllulosic biomass, an abundant and renewable feedstock, include cereal, straw, wheat chaff, rice husks, corn cobs, corn stover, sugarcane bagasse, nut shells, forest harvest, residue, wood process residues, energy crops on marginal and degraded lands. According to EIA report 2011[1], technical potential for bioenergy will be more than 1500 EJ in 2050. A book written by Dornburg et al. on sources of feedstock for biofuel and bioenergy, estimates the potential of agricultural and forestry residues at 85 EJ and that of surplus forest growth23 at roughly 60 EJ in 2050.

CLASSIFICATION OF LIGNO-CELLULOSIC BIOMASS

In general, lignocellulosic feedstocks are divided into three categories: (1) agricultural residues (e.g., crop residues, sugarcane bagasse), (2) forest residues, and (3) herbaceous and woody energy crops.

a. Agricultural residues

A wide range of agricultural residues (e.g. corn stover, straw, wheat straw, bagasse, etc) can be used for production of second generation biofuels. Such biofuels are generally considered sustainable as they use waste materials from food crop production, and do not compete with food crops for land. A number of conversion technologies can be used with agricultural residues. For example, conversion of agricultural residues to cellulosic ethanol can be done

via biochemical pathway, i.e., pretreatment, hydrolysis and fermentation. Another route can be gasification of residues for syngas formation which can be further converted to liquid fuels with the help of catalysts.

b. Forestry residues

Two main types of forestry resources are used for demonstrations of second generation biofuel production:

- Residues from harvesting of wood, such as branches, foliage, roots, etc
- Complementary felling which describe the difference between the maximum sustainable harvest level and the actual harvest needed to satisfy round wood demand.

Forest residues can also be converted to biofuels by means of thermo-chemical pathways. The world's first BioDME plant was initiated in Sweden, using black liquor from forest residues via gasification.

c. Herbaceous/ Woody Energy Crops

A number of energy crops can potentially be grown on marginal land (i.e. land that is not suitable for food production) to provide feedstocks for biofuels production. New energy crops, particularly perennial grasses (Miscanthus, switch grass, prairie grass and short rotation forest species (e.g. Eucalyptus, Poplars and Robinia) are being considered for the purpose. These crops can be high yielding when grown under good conditions and harvested over long seasons to provide a steady supply processing plant, thus avoiding costly storage of large biomass volumes for several months between harvests.

Forest residues have limitation because of forest products are used for several other products and energy production on marginal lands is controversial because of high energy requirements and adaptability of new crops to such soil conditions. Therefore, this paper is focused on agricultural based lignocellulosic biomass potential in developing countries.

It is, however, to be noted that large-scale use of biomass for second generation biofuels means constant supply of large amounts of wood, grasses, and ‘plant waste’. The removal of organic residues from fields will require greater use of nitrate fertilizers, thus increasing nitrous oxide emissions, nitrate overloading and its devastating impacts on biodiversity, on land, freshwater and in the oceans. It is also likely to accelerate topsoil losses.

3. PRODUCTION OF BIOFUELS FROM LIGNIOCELLULOSIC WASTES

Production of biofuels which do not compete with food and valorization of agro-waste from bio-based industry, is believed to be the main challenge for countries' building a sustainable bio-based industry of tomorrow. Second-generation biofuels share the feature of being produced from lignocellulosic biomass (lower-cost, non-edible feedstocks such as wheat straw, wood chips and a wide variety of different type of biomasses) thereby limiting direct food vs. fuel competition. As shown in the figure given below, second-generation biofuels can be classified in terms of the process used to convert the biomass to fuel: biochemical or thermochemical.

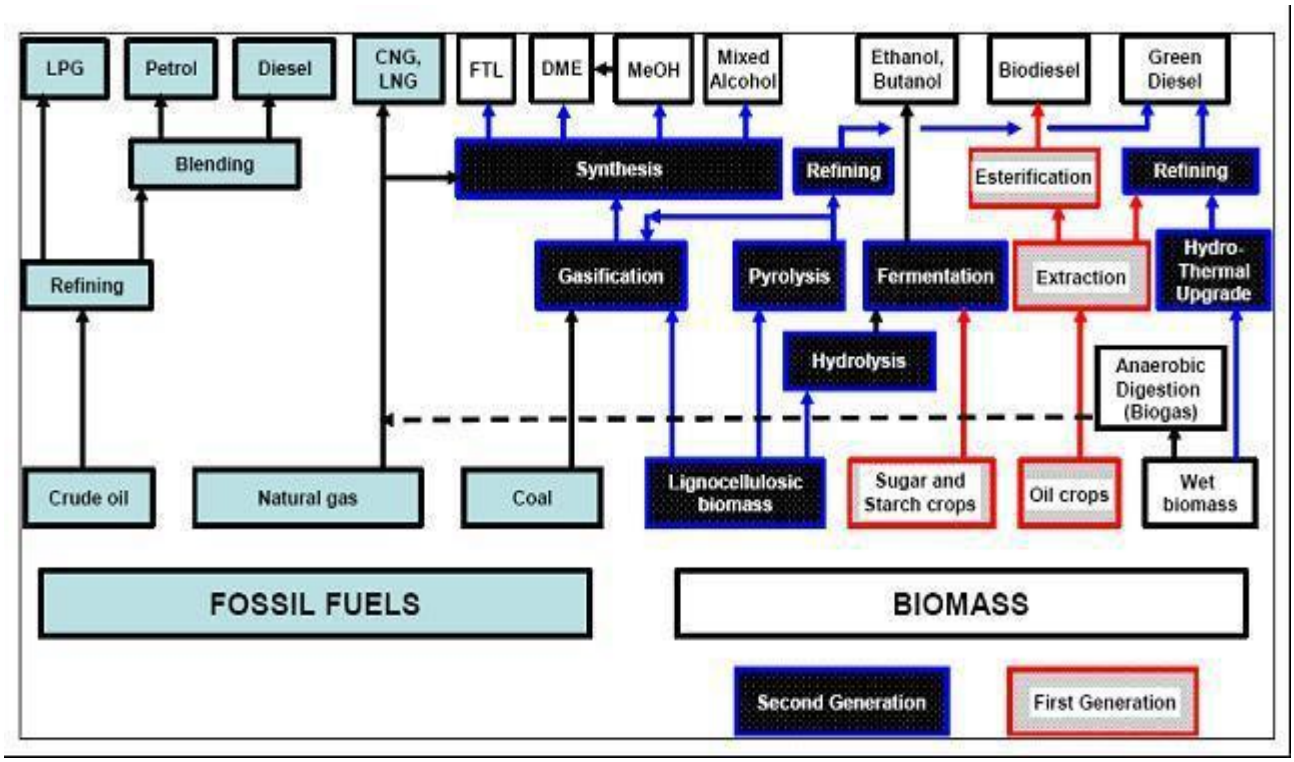

Fig. 1 Production pathways to liquid fuels from biomass and, for comparison, from fossil fuels [9].

Second-generation ethanol would be made via biochemical processing. On the other hand, second-generation thermochemical fuels include methanol, refined Fischer-Tropsch liquids (FTL), and dimethyl ether (DME), being made from fossil fuels using processing steps that in some cases are identical to those that would be used for biofuel production (Fig. 1). The other thermochemical biofuel in Fig, 1 is green diesel, for which there is no obvious fossil fuel analog. Unrefined fuels, such as pyrolysis oils, are also produced thermochemically, but these require considerable refining before they can be used in engines.

A variety of different process designs have been proposed for production of second generation ethanol. One relatively well-defined approach for ethanol production is the use of separate hydrolysis (or saccharification) and fermentation steps. Other concepts include one that combines the hydrolysis and fermentation steps in a single reactor [10] (simultaneous saccharification and fermentation), and one that additionally integrates the enzyme production (from biomass) with the saccharification and fermentation steps [11].

It is in the above context that the scientific community over the last couple of years have concentrated their research activities on the use of lignocellulosic biomass that could be specifically cultivated or easily recovered from agricultural, forests or agro-industrial wastes. Needless to say that increasing awareness about power generation and bioethanol production from lignocellulosic materials is certainly creating a lot of interest worldwide. Lignocellulosic materials such as agricultural, hardwood and softwood residues are potential sources of sugars for ethanol production. The cellulose and hemi-cellulose components of these materials are essentially long, molecular chains of sugars. They are protected by lignin, which is the glue that holds all of this material together.

The technological hurdles that are presented by the materials are:

- The separation of lignin from the cellulose and hemi-cellulose to make the material susceptible to hydrolysis.
- The hydrolysis of cellulose and hemi-cellulose takes place at different rates and over reaction can degrade the sugars into materials that are not suitable for ethanol production.
- The hydrolysis of these materials produces a variety of sugars. Not all of these sugars are fermentable with the standard yeast that is used in the grain ethanol industry. The pentose sugars are particularly difficult to ferment.

Agricultural residues and hardwoods are similar in that they have a lower lignin content and the hemi-cellulose produces significant amounts of pentose sugars. Softwoods have a higher lignin content, which makes the hydrolysis step more difficult, but they generally produce less pentose sugars.

Pretreatment, hydrolysis, fermentation and product recovery are important processes involved for the bioconversion of cellulose to ethanol.

It is, however, to be noted that in spite of good quality and availability of the raw material, it is necessary to improve the technologies for pre-treatment, enzymatic hydrolysis and separation of alcohol from the broth, apart from the valorisation of the current processes that of lignin and hemicellulose.

Breakthrough technologies to realize the potential of cellulosic biofuels can be expedited through below listed main research and development goals [12].

- Developing biomass feedstocks with physical and chemical structures that facilitate processing to ethanol, e.g. lower lignin content, higher cellulose content, etc.;
- Improving enzymes (also called cellulase) to achieve higher activities, higher substrate specificities, reduced inhibitor production and other features to facilitate hydrolysis;
- Developing new micro-organisms that are high-temperature tolerant, ethanol-tolerant, and able to ferment multiple types of sugars (6-carbon and 5-carbon).

Achieving these goals may be facilitated significantly by the application of genetic Engineering [13, 14]. Genetic modification of organisms appears to be generally accepted for applications involving micro-organisms contained in industrial processes, e.g. for cellulose hydrolysis or 5-carbon sugar fermentation.

A focused set of investments linking revolutionary biofuel technologies with advances from the biological, physical, computational, and engineering sciences will quickly remove barriers to an efficient, economic, and sustainable biofuel industry.

4. KEY PRETREATMENT TECHNOLOGIES

Cellulose and hemicellulose are densely packed by layers of lignin, that offer protect in against enzymatic hydrolysis. For production of ethanol using forest waste biomass, woody biomass and herbaceous biomass crops, it is very important to separate its main components (cellulose, hemicelluloses and lignin). So it is a must to break lignin seal and expose cellulose and hemicellulose to enzymatic action. To break down cellulose, the primary source of sugar in fibrous biomass, it is necessary to first get past hemicellulose and lignin, which surround the cellulose in a protective sheath. This is the job of pre-treatment.

An effective pre-treatment is needed to liberate the cellulose from the lignin seal and its crystalline structure so as to render it accessible for a subsequent hydrolysis step. By far, most pre-treatments are done through physical or chemical means. Physical treatment is often called size reduction to reduce biomass physical size. Chemical pre-treatment is to remove chemical barriers so that the enzymes can access to cellulose for microbial destruction.

To date, the available pre-treatment techniques include acid hydrolysis, steam explosion, ammonia fiber expansion, Organosolv, Sulfite Pre-treatment to Overcome Recalcitrance of Lignocellulose (SPORL), alkaline wet oxidation and ozone pre-treatment. Besides effective cellulose liberation, an ideal pre-treatment has to minimize the formation of degradation products because of their inhibitory effects on subsequent hydrolysis and fermentation processes. In wet oxidation pre-treatments, the material is treated with water and air at around 1200C.

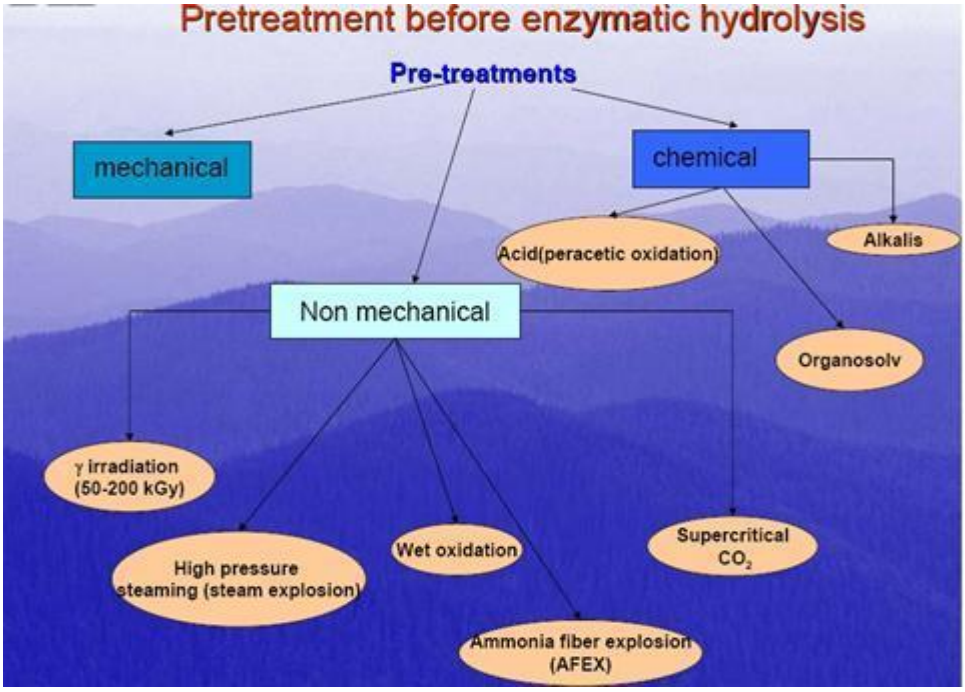

Fig. 2 Available pre-treatment techniques [15]

Although acidic wet oxidation (195°C, 15 min) offered good fractionation of bagasse, a significant part of polysaccharides was lost due to degradation and formation of byproducts, mainly carboxylic acids, but the enzymatic convertibility of the pre-treated feedstock was poor. Studies have shown that wet oxidation catalyzed transformation of hemicellulose from solid phase to liquid without major hydrolysis of the solubilized hemicellulose molecules accompanied by high production of xylose steam explosion produced more glucose.

Most pre-treatment processes are not effective when applied to feedstocks with high lignin content, such as forest biomass. Organosolv and SPORL are the only two processes that can achieve over 90% cellulose conversion for forest biomass, especially those of softwood species. SPORL is the most energy efficient (sugar production per unit energy consumption in pre-treatment) and robust process for pre-treatment of forest biomass with very low production of fermentation inhibitors. Organosolv pulping is particularly effective for hardwoods and offers easy recovery of a hydrophobic lignin product by dilution and precipitation.

4.1 SUITABLE PRETREATMENT BASED ON THE PROPERTIES OF LIGNOCELLULOSIC WASTES

Since many lignocellulosics have different physicochemical characteristics, it is necessary to deploy suitable pre-treatment technology based on their properties. Agricultural residues and hardwoods have low lignin and high pentose content compared to softwoods, and thus high temperature treatments are not effective for such biomass type thing to high thermal degradation quality of pentose.

4.1.1 AGRICULTURAL RESIDUES

Agricultural residues (straws, hulls, seeds, linter and other similar byproducts) have high pentose and low lignin content. Dilute acid treatment, low temperature steam treatment with acids, soaking in aqueous ammonia, and microwave-assisted treatment and wet oxidation, are used successfully.

4.1.2 STRAWS

Strong crystalline structure of cellulose in rice straw, and the complex structure of lignin, hemicellulose and cellulose limits accessibility of straw to hydrolytic enzymes. Therefore, various pre-treatment methods have been developed to open the crystalline complex of cellulose and so also to increase its exposure to hydrolytic enzymes.

Hydrothermal pre-treatments have proven to be effective in increasing enzymatic digestibility of wheat straw for and conversion into fermentable sugars for bioethanol production. It is reported that hydrothermal pre-treatments caused profound lignin relocalization and major wax and removal of a small fraction of hemicellulose.

It is possible to pre-treat wheat straw sufficiently without disrupting cell wall. Thus, only a modest pre-treatment is necessary in order carbohydrates are digested enzymatically.

4.1.3 BAGASSE

Pre-treatment methods for bagasse include steam explosion**,** hot water per acetic acid and with ammonia water. Steam explosion (220°C) for shorter reaction times, followed by acid hydrolysis, proved very effective for recovery of fermentable sugars from pine hemicelluloses. Steam explosion, with SO2 as acid catalyst, effectively

fractionates softwood carbohydrates, releasing soluble hemicellulose (80-90%) and thus enhancing enzymatic hydrolysis of the water-insoluble cellulose fraction.

4.2 STEAM EXPLOSION

Steam explosion with low environmental impact and producing highly biodegradable substrate seems the best suitable physical pre-treatment of straw as it partially hydrolyses hemicellulose and increases its enzymatic digestibility in the biomass residue.

The Steam Explosion (SE) is a hydrothermal treatment for making easier and less impactive the separation between the different fractions of the common vegetal substrates (hemicelluloses, cellulose and lignin). The process is based upon on the natural ability of the water vapour at high temperature and pressure to penetrate and breaking of chemical bonding of the polymeric, cellulose, hemicellulose and lignin, in the vegetal materials. Here, the material is kept at a certain temperature (180-230°C) for a short period (1-10 minutes) during which hemicelluloses is hydrolyzed and becomes soluble. Soon after the pressure is rapidly re-conducted to the atmospheric value to obtain a decompress explosion that further scrapers the biomass.

Steam pre-treatment is affected by steam temperature, residence time in the reactor, particle size, moisture content and the catalyst concentration. The final result is to make available the sugars contained in the feed material that otherwise could not be metabolized easily by the microorganisms used in the successive stages of bio-conversion.

Two experimental pilot plants both in batch and continuous version have been realized at Trisaia, to study Steam Explosion. The plant operating in continuous mode, called STELE, is capable of progressing nearly 300 Kg/h of wheat straw, wood chips and a wide variety of different type of biomass [16].

It is equipped with a system for the treatment of the stream of product exposed. Extraction with water, caustic solutions and filters are made on semi-industrial scale to separate cellulose and hemicellulose, and lignin.

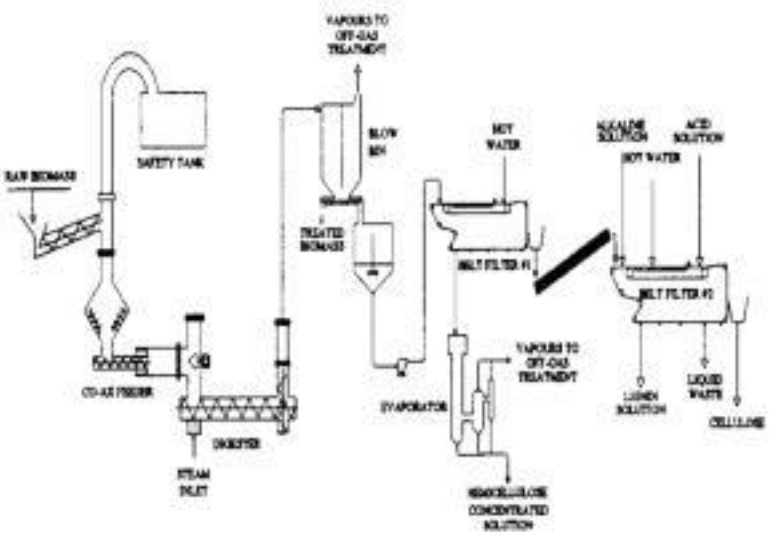

Fig. 3 Flow diagram of steam explosion plant

5. ENZYMATIC HYDROLYSIS

For cellulosic ethanol production, the primary challenge is breaking down (hydrolyzing) cellulose into its component sugars. In order that cellulose hydrolysis becomes economically feasible, it is important to identify methods that increase enzyme effectiveness and overcome barriers of enzymatic hydrolysis. Major factors that influence enzymatic conversion of lignocelluloses the fermentable sugars, include accessible surface area of lignocelluloses, enzyme loading and presence of inhibitors.

Attempts have been made to explore the causes of biomass recalcitrance and ways to overcome it using cellulases (enzymes that break down cellulose). The hydrolysis of the lignocellulose biomass to release the C6 fermentable sugars will be carried out via enzymatic hydrolysis.

External surface area of lignocelluloses can be increased by mechanical milling and grinding. More recently, addition of xylanase serves the same purpose and with cellulase, it proved to be the effective method for enzymatic hydrolysis of lignocelluloses. Ohgren et al obtained a near theoretical glucose yield (96-104%) from acid catalyzed steam pretreated corn Stover, using xylanase as supplement to cellulases during hydrolysis. Since high cost of enzyme limits large-scale lignocellulosic bioethanol production, it is desirable to use low enzyme loading to produce fermentable sugars with high yield.

Additives could be promising to improve enzymatic hydrolysis by restricting enzyme activity loss due to nonproductive adsorption. Use of surface-active additives (surfactants, proteins and polymers) has been reported to enhance enzymatic hydrolysis of lignocelluloses by preventing unproductive binding of cellulase to lignin. Addition of Tweed or polyethylene glycol (PEG) increased efficiency of enzymatic hydrolysis by getting adsorbed on the lignin surface. Ethylene oxide containing surfactants also have the same effect.

Addition of PEG to enzymatic hydrolysis medium at 50°C hindered deactivation of enzymes by their exclusion from lignin surfaces and increased cellulose conversion up to 70%. Surfactants have a more pronounced effect on acid and steam pre-treated straw than that of ammonia and hydrogen peroxide treated straws.

In another recent advance, enzymes are employed to enable milder pre-treatment. Although dilute acid pre-treatment can break down hemicellulose very effectively, the severe conditions require expensive processing equipment and tend to degrade the sugars. A milder pre-treatment process could cut process costs dramatically and eliminate sugar degradation losses. The challenge is to maintain a high level of effectiveness with the milder process, which is accomplished by using enzymes to further break down the hemicellulose after pre-treatment.
It has been reported that proper mixtures of enzymes can enhance hemicellulose hydrolysis. In an experiment on pre-treated corn Stover, adding a hemicellulase enzyme to break down the hemicellulose increased the yield of xylose (a sugar resulting from hemicellulose hydrolysis) by 12% across a range of pre-treatment conditions. Breaking down the hemicellulose also enhanced cellulose hydrolysis, resulting in a 6% higher glucose yield.

To make contact with cellulose, the enzymes must get past complex structures of maize plant. A unique array of microscopy tools and techniques available at NREL's Biomass Surface Characterization Laboratory enables researchers to image plant

structures down to the molecular level. To probe even further—visualizing structures and processes at scales that cannot (yet) be observed—NREL and its partners are building a sophisticated molecular dynamics model of the cellulose-cellulase system.

To accelerate cellulose conversion, it is critical to start with the best enzymes. The most active known cellulases are in the CelloBioHydrolase I (CBH I) family, derived from fungi. But not all CBH I enzymes are equal.

NREL recently confirmed the existence of CBH I enzymes that are twice as active as those from industrial sources.

These ultra-sharp laser microscope images were created with the Biomass Surface Characterization Laboratory's scanning con focal microscope, which can be used to build 3-D representations of plant structures.

5.1 IOGEN ENZYMATIC HYDROLYSIS PROCESS

The block diagram for the Iogen enzymatic hydrolysis process for converting lignocellulosic materials to ethanol is shown below.

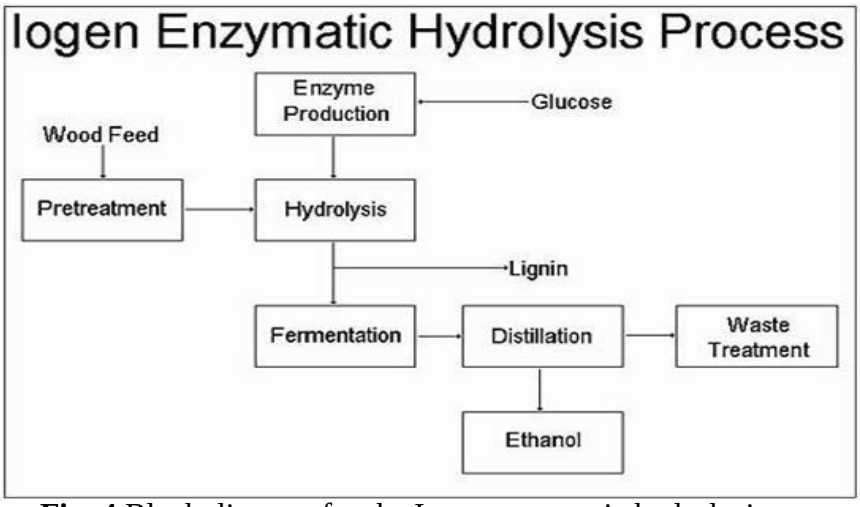

Fig. 4 Block diagram for the Iogen enzymatic hydrolysis process

The pre-treatment step involves steam explosion with dilute acid conducted at elevated temperatures and pressures. The hydrolysis and fermentation steps are undertaken at ambient temperatures and pressures. Distillation is the normal ethanol industry process. The Iogen process is currently suitable for agricultural residues such as wheat straw and corn stover. Hardwood residues are also a suitable feedstock. A single step pre-treatment process for agricultural and hardwood residues is able to produce a material that can be efficiently hydrolysed by the enzymes.

5.2 A TWO STAGE DILUTE ACID HYDROLYSIS PROCESS

The process is ideally suited to handle agricultural feedstocks and hardwoods. A two stage dilute acid hydrolysis process for the preparation of the sugar streams from its preferred feedstocks, is used. The hydrolysis is done in two stages, the first releasing the hemi-cellulose and the second the cellulose.

Both of these stages involve elevated temperatures and pressures and dilute sulfuric acid to keep the reaction times short.

As shown below, there are two separate fermentations although both use the same organism.

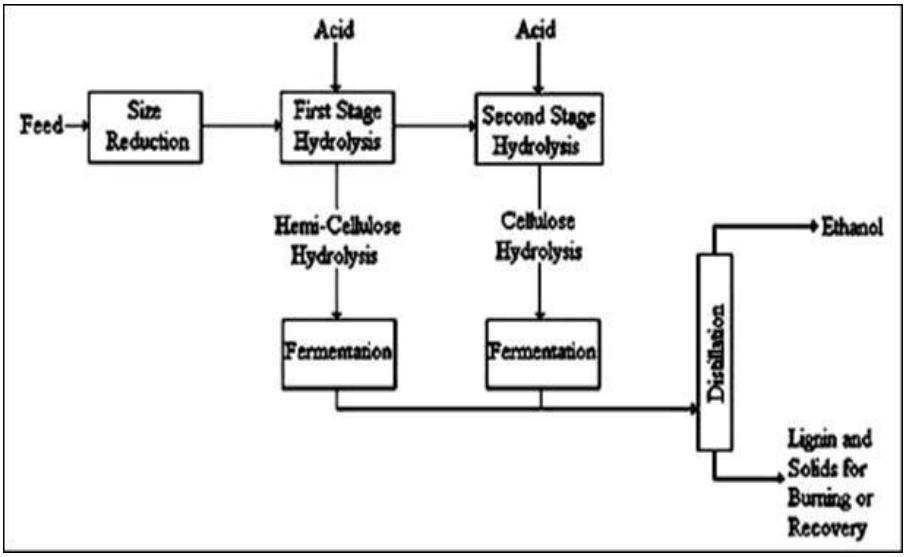

Fig. 5 A two stage dilute acid hydrolysis process for the preparation of the sugar streams

Advantage of the process is clearly its ability to ferment pentose and hexose sugars. That is particularly important for agricultural and hardwood residues but also has some impact on softwoods. *The two-stage hydrolysis is a complicated process with higher capital costs and higher operating costs.*

5.3 CONCENTRATED ACID HYDROLYSIS TECHNOLOGY

The advantages of the concentrated acid process, as shown below, are that the reaction is fast and is carried out at lower temperatures and pressures than those using dilute acid. These advantages result in less unwanted degradation products. The traditional disadvantages have been high costs of construction due to the concentrated acid and multiple process steps, and higher operating costs due to acid losses and high waste levels. *The concentrated acid technology is suited to softwoods*.

The process will produce lignin and gypsum as co-products of the process. The concentrated acid processes usually produce a lignin that has less potential for upgrading due to the amount of degradation that occurs in the processing.

Depending on the feedstock other products can also be produced such as silica when rice straw is used.

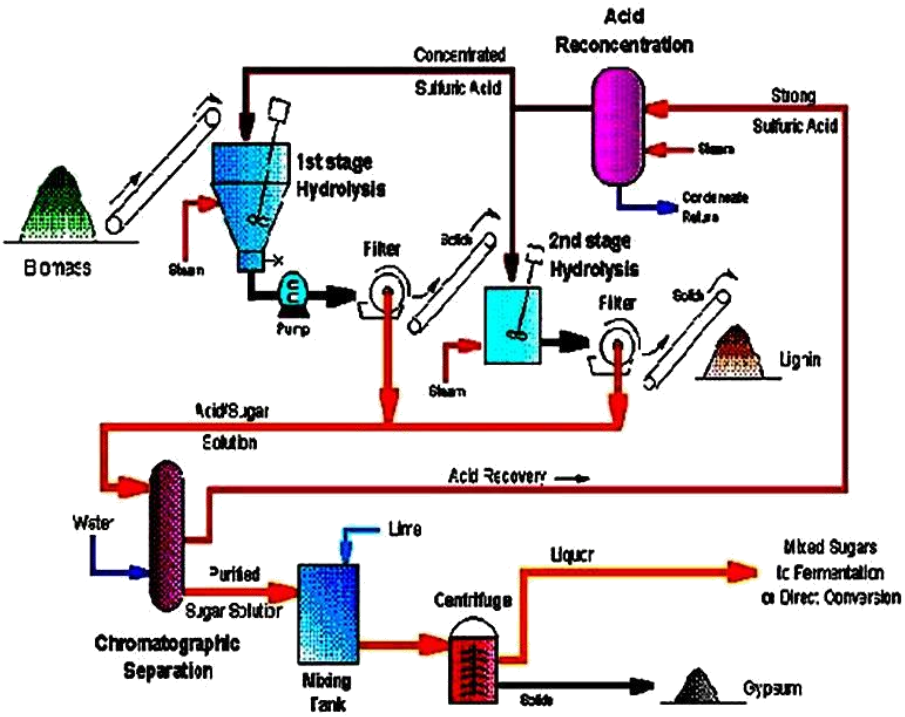

FIG. 6 Concentrated acid hydrolysis process

5.4 ACID CATALYZED ORGANOSOLV SACCHARIFICATION PROCESS

The process involves the solubilization of all components of lignocellulose with a concentrated solution of acetone with a small amount of acid. The reaction is carried out at temperatures around 200C and relatively high pressure of 40 bar. Residence times in the reactor are on the order of 0.5 hours.

The feedstock needs to contain moisture and be hammer-milled. The solvent to substrate ratio is closely monitored and maintained. A secondary hydrolysis is performed at about 100C for 20 minutes that drives off and recovers the remainder of the acetone. The lignin precipitates and is cooled, filtered and recovered. A block diagram of the ACOS process is shown below.

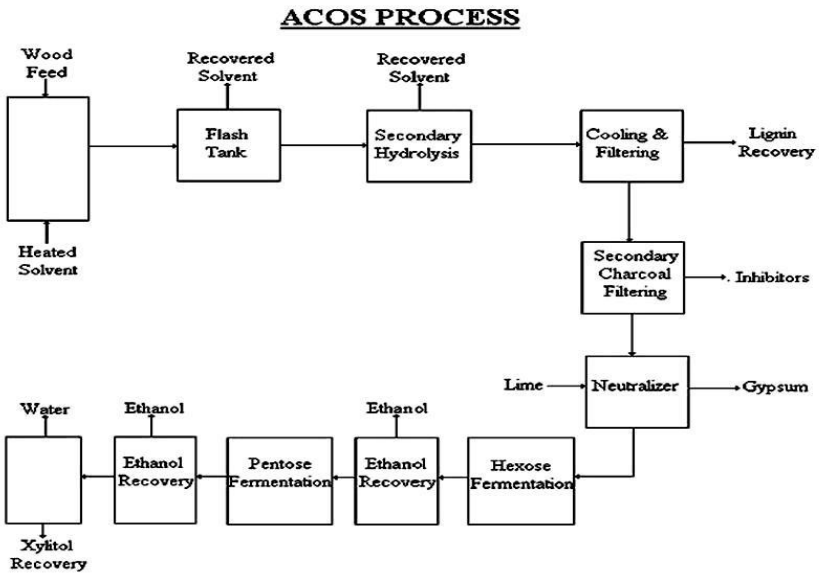

Fig. 7 Acid Catalyzed Organosolv Saccharification (ACOS) Process

The ACOS process has a number of unique aspects. It is claimed that a wide variety of feedstocks including hardwoods, softwoods, agricultural residues, and grain can be processed with the same conditions. The hydrolysis can process the hemi-cellulose and the cellulose at the same time without any significant degradation of the pentose sugars resulting in high yields. This single stage hydrolysis has the potential to lower capital and operating costs of the plant compared to the two stages. There is only one solids filtering step unlike the acid processes. The reaction times are short unlike the enzymatic process; again this helps to lower capital costs.

6. FERMENTATION

During fermentation, microorganisms (primarily fungi and bacteria) convert the sugars in biomass to ethanol. Under ideal conditions, these "bugs" will work contentedly, consuming sugars and producing ethanol and other products. But conditions in a cellulosic ethanol biorefinery are anything but ideal.

The hot soup, called a hydrolyzate, generated after pre-treatment and hydrolysis contains not only fermentable sugars, but also compounds (such as acetic acid) that are toxic to the bugs. Other things that are toxic in the fermentation process and the hydrolyzate are a high-solids concentration and a rising ethanol concentration. Because microorganisms found in nature do not function well in this hostile environment, there is a need to create "super-bugs" that thrive in it.

Yeasts are currently the fermentation organisms of choice for the corn ethanol industry. They are reasonably tolerant of ethanol, acid, and moderately high temperatures. However, existing yeast strains cannot withstand highly toxic hydrolyzates or ferment 5-carbon sugars and minor 6-carbon sugars efficiently. Also, development of a yeast capable of fermenting a particular 5-carbon sugar, arabinose, which constitutes up to 20% of the fermentable sugars in corn fiber, was reported. Three genes from a bacterium were inserted into the yeast Saccharomyces cerevisiae. This work resulted in the first ever demonstration, in 2000, of arabinose fermentation by yeast.

Use of a yeast alternative, the bacterium Zymomonas mobilis (Zymo) giving a high ethanol yield and tolerating high ethanol concentrations, is other option. Using genetic and metabolic engineering, acetic acid-tolerant Zymo strains that can ferment arabinose and the most important 5-carbon sugar, xylose, were developed by NREL. NREL also pioneered a technique to make the Zymo strain stable (the bacteria's offspring have the same genes as the parents) by inserting key genes into the genome.

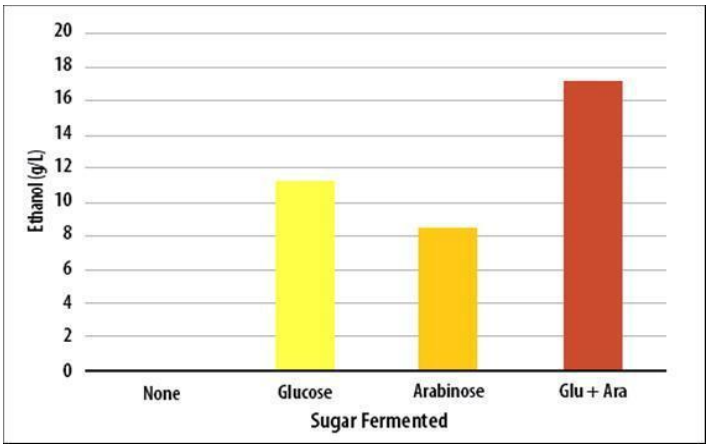

Fig. 8 Ethanol yield VS arabinose in a defined medium

These results show an ethanol yield of 83% from arabinose in a defined medium (not a hydrolyzate). From left to right, initial sugar concentrations were 0 g/L, 20 g/L glucose, 20 g/L arabinose, and 20 g/L glucose + 20 g/L arabinose. Expected ethanol from 20 g/L of sugar is 10.2 g/L at 100% yield.

7. THERMOCHEMICAL CONVERSION

Thermochemical biomass conversion involves processes at much higher temperatures and generally higher pressures than those found in biochemical conversion systems. Key intrinsic characteristics distinguishing thermochemical from biochemical biofuels are the flexibility in feedstocks that can be accommodated with thermochemical processing and the diversity of finished fuels that can be produced. Thermochemical production of biofuels begins with gasification or pyrolysis. The former is generally more capital-intensive and requires larger scale for best economics, but the final product is a clean finished fuel that can be used directly in engines.

The discussion here focuses on gasification based processing, by which a variety of different biofuels can be produced, including Fisher-Tropsch liquids (FTL), dimethyl ether (DME), and various alcohols.

Fischer-Tropsch liquid (FTL) is a mixture of primarily straight-chain hydrocarbon compounds (olefins and paraffins) that resembles a semi-refined crude oil. Converting biomass into FT liquids involves similar processing as for coal conversion [17-23]. FTL is synthesized by catalytically reacting CO and H_2.

Thus, any feedstock that can be converted into CO and H_2 can be used to produce FTL. In particular, coal, natural gas or biomass can be used as a feedstock for FTL production.

More recent activities are aimed at the development of gasifier dedicated to the production of syngas (to be used in an internal combustion engine), synthetic biofuels (sun-diesel, methanol) as well as hydrogen.

In this approach, heat and chemicals are used to break biomass into syngas (CO and H_2) and reassemble it into products such as ethanol. This method is particularly important because up to one third of cellulosic biomass, the lignin rich parts cannot be easily converted biochemically. Forest products and mill residues typically have high lignin contents, making them unattractive feedstocks for biochemical conversion yet suitable for thermo-chemical conversion. In an integrated bio-refinery, lignin-rich residues from the biochemical process could also be converted thermo-chemically.

However, syngas created from biomass is not “clean”—it contains contaminants such as tar and sulfur that interfere with the conversion of the syngas into products. These contaminants must be removed through tar-reforming catalysts and catalytic reforming processes that have demonstrated high levels of tar conversion—converting up to 97% of the tar into more syngas. This not only cleans the syngas, it also creates more of it, improving process economics and ultimately cutting the cost of the resulting ethanol.

The major components of the now-clean and concentrated syngas are carbon monoxide (CO) and hydrogen (H_2), usually with a small amount of methane (CH_4). The CO and H_2 react when passed over a catalyst (the CH_4 is inert) to produce liquid fuel. The design of the catalyst determines what biofuel is produced.

Further research work for regenerating the tar-reforming catalyst after it has been partially deactivated by sulfur poisoning has also been reported recently. Pure ethanol (or pure butanol) can also be made from syngas by micro-organisms that ferment the gas [24].

A second option for converting syngas to liquid fuel, one that is less well-developed commercially than the catalytic process just described, is represented by the dashed lines (Fig. 9). This combined thermo/biochemical route to a pure alcohol, if it can be made commercially viable, would enable the lignin in the biomass feedstock, as well as the hemicellulose and cellulose, to be converted to fuel, unlike the case for purely biochemical "cellulosic ethanol" discussed earlier. With this option, specially-designed micro-organisms ferment the syngas to ethanol or butanol.

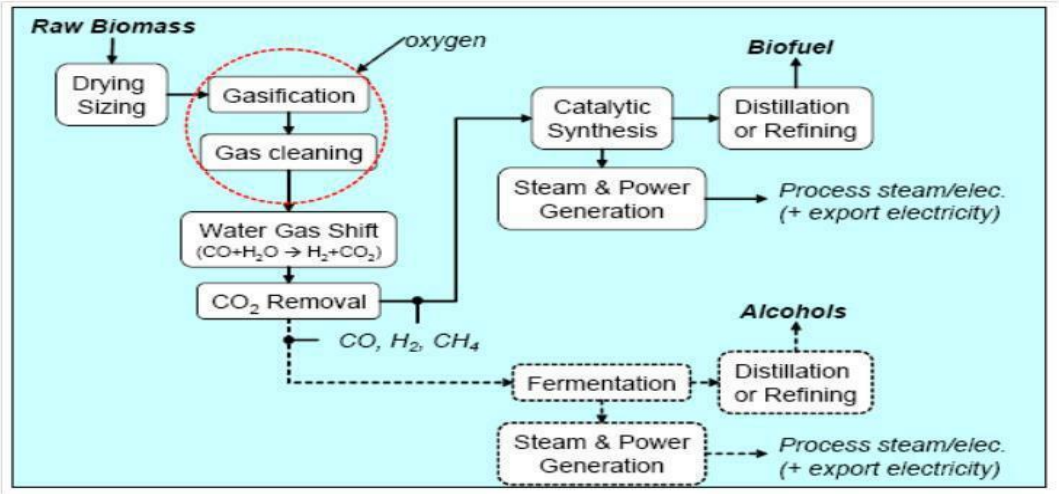

Fig. 9 Simplified depiction of process steps for thermochemical biofuels production

Most components of the equipment needed in a system for producing a thermochemcial biofuel by the catalytic synthesis route are commercially available today.
However, two areas needing further engineering development and demonstration are the feeding of biomass into large-scale pressurized gasifiers and the cleanup of the raw gas produced by the gasifier. The relatively low bulk density of biomass makes it challenging to feed into a pressurized gasifier efficiently and cost effectively.

Development is needed in the area of syngas cleanup (especially tar removal or destruction) because tolerance to contaminants of downstream fuels synthesis processes is low. Tars have been the most problematic of syngas contaminants and have been the focus of much attention since the 1970s. Methods for removal (or conversion to light permanent gases) are known, but still inefficient and/or costly.

Research, development and demonstration efforts are being pursued for syngas fermentation. The basic process flow for a novel fermentation process that can convert carbon monoxide and hydrogen to ethanol is shown below.

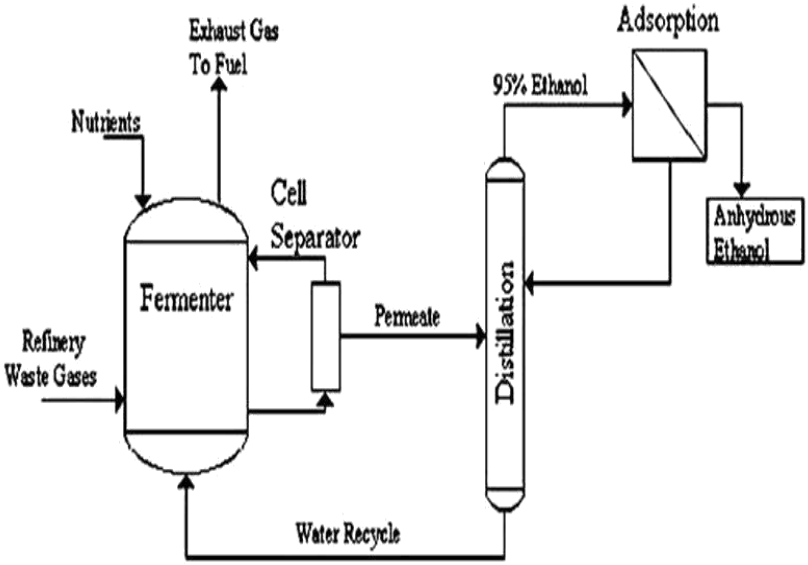

Fig. 10 Basic process flow for a novel fermentation process

The fermentation vessel operates at slightly above ambient temperatures (37 °C) but at moderate pressure (40psi) so that reaction rates are increased. Ethanol being toxic to the culture its concentrations are kept below 3% v/v in the reactor. The organism consumes carbon monoxide, carbon dioxide, and hydrogen to produce ethanol and acetic acid. The acetic acid production is minimized by the recycle of distillation bottoms containing some acid back to the fermenter. One of the distinct advantages of this route would be that bark could be processed as well as softwood sawdust and shavings.

There would be no co-products involved other than the excess energy generated by the system. This energy would be in the form of methane and could be used in a variety of applications including a gas turbine cogeneration system.
Dimethyl ether (DME), a colourless gas at normal temperatures and pressures is also an excellent diesel engine fuel due to its high ketene number and absence of soot production during combustion. However, an adequate purification of the product gas is obtained thanks to the inclusion of a high temperature ceramic filter in the cleaning section. By adding in the reactor a specific catalyst, the hydrogen content in the product gas can go over 50% and its quality can be further improved.

In the framework of its research activities focused on thermochemical conversion of waste biomass for both thermal and electric power, as shown on the next page, ENEA has developed an industrial scale FICFB gasifier at Trisaia [25]. The design of the reactor and the use of steam as gasification agent gives this process a nearly nitrogen free product gas with a high calorific value of around 12 MJ/Nm³ dry gas. By using a natural catalyst as bed material and gasification temperature above 800 °C, the tar content was reduced below 5 g/Nm³.

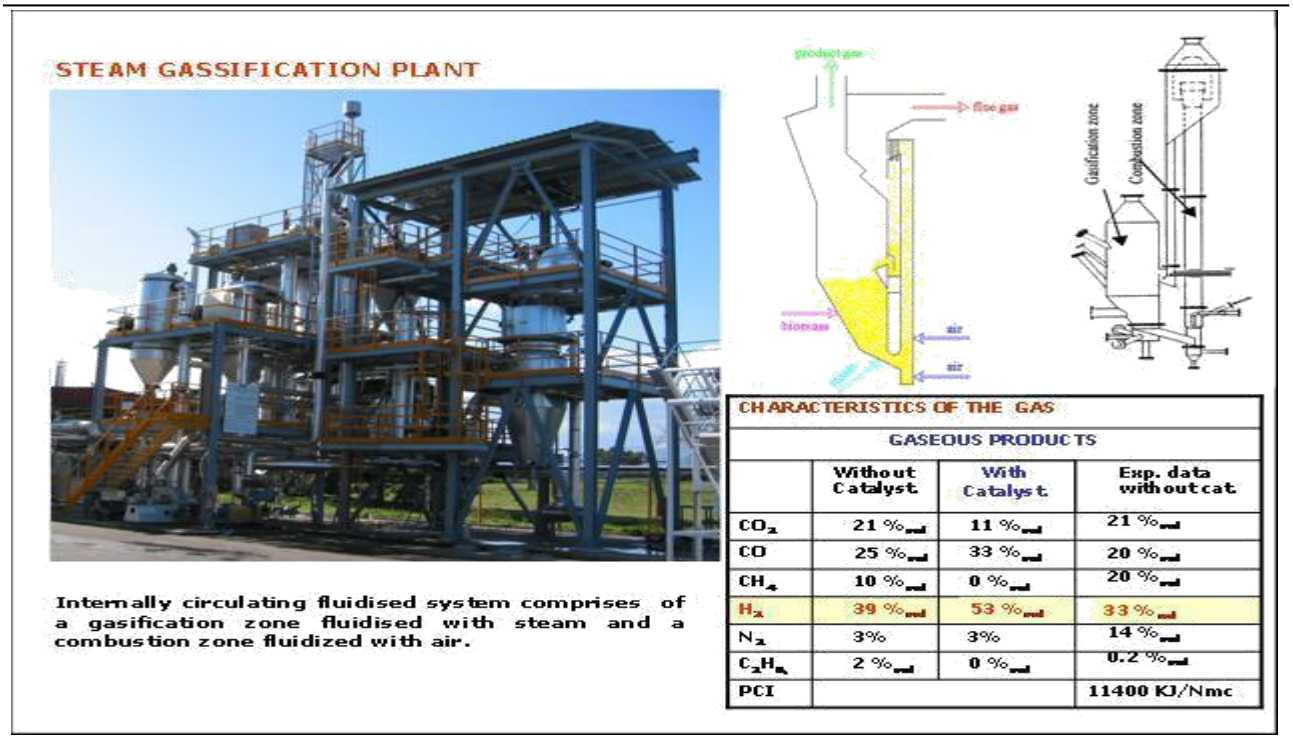

Fig. 11 Industrial scale FICFB gasifier designed, developed and experimented by ENEA

8. PREFERRED TECHNOLOGY ROUTE

Presently, there doesn't seems to be any clear commercial or technical advantage between the two pathways. Both sets of technologies are under continual development and evaluation, and have significant technical and environmental barriers yet to be overcome. For the biochemical route, much remains to be done in terms of improving feedstock characteristics; reducing the costs by perfecting pre-treatment; improving the efficacy of enzymes and lowering their production costs; and improving overall process integration. The potential advantage of the biochemical route is that cost reductions have proved reasonably successful to date, so it could possibly provide cheaper biofuels than via the thermo-chemical route.

Conversely, as a broad generalization, there are less technical hurdles to the thermo-chemical route since much of the technology is already proven. The main problem appears to be the availability of large enough quantity of feedstock at a reasonable cost. Reliable and economic gasification of biomass still needs to be improved.

One key difference between the biochemical and thermo-chemical routes is that the lignin component is a residue of the enzymatic hydrolysis process and hence can be used for heat and power generation. In the BTL process it is converted into synthesis gas along with the cellulose and hemicellulose biomass components.

Both processes can potentially convert biomass to energy carrier in the form of biofuels giving an overall biomass to biofuel conversion efficiency of around 35%. Overall efficiencies of the process can be improved when surplus heat, power and co-product generation are included in the total system.

A second major difference is that biochemical routes produce ethanol whereas the thermo-chemical routes can also be used to produce a range of longer-chain hydrocarbons from the synthesis gas. These include biofuels better suited for aviation and marine purposes.

As said earlier, currently there doesn't seems to be any clear commercial or technical advantage between the two pathways so only time will tell which conversion route will be preferred.

For second-generation biochemical ethanol production, advances in engineering of biological organisms and processes, and in lower-cost production of lignocellulosic feedstocks such as switch grass, the commercial ethanol production costs will be competitive with ethanol from corn.

In the longer term, both low feedstock costs and large production scales are projected to be needed to reach costs below corn-ethanol costs. Many developing countries may have a comparative advantage due to natural climatic conditions, and there is a greater probability that sustainable low-cost biomass production can be achieved in such places.

For second-generation thermochemical systems, since many of the equipment components needed for biofuel production are already commercially established from applications in fossil fuel conversion, with relatively modest further development and demonstration efforts, thermochemical biofuels could be in commercial production within a few years. With the present understanding of technology, a large-scale biomass-FTL production facility could be realized. Where thermochemical biofuel production can be integrated with a facility producing biomass by-products usable for energy – e.g. the pulp and paper industry – it could be competitive at much lower oil prices and/or at smaller scale. Moreover, in countries where biomass production costs are lower and construction and labour costs are also lower, thermochemical biofuels will compete with oil prices.

9. ECONOMICS

A general characteristic distinguishing second-generation biofuels production from first generation technologies is the larger capital cost per unit of production. Lower-cost feedstocks will offset this greater capital intensity to yield lower total production costs. For second-generation biochemical ethanol production, advances in engineering of biological organisms and processes, and in lower-cost production of lignocellulosic feedstocks such as switchgrass, are expected to be commercial competitiveness of biological fuel ethanol over the next 10 to 20 years. Production of cellulosic ethanol with today's known technologies, especially, in many developing countries, may have a comparative advantage due to possible sustainable low-cost biomass production in such places.

For second-generation thermochemical systems, it is expected that with relatively modest further development and demonstration efforts, thermochemical biofuels could be in commercial production within a few years. In case, thermochemical biofuel production can be integrated with a facility producing biomass by-products usable for energy – e.g. the pulp and paper industry, thermochemical biofuel production can be competitive at much lower oil prices (~$40-50/barrel of oil) and/or at smaller scale
[27]. In countries where biomass production costs are lower (due to better growing climates) and where construction and labour costs are also lower, thermochemical biofuels will be more competitive.

Given the still-early point in commercial development of second-generation biofuel technologies, it is difficult to project the role that developing countries will take in a global biofuel economy in the long term.

9.1 COST PREDICTION

The chart provided below presents data on what the NREL expects the costs of cellulosic ethanol to be in future.

It can be observed from the above illustration that significant reductions are expected in all the main three cost contributors – feedstock costs, enzyme costs and conversion costs. In the longer term, both low feedstock costs and large production scales are projected to be needed to reach costs below corn-ethanol costs. The achievability of supplying large volumes of biomass at an average cost of $30/ton or less (as assumed in Fig. 12 by NREL) will be a most challenging task.

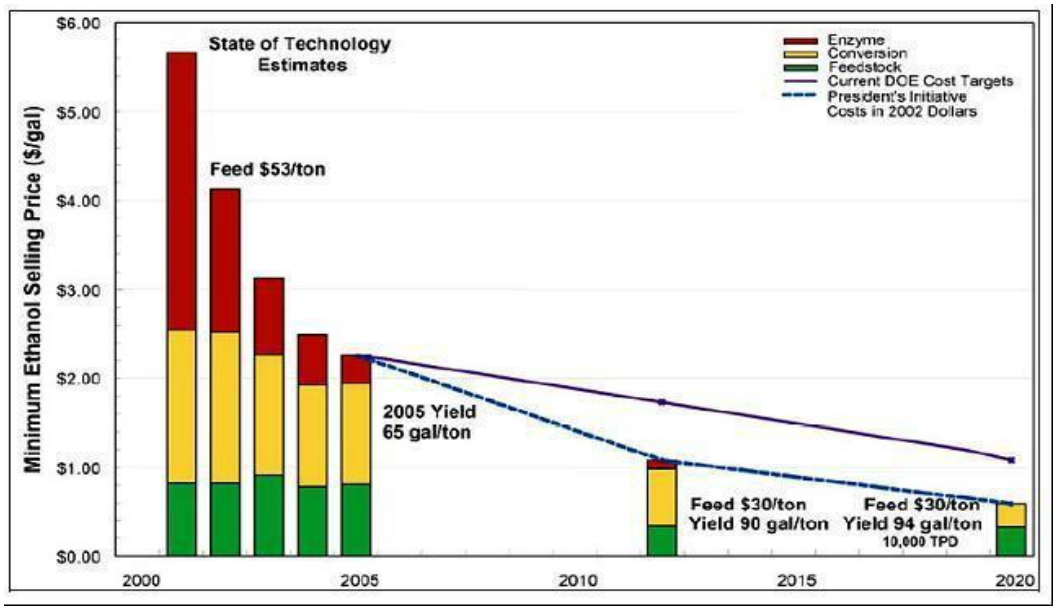

Fig. 12 Costs and cost targets for cellulosic ethanol production projected by NREL[27]

In the longer term, both low feedstock costs and large production scales are projected to be needed to reach costs below corn-ethanol costs (Fig. 12).

It is worth to note that as per projection from NREL laboratory, it is expected that by the year 2012, feedstock costs will decrease by over 40%, conversion costs will decrease by over 40% whereas enzyme costs to decrease by almost 70%. Lignocellulosic ethanol is estimated to become cost competitive with fossil fuels currently at a crude price of about $100 per barrel, and by 2030, it is expected to be competitive at a crude price of $75.

Needless to say that processing cost reduction benefits could result from various efficiency efforts. The largest of these reductions are likely to come from concepts such consolidated bioprocessing, efficiencies in pre-treatment methods, and a more optimal utilization of cellulose enzymes. It is expected that through reduced energy usage, reduced enzyme costs, reduced raw material requirements and capital expenses, it is possible to achieve the target value.

Based on above information and data and using other reference sources, it is estimated that the following is the likely trend for cellulosic ethanol costs in future.

Table 1 Future projections for cellulosic ethanol costs

All cost data in $ / gallon

Cost Component	2001	2005	2012	2020
Feedstock	0.8	0.8	0.5	0.35
Enzyme	3.2	0.4	0.3	0.1
Conversion	1.7	1.2	0.8	0.6
Total cost per gallon	5.7	2.4	1.6	1.05
Total cost per gallon equivalent of gasoline*	9.3	3.9	2.6	1.7

* : 1.63 gallons of ethanol is the equivalent of 1 gallon of gasoline, in terms of calorific value / energy density.

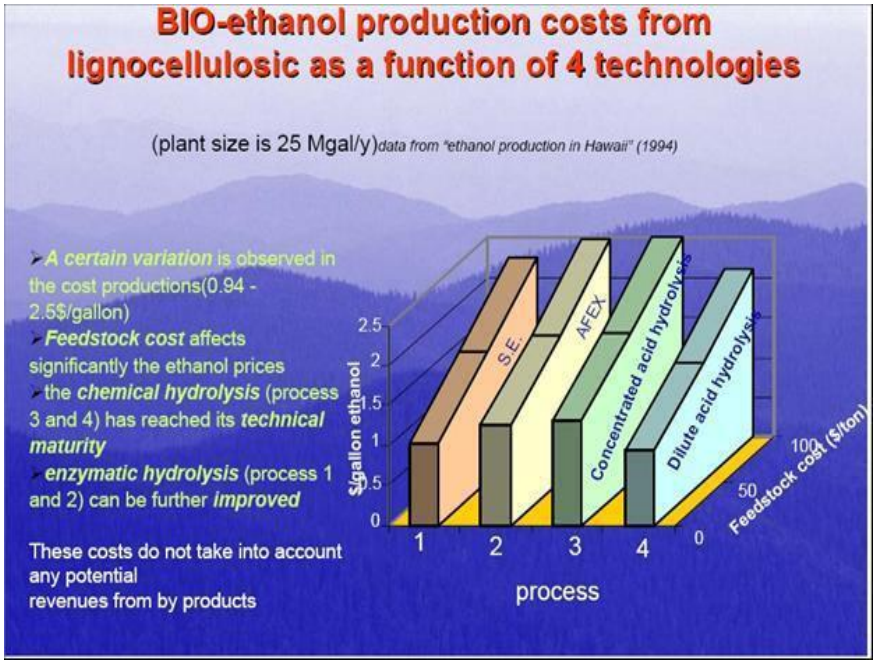

Fig. 13 Bioethanol production costs from lignocellulosic as a function of technologies

10. INVESTMENT POTENTIAL

Keeping in view the overall global production and, moreover, to meet its targets for renewable energies, a marketing report produced by the European Renewable Energy Council has predicted an overall investment of Euro 443 billion (by the year2020), in Europe.

TABLE 2 WORLD ETHANOL FUEL PRODUCTION IN MILLION LITRES

WORLD ETHANOL FUEL PRODUCTION IN MILLION LITRES						
	2006	**2007**	**2008**	**2009**	**2010**	**2011**
Europe	1,627	1,882	2,814	3,683	4,615	5,467
Africa	0	49	72	108	165	170
America	35,625	45,467	60,393	66,368	77,800	79,005
Asia/ Pacific	1,940	2,142	2,743	2,888	3,183	4,077
World	39,192	49,540	66,022	73,047	*85,763*	*88,719*
					Source: F.O. Licht	

Needless to say that a pre-set target share of 20% from renewable in total energy consumption will have economic opportunities for new industries and new industrial and craft jobs through production, installation and maintenance of such energy systems.

To reach both the overall target and the sector targets, which are feasible, specific support actions for some technologies such as lignocellulosics waste, needs to be taken soon. Using biological fuels or other renewable fuels to replace diesel or petrol, in each member state, can guide policy-makers and send important signals to the investors.

Moreover, the effective implementation of proposed biofuels directives will certainly needs a considerable amount of investments in this sector.

Given the present state of market progress and a strong political support, it is worth mentioning that concrete steps needs to be taken to achieve significant contribution from biofuels toward energy consumption in the transport sector.

Ethanol production is expected to hit 88.7 billion litres in 2012, with net growth of over 3% compared to the global production during the year 2011 of 85.8 billion litres. The United States continues to be the largest ethanol producer in the world with production levels expected to reach

over 51 billion litres, in 2011. Europe is expected to produce 5.4 billion litres of ethanol this year which is a 15 per cent increase over 2010. The African continent has tremendous potential for biofuels production. High energy prices and the availability of productive land represent enormous opportunity for African biofuels production.

This year will be critical for Europe as member counties ramp up their production and use of ethanol to meet the European Union's Renewable Energy Directive.

There is no doubt that ethanol production today is able to reduce reliance on foreign oil, but still there is lot more to do and we should do.

11. CONCLUSIONS

a. It is true that the technology applied for the production of bioethanol from sugar and starch crops (sugar cane, sugar beet, maize, etc.) is mature enough to permit to achieve liquid fuel competitive, both for price and performances, to gasoline and diesel but the fact remains that have proven grossly inadequate to augment rising global requirements. Also, their continued use has contributed towards global food for fuel crisis.

b. Production of biofuels which do not compete with food and valorization of agro-waste from bio-based industry, is believed to be the main challenge for countries' building a sustainable bio-based industry of tomorrow. Hence, the priority is to make use of lignocellulosic biomass both forest (woody) and agricultural.

c. Use of biofuels in transport are important for reducing emission of green house gases (GHG) and the EU duly recognizing the roles biofuels have to play support the need for increasing the share of biofuels in the transport sector, especially in road transport that generates nearly 85% of the transport sector's emission. Second generation biofuel technologies such as cellulosic ethanol or syndiesel, with greater environmental benefits, can save CO_2 up to 90% and higher.

d. Innovation in the industrial biotechnology, especially the development of enzymes that can convert (hemi) cellulose with improved efficiency, is key to the development of second generation biofuels with focus on using residual non-food parts of current crops as well as other crops that are not used for food purposes, such as switch grass, cereals that bear little grain and more fibre, wood chips, etc.

e. Pre-treatment of lignocellulosic biomass for ethanol production, new and advanced technologies for hydrolysis and/or fermentation of lignocellulosic biomass, high purity syngas cleaning technologies for biofuels, biological conversion of syngas into liquid biofuels and the development of the Bio-refinery concept, as well as alternative routes to renewable fuel production, are important technical aspects that needs to be addressed on priority basis.

f. For second-generation fuels, many developing countries have the potential to produce biomass at lower cost than in industrialized countries due to better growing climates and lower labour costs, and so may be able to gain some comparative advantage.

g. In view of significant gains on energy and environmental benefit, it is very important to have a close collaboration with countries having ever increasing demand for energy for sustainable development, like, India and China, in the near future. For successful technology adoption and adaptation, it will be essential to have in place a technology innovation system in a country. This includes the collective set of people and institutions able to generate fundamental knowledge, to assimilate knowledge from the global community, to form effective joint ventures with foreign companies, joint collaboration in the field of research and technology development, etc.

h. For the purpose of technical know-how transfer, production of the fundamental data on the cultivation and exploitation, marketing strategies, capacity development and co-ordination and execution of the necessary (predictive) research on various aspects of new generation biofuels, co-operation at the international level, is a must.

i. To build trust, good interface with all stakeholders including the vehicle manufacturers and oil companies, is a must.

ACKNOWLEDGEMENT

Author would like to express his sincere thanks to all the researchers worldwide, whose valuable work has been cited in this document.

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