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Developments In Bio – Refinery and Its Impact On Pulp & Paper Industry

ABSRACT

Environmental sustainability and energy security, put pressure on the use of renewable or recyclable resources with zero impact on environment for meeting the growing needs of energy. Further mandates and regulations facilitate the use of bio-fuels in transport vehicles. Technological developments have now made it possible to use the renewable resource, namely biomass to produce bio-fuel, power and chemicals in a bio-refinery. Global bio-fuel production is currently estimated at 100 billion liters per year. Food crop, wood, agricultural residues, etc based bio-refineries have emerged as one of the solutions to the global energy problem. Commercial scale bio-refineries are in operation in several countries and some are under construction. Various technologies have been developed for producing bio-fuels, power and or chemicals from varieties of biomasses. This paper reviews the developments in bio-refineries, and its impact on pulp and paper industry.

INTRODUCTION

One of the serious challenges faced by the world is the growing population and the consequent growing demand for energy. In addition, anthropogenic climatic change is a severe threat to mankind and requires that the current greenhouse gas (GHG) emissions be reduced to avoid detrimental consequences for the globe. Efficiency improvements in energy generation and consumption alone cannot achieve this reduction in the long run. Alternative energy sources such as solar, hydro, wind, biomass, etc need to be increased to substitute the reliance on fossil fuels. Environmental sustainability and energy security, put pressure on the use of renewable or recyclable resources with zero impact on environment for meeting the growing needs of energy. Hence the global bio-fuels industry has grown significantly in recent years and is making a significant contribution to the individual economies of producing countries and to the global economy as a whole.

Industrial bio-refineries were identified by the World Economic Forum, as one potential solution that may help mitigate the threat of climate change and the seemingly boundless demand for energy, fuels, chemicals and materials. To promote the growth of this bio-fuel industry, several countries have established mandates and regulations to facilitate the use of bio-fuels in transport vehicles.

Bio-fuels are produced from corn, sugarcane, coarse grains, wheat and sugar from beet, etc. However, LINGO-cellulose based feedstocks such as straw, wood chips, bagasse, etc are now being used for production of bio-fuels. Some of the cellulosic feed stocks are also used in pulp and paper industry for

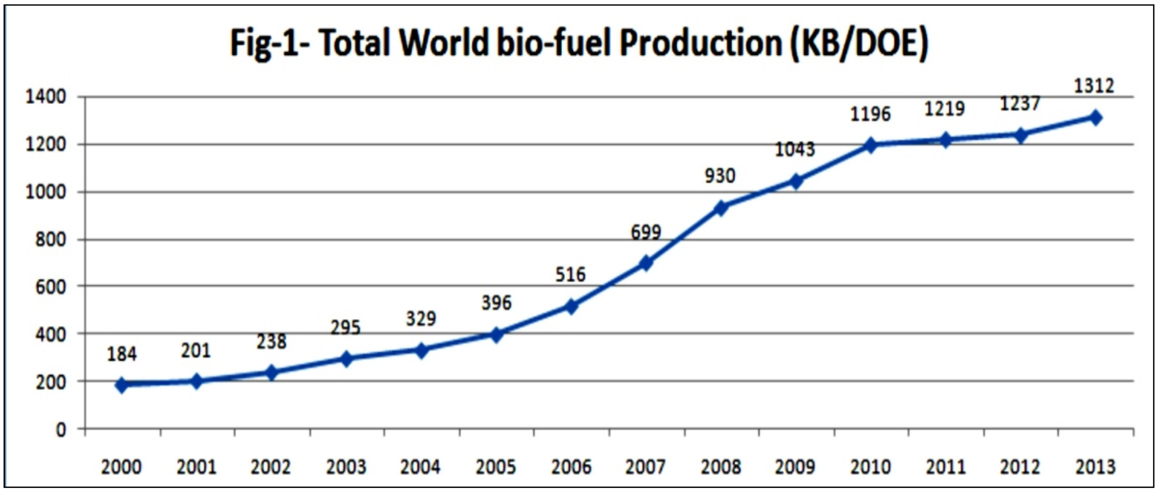


Fig-1- Total World bio-fuel Production (KB/DOE)

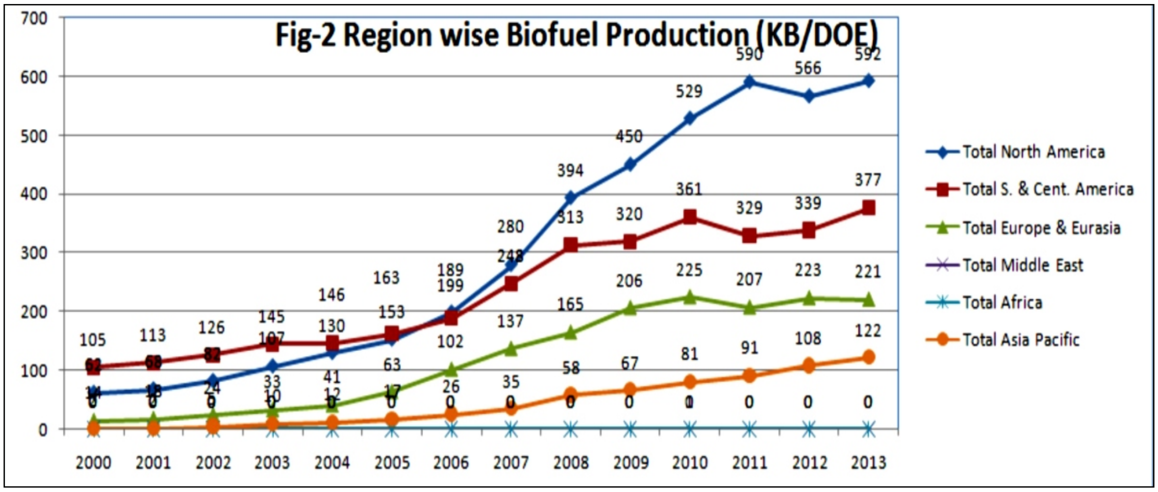


Fig-2 Region wise Biofuel Production (KB/DOE)

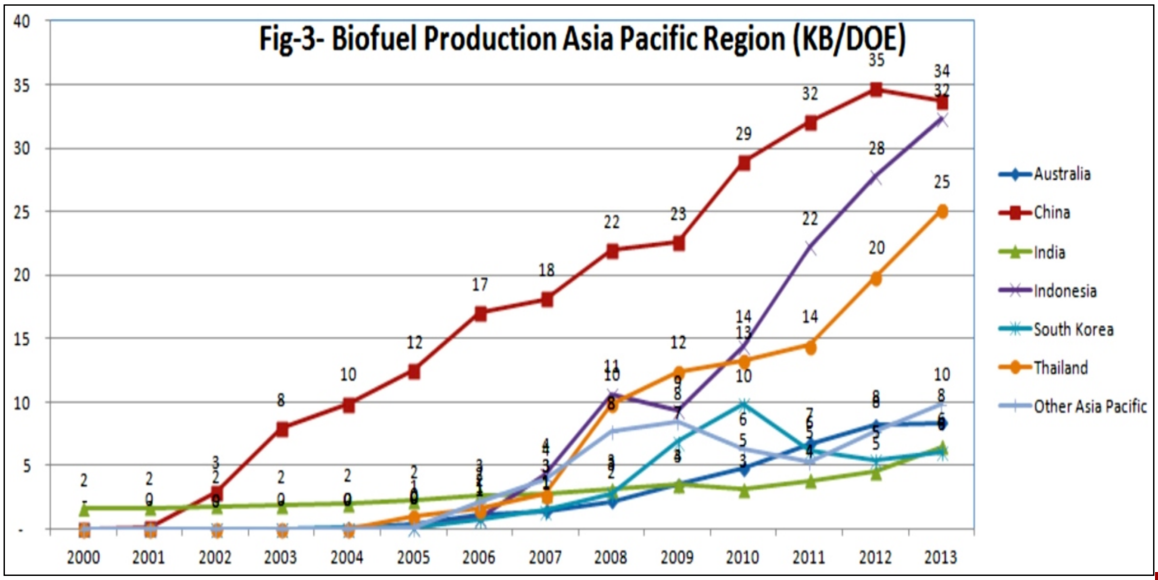


Fig-3- Biofuel Production Asia Pacific Region (KB/DOE) making paper. Hence the pulp and paper industry has to learn from the developments in bio-refinery industry. This paper reviews the global production scenario of biofuels, feed stocks used, and technologies adopted and the details of bio-refineries in operation. Further the impact of biorefinery technology in pulp and paper manufacturing is discussed.

GLOBAL SCENARIO

BP Statistical Review of World Energy 2014 [1] estimates the global bio-fuel production at 1312 KB/DOE (Thousand barrels per day of oil equivalent) in the year 2013 (Fig.1). It has grown more than four fold during the last 10 years with an annual average growth rate of 16%. US, Brazil and Europe are the front-runners in producing the bio-fuels. As seen in Fig.2, North America produced the highest bio-fuel followed by South and Central America (mostly Brazil) and followed by Europe. The scenario in Asia Pacific is far behind (see Fig.3). Among the Asia Pacific nations, china, and now Indonesia produce maximum quantities of bio-fuels.

USA have high targets for the replacement of fossil transportation fuels through wide range of support schemes including grants, tax credits, loan guarantees, etc. Focus is on bio-ethanol. Public support during last 5 years approximates € 1.2 billion. Brazil has world's leading first generation biofuel production capacity. Some commercial 2G bagasse refineries are in operation and aggressive government growth targets for bioethanol by 2025. EU has also set high targets for the replacement of fossil transportation fuels but focus is on biodiesel/ bio-chemicals and public support during last 5 years is approximately € 200 million. China has planned large-scale investment in bio-refineries and plans to substitute 20% of crude oil imports by 2020. Lane [2], gives following mandates for biofuels around the world for 2014.

The proposed statutory volumes are (in billions of US gallons)

Cellulosic	1.750
Biomass-based diesel	1.000
Advanced biofuel	3.750
Renewable Fuel	18.150
Corn Ethanol	14.14

Brazil: Mandates a minimum ethanol content of 20 percent. On the biodiesel side, the mandate is 5%. EU: The EU currently has a 5.75 percent mandate directive in place, and was scheduled to move to 10 percent by 2020.

China: Overall, the country seeks to move to a 10 percent biofuels mandate by 2020, and currently has a 15 percent overall target for 2020

India: The country has an E5 ethanol mandate, scheduled to move to E10 as soon as production is in place, and ultimately has set a goal of 20 percent for all biofuels content by 2017.

FEED STOCK AND TECHNOLOGIES ADOPTED

Currently, most biofuels are produced from crops that can also be used for food production (e.g. corn, wheat, sugar cane, sugar beet, palm oil, rape seed, soy, etc). Although biofuels offer a number of benefits to society, there has been a global debate in recent years concerning the impacts of biofuels (and bioenergy) on food production and prices. A wide diversity of 'non-food' feedstocks are potentially available globally for biofuel production including energy crops (e.g. Miscanthus, Jatropha, Short Rotation Copice), wastes (e.g. waste oils, food processing wastes, etc), agricultural residues (straw, corn stover, etc), forestry residues and novel feedstocks, such as algae.

Gołaszewski et al. [3] provides a conceptual framework of bioethanol production from lignocellulose. The various production technologies for producing ethanol, FT liquid, SNG, biodiesel, and other value added products from biomass are classified as follows

- Biochemical conversion
- Thermo-chemical conversion
- Chemical conversion

They defined the technological development (Table 1) in following three phases for ethanol.

Table - 1 Bio-Refinery Proceses

Biomas	Process	Bio-products
Sugar Crops	Fermentation, Distillation	Bioethanol
Sugar Crops	Conversion into monosaccharide, Fermentation, Distillation	Bioethanol
Ligno-cellulose materials	Pre-treatment, Conversion into monosaccharide, Fermentation, Distillation	Bioethanol lignin, power, chemicals

- Biorefinery, 1st Phase 1st generation biofuel made from sugar crops, starch crops, and vegetable oil.
- Biorefinery, 2nd Phase 2nd generation biofuel: biofuel made from lingo-cellulose based biofuels and integrated power generation
- Integrated Biorefinery, 3rd Phase integrated biorefining processes and power generation processes producing products including biofuel, power, other chemicals, fertilizers, etc

Biochemical Conversion

Bioethanol, as a fuel for motor vehicles has been produced, for tens of years, from the natural resource such as crop that is rich in sugar (sugarcane, sugar beet) or starch (grains, potato crops), is 1st generation biofuel. Characteristic feature of 1st generation biofuel includes natural competitiveness as compared to fodder or food production, relatively high production cost as compared to petrochemical fuel (low competitiveness) and low environment-friendly impact [3]. The aforementioned drawbacks are non-existent in the case of 2nd generation biofuel obtained from woody crops or agricultural waste or residues of high cellulose content called cellulose or lignin-cellulose or more often lignocellulose crops to highlight the substantial content of lignin polymer that is hard to convert into simple chemical compounds, and which may serve, beside nonpower opportunities, as the hard fuel for gasification processes and pyrolysis and further conversion into biofuel, and bioethanol too. The biorefinery integrating biofuel processes produce products through two kinds of processes biochemical process (the so called sugar platform) and thermal and chemical process (the so called syngas platform). The process of digesting sugar extracted from a variety of biomass serves the basis for the sugar platform of the biorefinery, whereas the syngas platform converts biomass through the thermal gasification process or pyrolysis into gaseous or liquid semi-products that may subsequently be used for producing several biofuels and other bioproducts (chemicals).

In contrast to the traditional bioethanol production from sugar and starch, the production based on lignocellulosic material requires additional processing steps. The reason is that the ellulose (source of C6 sugars such as glucose) as well as hemicellulose (mainly source of C5 sugars such as xylose) is not accessible to the traditional bioethanol producing microorganisms. Following processing steps may be found in a general lignocellulose to bioethanol production processes:

- Biomass size reduction
- Pretreatment
- Hydrolysis
- Fermentation
- Distillation

Thermo-chemical Conversion

Although thermo-chemical processes include gasification, pyrolysis and torrefaction, currently gasification technology is widely deployed. The production of biofuels using the thermochemical route differs significantly from the lignocellulosic ethanol production. Within this production scheme the biomass is first thermally fragmented to synthesis gas consisting of rather simple molecules such as hydrogen, carbon monoxide, carbon dioxide, water, methane, etc. Using this gaseous material the BtL fuels may be re-synthesized by catalytic processes. Alternatively methanation may be performed in order to obtain bio-SNG as substitute for natural gas.

After the size reduction, the material is moved into the gasifier where it transforms into gas (mainly composed of hydrogen and carbon monoxide) and solid by-products (char or ashes and impurities). Gasification takes place under shortage of oxygen. The product gas has a positive heating value, and, if char is produced, this also has a positive heating value. By reducing the amount of available oxygen, other processes are triggered, called pyrolysis and liquefaction. The gasification processes may be distinguished according to the used gasification agent and the way of heat supply. Typical gasification agents are oxygen, water, and air (carbon dioxide and hydrogen are also possible). Two types of processes are distinguished based on how heat is supplied. In one of the processes, the heat is provided through partial combustion of the processed material in the gasification stage. In the second type of processes, the heat is provided externally via heat exchangers or heat transferring medium. In these processes the heat may come from combustion of the processed material (i.e., combustion and gasification are physically separated) or from external sources. The amount and kind of impurities depend on the type of biomass used as fuel. Impurities can cause corrosion, erosion, deposits and poisoning of catalysts. It is therefore necessary to clean the product gas. Dust, ashes, bed material and alkali compounds are removed through cyclones and filter units, the tar through cooling and washing the gas using special solvents or by condensation in a wet electro-filter. Components having mainly poisonous effects are sulphur compounds that can be withdrawn by an amine gas treating, a benfield process or similar process, and nitrogen and chloride for which wet washing is required. The cleaned product gas will then be upgraded.

Fuel Synthesis - Fischer-Tropsch Liquids

Starting form the synthesis gas (the cleaned and upgraded product gas) several fuel processing pathways are possible. One of these is the Fischer-Tropsch (FT) process, through which alkanes are produced in fixed bed or slurry reactors using mostly iron and cobalt as catalysts. In the case of the High Temperature Fischer-Tropsch (HTFT) synthesis (300 – 350°C and 20 – 40 bar), products obtained are basic petrochemical materials and gas. The Low Temperature Fischer-Tropsch (LTFT) technology (200 – 220°C and less than 20 bar) provides outputs for diesel production. The raw product, though, cannot be directly used as fuel, it needs to be upgraded via distillation to split it into fractions; via hydration and isomerization of the C5 – C6 fraction and reforming of the C7 fraction in order to increase the octane number for petrol use; and via cracking by application of hydrogen under high pressure in order to convert long-chain fractions into petrol and diesel fraction.

Synthetic Natural Gas

The upgrading to SNG (synthetic natural gas) requires methanation of the product gas, desulfuration, drying and CO removal. In the methanation step (catalyzed by nickel oxide at 20-30 bar pressure conditions) carbon monoxide reacts with hydrogen forming methane and water: The withdrawal of CO can be performed by water scrubbing (a counter-current physical absorption into a packed column) and Pressure Swing Adsorption (an absorption into a column of zeolites or activated carbon molecular sieves followed by a hydrogen sulphide removing step) technologies. Natural gas quality is reached at 98% methane content. The final step is the gas compression (up to 20 bar for injection into the natural gas grid, up to 200 bar for storage or for use as vehicle fuel).

Mixed Alcohols

Starting form a suitably upgraded product gas, it is possible to synthesize alcohols as main products via catalytic conversion. The product upgrading of the obtained alcohol mixture consists typically of degassing, drying and separation into three streams: methanol, ethanol and higher alcohols.

CLASSIFICATION OF BIO-REFINERIES

Cherubini et al. [4] developed a bio-refinery classification approach. This classification approach relies on four main features: (1) platforms; (2) products; (3) feedstock; and (4) processes. Selected examples of bio-refinery classification are (1) one platform (C6 sugars) bio-refinery for bio-ethanol and animal feed from starch crops (corn); and (2) four platforms (lignin / syngas, C5/C6 sugars) bio-refinery for synthetic liquid bio-fuels (Fischer-Tropsch diesel), bio-ethanol and animal feed from LINGO-cellulosic crops (switch grass).

In bio-refinery systems, several technological processes are applied to convert biomass feedstock into marketable products. This classification approach identifies four main subgroups of processes.

1. Mechanical/physical (e.g., pressing, pre-treatment, milling, separation, distillation), which do not change the chemical structure of the biomass components, but they only perform a size reduction or a separation of feedstock components.
2. Biochemical (e.g., anaerobic digestion, aerobic and anaerobic fermentation, enzymatic conversion), which occur at mild conditions (lower temperature and pressure) using microorganisms or enzymes.
3. Chemical processes (e.g., hydrolysis, transesterification, hydrogenation, oxidation, pulping), where a chemical change in the substrate occurs.
4. Thermo-chemical (e.g., pyrolysis, gasification, hydrothermal upgrading, combustion), where feedstock undergoes extreme conditions (high temperature and/or pressure, with or without a catalytic mean).

These four features, with their subgroups, are used for the classification of bio-refinery systems. The generic bio-refinery pathway starts with a feedstock that is converted to one of the platforms, from which final energy and material products are produced. An

S.no	Name	Platforms	Main Product	Other Products	Feedstock	Processes
1	One-platform (C6 sugar) biorefinery for bioethanol and animal feed from starch crops	C6 sugar	Bioethanol	Animal feed	Starch crops (com)	Hydrolysis, fermentation
2	One-platform (oil) biorefinery for biodiesel, animal feed and glycerine from oil crops	Oil	Biodiesel	Animal feed (rape cake), glycerine	Oil crops (rapeseed)	Pressing, transesterification
3	One-platform (syngas) biorefinery for synthetic biofuels and chemicals	Syngas	Synthetic biofuels (FT-fuels)	Chemicals (alcohols)	Linocellulosic residues (straw)	Pre-treatment, gasification, FT synthesis, alochol synthesis
5	Two-platform (biogas and organic juice) biorefinery for biomethane, lactic acid, amino acid, biomaterials and fertilizer from grasses	Biogas, organic juice	Biomethane	Chemical (lactic acid, amino acid), biomaterials (fibers)	Grasses	Pressing, fiber separation, anaerobic digeston, upgrading
5	Four-platform (C6/C5 sugar and lignin/syngas) biorefinery for synthetic biofuels, bioethanol and animal feed from lignocellulosic crops	C6/C5 sugar, lignin, syngas	Synthetic biofuels (FT, fuels) bioethanol	Animal feed	Lignocellulosic crops (switchgrass)	Pre-treatment, hydrolysis, fermentation, gasification, FT synthesis

example of a bio-refinery system producing bio-ethanol from corn consists of mechanical treatment; corn is hydrolyzed to C6 sugars (the platform) and then fermented to bio-ethanol (the energy product), with animal feed as co-product (the material product).

Since there are some processes which are suitable for more than one platform, some platforms and conversion processes are linked together as well (Table 2), thus combining two or more individual bio-refinery systems. A particular role is played by the electricity and heat platform, which can be reached from almost all the biomass feedstocks and other platforms via combustion. This heat and power can be used to meet the energy demand of the biorefinery itself, used as an energy source from a nearby individual biorefinery system or sold to the public grid.

BIOREFINERY PLANT IN OPERATION - EXAMPLES

Many bio-refineries are in operation and some are under construction stage. In this section, few lignocellulosic bio-refineries in operation are discussed. Bio-fuel Digest [5], has released data on various bio-refineries across the globe in their web site. The database "SuperDataFree-062413.xls" contains information about 953 bio-refineries with total annual capacity of around 26 billion gallons per year. There are 805 first generation plants, 148 are second generation bio-refineries. Some of the major bio-refineries are discussed here

(i) Neste Oil: Neste Oil has production facilities in Netherlands (240 mgpy), Finland (109 mgy) and Singapore (223 mgy) for producing bio-diesel from renewable materials such as waste fat from fish processing, palm oil residues, technical corn oil, spent bleaching earth oil and vegetable oil such as Palm oil, Rapeseed oil, Camelina oil, Jatropha oil, and Soybean oil based on hydro-processing technology.

(ii) REG Geismar (formerly known as Dynamic Fuels, LLC Dynamic Fuels), USA has production facility (75 mgpy) for producing bio-diesel from animal waste based on Fischer-Tropsch gas to liquid technology.

(iii) Netherlands' BioGasols production facility (60 mgpy) adopts biomass fractionation technology, unlocks sugars from plant material (biochemical conversions) and fermentation of all sugars into ethanol simultaneously at high temperatures.

(iv) Brazil's Braskem is the world leader in the field of biopolymers because of production of green poly ethylene, first from sugar cane ethanol (57 mgpy) on a commercial scale started in September 2010. The production process comprises of sugar cane crushing, fermentation, distillation, dehydration, polymerization, extrusion and transformation.

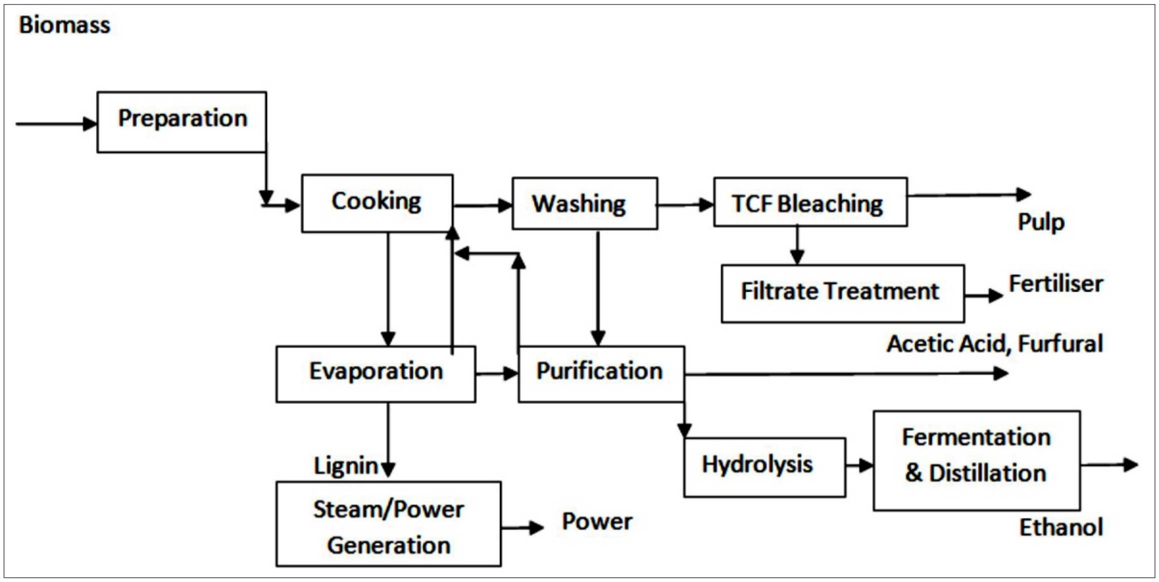
(v) Nature works, USA make (37 mgpy) biopolymers from dextrose (sugar) that is derived from field corn. The starch in the corn is converted into dextrose by hydrolysis. Then microorganisms are used for converting the dextrose into lactic acid through fermentation. Then biopolymers are produced through the polymerization process.

BIOREFINERIRS IN PULP AND PAPER INDUSTRY

Chempolis

In Finland, Chempolis [9] is running its pilot-scale biorefinery for processing cellulosic ethanol from agriculture and paper industry waste, at Oulu in northern Finland. The company has invested $24.4 million in its 68 tons per day facility, which also functions as a development and marketing centre for testing customer-sourced raw materials, and for producing sample batches of bioethanol, biochemicals, and papermaking fibers. Chempolis has patented third generation (3G) technologies for biorefining of non-food biomasses. Chempolis offer a 3G non-food biorefining platform which produces pure cellulosic sugars, biochemicals and solid biocoal. With this patented and proven technology, the conversion of bagasse, wheat and rice straw, corn-stover to non-food bioethanol and biochemicals is already proved. The technology makes it possible to produce simultaneously pulp for paper making, cellulosic ethanol, chemicals, lignin, fertilizer, etc. The process flow diagram is presented here in Fig. 4. There are significant technological and cost

Fig. 4 Chempolis's Biorefinery and Pulp Production Process



differences between the biofuel technology generations. Currently, commercial bioethanol is produced by 1G technology from food crops. The second and third generation (2G and 3G) technologies use non-food lignocellulosic biomasses and are on a threshold of commercialization. The unique advantage of Chempolis 3G technology is the selective fractionation of biomass resulting in reduced requirement for costly enzymes and higher purity of products. Compared to other typical approaches for the production of cellulosic ethanol, co-production of ethanol and biochemicals by this technology gives 40% more sales revenues. Because cellulose has been purified before hydrolysis, enzyme and overall operating costs are also favourable. For example, this Pasi Rousu claims that this 3G technology would provide approximately three-fold revenues by the use of bagasse when compared to current use in co-generation at sugar mills.

Chempolis' biorefinery integrates biomass conversion processes and equipment to produce fibres, multiple fuels, power, heat and chemicals from biomass at low pressure and temperature operation and 100% energy self-sufficiency and no need of fossil fuels. Besides these, other features are no pollution, full recovery of chemicals and water and 95-98 % removal of lignin and hemicelluloses. Hydrolysis of clean open structure cellulose fibre to glucose is very easy and lesser quantity of enzyme is needed, fermentation of pure glucose is easy and is proven in mill scale in Finland. TCF-bleaching of clean cellulose fibre is easy and no chlorine-based chemicals (ClO_2) are needed and high quality paper can be manufactured.

In India about 413 billion dry metric ton of agricultural residues (straw, bagasse, etc) are produced annually. Pasi Rousu [9] estimates that if 27 % of the available residues were used in 3G biorefining, it would enable bioethanol production of 18 Mt/a in 400 biorefineries which will replace completely gasoline by ethanol and reduce imports of crude oil by 25% and reduce CO_2 emissions by 40 Mt/a.

IMPACT ON PULP AND PAPER INDUSTRY

Bio-refineries will be increasingly competing with the pulp and paper industry for the biomass (wood as well as other agro-waste and even waste paper) for their raw material for production of bio-fuels to save the environment. Further, the Internet penetration significantly decreases aggregate paper consumption [10]. Estimates show that Internet growth reduces consumption of the paper categories that are more likely to be affected by the diffusion of the Internet (paper used to print newspapers and books and magazines). For example, in the US, the paper per capita consumption has reduced from 340 kg in 1999 to 230 kg in 2009 while the Internet penetration has increased from 35% to 70% during the same period. This will have impact on the existing mills. Even in Europe, many mills are closed down due to the same reason. Hence the option for the existing mills are to switch over to producing the bio-fuels as an alternative to the paper product but with the same raw materials with modifications in their production processes. Mills, which have investment capacity, can now go for completely new biorefineries and produce multiple products (such as bio-fuels, lignin, bio-chemicals and fertilizers) in addition to paper. Opportunities now exists for even existing mills to bring down the effluent quantities as well as qualities, eliminate the use of fossil fuels and use only the lignin for steam production by deploying the new biorefinery technologies.

Chambost [11] argues that pulp and paper mills proactively and strategically make decisions suitable for transforming their company into a unique new biomass-processing company making profits sustainable into the long term. For this the identification of a long-term business model, and the proactive creation of quality partnerships are essential for consolidating and securing value creation.

CONCLUSIONS

Many paper mills already have a tradition to utilize residual biomass such as bagasse, straw, etc from agriculture, for making paper. Due to the current limited domestic supply, the oil companies have had difficulties in fulfilling the E5 mandate. Further international pressures are mounting on improving India's environmental sustainability. Hence there is an opportunity market for producing and supplying more biofuels in India. The availability of residual biomasses, such as straws and bagasse is annually over 400 million tonnes in India. Using 30% of these available residues in 3G biorefining would enable bioethanol production of 20 million tonnes per annum. By utilizing cellulosic biomasses, co-produced annually by Indian agriculture, biorefining of domestic raw materials could potentially lead to 100% replacement of gasoline with domestic cellulosic ethanol.

Pulp and Paper industry can integrate the biorefinery in their production process and become a multi product (paper, fuel, chemical, fertilizer, etc) industry.

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