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Biorefineries from the perspective of sustainability: Feedstocks, products, and processes

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ABSTRACT

Today, sustainability is the buzzword in the developmental parlance. This has brought the issue of availability and utilization of energy into sharp focus. There is an urgent need to find viable alternative to fossils, mainly petroleum. It not only provides the major share of our present energy needs but also feeds the organic chemicals industry with vital raw materials. Among many alternative energy sources being explored biomass is the only one that has the potential for such dual application. Comprehensive yet judicious exploitation of biomass is, therefore crucial. The emerging concept of biorefineries is important in this context which advocates multiprocess and multiproduct biomass based industries. But everything green need not always be clean and sustainable as populism often makes it to be. Needless to say, the choices of feedstocks, processes as well as product mix are many. There is a need to critically examine them. This paper presents a status review of biorefineries from the stand point of feedstocks, products and processes.

Contents

1. Introduction

The World Commission on Environment and Development (WECD) in its report of 1987 defined sustainable development as development that meets the needs of the present without compromising the ability of future generations to meet their own needs [1]. The UN General Assembly welcomed the report in its 96th plenary

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meeting with a belief that it should become a central guiding principle of the United Nations, Governments and private institutions, organizations and enterprises [2]. This was reasserted in the 1992 United Nations Conference on Environment and Development, stating that "The right to development must be fulfilled so as to equitably meet developmental and environmental needs of present and future generations" [3]. Dependence on fossil fuels and their exhaustive use is certainly an antithesis to sustainability and mandates search for an alternative. In continuation to such efforts, the 2002 World Summit on Sustainable Development adopted a Plan of Implementation [4] to attain the goal of sustainable development. It unequivocally identifies the importance of "access to reliable, affordable, economically viable, socially acceptable and environmentally sound energy services and resources" and in this context "Promote a sustainable use of biomass". The common perception of biomass is one of low grade low cost energy source only meant for marginal use. Even with value addition, it is only the energy potential of biomass that is generally recognized. This view has to change. Biomass is the only carbon rich material available besides fossils. If we were to look beyond an economy based on fossils, harnessing and appropriate utilization of biomass becomes indispensible. Here comes the concept of biorefineries. The term biorefinery refers to co-production of transportation biofuels, bioenergy and marketable chemicals from renewable biomass sources [5] and aims to replace today's 'Petroleum Refineries' which produces multiple fuels and products from petroleum. International Energy Agency (IEA) Bioenergy Task 42 defines biorefinery as sustainable processing of biomass into a spectrum of marketable products (food, feed, materials, and chemicals) and energy (fuels, power, and heat) [6]. According to American National Renewable Energy Laboratory, "biorefinery is a facility that integrates biomass conversion processes and equipment to produce fuels, power, and chemicals from biomass" [7].

Biorefineries are classified based on their system components [6]; viz. platforms, products, feedstocks, and conversion processes as explained below:

- Platforms refer to intermediates connecting biorefinery systems and their processes. More the number of platforms more complex is the system. For example, C_5/C_6 sugars, syngas, and biogas.
- Products are both energy products like bioethanol and biodiesel or material products like chemicals.
- Feedstocks can come from energy crops from agriculture (corn, sugarcane, etc.). They can also be sourced from agricultural residues, forestry residues, and industrial wastes (straw, bark, used cooking oils, paper mill black liquor, etc.).
- Currently four major groups of conversion processes are involved in biorefinery systems. These are biochemical (e.g. fermentation), thermochemical (e.g. pyrolysis), chemical (e.g. esterification) and mechanical (e.g. size reduction).

This paper critically examines the emerging idea of biorefineries in the light of sustainability.

2. The driving forces

2.1. The future of fossil feedstocks

The last century has witnessed an unprecedented growth in energy demand as the economies expanded rapidly and the living standards improved dramatically in the developed world. The other nations were soon to join the bandwagon. This quest for an open ended developmental agenda led to digging deeper and deeper into the natural resource base and stressed our natural environment. And this race is far from finished. If the recent IEA reports [8,9] are to be believed, world energy demand is growing at a rate of about 1.6% per year. It is expected to reach about 700 EJ/y by 2030, with more than 80% of worldwide primary energy production still coming from combustion of fossil fuels [8,9]. The Energy Information Administration of the US Department of Energy estimates the world energy consumption to rise by an average annual 1.4% between 2007 and 2035 [10]. While the OECD countries' energy use is likely to rise at only 0.5% per year the energy demand in non-OECD countries is projected to expand at 2.2% per year [10]. In addition to energy, we are dependent on petroleum for over 90% (by tonnage) of all organic chemicals produced [11]. Against this backdrop a reality check on the available fossil reserves, the predominant primary source of energy at present, paints a grim picture. The oil reserves are likely to last for only 40 years and natural gas for 60 years [12]. Furthermore, as only 50% of the reserves are classified as conventional, the exploration and the processing of the remaining 50% may be hiding unattractive margins [13]. Concern for energy security and availability of feedstocks for organic chemicals are major driving forces for exploring the idea of biorefineries. It is to be noted that among all the renewable sources of energy only biomass has the potential to fulfil the requirement of organic chemicals feedstock.

2.2. The environmental crisis

A second reason, and possibly the more pressing one, that warrants a changeover from fossil fuels is the damaging impact on the environment caused by them. Burning of fossil fuels is the major source of Green House Gases (GHGs) emissions and result in climate change which is an issue of grave significance [14]. To cite the IPCC report, "For the 1995 to 2005 decade, the growth rate of CO_2 in the atmosphere was 1.9 ppm per year and the CO_2 Radiative Forcing (RF) increased by 20%: this is the largest change observed or inferred for any decade in at least the last 200 years. From 1999 to 2005, global emissions from fossil fuel and cement production increased at a rate of roughly 3% per year [14]. The global mean CO_2 concentration in 2005 was 379 ppm [14]. The projected values by the coupled climate-carbon cycle models range between 730 and 1020 ppm by 2100 [14]. These are alarming projections with impacts that could be serious to catastrophic. There exists, therefore, an urgent need to address the problem. Liquid transportation fuels from petroleum are major contributors to GHG emissions. In EU alone, in the period from 1990 to 2010 about 90% of CO_2 emissions will be attributable to transport [13].

While fossil fuels release ancient carbon and other greenhouse gases into the atmosphere significantly contributing to global climate change processes, biomass fix carbon from the atmosphere [14]. Annual crops sequester carbon from the atmosphere in annual cycles, while woody biomass does so over a few decades. They are, thus, carbon neutral compared to fossils which are distinctly carbon positive. Replacement of fossil fuels with biofuels can have a major mitigating impact on CO_2 emission. In combination with CO_2 capture and storage (CCS) bioenergy can even be carbon negative [15,16]. Bioethanol in place of gasoline in transportation can potentially save the emission of 198 g CO_2 equivalent per km of vehicle travelled while electricity produced from biomass in CHP mode can save 731 g CO_2 equivalent per kWh over electricity produced from natural gas [5]. The net carbon emissions from a biomass fed power plant is estimated to be approximately 5% of the emissions resulting from a coal fired power plant after netting out the CO_2 absorbed during tree growth [17]. Studies suggest that to stabilize the CO_2 concentration at 550 ppm by the end of the 21st century, the share of the biomass derived energy has to be the same as that of fossil fuels at the beginning of the century [18]. Some prefer heat or combined heat or power generation from biomass over production

Table 1
Biorefinery feedstocks.

Feedstock			Remarks
Dedicated crops	Oil crops	Soybean Sunflower Rape Palm Jatropha	• Possible alternative use as human feed or animal fodder • Pressure on arable land • Availability dependent on priorities of farming communities
	Sugar crops	Sugarcane Beet	
	Starch crops	Corn Potato Wheat Cassava Sorghum	
	Woody plantations	Hardwoods Softwoods	
	Grasses & herbs	Switch grass Alfalfa	
Residues/wastes	Lignocellulosic	Black liquor Paper mill waste sludge Timberhouse waste Saw mill waste Wheat straw Rice straw Bagasse	• Availability and characteristics depend on ○ Choice of technology ○ Scale of operation ○ Administrative policies
	Oils and fats	Fat from slaughterhouse Waste cooking oils	
	Others	Slaughterhouse trimmings and bones Vegetables and fruit processing wastes Pith Poultry litter Animal farm wastes Molasses Municipal wastes	

of liquid biofuels in order to maximize CO_2 emission mitigation [19,20]. However, under very high CO_2 charges liquid biofuels may be an effective choice in the transport system, especially if carbon-neutral hydrogen or electricity is not readily available for transport [21,22]. And it can only be logical to extend the 'energy from biomass' idea to an elaborate refinery framework to incorporate the entire gamut of biomaterials.

3. Biorefinery feedstocks

Since the sustainability debate stems from the unsustainability of petroleum refining, a biorefinery feedstock should have many of the favourable traits of petroleum, if not all. The biggest benefit of petroleum as a refinery feedstock is the fact that it has no other use than refining. On the contrary, many biomass feedstocks can be used for purposes other than refining. This can lead to conflict of interest. Biomass is a renewable material, which is certainly advantageous for sustainability. But this also limits its maximum rate of utilization. The theoretical maximum availability of biomass is limited by the primary production capacity of the biosphere. All the scientific advancements notwithstanding, our understanding of the working of the biosphere and its subset ecosystems are far from complete. Any use of biomass for non-food use takes it out of the food web, the basic functional mechanism of any ecosystem. How much of this takeaway is actually safe? We do not have a precise answer for this. It is the collective responsibility of the humankind to see that this safe limit is not exceeded in our quest for development.

To be a viable alternative to petroleum refineries, the biorefineries must have dependable supply of feedstocks over its entire lifespan, which can be 10–30 years or even longer [23]. Feedstocks represent 40–60% of the operating costs of a typical biorefinery [24]. Considerable research effort has gone into the scheduling and optimization of biomass feedstock supply [25–27]. There cannot be a universal rule for the choice of feedstocks as it is dictated by many factors. Climatic and weather conditions, location, socioeconomic issues and government policies can all affect the availability of feedstocks. Since the main driver for the establishment of biorefineries is sustainability, the feedstock supplies should conform to these parameters. A biorefinery can get its feed from dedicated crops, either from agriculture or from forestry. Getting dedicated crops from agriculture to feed biorefineries, however, is a contentious issue because it is seemingly in conflict with food availability. A judicious assessment of priorities is, therefore needed. Feedstocks can also come from residues from a range of activities. Table 1 shows possible feedstocks for biorefineries. A biorefinery would be more sustainable if it has a diverse feedstock portfolio, thereby reducing the supply side uncertainties.

3.1. *Dedicated crops*

The so called first generation biofuels came from dedicated crops traditionally used as food. Among the dedicated crops for biorefineries corn is one of the frontrunners, especially in North America. There are several corn to ethanol biorefineries working in the United States while soybean is the main source of biodiesel [28]. Sugarcane is an important dedicated crop for bioethanol production in Brazil. Recently, Brazil also embarked upon a biodiesel programme based on soybean. In China, 80% of fuel ethanol production is from corn [29]. In India, the primary product from sugarcane is sucrose (edible sugar) while bioethanol is principally produced from the molasses that is left behind. Palm oil biodiesel in Malaysia and oilseed rape biodiesel in Germany have matured commercial markets. Numerous other oilseed crops are being investigated – including canola, sunflower, safflower, cottonseed, palm, and jatropha. Compared to lignocelluloses, starch based biorefineries are commercially more established [13]. Some other dedicated crops that can be used as biorefinery feedstock are sweet potato, cassava, barley, and sweet sorghum [30].

It is, however, imperative to note here that all first-generation biofuels ultimately compete with food production for land, water, and other resources. This raises the question of social sustainability. Is it ethical to divert food crops or area under agriculture for biofuel production when a large proportion of human population still remains malnourished or undernourished? Food commodities have witnessed runaway inflation in prices in recent times. In the short span of biofuel enthusiasm of the past few years the high food prices attributed to global biofuel production have caused 30–75 million people to fall into poverty and to jeopardize the livelihoods of 100–220 million people [31]. Such factors can be crucial for densely populated countries like India and China. Further, a high inventory holding cost is also involved due to the seasonal availability of the crop. On the other hand, cultivating dedicated crops on land converted from rainforests, peatlands, savannas, or grasslands result in release of several times more CO_2 in the atmosphere than is saved by the use of produced biofuels [32].

3.2. Agricultural residues

In terms of abundance lignocelluloses fare much better than dedicated crops. They are not meant for human food consumption either. Agricultural residues constitute an important category of potential biorefinery feedstock that is not in confrontation with food availability. These lignocellulosic materials have three basic constituents; cellulose, hemicelluloses, and lignin, and can be transformed into a multitude of products. A typical composition of agricultural residues is cellulose 40–50%, hemicelluloses 25–35%, and lignin 15–20% [33]. Their widespread availability, at relatively lower cost in many countries, makes them an attractive option. Worldwide their availability is estimated to be 10^{10} Mt, corresponding to an energy value of 47 EJ [34]. Of this, the cereal residues make up for the two thirds amounting to about 3.8×10^9 Mt [35]. Straw (wheat and rice) is extensively used as a papermaking raw material in China and India, but still their full biomass potential is not utilized. In some parts of India, there is a disturbing practice prevalent in the farming community to burn the straw lying in the field, after harvesting the grains. This has severe detrimental impact on the environment. Other important agricultural residues that have potential as biorefinery feedstock are corn stover, cotton stalk, barley stalk, sugarcane bagasse, empty oil palm fruit bunch, to name a few [5,23,36,37].

Several issues are, however involved in the life cycle context of their utilization, and hence, sustainability. Scattered availability and bulkiness can be an impediment in transportation as well as the seasonal variations in yield [38]. Delivered cost of the agricultural residue would include harvesting cost and logistics cost. The latter part, accounting for as much as 90% of the delivered cost, may play a significant role in the overall profitability of a biorefinery. On this account, the agricultural residues may not score much over the fossil resources. The technical literature provides a range of figures for the delivered cost of agricultural residues as biorefinery feedstocks [23,27,39]. This can have important bearing on the economic sustainability of any biorefinery. They also carry a high inventory holding cost like the dedicated crops. Their removal from the fields can affect the processes like soil organic matter turnover, soil erosion, crop yields, N_2O emissions from soils and others [5,28]. Removal of agricultural residues from the fields can change the soil organic content to the extent of 0.2–0.35 tonnes C/ha, thereby affecting the overall GHG balance of these operations over their entire life cycle [5,34]. Removal of wheat straw from the field can contribute to global warming potential of 1 tonne CO_2 equiv./ha [34]. On the positive side, removal of the residues can lower the emission of N_2O from the soil because of lower rates of denitrification [40]. Additional fertilizers are needed to make up for the nutrient value of the removed residue, with their associated ecological impacts from production to end use like groundwater contamination and eutrophication. Production of these fertilizers as well as their use in the field would partly offset the benefits gained by the use of the agricultural residues as biorefinery feedstock. The effects are further complicated by climate and soil type [35,41]. In fact there is a big ongoing debate on the benefits and disadvantages of agricultural residues as biorefinery feedstock. But even taking these factors in account, every ton of agricultural residue utilized in a biorefinery framework can save the emission of GHGs to the extent of 0.25–0.35 tonnes CO_2 equiv. while providing renewable energy output 4–5 times the non-renewable energy utilized in the process [5].

3.3. Woody biomass

Woody biomass is another important feedstock option for biorefineries. These lignocellulosic materials have composition similar to agricultural residues, but generally with higher lignin content [27,33]. Forest derived woody biomass is less seasonal than agricultural residues. But the economic and environmental sustainability is largely dependent on the location and type of the forests. Countries of North America and Northern Europe already have established forest based industries that can be expanded into biorefineries. For example, Switzerland produced just under 1 million litres of bioethanol in 2005 from wood cellulose [42]. These are mainly dependent on large stretches of coniferous forests in these regions. Normally, the transportation cost for woody biomass is less than that for agricultural residues [40]. Tropical evergreen and deciduous forests present more restricted accessibility. Getting biomass feedstock from these forests is trickier. It often involves tinkering with their rich biodiversity and delicate ecosystems that go against the idea of sustainability. Woody biomass can be available for biorefineries as residues from timberhouses and saw mills. Purpose-grown energy crops such as vegetative grasses and short rotation forests are another important source [43]. Herbaceous crops like switch grass and alfalfa are still other sources [44]. But, land availability is again an issue. Any land use change for growing biomass feedstocks should be critically examined for its net impact on the environment, which is often found to be negative. The perennial grasses like kahi grass and sarkanda (*Sachrum Munda*) can be grown on marginal lands not suitable for food production. Such practices can have important socio-political ramifications.

3.4. Aquatic biomass

While biorefineries based on the terrestrial biomass are steadily being developed and expanded, there is a new focus on using aquatic biomass that do not compete with food commodities. Many believe these resources to be sustainable [43,45]. Algae merit a special mention here. For equivalent production they require considerably less land use than terrestrial biomass [28]. Algal species can grow at mild conditions, offering much higher (solar) energy yields in comparison with terrestrial plants [46]. They can be grown in large scale in open ponds or specially designed photosynthetic bioreactors [47,48]. Special mention must be made of some algal species that produce and accumulate hydrocarbons in their bodies [13]. Large scale commercial utilization of these resources, however, warrants a cautious approach. Cultivating algal biomass in man-made water bodies has only limited scope, because of limited land availability. Harvesting them in natural water-bodies would be tantamount to increasing the primary production of the aquatic ecosystem, thereby affecting its overall health.

Table 2
Biorefinery products.

Biorefinery products			Remarks
Energy products	Biochemical	Methanol Ethanol Higher alcohols Biogas	• Alcohols and heat are traditional products from biomass • Biomass derived energy often suited to decentralized applications • Electricity from waste biomass may be economically competitive with that from fossils • Products like DME, FT diesel, SNG, and hydrogen still to find wide acceptance
	Chemical	Biodiesel DME FT diesel Biocrude	
	Thermochemical	Heat Electricity Syngas SNG Hydrogen Methane	
Biomaterials	Cellulose based	Paper and paperboard Rayon Cellophane Adsorbents	• Cellulose based products have well established markets • Development and utilization of lignin based products outside of energy realm is still not so widespread
	Hemicellulose based	Furfural	
	Lignin based	Adhesives Dispersants Emulsifiers Adsorbents Vanillin Soil conditioners	
	Miscellaneous	Particle board Carbon products Animal feed	

4. Biorefinery products

4.1. Energy products

An illustrative list of biorefinery products is given in Table 2. Bioethanol is by far the most important biomass based energy product, mainly used in the transportation sector. In recent years biodiesel has also gained in importance as a transportation fuel. Major nations have drawn ambitious plans to improve the share of biofuels in the transport sector. Between 2001 and 2006 alone, the global annual production of biodiesel and ethanol grew by 43% and 23%, respectively [49]. According to the European draft directive on renewable energy, the target for biofuels share is 10% by the year 2020 [50]. The International Energy Agency (IEA) aims a contribution of 10–20% biofuels in transportation market in 2030 [8]. In US, the Renewable Fuels Standard (RFS), a provision of the US Energy Policy Act of 2005, expects the supply of renewable energy to increase from 4 billion gallons in 2006 to 7.5 billion gallons by 2012 [51]. Gaseous fuels like biogas and syngas are also derived from biorefineries. Pyrolysis products can be chemically modified to yield dimethyl ether (DME), Fischer–Tropsch diesel, and synthetic natural gas (SNG). Biogas is important from the point of view of decentralized production which can be helpful for sustainable development in rural areas.

Environmental sustainability of biomass derived energy has never been in doubt thanks to their potential to cut emission of GHGs and other air pollutants. Economic sustainability, however, is the key issue, where it has to compete with the present fossil derived energy. On a purely economic basis untaxed gasoline or diesel is far more competitive than presently produced biofuels. These biofuels, thus, often require some economic incentives or policy interventions to compete. In the late 1990s U.S. ethanol subsidies amounted to over 50% of product sale price [52]. Ethanol suppliers received, on average, a US$ 0.54 per gallon subsidy [53]. Biofuel industries in OECD countries have enjoyed financial support of the order of US$ 10 billion a year in excise tax exemptions and income tax credits for the current levels of production [42]. This would increase to US$ 100 million a year or more if the target of 30% share of biofuels in liquid transport fuels is to be achieved. In China, the subsidies have been of the order of US$ 0.4 per litre ethanol [29]. To add to it several countries have also provided financial incentives to spur capital investment. Interestingly, there even have been cases of Govt. backing off from its promised subsidy, for example in Indonesia and Malaysia [54,55], indicating that it is not a win win situation all the time. This caution is reflected in the EU Directive which finds it essential to develop and fulfil effective sustainability criteria for biofuels and ensure the commercial availability of second-generation biofuels [50]. It is not totally unwarranted to boost a nascent industry with potential future benefits in its formative years. But, this practice in the long term would be counterproductive and against the ideals of sustainable development.

Environmental benefits are largely considered as economic externalities so that these are kept outside the realm of economic estimates. It is high time that the environmental advantages are translated into tangible economic instruments and internalized in the economic estimates. With the environmental costs internalized, one can have a more objective assessment of the sustainability of bioenergy. Some analyses on these lines have been carried out. One such study suggested that for carbon prices above US$ 70, biofuels dominate all other agricultural mitigation strategies, but for carbon prices below US$ 40 per tonne they are not sustainable [52]. The technology involved in petroleum refining is mature and any drastic fluctuation in the prices of petro-products on account of technological advancements is very unlikely. The volatility often observed in their prices is mainly due to the volatility of crude prices. These are governed more by geopolitical reasons than anything else. On the contrary, the price of bioenergy, especially the biofuels, can see downward trends with advancements in technology and increased market penetration. Here also, it should be mentioned that dramatic technological breakthroughs in

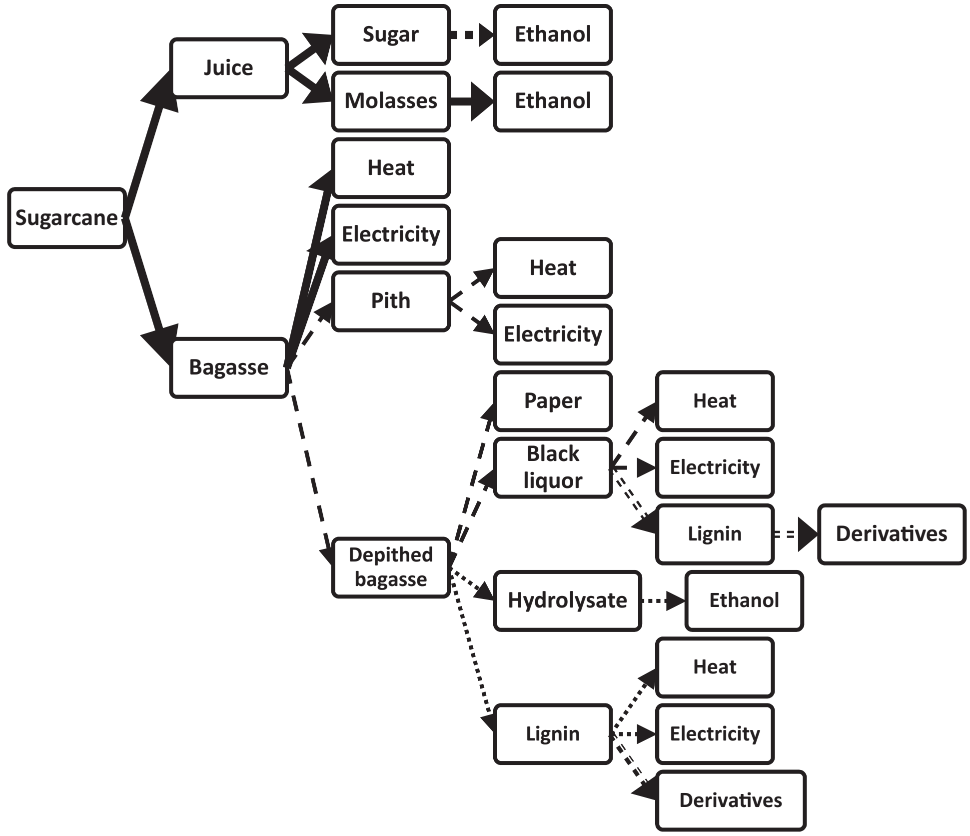

Fig. 1. Possible processing pathways for sugarcane. Thick solid arrows represent conventional processing. Different dotted arrows present alternative processing pathways in biorefinery framework.

bioethanol production from starchy feedstock and the basic transesterification process to produce biodiesel is very unlikely [8]. For these products the future of economic sustainability lies in comprehensive utilization of byproducts and residues, i.e. the biorefinery approach. While the bioethanol production from corn and sugarcane is commercially established, the production from cellulose and hemicelluloses is still in its initial development phase. The production costs are high, of the order of US$ 1 per litre on a gasoline equivalent basis [8]. Much scope for improvement remains here. Some reports from Brazil already mention lower production costs of US$ 0.41 per litre on gasoline equivalent basis for bioethanol from bagasse in integrated sugar–ethanol complexes [42]. The same is true for synthetic fuels like FT diesel, green diesel and SNG.

4.2. Biomaterials

Biorefineries can provide an array of chemicals like adhesives, cleaning compounds, detergents, dielectric fluids, dyes, hydraulic fluids, inks, lubricants, packaging materials, paints and coatings, paper and box board, plastic fillers, polymers, solvents, and sorbents [5]. Corn to ethanol biorefineries can produce fiber, germ, and gluten besides Distillers' Dried Grains (DDG) as animal feed [56,57]. Corn fiber, rich in hemicelluloses, can be further hydrolyzed and fermented to yield additional ethanol. Alternatively, it can be processed into corn fiber oil [56], characterized by its low cholesterol content [44], and corn fiber gum [57,58], which have high commercial value. Gluten rich zein is also a high value product. It has important applications in adhesive, coating, cosmetic, textile, and biodegradable plastics [59,60]. Thus, expanding the corn to ethanol production into a biorefinery framework can provide vital product diversification making the business venture much more economically sustainable. Compared to conventional single product approach, recovering germ alone in a large capacity plant can reduce the bioethanol cost by 2.69 ¢/L [57]. Glycerine is the important byproduct of biodiesel manufacturing and its effective utilization and possible further value addition is important in the sustainability context.

Paper and paperboard are the traditional products obtained from woody biomass from forest. Paper manufacturing, worldwide, has experienced stagnation in the recent past due to competitive products from fossil resources. Off late there has been a rethinking on these operations to expand them as forest biorefineries (FBR). A similar approach can also be applied to agricultural residue based paper production, especially in many developing countries. This can be a much better option than starting a greenfield biorefinery. Such integrated biorefineries can produce ethanol, syngas, DME and electricity among possible energy products and paper/paperboard, fiber reinforced bio-composites, and lignin derivatives as functional biomaterials [44]. Besides, natural health food components, like phytosterols, folates, and phytates can also be produced [46]. Lignin is the component of the lignocelluloses which has been traditionally neglected. Lignin is the second most abundant organic substance on earth after cellulose. But currently it is recognized only as a low value biofuel. There has been extensive research worldwide to find better uses for lignin. The largest current application of unaltered lignin is its use as a replacement of phenol in phenol–formaldehyde adhesives or resins [61–63]. However, it can be used in many other polymer formulations [64–66], as adsorbents and carbon precursors [67–69], and raw material for an array of low molecular weight aromatic substances [11,69,70]. If used as a raw material for specialty chemicals, lignin can fetch much higher price than when used as a biofuel [71,72]. Use of lignin outside the energy domain can significantly improve the economic and environmental sustainability of lignocelluloses based biorefineries.

As an illustrative example, Fig. 1 conceptualizes a sugarcane based biorefinery with different alternative processing pathways and resulting product mix. It is evident that compared to conventional processing (as shown by solid arrows) working in a biorefinery framework can give a lot of operational flexibility, as well as product mix to choose from. This can enable the company to fine tune their corporate strategy in line with economic and market realities, while minimizing the wastage of precious biomass resource. Similar reasoning can be extended to the processing of other important feedstock categories like starchy crops, agricultural residues, and woody biomass.

5. Biorefinery processes

As discussed in Section 4, the sustainability of a biorefinery depends on the comprehensive utilization of the biomass feedstock so as to give a diverse product portfolio. This would only be possible with an optimal mix of processes. Biorefinery processes can be thermochemical, biochemical, chemical, or a combination of them. A full realization of the utilization potential of any biomass resource often requires a complex set of operations. Besides the actual chemical transformation steps, a multitude of physical processes are involved in the raw material pretreatment as well as in the separation of intermediates and products.

5.1. Thermochemical processes

Though combustion is the most apparent thermochemical route to harness energy from biomass, this is certainly not the most efficient one. Further, it contradicts the multiproduct approach of a biorefinery. Main thermochemical conversion processes are pyrolysis, gasification, and liquefaction [73]. While combustion is the complete oxidation of biomass in the presence of stoichiometric or excess amount of oxygen, pyrolysis is the fundamental chemical reaction that occurs when biomass is heated in the absence of oxygen. In between these two extremes, a full spectrum of reaction alternatives is available depending upon the amount of oxygen used. These processes are commercially known as gasification. Further variations in terms of reaction temperature and pressure add to the versatility of the process. Liquefaction is a catalytic process in the presence of water and carbon monoxide/hydrogen [74,75].

Biomass gasification is a promising option. It can give intermediates which can be further transformed for value addition, both as energy products and biomaterials. Biomass gasification in CHP mode can simultaneously generate liquid biofuels, electricity, and heat [76–78], and it achieves more energy conversion efficiency than combustion based processes. For sustainability, a gasification based biorefinery must be configured not only to suit the available feed stock, but also to the market needs for biofuels, electricity, and heat. Lignin, most readily available as spent black liquor from paper mills [79,80], is a fit candidate for gasification and further processing, if its isolation and valorization is immediately not on the horizon. The overall annual world production of black liquor is approximately 500 million tonnes [81]. Of this, about 50 million tonnes is estimated to be lignin [82]. Black liquor gasification [83–85], therefore, is an integral part of any attempt to upgrade existing paper mills into FBRs.

Higher temperatures maximize the gas yield [73] in biogasification but the gas composition depends on several parameters like temperature, quantity of oxygen/air, and type of biomass [75,86]. The preferred pyrolysis technology today is fast or flash pyrolysis wherein the biomass is rapidly heated to high temperatures in the absence of oxygen for short residence times of the order of few seconds [73,87]. At low temperature the product is mostly a liquid biocrude that can be processed into liquid biofuels [73]. Hydrothermal liquefaction (HTL) can produce valuable bioproducts like biocrudes from waste biomass streams [88]. A modification is the hydrothermal upgradation (HTU) that uses liquid water at high temperature and pressure [89].

As already discussed above lignin can be a much valuable product as a raw material for specialty chemicals. Studies suggest that with energy saving measures paper mills can spare a part of the lignin present in the black liquor from energy use [71,72]. This requires isolation of lignin from black liquor. Acid precipitation is the most widely used method at present; but it is associated with many difficulties [70–72]. Membrane based techniques have shown limited success but they are still not cost effective and also have operational problems [90–92]. Recently, electrolysis has been found to be suitable for partial removal of lignin from black liquor [93–95]. A perfected technology for lignin isolation from black liquor and breakthroughs in industrial chemistry and chemical technology for deriving value added products from lignin can dramatically transform a biorefinery based on lignocelluloses.

5.2. Biochemical processes

Fermentation of sugars to bioethanol is a well established process. Both starch and cellulose can be converted into fermentable sugars by enzymatic hydrolysis. Liquefaction of starch is the commercial process of hydrolyzing starch into glucose syrup using emylase enzymes at a relatively high temperature of 140–180 °C [96,97]. Biochemical conversion of cellulose into bioethanol involves an initial step of enzymatic depolymerization of cellulose into glucose monomers [98,99] followed by usual fermentation. Fermentation of hemicelluloses is important for inclusive utilization of lignocelluloses [100]. Corn fiber, rich in hemicelluloses, can be fermented to ethanol by strains of *Escherichia coli* [101]. Enzymatic hydrolysis of cellulose and hemicelluloses to monomeric fermentable sugars is harder than that of starch. This step usually is confronted with several difficulties owing to a multitude of parameters [102–105]. Fermentation of the resulting hydrolyzate is also difficult owing to the presence of mixed sugars and inhibitory substances [96]. General recalcitrance of lignocelluloses to biological degradation is a technical challenge to be overcome for large scale application of such processes [28]. Also, fermentation by its very nature is a rather inefficient process with a significant amount of substrate/reactant required for cell energy, cell growth and other products [106]. This shortcoming, in recent years, has been overcome to some extent through genetic and metabolic engineering to develop new microbial strains. Another approach, the so called microbial catalysis, is to grow the cells first and subsequently carry out the reaction to increase the yield. In such circumstances process parameters can be optimized to enhance the product yield irrespective of cell growth. One can choose the optimal cell concentration, for example [107]. Still better is to isolate the specific enzyme and to use it as immobilized or in solution. Anaerobic digestion is an important process in biorefinery context [108,109]. It can be an important downstream process for generation of biogas from the stillage after the distillation of bioethanol [110,111]. Anaerobic digestion is also suited to lignin containing wastewaters and process streams [112,113], as well as other waste biomass [114,115].

5.3. Other chemical processes

Besides the thermochemical and biochemical processes, there are a number of chemical processing steps that may be involved in biorefinery operation. These may be pretreatment steps as well as downstream modifications. In the overall context of the sustainability of a biorefinery, these processes can be extremely important. Acid hydrolysis is important for converting hemicelluloses and even cellulose into monomer sugars. Under controlled conditions, mild acid treatment of lignocelluloses hydrolyzes the hemicelluloses fraction, especially xylan into xylose, with the cellulose and lignin fractions remaining unaltered [96]. Hydrolysis of cellulose into constituent sugars requires stronger acidic conditions. Dilute acid hydrolysis of lignocelluloses, therefore, often involves two steps. At low temperature hemicelluloses is hydrolyzed followed by a high temperature hydrolysis of cellulose [116–118]. Concentrated acid hydrolysis gives rapid and more complete breakdown of polysaccharides and higher sugar yields, but at the same time more glucose degradation [118–120]. An optimized prehydrolysis step for the lignocellulosic biomass is the key to their successful comprehensive utilization in the biorefinery framework generating second generation biofuels.

Another important chemical transformation is the catalytic Fischer–Tropsch Synthesis (FTS) of liquid hydrocarbons from syngas [121–123]. Syngas from biomass gasification is rich in CO and H_2. Besides FTS, it can be subjected to a variety of other chemical transformations like methanol synthesis, hydroformylation, and methane synthesis [73]. Transesterification, to produce biodiesel from vegetable oils is yet another important chemical processing step for a biorefinery [28,124]. Unlike transesterification, catalytic hydroprocessing of vegetable oils gives 'Green Diesel' which is identical to petroleum derived diesel [124,125].

6. Policies and future directions

Though biofuels have been on the political agenda for quite some time now, it is only recently that policymakers are coming to terms with the potential advantages of biorefineries. These policy initiatives have been few, mostly in some of the developed nations. The bulk of the policies and programmes still venture around the biofuels route. Here also, many nations are yet to look beyond the first generation biofuels.

United States has a well defined biorefinery development programme with clear cut objectives and targets. They have aggressively pursued the biofuel production as a means to reduce their dependence on foreign oil and have well laid out legislations and policies. Energy Policy Act of 2005 envisaged encouraging collaboration among government, industry, and academic institutions to develop advanced technologies for production of biofuels so as to produce 7.5 billion gallons per year of bioethanol by 2012 [126]. The Energy Independence and Security Act was signed into law in the USA in December 2007. It sets a target of 36 billion gallons of renewable fuel use by 2022, of which a minimum of 15 billion gallons should come from corn ethanol and 16 billion gallons from lignocelluloses [127]. On the chemicals front, the USDOE [128] aims at (1) achieving at least 10% of basic chemical building blocks from plant-derived renewable resources in 2020, and 50% in 2050; (2) establishing commercial demonstration industry system chains to produce chemicals from plant-derived renewable resources; (3) building further collaborative partnerships to improve vertical integration and supporting success via enhanced rural development. A detailed roadmap "Biomass technology in the United States" has been drawn by the Biomass R&D Technical Advisory Committee [129]. In Canada, the impetus have more been on biofuels and the associated environmental benefits through initiatives like federal Ethanol Expansion Program; Future Fuels Initiative; the Transportation Energy Technologies Program; and the FleetWise and Fleet$mart programs [130,131]. The European Commission aims to increase the share of biofuels in total fuel consumption to 10% by 2020 [50,132]. There are other policy incentives in the form of carbon tax, quota obligation, and green energy certificates in many EU member states [76]. Development of FBRs is earnestly being promoted in many Scandinavian countries. Brazil has one of the oldest and well established bioethanol programmes which has witnessed huge commercial success. They started an ethanol fuel production programme way back in 1975 which currently provides 40% of Brazilian petrol consumption [96].

In comparison, the Asian countries, by and large have been sluggish in identifying the full potential of biomass utilization in the framework of biorefineries. Consequently, most of the activities hover around first generation biofuels only. Even in these areas, a comprehensive policy push is often missing. Thailand and Indonesia have well defined biofuels expansion targets. Indonesia, though with significant petroleum reserves, established its first national policy on biofuels as part of the National Security Act in 2006. It aims at 3% share of domestic biofuels in their total energy consumption by 2015, and to further increase it to 5% by 2025 [54,133]. One of the goals was to create rural jobs and energy self sufficiency in villages. The focus is mainly on biodiesel. However, the policy has already run into rough weather owing to poor economic foresight. And it is almost similar scenario in the neighbouring country Malaysia. Malaysian federal govt. developed ambitious biofuel policies in 2005 in the hope that its abundant production of palm oil can be profitably converted into biodiesel which turned out to be economically unsustainable [55]. China is the third largest producer of bioethanol in the world after USA and Brazil [134]. It launched its Ethanol Promotion Programme in 2002 and targets to produce 10 million tonnes of fuel ethanol per year by 2020 [29]. Being a net importer of vegetable oils, it does not promote biodiesel as a transport fuel. Malaysia, being one of the largest producers of palm oil in the world has an interest in biodiesel. India traditionally has a large sugar industry base which provides molasses as the raw material for bioethanol. The Govt. in Japan has set a target of using 6 billion litres of biofuels in transport (10% of total transport fuel consumption) by the year 2030 [42]. In India the policy support and development for biomass has mainly been energy centred with the idea of biorefineries yet to be recognized. National Bio-energy Board (NBB), under the Ministry of New and Renewable Energy (MNRE), is the apex coordinating agency. It has drawn a National Master Plan (NMP) for waste-to-energy to target both municipal and industrial wastes [135]. It identifies a power generation potential of 462 MW from municipal liquid wastes and 4566 MW from municipal solid wastes by the year 2017. In addition, a total of 1997 MW power is intended to be generated from different industrial wastes. National Policy on Biofuels was approved by Govt. Of India in 2009 which set a target of 20% blend of biofuels with gasoline and diesel by 2017 [136,137]. As a modest beginning, the Technology Information, Forecasting, and Assessment Council (TIFAC), Under the Department of Science & Technology, Govt. Of India, has launched the Bioprocess & Bioproducts Programme in January, 2007 [138]. It recognized the tremendous opportunity to derive not only energy and fuel but a wide range of chemicals from biomass. Some economic incentives for family size biogas projects also exist.

7. Conclusion

With the emphasis on sustainable development we have to look beyond fossil fuels for both energy needs as well as chemical feedstocks. Limited reserves and adverse environmental impact of their use mandate a switch to renewables. Here, biomass certainly offers an alternative. But harnessing of biomass for commercial ends cannot always be sustainable. Possible conflict of interest with other alternative uses of biomass must be carefully examined; especially when dedicated crops are diverted from being used as food. For the abundantly available and seemingly waste lignocelluloses, economic sustainability is an issue. In this context the biorefinery concept is attractive as it looks for comprehensive utilization of biomass to yield energy/fuel along with multiple chemical products. Biorefineries can improve the sustainability of biomass utilization by diversifying the product portfolio. Diversity of feedstocks and processing technologies can provide various combinations so as to suit different needs vis-a-vis geographical location, economy of scale and national priorities. However, this large potential is still not widely recognized. Barring some of the developed nations, others still look at biomass essentially as an energy source alone. This notion should change.

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