

BIOBASED PRODUCTS INDUSTRIAL UTILIZATION LIMITATIONS

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Abstract. A number of substances of commercial significance may be produced from bio-based products through the use of commercial enzyme cocktails, simultaneous saccharification and fermentation, lengthening of carbon chains, deoxygenation and hydrogenation processes. To achieve these chemical transformations with decreasing negative environmental impact, chemistry plays a strong economic role given bio-based products diversified chemical constitution. The conversion of plant biomass for industrial applications is limited due to the cost of pretreatment to separate or access the biomass's three main usable components, cellulose, hemicellulose, and lignin. This study was to identify the current status-quo of knowledge of the industrial uses to which the biomass can be applied, and to identify the challenges that this technology faces so as to encourage clearly defined goals for increasing the use of biomass-derived feed stocks in industrial chemical production.

Keywords: *bio-based products, bio-renewable resources, functional group, biomass, industrial products.*

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1. Introduction

The world is currently challenged to formulating effective responses to pressing global challenges such as climate change, CO₂ emissions, resource efficiency, sustainable economic growth, global food security and health. Humans, in their effort to survive, have designed various forms of intervention to ensure the sustainability of very important resources. Scientific studies and social researches have been advanced to find ways of developing sustainable projects, which can empower people to meet economic needs without relying on methods that can adversely affect the environment (Ugoala *et al.*, 2012). Supplementing petroleum consumption with renewable biomass resources is critical for long-term security and continued economic growth.

Biomass is a sustainable source of hydrocarbons that is renewable as well as being carbon-neutral. Biomass can be a source of industrial chemicals and fuels and also serve as a renewable source of hydrogen in the long term. Biomass includes trees, grasses, agricultural crops, and even animal manure. Triglycerides, sterols, alkaloids, resins, terpenes, terpenoids and waxes are other biomass components, which are generally present in minor amounts. Primary biomass resources are produced directly by photosynthesis and are taken directly from the land. They include perennial short-rotation woody crops and herbaceous crops, the seeds of oil crops, and residues resulting from the harvesting of agricultural crops and forest trees (e.g., wheat straw, corn stover, and the tops, limbs, and bark from trees). Secondary biomass resources result from the processing of primary biomass resources either physically (e.g., the production of sawdust in mills), chemically (e.g., black liquor from pulping processes),

or biologically (e.g., manure production by animals). Tertiary biomass resources are post-consumer residue streams including animal fats and greases, used vegetable oils, packaging wastes, and construction and demolition debris. Biomass is a universal feedstock due to its versatility, domestic availability, and renewability.

A bio-economy has the potential to contribute significantly to the reduction in CO₂ emissions by lessening of dependence on non-renewable resources increase in markets for farm products, and the potential for new industries that should reduce dependence on petrochemical-based industrial products. Products produced from bio-based products are considered carbon-neutral because the carbon dioxide that may be released during transformation of the raw material is already part of the carbon cycle. Bio-based products have eco attributes that offer an answer to maintaining sustainable development of economically and ecologically attractive materials with respect to ultimate disposability and raw materials use.

The advanced standard of performance brought by petroleum-based industrial products and advances in genomics, proteomics, enzyme technologies, materials science, separation science, and many other technologies have opened a host of new opportunities to the growing enthusiasm for the development of a new bio-products industry. Utilization of biomass truly involves an interdisciplinary field of research necessary to understand and interrogate the numerous structures encountered (Ugoala *et al.*, 2014). Bio-based products are rich source of structurally novel and biologically active metabolites. These metabolites may be potential bioactive compounds of interest in the pharmaceutical industry (Ugoala *et al.*, 2016). These metabolites can be sources of new leads for treatment of many diseases such as cancer, AIDS, inflammatory conditions, and a large variety of viral, bacterial and fungal diseases. They also have an important role in aquatic ecology such as plant herbivore interactions, toxicity for defense, space competition and antifouling.

In fact, nano-materials have been generated from agricultural crop and beverage processing by-products. Rice straw and grape pomace has been fractionated into cellulose, hemicellulose, lignin and silica streams from which further functional nano-products are engineered. The phenolic components are being explored as precursors for carbon nano-fibers and porous products. These bio-based nano-materials and nano-fibres demonstrate viable strategies for utilizing under-utilized by-products to achieve novel functionality for advance material applications. Organic acids are examples of valuable by-product of the fermentation of high carbohydrate containing industrial substrates. This knowledge base offers opportunities for new bio-based products and bio-nano materials as well as solutions to expanded value-added utilization of bio-renewable resources. They have the potential to result in significant environmental and socio-economic benefits. Therefore the bio-products industry is of strategic importance to strategic economic growth, environmental sustainability and rural diversification.

Such knowledge base of bio-based resources encourages the development of efficient and sustainable technologies that are poised to create major bio-based product breakthroughs benefiting consumers as well as the agriculture, fibre, polymer/plastic and consumer/industrial product industries. But the use of biomaterials to produce higher value chemicals products, are limited due to biomass feedstock preparation, accumulation logistics, and economics. Raw biomass materials are disadvantaged in having low bulk density, high moisture content, hydrophilic nature, and low calorific value. High moisture in raw biomass reduces the efficiency of any conversion process,

leads to natural decomposition (loss of quality), and causes uncertainty in bio-renewable resources physical, chemical, and microbiological properties.

The diverse range of bio-based products industrial applications depends on their physicochemical properties, which are governed by the chemical compound make-up, size, functional groups present. These functional groups provide linkages within the individual components of bio-based products (intra-polymer link-ages), and connect the different components to form the complex (inter-polymer linkages). The ether bond holds the glucose monomers in a polymer chain (glucosidic linkage). In the hemicellulose polymer, it is the acetyl group that forms ester bond with a hydroxyl of the main chain of the polysaccharides. Cellulose fibres are insoluble in water due to hydrogen bonds while increase in the formation of hydrogen ions causes the gumming of materials. Therefore a heterogeneous composition creates mixtures of chemical units which can impose unexpected chemical behavior (Li and Gellerstedt, 2008). This would mean that the processing of mixed bio-based biomass with varying composition would be challenging than the bioconversion of single biomass (Lal, 2005 and Ragauskas *et al.*, 2006). This is due to the inherent recalcitrance of some biomass to enzymatic and microbial deconstruction, imparted by the constituent chemical compounds (Himmel *et al.* 2007; Yang and Wyman, 2008). Therefore, complex bio-based products like lignocellulosic material, oils, algae and sugar crops are usually biorefined to promote broader applications (Dembras, 2009; Cherubini, 2010).

The present article deals with the limitations encountered in the utilization of bio-based products for possible biotechnology applications.

2. Bio-products market demand

According to the World Economic Forum, there are great prospects in the utilization of biomass feedstock and conversion technologies in the production of biomass-related chemical products (bio-based acids, bio-based oils, and specialty chemicals). Therefore, a long term and sustainable market can be envisaged for technologies that produce chemicals, materials, and pharmaceuticals from plant-based feed stocks, which will supplement the emerging demand for bioenergy feed stocks and the still growing demand for food and other agricultural products. Such a development will need to be supported by processing steps that are energy efficient and cost-effective.

Presently, many of the current biomass-based chemicals being developed are focusing on intermediates such as succinic acid, n-butanol, acrylic acid, adipic acid, acetyls and even methyl methacrylate. Advances in genomics, proteomics, enzyme technologies, materials science, and separation science as well as bio-refineries should make important contributions to the growing enthusiasm for the development of a new bio-products industry. These concepts, along with the need to develop human capital to meet the growing demands of a bio-based economy, will bring new challenges and opportunities to universities and governments alike.

Biofuels

Liquid biofuels include pure plant oil, biodiesel, and bioethanol. Biodiesel is based on esterification of plant oils. Ethanol is primarily derived from starchy crops. Biofuels hold the greatest potential for major impact on both the agricultural economy and on greenhouse gas (GHG) reduction. The effective utilization of low-cost high-

volume agricultural and forest biomass for the production of biofuels and bio-based materials will play a vital role in addressing this concern (Lal, 2005).

Fermentation routes to fuel ethanol have been used in most research studies and commercial developments to date. However, a new approach is to use a gasification route. In this method, the biomass material would be gasified to a mixture of carbon monoxide and hydrogen. In the presence of the appropriate metallic catalyst, this mixture could be converted into ethanol. This approach can utilize biomass materials such as bark, which are not suitable for ethanol production by fermentation methods. Moreover, high gravity fermentation can be used to produce ethanol from grains with significant reductions in costs while at the same time achieving improvements in productivity (Ingledeew, 2002).

However, there is need to improve technology in both the starch and lignocellulosic route to biofuel production: improve crop yields during drought years, reduce nitrous oxide emissions from crop production, develop hay crops suitable for ethanol production, develop techniques to improve farmers' income from production of raw materials, develop new co-products from ethanol production to increase total revenue and reduce ethanol production costs, and improve methods to cheaply produce simple sugars from lignocellulosic raw materials.

A new technology David Boocock of the University of Toronto uses animal wastes in biodiesel production. This new process employs an inert solvent, such as tetrahydrofuran, to form a single phase between the oil to be reacted, the alcohol and the catalyst. This greatly increases the rate of reaction.

Generally, biofuels had evolved in the following stages:

First generation Biofuels: produced through cold pressing/extraction, transesterification, hydrolysis and fermentation, and chemical synthesis from sources such as starch, sugar, animal fats, and vegetable oil

Second Generation Biofuels: produced from lignocellulose through more advanced processes (hydro treatment, advanced hydrolysis and fermentation, and gasification and synthesis). Second-generation biofuels not yet commercial on a large scale as their conversion technologies are still in the research and/or development stage. Biodiesel, bioethanol, synthetic fuels, and bio-hydrogen are second generation biofuels.

Third generation Biofuels: use photosynthetic microorganisms (i.e. microalgae) to directly convert CO₂ into fuel molecules or fuel precursors, eliminating the biomass intermediate

Fourth generation Biofuels: GMO carbon-negative Energy crops Corn-grain-derived ethanol and soybean-based biodiesel yield 25% and 93% respectively more energy than is needed to produce it (Crocker and Crofcheck, 2006).

Bioplastics

Bio-based plastics include starch plastics, cellulosic polymers, polylactid acid (PLA), polytrimethylene terephthalate (PTT) from bio-based 1,3-propanediol (PDO), bio-based polyamides (nylon), polyhydroxyalkanoates (PHAs), bio-based polyethylene (PE), polyvinyl chloride (PVC) from bio-based PE, other bio-based thermoplastics (polybutylene terephthalate (PBT), polyphenylene sulphide (PBS), polyethylene terephthalate (PET), polyethylene-co-isosorbide terephthalate polymer (PEIT), further polyesters based on PDO), polyurethane (PUR) from bio-based polyols and bio-based thermosets. Starch-based bio-plastics are applied as packaging materials, kitchenware, car interiors, horticulture devices, and diapers. Starch plastic application offers a major

end use for cassava (*Manihot esculenta*), maize, and wheat (*Triticum aestivum*). Starch properties depend on the amylose/amylopectin ratio and size of starch granules. Amylose ethers offer biodegradable alternatives for polyethylene and polystyrene. Commercially interesting polyesters, made from starch or sugar via fermentation, include polylactic acid (PLA) and polyhydroxyalkanoate (PHA). The PLA is competing with fossil polymers like PET and links to the large market of packaging and fibre/fibre fill materials. Fossil fibres like polyester or nylon offer large opportunities for bio-based feed stocks.

Bio-composites

Bio-composites fibres have the potential to reduce GHG emissions by lowering component weight, reducing the use of energy-intensive products (e.g. glass fibres, cement) and limiting the need for energy-intensive pesticides and herbicides (in the case of industrial hemp). Developing resins made from bio-based sources, and ensuring adhesion between natural fibres and the polymer matrix needs to be addressed.

Natural fibres can be applied in high value-added composite materials using cellulosic feed stocks from wood and straw, plus classical crops like kenaf (*Hibiscus cannabinus*), sisal (*Agave sisalina*), jute (*Corchorus spp.*), flax (*Linum usitatissimum*), and hemp (*Cannabis sativa*). Additionally, eucalyptus (*Eucalyptus spp.*) may replace synthetics like rayon. Composite materials based on cellulose offer special qualities (reduced weight, improved safety, and good acoustic properties), and natural fibres are being used to reinforce synthetic materials rather than replace them.

Bio-lubricants

Bio-lubricants are currently being used in cutting fluids, chainsaw lubricants, metal working fluids, hydraulic oils, 2-stroke engine oils, marine oils and drilling fluids due to their distinct performance properties and environmental benefits (biodegradability, lower toxicity), which enable their use in sensitive environments and contributes to pollution prevention. Bio-lubricants and hydraulic fluids represent one of the most important bio-product areas for reducing GHG emissions (Johnson, 2000). High oleic canola and high erucic rapeseed oils have been identified as raw materials to make industrial lubricants and other products in the plastics and cosmetics industries. However, oxidative instability of these raw materials due to the presence of polyunsaturated fatty acids, as in linoleic acid and linolenic acid is a major hindrance. Recent developments to circumvent such hindrances include e.g. additive technology, chemical transformation and polymerisation, trans-esterification and genetic modification.

Bio-solvents

Bio-solvents are volatile organic compounds (VOC) free. They include soy methyl ester (soy oil esterified with methanol), lactate esters (fermentation derived lactic acid reacted with methanol or ethanol) and D-Limonene (extracted from citrus rinds). Bio-solvents are used as degreasing agents (cleaning of metals, textiles), additives and diluting compounds (paints, varnishes, inks, glues, pesticides), stripping agents (paint, varnish, glue removers) and extraction solvents (perfumes, pharmaceuticals). Bio-solvents naturally degrade through UV light and soil microbes.

Bio-solvents are promising industrial alternatives for environmentally benign synthesis strategies. They are characterized by their low miscibility with water, toxic, boiling point, remarkable stability. Bio-solvent production at lower cost and higher purity is now possible through pervaporation.

Bio-surfactants

Bio-surfactants are commonly derived from plant oils such as coconut and palm oils, from plant carbohydrates such as sorbitol, sucrose and glucose or from animal fats such as tallow. Surfactants are used in many industries such as household detergents, personal care, industrial cleaners, food processing, oleochemicals, agricultural chemicals, textiles, emulsion polymerization, paints and coatings, lubricant and fuel additives, metal working, mining chemicals, pulp and paper production, leather processing, etc. Bio-surfactants are surfactants in which at least one of the two groups (hydrophilic or hydrophobic) is obtained from plants: they are therefore not necessarily 100% plant-derived (Omni Tech International, 2008). Advantages of naturally-derived surfactants include biodegradability, low toxicity and raw material availability as they can be produced from industrial waste or by-products.

New surfactants are being developed using biotech processing. Sophorolipids and rhamnolipids are examples; both are glycolipids that can be used to produce bio-surfactants via a fermentation process (ICIS, 2010)

Bio-plasticizers

Bio-plasticizers composed of phthalate- and lead-free material, offer flame resistant protection and performance using a renewable material alternative to traditional PVC plasticizer wire insulation and jacketing.

Adhesives

Volatile organic chemicals (VOC) emissions from petrochemicals based adhesives and the expanding array (wood and paper products industry) of new uses for adhesives is driving the use of renewable materials research interest in bio-based adhesives. Much of the current research is focused on bio-based adhesives with corn and soy being used as the starting material.

Platform Chemicals

A number of potential platform chemicals that can be produced from agricultural feed stocks includes citric acid, lactic acid, levulinic acid, succinic acid, and 1,3-propanediol, etc. In the production of each of these platforms, cheap lignocellulosic wastes are used to make sugars, which can be used as a platform for deriving various bio-chemicals. Therefore, for the production of platform chemicals to be economically viable, access to large amounts of cheap lignocellulosic feed stocks; a ten-fold reduction in enzyme costs; and access to an existing ethanol and/or starch processing infrastructure that can act as a bridge for the production of other chemicals must be pursued.

3. Bio-renewable resource conversion technologies

Raw material source shapes the structure of the industry that utilises it. From the technological point of view, there are three different ways to utilise bio-renewable resources.

Dry biomass pretreatment

Thermal treatment

The dry biomass has a moisture content of significantly less than 50 %, but not more than 90% can be treated thermally by gasification or pyrolysis to breakdown complex macromolecules into smaller molecules in gaseous or liquid state (with a remaining solid product containing ash and, dependent on the technology, solid carbon), which may subsequently be used as the building blocks for further synthesis.

Table 1. Pyrolysis processes in relation to their common feed stocks, typical products

Feedstock	Process	Product
Agricultural waste (wheat straw, coconut shells, waste wood, etc)	Fast pyrolysis (anhydrous) Slow pyrolysis (low temp. 450-550°C, O ₂ -free, some-times steam) Gasification (high temperature, fast heating rate, O ₂ present) Fermentation, anaerobic digestion and mechanical bio-treatment	Synthesis gas Bio-oil liquid Biochar solid Syngas and Biochar Combustible methane and ethane Ethanol
Compost (green waste)	Slow pyrolysis (high temp. 600-900°C, O ₂ -free)	Activated Biochar and syngas
Manure/ animal waste	Carbonization (brown at 300°C Black at 380°C) Gasification (high temperature, fast heating rate, O ₂ present)	Charcoal Combustible methane and ethane, and Biochar
Waste plastic, food, etc	Gasification (high temperature, fast heating rate, O ₂ present)	Combustible methane and ethane, and Biochar
Sewage sludge	Gasification (high temperature, fast heating rate, O ₂ present)	Combustible methane and ethane, and Biochar
Biomass energy crops (corn, cereals, wood pellets, palm oil)	Fermentation, anaerobic digestion and mechanical bio-treatment	Ethanol, methane and sludge

Agricultural biomass carbonized to biochars undergoes a dehydroxylation/dehydrogenation and aromatization process, mainly involving the cleavage of O-alkylated carbons and anomeric O-C-O carbons in addition to the production of fused-ring aromatic structures and aromatic C-O groups. With increasing charring temperature, the mass cleavage of O-alkylated groups and anomeric O-C-O carbons could occur prior to the production of fused-ring aromatic structures.

Slow heating rate (SHR) and high heating rate (HHR) pyrolysis techniques produces certain levels of valuable co-products meat browning and food flavoring agents, wood preservatives, adhesives and other useful chemical components (Czernik & Bridgwater, 2004).

Bio-oil is unstable and acidic, contains char particles, and has about half the heating value of petroleum liquid fuels. Acidity, high viscosity, high oxygen content, difficulties in removing char particles, and immiscibility with petroleum liquids have restricted the use of bio-oil. A catalytic pyrolysis process has been found to be effective in alleviating some of the negative properties of the bio-oil. The catalytic process which uses some selective zeolites, involves the cleavage of C-C bonds associated with dehydration, decarboxylation, and decarbonylation, and produces aromatic compounds.

Table 2. Thermal Depolymerization processes in relation to feed stocks, typical products

Feedstock	Process	Product
complex organic materials (like manure, slaughterhouse wastes, and food processing wastes)	Depolymerization	Oils and gases short-chain hydrocarbons (18 carbons).

NMR studies revealed the presence of maximum aliphatic lignin components with absence of the aromatic lignin in pretreated samples. The presence of maximum hexosans and xylans reveals that presence of aliphatic lignin components could be a helpful way of retaining the monosaccharides (Sonali *et al.*, 2017)

Lignin is depolymerized usually by selectively oxidizing cleavage of C-C and C-O bonds to Aromatics

Table 3. Incineration process in relation to common feed stocks, typical products

Feedstock	Process	Product
Biomass	biomass co-combustion	Synthesis Gas

Stable aromatic and heterocyclic carbons are the main functional groups of dry treated biomass. Their stability is large due to their chemical recalcitrance (Lehma and Joseph, 2009; Mao *et al.*, 2012). The observed properties depend on the production conditions (temperature) and the biomass type (Lehma, 2007; Meyer *et al.*, 2011; Harvey *et al.*, 2011).

4. Wet biomass conversion technologies

Biotechnological conversion

Wet biomass is normally treated biochemically under moderate conditions. In these processes biological agents take over the task of facilitating the synthesis of products. These products may be as simple as ethanol or acetone or may be highly complex like antibiotics or proteins. The processes may require energy for tasks like sterilization, fermenter aeration, stirring and occasionally cooling as well as products separation and conditioning.

5. Fermentation technology

Plant biomass like sugarcane bagasse and straw, cotton fibres are mostly composed of lignocellulosic materials. The recalcitrance offered by lignocellulose to get converted into simple sugars makes its conversion process complicated, hence pretreatment is required prior to enzymatic hydrolysis and fermentation.

There exists intra- and intermolecular hydrogen bonds that make the crystalline and amorphous regions in the cellulose.

Table 4. Simultaneous Saccharification and Fermentation (SSF)

Feedstock	Pretreatment	Process	Product
Lignocellulosic materials	Removal of lignin and hemicelluloses and subsequent enzymatic saccharification of cellulose	Simultaneous yeast/bacteria fermentation of sugars to alkanol in the same vessel	

Table 5. Simultaneous Saccharification and Extractive Fermentation (SSEF)

Feedstock	Process	Product
Concentrated lignocellulosic	Simultaneous yeast fermentation of sugars to alkanol by adsorption onto polymeric materials or carbon	
Cotton stalk, Soybeans, Rice straw, Wheat straw, Maize Stalk, Jute stalk, Sugarcane tops, Ground nut straw	Resulting alkanol is vapourised and condensed Process reduces water requirement and downstream distillation.	

Table 6. Solid state Fermentation (SStF)

Feedstock	Process	Product
Complex composition of agro-substrates (sweet sorghum, corn, apple, grape, sugar cane, sugar beet, fodder beets)	Cultivation of micro-organisms on moist solid substrates, natural or an inert carrier with air as a continuous phase Occurs in the absence or near absence of free water	Production of alkanols, enzymes, enzyme activity studies, cellulose production and development, chitinase production from shellfish processing, citric acid production from pineapple waste, lactic acid fermentations, secondary metabolites, culturing of micro-organisms and antibiotic production

Table 7. Consolidated Bio-processing (CBP)

Feedstock	Process	Product
Rice Husk, Rice Bran, Maize cob, Maize Husk, Coconut shell, Coconut husks, Ground Nut Husk, Sugarcane bagasse, Coffee husk, Saw Dust	Use of one micro-organism or a consortium of micro-organisms in a single bioreactor to convert raw materials into alkanol	Production of alkanol, cellulolytic enzymes, hydrolysis of biomass

6. Direct extraction of bio-renewable materials technologies

In these techniques, processes are focused on single products with the main emphasize on high efficiency in extracting that target product(s). The rest of the material is degraded into low grade side products, re-integrated into agriculture or

downright disposed of as waste. This means that the target product(s) has to pay for the raw material, the process and all subsequent steps like waste treatment and disposal. Products like fibres, vegetable oils and fats as well as more complex products like essential oils, amino acids and proteins may be recovered directly from biomass without further synthesis steps.

Table 8. Bio-refineries

Bio-refinery Type	Raw materials	Process Technique	Products
Green	grass	Pressurization of wet biomass (green grasses and green crops)	liquid phase containing water-soluble compounds (lactic acid, amino acids) and a solid phase mainly consisting fibres
Whole Crop	Cereals (rye, wheat, maize)	Dry or wet milling of biomass Mechanical separation (milling) into grain (20 wt%) and straw (80 wt%) fractions Both streams further processed separately. Wet milling releases value-added products. Wet milling saves natural structures of starch, cellulose, and proteins	fuel grade ethanol
Lignocellulosic Feedstock		Fractionation of lignocellulosic-rich biomass sources into the intermediate output streams cellulose, hemicellulose and lignin	cellulose, hemicellulose, lignin
Thermo Chemical	fatty acids, fatty esters and glycerol from oil crops	Torre-faction Pyrolysis, Gasification Hydro-Thermal-Upgrading (HTU)	platform chemicals, functional monomers, lubricants and surfactants
Marine	microalgae and macro-algae		Proteins, Carbohydrates, Lipids, valuable Compounds
Two Platform Concept	Biomass	Fractionation of biomass into mainly a sugar (cellulose and hemicellulose) and a lignin fraction.	

Cotton fibres have strong hydrogen bonding that keeps the molecules together. These bonds needs to be cleaved in order to improving the refinery utilization of cotton

7. Bio-renewable resources industrial utilisation limitations

Limitations on Aquatic Biomass Production

Strain Selection

There are many species of aquatic plants with high potential value for biotechnology development. Therefore, there is need to identify species for specific purposes. Meanwhile, algal strain genetic improvement has lagged behind, hindered by a combination of the small numbers of families evaluated and lack of phenotypic information. Maintaining genetic diversity will be essential for providing a genetic basis

for current and future breeding programs that will develop strains with efficient performance in different climates and production systems.

Temperature

For effective growth of microalgae cultures an appropriate temperature range must be maintained depending upon the requirements of the strain. Every microalgae strain has a specific requirement for optimum temperature for maximum growth rates. Generally, temperatures between 15–25°C are acceptable for microalgae. Algae exhibit normal temperature to biological activity relationship with activity increasing with temperature until an optimum temperature is reached. Above the optimum temperature, biological activity declines, sometimes abruptly, to zero (Lowrey, 2011). Temperatures beyond the optimal temperature range will slow down the growth or kill the algae. Temperature tolerance may be found in some species or strains through screening, or may be trained through acclimation. In regions where winter is extremely cold, the algae production facility may be enclosed in a greenhouse to maintain a suitable temperature.

Bacterial Control

Although in laboratory research pure or unialgal species in the culture system are possible, in reality contamination of algae with other aquatic organisms and lower metazoan is unavoidable, and is sometimes beneficial but often times disastrous. Bacteria are one of the major sources of contamination. Laboratory work showed that many bacteria if co-cultured with algae inhibit growth of algae probably by secreting toxic factors and interfering with algal metabolisms. However, some bacteria when introduced into the algal culture system could promote algal growth. They are thus called growth-promoting bacteria. It is believed that these growth promoting bacteria are capable of generating and releasing some beneficial biofactors, but the identities of these biofactors remain unknown in most situations.

Microscopic Nature

Micro-algal strains due to their microscopic nature (typically 3-20 microns) and their low concentrations in which they can be grown (typically less than 2 g algae/L water) are difficult to harvest in a conventional way. Microalgae which are about 5-50 micro-metre in size form stable suspensions due to their negatively charged surfaces. Suspensions tend to be relatively dilute, adding to the difficulty in harvesting algae. A compounding problem is the sensitivity of the cell walls in many species to damage in high shear processes (e.g., centrifuging), which can result in leaching of the cell contents. Methods for the harvesting of algae include concentration through centrifugation, foam fractionation, flocculation, membrane filtration and ultrasonic separation. All these harvesting methods contribute to the total cost of algae biomass. Filtration is normally performed using a cellulose membrane and a vacuum being applied in order to draw the liquid through the filter. Although this method is simple, the membrane tends to become clogged, rendering the process extremely time consuming. Centrifuging, in a continuous or semi-continuous process, appears to be more efficient in this regard; however, it is extremely energy intensive and cannot readily be scaled to very large applications. The third option, flotation, uses a bubble column. Gas is bubbled through the algae suspension, creating a froth of algae that can be skimmed off.

Algae biomass dewatering

Live microalgae are tiny particles (1 to 30 μ m) suspended in the culture media. Therefore separating and collecting these fine particles with low specific gravity from

the bulk liquid is challenging and costly. Cost-effective and efficient concentration processes have been identified as a key technical hurdle for the commercialization of algae. Several physical, chemical, and mechanical harvest methods, individually or in combination, have been tested. Membrane filtration with the aid of a suction or vacuum pump is usually the preferred method. However, membrane fouling and clogging are major problems associated with cell penetration into the membrane structures and cell packing. Chemical flocculation also appears to be a viable method. Microalgae have negative charges on their surfaces that keep individual cells separated in suspension. When adding coagulants (e.g., iron, alum, lime, cellulose, salts, polyacrylamide polymers, surfactants, chitosan, and other man-made fibres), the negative surface charges are disrupted, causing microalgae in suspensions to flocculate and settle. Air flotation, dissolved air flotation, and suspended air flotation (Wiley *et al.*, 2009) are methods in which fine air bubbles are generated through air injection and adhered to algal cells, causing algal cells to float as foam to the top of a treatment column. The foam with concentrated algae is removed from the top, or the water below the foam is drained or siphoned off. Flotation methods are commonly combined with chemical flocculation. Flotation methods can be expensive to operate because they involve energy-intensive air compression. Centrifugation is another widely tested method. It may be used alone or as a second step to further remove water from concentrated algae collected with other methods. Centrifugation of large volumes of algal culture may be carried out using large centrifuges such as a cream separator. Algal cells are deposited on the walls of the centrifuge head as a thick algal paste. Ultrasound wave is a relatively new method in which algal cells experience low energy ultrasound waves and move to the low pressure nodes of ultrasound waves, causing the algal cells to agglomerate. The cell agglomeration is aided by the acoustic interaction forces and particle-particle interaction forces. Algae aggregates grow to such a size that they settle due to gravity when the ultrasonic field is turned off. The advantages of this technique are that it is non-fouling, causes no shear, and is free of mechanical failures because it does not involve moving parts and offers the possibility of continuous operation. Its major disadvantages are high power consumption and low concentration factors compared with traditional centrifugation and flocculation methods.

Drying of Algal Biomass

Drying of algal biomass also poses a major challenge towards commercialization because of aquatic (rich water content) nature of algae. Drying to 50 % water content is required in order to produce a solid material that can be easily handled. Given the fact that algae paste, as obtained by centrifuging or filtering, typically consists of 90 % water, drying algae is an energy intensive proposition. Consequently, solar drying is the main approach that has been considered to date. Solar drying is used commercially for drying grains and timber, and is inherently inexpensive; however, drying large quantities of algae would necessitate the use of considerable areas of land. Considering the methods available for algae harvesting, it is clear that more research is needed in order to improve efficiency and to reduce the required energy input. Flocculation appears to be a promising alternative to the technologies described above, providing that the necessary flocculants are either very inexpensive or can be recycled. Rather than using solar energy for subsequent dewatering/drying of the algae, a better approach might be to develop processes that make use of low-grade waste heat from an existing CO₂ source (e.g., power plant).

8. Physical limitations

Increasing World population

The use of agro-products (perennial grasses and trees grown on agricultural land) for industrial biomass utilization could drive up prices of both food and land due to increasing population. Food prices may rise if a major percentage of grain crops are grown for industrial utilization. The price increases could affect impoverished populations in developing countries, in particular. A person needs some 100 W of food energy (2000 Cal/day).

Agro-products industrial utilization may be in direct competition with food production for land, for water, and for fertilizer. It is no secret that humankind is already struggling to eliminate hunger; therefore, to take land, water, and fertilizers away from food production may not be a prudent option in global perspective. For example, to run one SUV on ethanol would require an amount of grain sufficient to feed 26 people (Lester, 2006). The bio-energy sector and the chemical production will compete for the same raw material source. In the case of forestry, the pulp and paper industry, the construction sector and the fiber board production will compete

Furthermore, large biomass sourcing, like agriculture, is an enemy of biodiversity. Any land taken away from wilderness destroys habitat and contributes to the mass extinction of species. However, this will inevitably happen with increasing use of biomass. Indonesia is planning to cut down rainforests in order to supply more palm oil (Eric, 2006). Brazil threatens the Amazon rain forest by exporting ethanol from sugarcane, and soya based diesel fuel (Bio-fuel watch, 2006).

Global limits to Food and Energy Crops

A study of net primary productivity and energy fixation for the world, confirms the low efficiency of biological conversion of solar energy (Lieth, 1975). Tropical rainforests and wetlands generate biomass energy at a rate of 1 W/m² while other forms of vegetation have lower yields. According to the study, about 1.4*10¹³ m² (2150 m²/person) of land worldwide is cultivated or used for permanent crops. The land used worldwide for agriculture produces biomass energy at a rate 0.36 W/m² (774 W/person). Systematic utilization of agricultural waste and byproducts of the food system can contribute a few hundred watts per person to the total power consumption. However, to supply the remaining present energy needs from biomass is physically not feasible, as it requires additional 4000 m²/person of biologically productive land, which may not be available on earth.

Within this invigorated competition the food sector (for agriculture) as well as the trade in saw logs (for forestry) pertains to markets with generally higher product prices. This means that these demand sectors will, in a stiffer market, command high quality product segments. In order to keep raw material costs in check, chemical processes and energy provision will have to concentrate on lower quality renewable raw materials. This includes surplus products (like grass, algae); harvest residues from crops that will go to the food sector (e.g. straw) as well as by-products and wastes from processes in the food sector (e.g. whey), from forestry or from society (e.g. waste cooking oil). Besides their low price, these raw materials offer the advantage that they have already been recovered from the land, so that costs and efforts for harvesting them will be low (or at least shared with more valuable products). High grade raw materials (like cereals) or specific raw materials (like herbs, fruits or specific animal parts) will remain reserved

(at least with regard to process industries outside the food sector) for the production of high value goods, especially in the pharmaceutical and cosmetics sector.

Bio-Renewable Resource Solar Energy Conversion

The solar constant at the Earth's orbit is 1370 W/m² perpendicular to the solar rays. 30 % is reflected back into space. Thus, the Earth receives 960 W/m² of its cross section (1.27 *10¹⁴ m²), which is a total insolation available at the Earth's surface of 1.22*10¹⁷ W (19 MW/person). Therefore, solar energy received at the Earth's surface is about 10 000 times more than humans are presently using from other resources. Distributed over the surface of the sphere, which is 4 times the cross section yields a day and night global average of 240 W/m² on the surface. Equatorial regions get some 400 W/m², while the inhabited regions in higher latitudes will receive around 200 W/m² on a horizontal surface (Pidwirny, 2005). Using the global average insolation, 10 m²/person of horizontal surface receive the amount of energy presently used by humans on a global average.

Plants capture solar energy as fixed carbon, converting carbon dioxide and water to sugars and oxygen, (CH₂O)_x: CO₂ + H₂O + light → (CH₂O)_x + O₂.

Biomass conversion of solar energy is less efficient, and requires water, fertilizers, and biologically productive land. Therefore the type and scale of any ecological change related to biomass production will depend on the method, the level of production and the physical, chemical, and biological characteristics of the area in question.

9. Chemical limitations

Low energy density of biomass

Biomass has a low energy density compared to that of coal, liquid petroleum, or petroleum-derived fuels. When moist (50% by weight), the energy content is further reduced. Thus, without substantial drying, the energy content of a biomass feed per unit mass is even less.

Non-selective conversion of biomass

The production of liquid fuels from biomass through direct thermochemical conversion processes (pyrolysis, liquefaction, and solvolysis) is non-selective, producing a wide range of products.

High temperatures conversion of biomass

Biomass contains a multitude of components (cellulose, sugars, fatty acids and proteins). This means that biomass would contain more functional groups including alcohols, aldehydes and amines. Sugars and proteins cannot resist high temperatures. As a result biomass components are often less stable at higher temperatures, which is unfavourable for application in products such as sustainable plastics. This can be corrected by reducing the number of unwanted functional groups by means of catalytic oxidation or hydrogenation.

Thermochemical conversion of biomass occurs at very high temperature (1600-1800K) in a stream of oxygen or steam. The higher temperature produces more volatile hydrocarbons and carbon chars which significantly increases the source of particulate organic carbon in the atmosphere. The organic carbons absorb and scatter the solar radiation, and indirectly through their ability to act as cloud condensation nuclei (CCN) affect the energy balance of the atmosphere.

Breakdown of lignocellulose

Lignocellulose, being the cheapest and most abundant forms of biomass, is composed of sugar polymers such as cellulose, lignin and starches. The cellulose and hemicellulose fractions can be readily broken down to their constituent monomers by hydrolysis, preparatory to conversion to ethanol or other chemicals. The lignin fraction is a complex structure containing aromatic groups and being relatively unreactive material is difficult to breakdown.

Lignocellulosic feedstock processing encompasses transformation of lignocellulosic biomass into intermediate outputs (cellulose, hemicellulose and lignin) with multiple functional groups that have a high transformation potential into new families of useful molecules. Examples of sugar-based platform chemicals are ethanol (C2), glycerol (C3), succinic acid (C4), xylitol (C5) and sorbitol (C6). The limitations of Lignocellulosic feedstock breakdown include

- i. Pre-treatment stages are the most complex step because the process produces single product. The obstacles in the pretreatment processes of lignocellulosic materials include insufficient separation of cellulose and lignin (which reduces the effectiveness of subsequent enzymatic cellulose hydrolysis), formation of by-products that inhibit ethanol fermentation (e.g. acetic acid from hemicellulose, furans from sugars and phenolic compounds from the lignin fraction), high use of chemicals and/or energy, and considerable waste production (Harmsen *et al.*, 2010).
- ii. Saccharification requires complex enzymes
- iii. Fermentation techniques in use are established for glucose. Therefore, new technology are required for pentose innovations for better performance and cost
- iv. Separation/Purification stages require novel dehydration technologies. The profile of the separation operations is vastly different in renewable resource processes than in fossil-based. The dominance of thermodynamic separation processes like distillation and absorption are now challenged by separation processes that are more geared to separate complex, larger molecules. In this regard membrane processes, electrophoresis and chromatography are becoming widely used even in the production of bulk chemicals.

Extensive de-oxygenation and hydrogenation

Triglycerides are good feedstock of biofuel because of its high energy density. However, corrosion induced by the long term storage of triglycerides needs to be solved by the removal of oxygen atoms in triglycerides. Hydrodeoxygenation (HDO) and deoxygenation (DO) without hydrogenation are two major solutions. The considerable hydrogen consumption limits the widespread use of the HDO process. In DO, deactivation of the catalysts by coke deposition has been a major problem to be overcome (Chang Hyun Ko *et al.*, 2012).

Limited conversion of Biomass

Fermentation, pyrolytic processes reactions has become more efficient, it is still limited to a 67% yield due to the loss of one-third (1/3) of the available carbon as carbon dioxide gas. Pyrolytic reactions also lose carbon as gases' and char but may achieve about 80% carbon conversion.' While most pyrochemical processes usually require nearly dry feedstock, the Shell Hydrothermal Upgrading (HTU) process requires a 3:1 ratio of water to biomass.² However, HTU produces only 50% biocrude which still contains 10-15% oxygen. Obviously, there remains a need for a variety of fuels

from many sources, especially conventional liquid fuels for transportation purposes. To resolve this fuel problem and to use a renewable resource, a strategy was selected to prepare valuable liquid hydrocarbons from biomass by a new chemical process.

Diverse Hydrocarbon structure

Biomass is primarily hydrocarbons. The industrial utilization of biomass requires diverse technical techniques because of the diversity of inherent hydrocarbon structures of the biomass. This means that processes are adapted to the respective needs to treat different raw materials but still producing the same product in different biomass systems.

Chemical groupings can be of significance in the manifestation of a particular type of biological activity, due perhaps to a special type of chemical reactivity or stereo chemical arrangement. Secondly, individual groups may exert characteristic effects in modifying the intensity of a type of biological activity which is exhibited in compounds having a common molecular basis. If the grouping is very reactive, the substance may react easily with a variety of cell constituents. At the other extreme, if the chemical reactivity is too low, biological activity will be diminished, perhaps to the point of disappearance (Ross, 1958).

Hydrocarbon structure determines the effect on the physical properties of an organic substance. The longer the chain or in the case of branched chains the higher the molecular weight, the greater the effect. The methyl group is unique among the alkyl groups because it aids in the replacement of active hydrogen atoms, thus distorting the general chemical reactivity of the molecule, either by blocking chemically reactive positions or by activating other positions (Preussmann, 1958).

Polyhydroxyl compounds are characterized by their capacity to enter into union with other molecules, and within themselves, by H-bonding.

Unsaturation in compounds may influence its stereo chemical considerations especially where the possibility exists in the unsaturated compound of *cis-trans* isomerism. One of the isomers of the unsaturated form may have some characteristic activity which is either not shown by the saturated substance or is only shown to a diminished degree. Unsaturation in compounds may also affect their physical properties. Chemically, an isolated double bond does not appear to possess a sufficient degree of reactivity to enter into ready unions with cell constituents, for if it were otherwise, the unsaturation hydrocarbons might be expected to exhibit a greater variety of actions than they actually do. However, when the double bond is chemically activated by a neighboring group, a different state of affairs prevails (Brookes, 1960).

In order to transform biomass into higher value products, the chemical transformation must break C:H bonds and mediate the formation of new bonds of carbon with other heteroatoms, e.g. $\text{RH} \rightarrow \text{ROH}$, is a major chemical change since additional reactions may occur in the process. Therefore such transformations usually require insight from complementary backgrounds, including bioinorganic, organometallic, electrochemistry and computational chemistry to develop pathways for these transformations.

The following reactions may occur

- Esterification of acids with alcohols
- Transesterification of esters
- Homopolymerization of aldehydes
- Hydration of aldehydes or ketones

- Hemiacetal formation with aldehydes and alcohols
- Acetalization of aldehydes and alcohols
- Phenol/aldehyde reactions to form resins
- Polymerization of furan derivatives
- Dimerization of nitrogen compounds from proteins with aldehydes.

Heteroatom concentration

Nature functionalizes biomass using heteroatoms in which one of the atoms is in a high oxidation state (i.e. electron deficient). Therefore transformations that may replicate such activities are usually limited. It however requires expertise in bioorganic chemistry, heterogeneous and homogeneous catalysis that provide more controlled hydrocarbon functionalization chemistry.

Heteroatom speciation

Biomass is primarily associated with the presence of particular groupings essential for the manifestation of a particular type of activity, due perhaps to a special type of chemical reactivity or stereochemical arrangement. However, the identification of heteroatoms responsible for particular chemical reactivity in a molecule are usually difficult, especially oxygenated species. The tracking of hydrogen species is done through solid state measurements which involves expensive equipment like Nuclear Magnetic Resonance Spectroscopy and Fourier transform Infrared spectroscopy.

Oxygen concentration

Biomass can be converted into useful products either through thermo-chemical or biochemical processes. Yeasts, fungi and bacteria, under anaerobic conditions are able to convert biomass into ethanol with some limitations. The anaerobic conditions do not allow these microorganisms to fully utilize the range of carbohydrates present in the biomass while producing ethanol at high yield. For various stages in the bioprocess conversion, differing levels of oxygen are required.

SCIOECONOMIC CHALLENGES

Cost

Producing micro algal biomass is generally more expensive than growing crops. The cost of culturing *Botryococcus braunii* typically varies between \$5–10 per kilogram (Chisti, 2007). Production costs vary significantly with production scale and the system of production. Energy is used to produce the crops (in the manufacture of the fertilizer, in the sowing, looking after and harvesting the crops and their transport to the refineries). Energy is also used in the fermentation processes and in the subsequent purification of the fuels. However an integrated bio-refinery, where valuable co-products (oils, proteins and carbohydrates) would complement production cost (Pienkos and Darzins, 2009). The driving cost factors are biological, and not engineering or environmentally-related. High productive organisms capable of near-theoretical levels of conversion of sunlight to biomass are needed. Thus, much work should be devoted to ensure that the energy inputs are reduced substantially and that the carbon dioxide produced is captured.

Funding

Economics of bio-product utilization is gradually becoming more complex and evolving rapidly. For example, new inputs to cost models including carbon recycling and environmental reclamation opportunities are being considered. However, regardless of technological and biological breakthroughs or carbon mandates, commercial marketplace may not fund capital intensive biomass projects unless the risk-return ratio is acceptable to debt and equity financiers. The capital costs are usually divided into costs associated with biomass production, harvesting and industrial utilization systems.

Carbon Life-Cycle Assessment

Accurate estimation of carbon lifecycle impacts on human health, wildlife and the environment is critical for the development of biomass production technologies. These impacts present significant hurdles for various approaches to the bio-fixation of CO₂. Algae require approximately 2g of CO₂ for every gram biomass generated and thus have a tremendous potential to capture CO₂ emissions from power plant flue gases and other fixed sources. In photo-bioreactors, CO₂ can be used as both an input to photosynthesis, as well as a pH controller. As microalgae grow and uptake CO₂ within a closed system, the growth media exhibits an increasing pH. When CO₂ is added to the photo-bioreactor, it drives the formation of carbonic acid, thereby lowering the the pH (Mehlitz, 2009).

Land Ownership and Utilization

Farm land is a major unit of property, status, socialization, and welfare for a family in a rural society. Levels of land ownership included government, private (men, women), and communal. Land acquisition by individuals affects its use. As individualization of land ownership increases, use may likely decrease. The pattern of land ownership has several implications as to who is likely to make decisions about which crops are grown. Management of a farm system and the division of labor are likewise related to patterns of inheritance, responsibility, and authority over the land. Land ownership in most developing nation's still remains male dominated. Land degradation is usually attributed to increase over farming and harvesting of trees for firewood. Increased land degradation and encroachment by thickets reduces the quality and quantity of pasture biomass available, thus lowering animal productivity. Increased utilization of land for agricultural activities results in increased conflicts due to competition for space, consequently reducing animal productivity.

Location and Ownership of Bio-resources

Bio-resources are usually of public or communal ownership. This means that the responsibility for its maintenance is not owned by any individual. Public or communal ownership directly affects their Management.

Bio-renewable resources are most often, produced dispersedly and de-centrally. Therefore, further processing of intermediaries is dependent of logistic considerations. In addition to their dispersed emergence, renewable raw materials are, in many cases, generated discontinuously, are perishable and require large transport volumes (or have low concentrations of the targeted material or are accompanied by large amounts of moisture). All these factors increase efforts and costs for transporting and storing raw materials.

Public Policy

To break away from the subsistence system, governments can accelerate agricultural development by changing the land tenure system, transferring Western technology and mechanization, introducing mono-cropping, and encouraging agricultural entrepreneurship.

Public policy and implementation have direct impacts on agro-ecosystems, farming systems, and decision making of farmers. The delivery of subsidies, technical and chemical inputs, as well as extension services, have generated changes in agricultural practices and, at times, have fostered resistance from farm level communities.

10. Conclusion

Bio-renewable resources from the food, agricultural and forestry sectors have industrial applications as feed stocks for producing high-value substances. Thermodynamic separation processes (distillation and absorption), membrane processes, electrophoresis and chromatography techniques are needed to separate complex, larger molecules in the production of bulk chemicals. These technologies provide a way for the benefit of currently underutilized food by-products, particularly through the manufacture of phytochemicals with potential health benefits for the pharmaceutical, cosmetic and food industries. Combinations of adsorption stages with other conventional and/or emerging technologies provide opportunities to develop effective and environmentally friendly processes enabling the manufacture of concentrates enriched in defined target compounds, suitable for commercial exploitation.

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