

Production of first and second generation biofuels: A comprehensive review

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ABSTRACT

Sustainable economic and industrial growth requires safe, sustainable resources of energy. For the future re-arrangement of a sustainable economy to biological raw materials, completely new approaches in research and development, production, and economy are necessary. The ‘first-generation’ biofuels appear unsustainable because of the potential stress that their production places on food commodities. For organic chemicals and materials these needs to follow a biorefinery model under environmentally sustainable conditions. Where these operate at present, their product range is largely limited to simple materials (i.e. cellulose, ethanol, and biofuels). Second generation biorefineries need to build on the need for sustainable chemical products through modern and proven green chemical technologies such as bioprocessing including pyrolysis, Fisher Tropsch, and other catalytic processes in order to make more complex molecules and materials on which a future sustainable society will be based. This review focus on cost effective technologies and the processes to convert biomass into useful liquid biofuels and bioproducts, with particular focus on some biorefinery concepts based on different feedstocks aiming at the integral utilization of these feedstocks for the production of value added chemicals.

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1. Introduction

In the twentieth century major research emphasis was given for the development of petroleum, coal, and natural gas based refinery to exploit the cheaply available fossil feed stock. These feedstocks are used in industry to produce multiple products such as fuel, fine chemicals, pharmaceuticals, detergents, synthetic fiber, plastics, pesticides, fertilizers, lubricants, solvent, waxes, coke, asphalt, etc. to meet the growing demand of the population [1,2]. Currently, the fossil resources are not regarded as sustainable and questionable from the economic, ecology and environmental point of views [3]. The burning of fossil fuels is a big contributor to increasing the level of CO₂ in the atmosphere which is directly associated with global warming observed in recent decades [4]. The adverse effects of greenhouse gas (GHG) emissions on the environment, together with declining petroleum reserves, have been realized. Therefore, the quest for sustainable and environmentally benign sources of energy for our industrial economies and consumer societies has become urgent in recent years [5]. Consequently, there is renewed interest in the production and use of fuels from plants or organic waste.

The biofuels produced from the renewable resources could help to minimize the fossil fuel burning and CO₂ production. Biofuels produced from biomass such as plants or organic waste could help to reduce both the world's dependence on oil and CO₂ production. These biofuels have the potential to cut CO₂ emission because the plants they are made from use CO₂ as they grow [6]. Biofuels and bioproducts produced from plant biomass would mitigate global warming. This may due to the CO₂ released in burning equals the CO₂ tied up by the plant during photosynthesis and thus does not increase the net CO₂ in the atmosphere. Additionally, biofuel production along with bioproducts can provide new income and employment opportunities in rural areas. 21st Century is looking for a shift to alternate industrial feedstock and green processes to produce these chemicals from renewable biomass resources [7].

'First generation' biofuels can offer some CO₂ benefits and can help to improve domestic energy security. But concerns exist about the sourcing of feedstocks, including the impact it may have on biodiversity and land use and competition with food crops. A 'first generation' biofuel (i.e. biodiesel (bio-esters), bio-ethanol, and biogas) is characterized either by its ability to be blended with petroleum-based fuels, combusted in existing internal combustion engines, and distributed through existing infrastructure, or by the use in existing alternative vehicle technology like FFVs ("Flexible Fuel Vehicle") or natural gas vehicles. The production of 1st generation biofuels is commercial today, with almost 50 billion liters produced annually. There are also other niche biofuels, such as biogas which have been derived by anaerobic treatment of manure and other biomass materials. However, the volumes of biogas used for transportation are relatively small today [4].

However, the first generation biofuels seems to create some skepticism to scientists. There are concerns about environmental impacts and carbon balances, which sets limits in the increasing production of biofuels of first generation. The main disadvantage of first generation biofuels is the food-versus-fuel debate, one of the reasons for rising food prices is due to the increase in the production of these fuels [8]. Additionally it is claimed that biodiesel is not a cost efficient emission abatement technology.

Therefore, for the abatement of GHG, it is recommended to have more efficient alternatives based on both renewable and conventional technologies [9].

Therefore, lignocellulosic feedstock can offer the potential to provide novel biofuels, the biofuels of the 'second generation' [10]. Second-generation biofuels produced from 'plant biomass' refers largely to lignocellulosic materials, as this makes up the majority of the cheap and abundant nonfood materials available from plants. But, at present, the production of such fuels is not cost effective because there are a number of technical barriers that need to be overcome before their potential can be realized [9]. Plant biomass represents one of the most abundant and underutilized biological resources on the planet, and is seen as a promising source of material for fuels and raw materials. At its most basic, plant biomass can simply be burned in order to produce heat and electricity. However, there is great potential in the use of plant biomass to produce liquid biofuels. However, biofuel production from agricultural by-products could only satisfy a proportion of the increasing demand for liquid fuels. This has generated great interest in making use of dedicated biomass crops as feedstock for biofuel production [11]. The examples of 2nd generation biofuels are cellulosic ethanol and Fischer–Tropsch fuels. The production of 2nd generation biofuels is non-commercial at this time, although pilot and demonstration facilities are being developed. Therefore it is anticipated that, these 2nd generation biofuels could significantly reduce CO₂ production, do not compete with food crops and some types can offer better engine performance. When commercialized, the cost of second generation biofuels has the potential to be most comparable with standard petrol, diesel, and would be most cost effective route to renewable, low carbon energy for road transport [4].

Therefore due to many advantages and disadvantages of the 1st generation biofuels and obvious advantages of 2nd generation biofuels as shown in Fig. 1, the approaches to integral utilization of biomass for sustainable development are more reasonable, where all parts of the plant such as leaves, bark, fruits, and seeds can be utilized to useful products. The term 'Biorefinery' was initially established by NREL during 1990, for the utilization of biomass for production of fuels and other bioproducts. This term refers to a facility (or group of facilities) which combines the production of materials, chemicals, or fuel products with energy production [12]. The biorefinery system includes biomass production, biomass transformation/processing, and end use. The total biomass production on earth is approximately 100 billion tones organic dry matter of land biomass per annum and 50 billion tones of aquatic biomass. The part of it is used as food, feed, energy and industrial raw materials, where food use is only 1.25% of the entire land biomass. The rest of the biomass is unused or recycled in to the earth system, which can be used as raw material for chemical production. Currently, starches, sugar, oils and fats, cellulose, rubbers have been used industrially as well [6].

So far many research papers on the biorefinery concept have been published: wheat straw biorefinery [13], corn biorefinery [14] and forest residue based biorefinery [5], etc. Also, many review papers are available in the literature i.e. bioethanol from biomass, green diesel, chemicals from glycerol, etc. but the information on the first, second generation biofuel and related chemicals from non-food crops are scanty. In this paper an attempt has been made

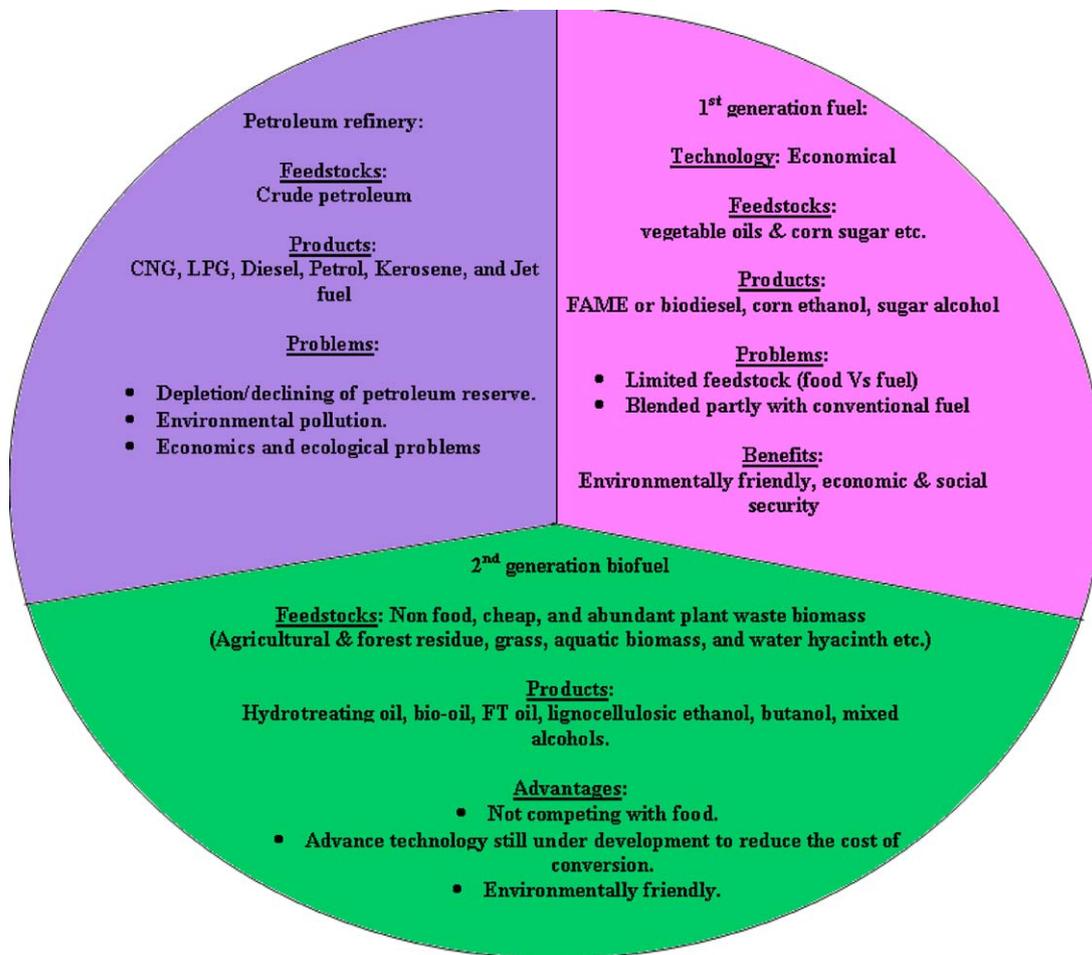


Fig. 1. Comparison of first, second generation biofuel and petroleum fuel.

to review the literature on first and second generation biofuels and anticipated biochemicals from the non-food crop biomass. In this respect, the present paper is a part of research program aiming at the integrated utilization of *Jatropha* in India and cereal crop residues in Canada, attempting to contribute to the first generation biofuels production (i.e. biodiesel) and parallel use of the residues for energy and 2nd generation biofuels production. In addition some biorefinery concepts based on different biomass feedstocks for 2nd generation biofuels and their bioproducts with example have been discussed.

2. Biomass as multiple feedstocks for biorefinery

Biomass derived from trees, agro-forest residues, grasses, plants, aquatic plants and crops are versatile and important renewable feed stock for chemical industry as shown in Fig. 2. Through photosynthesis process, plants convert carbon dioxide and water in to primary and secondary metabolite biochemicals. Both of these are industrially important chemicals. Primary metabolites are carbohydrate (simple sugar, cellulose, hemicellulose, starch, etc.) and lignin called lignocellulose present in high volume in biomass. The lignocellulosic biomass can be converted into biofuels. The secondary metabolite are high value biochemicals such as gums, resins, rubber, waxes terpenes, tepenoids, steroids, triglyceride, tannin, plant acids, alkaloids, etc. are present in low volume in the plants [15]. The secondary metabolites can be utilized for production of high value chemicals such as food flavors, feeds, pharmaceuticals, cosmoceuticals, and nutraceutical, etc. using integrated processing technique.

Enhancement of biomass utilization requires tremendous effort to develop new biomass systems in which production, conversion and utilization of biobased products are carried out efficiently in near harmony with nature [6]. However, success depends on how far it is possible to change today's production of goods and services gradually from fossil to biological raw materials. Therefore many researchers around the World are working on the development of possible biomass integrated conversion technologies. For example, Huang et al. [14] reviewed on separation methods and technologies related to lignocellulosic biorefineries for production of ethanol and other products. The paper critically has reviewed the current and future technologies used for corn to ethanol biorefinery, lignocellulosic biomass to ethanol biorefinery, integrated lignocellulose/forest biorefinery (ILCB), pre extraction of hemicellulose and other value added chemicals (corn germ, fiber, zein or gluten from corn-ethanol plant), detoxification of fermentation hydrolyzates, and ethanol product separation and dehydration. For future biorefineries separation processes like extractive distillation with ionic liquids and hyperbranched polymers, adsorption with molecular sieve and biobased adsorbents, nanofiltration, extractive-fermentation, membrane pervaporation in bioreactors, and vaccum membrane distillation (VMD) hold significant potential and great promise for further investigation, development and application. Clark et al. [16] reported the use of green chemical technologies to transform low value waste biomass to green chemicals like, waxes and ethanol, etc. However, Chew et al. [17] have reported on different types of catalysts and their role in the catalytic processes for production of biofuels in a typical palm oil and oil palm based refinery in Malaysia. Rowlands et al. [18] reported the biorefinery challenges,

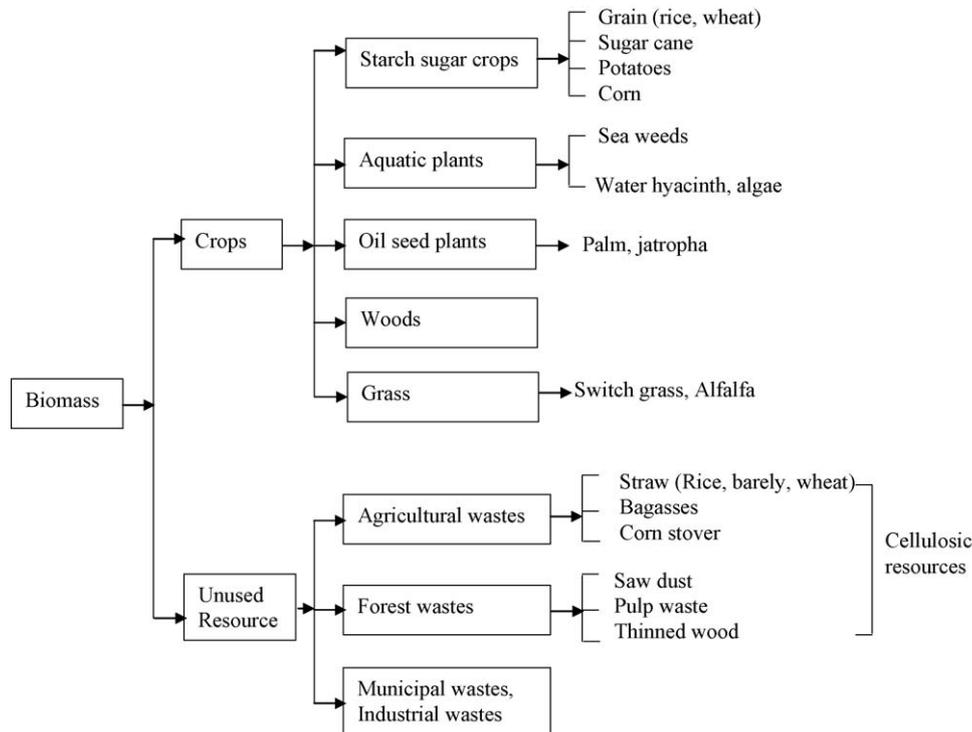


Fig. 2. Biomass as renewable feed stock for biorefineries.

opportunities in the context of Australian perspective. Mabee et al. [5] have assessed the emerging biorefinery sector in Canada. Gomez et al. [11] reported on the underpinning research necessary to enable the cost effective production of liquid fuels from plant biomass, with a particular focus on the aspect related to plant cell walls and their bioconversion.

For the second generation biofuel non edible oilseeds like *jatropha curcas*, high erucic mustard, Indian beech (*pongamia pinnata*), green seeds canola and micro algae, etc. can be used for biofuels including green diesel and whereas, aquatic biomass can be utilized for bioethanol and biodiesel. This paper also reviews the current status and future scope of biorefineries in the context of first and second generation biofuel by utilizing different biomass.

2.1. Biorefinery concept/system

The biorefinery system is based on biomass as processing input (feedstocks) for production of multiple bio-based products. The basic concept of the biorefinery system is to produce biofuel and platform of chemicals from biomass. The detail flow chart on conversion processes such as physical, chemical, biological, and thermal or combination of processes with products is shown in Fig. 3. The earlier papers differentiated three types of biorefineries based on feed stocks, processing flexibilities and products. The first one has fixed processing capabilities and uses dry grain as feed stocks to produced ethanol, dried distillers grain (DDG)/feed products and carbon dioxide. The second type biorefineries used same feedstock and has more processing flexibilities than first one. It can produce starch, high fructose syrup, ethanol, carbon dioxide, DDG and corn oil. Third type of biorefinery is most advanced and can use a mix of biomass feed stocks and produced different products by employing combination of technologies. It is based on both the High Value Low Volume (HVLV) and Low Value High Volume (LVHV) out put principle. The third type of biorefinery are again classified in three categories like, Whole Crop, Green and Lignocellulose feedstock biorefineries, which are in research and development stage [12].

The overview of biorefinery system for producing bioproducts from biomass was also reported by Kamm et al. [3] and Fernando et al. [12]. There are many research papers which give the information on biorefinery concept which uses different feedstocks such as crops and crop residues, forest residues, green grasses, lignocellulosic biomass, and industrial waste [3,14,17,19].

According to National Renewable Energy Laboratory, a biorefinery is a facility that integrates biomass conversion processes and equipments to produce fuels, chemicals and power from biomass. The goal of a biorefinery is to transform biomass into useful products using technology and processes. Biomass conversion required deep understanding of production technology, chemistry, conversion technology of biomass, economics and environmental related issues [20].

The development of comparable biorefineries—however not in the sense of a direct copy of petroleum refinery, it is necessary to produce a broad variety of biobased products in an efficient construction set system. Each biorefinery refines and converts its corresponding biological raw materials into a multitude of valuable products. The product palette of a biorefinery includes not only the products produced in the petroleum refinery, but also in particular products that are not accessible in petroleum refineries [21]. Therefore it is necessary to develop new technologies such as (i) lignocellulosic feedstock biorefinery, including LCF pretreatment and effective separation in lignin, cellulose, and hemicellulose, (ii) further development of thermal, chemical, and mechanical processes, (iii) development of biological processes, (iv) combination of substantial conversions, such as biotechnological and chemical processes [3].

3. First generation biofuels

The dramatic rise in oil prices seen in the last decade has also enabled liquid biofuels to become cost-competitive with petroleum-based transportation fuels, and this has led to a surge in research and production around the world. The three main types of first generation biofuels used commercially are biodiesel

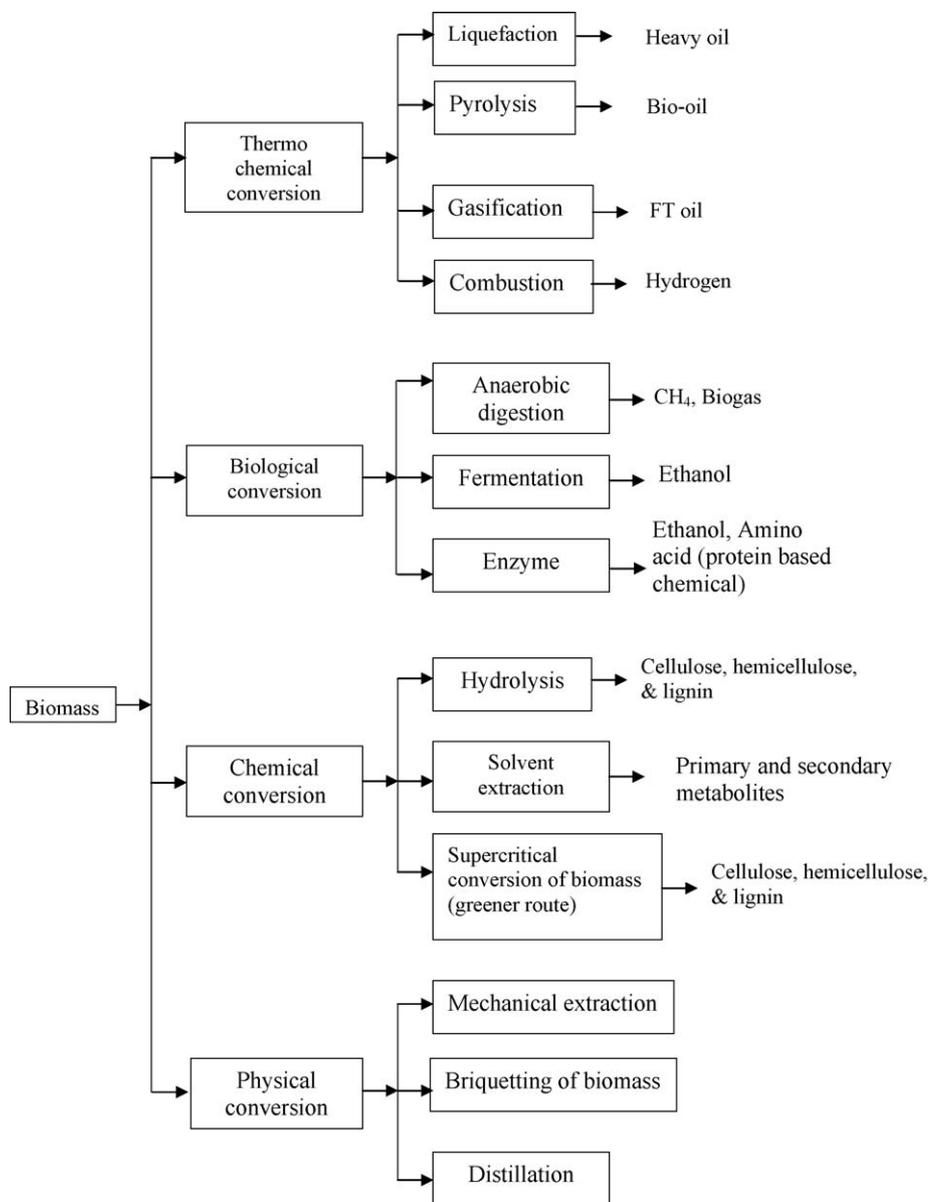


Fig. 3. Biomass conversion processes.

(bio-esters), ethanol, and biogas of which world wide large quantities have been produced so far and for which the production process is considered 'established technology'. Biodiesel is a substitute of diesel and is produced through transesterification of vegetable oils, and residual oils and fats, with minor engine modifications; it can serve as a full substitute as well. Bioethanol is a substitute of gasoline and it is a full substitute for gasoline in so-called flexi-fuel vehicles. It is derived from sugar or starch through fermentation. Bioethanol can also serve as feedstock for ethyl tertiary butyl ether (ETBE) which blends more easily with gasoline. Biogas, or biomethane, is a fuel that can be used in gasoline vehicles with slight adaptations. It can be produced through anaerobic digestion of liquid manure and other digestible feedstock. At present, biodiesel, bioethanol and biogas are produced from commodities that are also used for food. The demands of edibles oils are increasing trend, so it difficult to use the agricultural food crop for biofuel production [22]. There are some potential crops for biodiesel production, which can be taken up as Industrial crop on unproductive lands. Such multipurpose uses oilseeds crops can be introduced, so that the biomass produced by

them can be utilized for production of various bioproducts. In that respect, example of whole crop biorefinery as shown in Fig. 4, has been discussed aiming at the integrated utilization of *Jatropha* in India, attempting to contribute to sustainable biodiesel production and parallel use of its solid residues for production of other valuable chemicals and utilization of its lignocellulosic biomass for 2nd generation biofuels production.

3.1. Conversion processes for first generation biofuels

3.1.1. Transesterification

The vegetable oil based fatty acid methyl esters (FAME), popularly known as biodiesel, is gaining importance as an environment-friendly diesel fuel substitute or extender. Biodiesel is an alternative diesel, made from renewable biological sources such as vegetable oils and animal fats by chemically reacting oil or fat with an alcohol, in the presence of a homogeneous and heterogeneous catalyst. The product of the reaction is a mixture of methyl esters, which are known as biodiesel, and glycerol, which is a high value co-product [23,24].

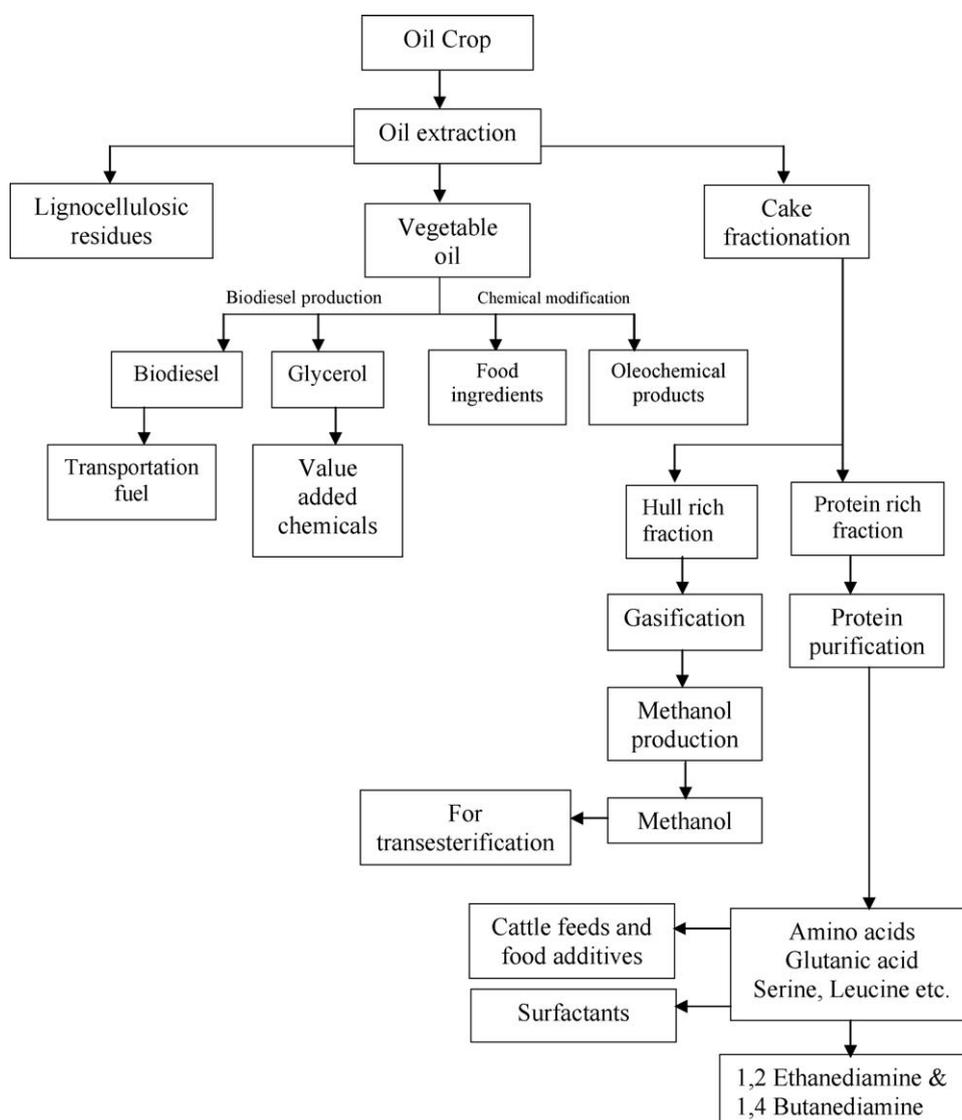
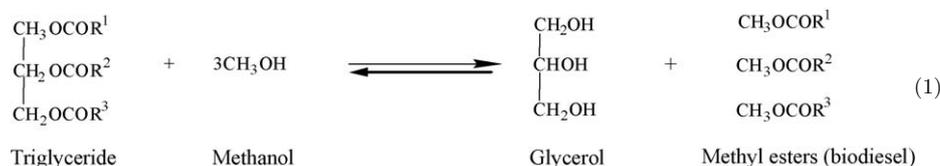


Fig. 4. Whole crop biorefinery.

3.1.1.1. *Homogeneous catalysis.* Transesterification is a reversible reaction and proceeds essentially by mixing the reactants in which the catalysts is a liquid acid or a liquid base. The process known as transesterification, as shown in Eq. (1) (Transesterification (alcoholysis) process).

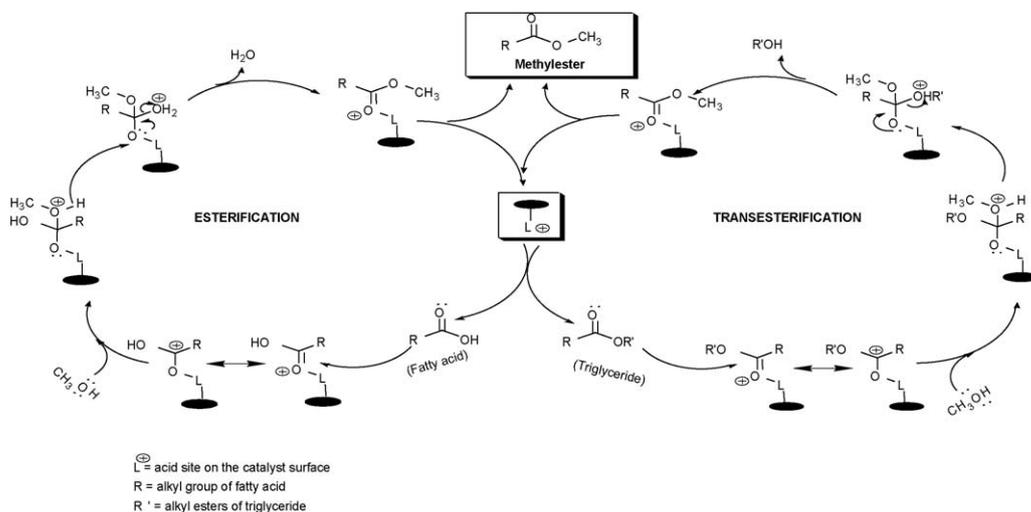


3.1.1.2. *Heterogeneous catalysis.* It is not possible to perform a basic transesterification process for high free fatty acid (FFA) content oil and decreases the conversion of oil to methyl ester due to saponification reaction. The use of solid catalyst is recommended for high free fatty acid containing oil. This is because the solid acid catalysts can simultaneously catalyze the transesterification of triglycerides and esterification of free fatty acid (FFA) present in oil to methyl esters. Solid acid catalysts have the strong

potential to replace homogeneous catalysts, eliminating separation, corrosion and environmental problems [23].

The solid acid catalyzed biodiesel production by simultaneous esterification and transesterification of low quality oil containing high FFA was performed by Kulkarni et al. [23]. The reaction

mechanism of simultaneous esterification and transesterification using Lewis acid is as shown in Scheme 1. The esterification takes place between free fatty acids (RCOOH) and methanol (CH₃OH) whereas transesterification takes place between triglyceride (RCOOR') (taken as representative of triglycerides in this case) and methanol adsorbed on acidic site (L⁺) of catalyst surface. The interaction of the carbonyl oxygen of free fatty acid or mono-glyceride with acidic site of the catalyst forms carbocation. The



Scheme 1. Solid acid catalyzed simultaneous esterification and transesterification [23].

nucleophilic attack of alcohol to the carbocation produces a tetrahedral intermediate (Scheme 1). During esterification the tetrahedral intermediate eliminates water molecule to form one mole of ester (RCOOCH_3). The transesterification mechanism can be extended to tri- and di-glyceride. It is well known that transesterification is a stepwise reaction. In the reaction sequence the triglyceride is converted stepwise to di- and monoglyceride and finally glycerol. The tetrahedral intermediate formed during reaction eliminates di-, monoglyceride and glycerol when tri-, di- and monoglyceride come in contact with the acidic sites, respectively, to give one mole of ester (RCOOCH_3) in each step. In cases, esterification and transesterification produce methyl ester, the same final product. Also, as shown in Scheme 1, the catalyst is regenerated after the simultaneous esterification and transesterification reactions. Use of excess alcohol favors forward reaction and thus maximizes the ester yield [23].

3.1.1.3. Ethanol conversion processes. A wide variety of carbohydrates containing raw materials have been used for production of ethanol by fermentation process. These raw materials are classified under three major categories:

- Sugar containing crops: Sugar cane, wheat, beet root, fruits, palm juice, etc.
- Starch containing crops: Grain such as wheat, barely, rice, sweet sorghum, corn, etc. and root plants like potato, cassava.
- Cellulosic biomass: Wood and wood waste, cedar, pine, wood, etc. agricultural residues, fibers.

The alcohol produced from food crops like corn, wheat, barley, sweet sorghum is called grain alcohol, whereas ethanol produced from lingo-cellulosic biomass such as agro residue (i.e. rice straw, wheat straw) grasses (switch grass) is known as biomass ethanol or bioethanol. Both these alcohols are produced through biochemical process [25].

Chemical structure of starch consists of long chain polymer of glucose. The macromolecular starch cannot be directly fermented to ethanol by conventional fermentation technology. The macromolecular structure first broke down into simpler and smaller glucose. In this process, starch feedstocks are grounded and mixed with water to produce a mash typically contained 15–20% starch. The mash is then cooked at or above its boiling point and treated subsequently with two enzyme preparation. The first enzyme hydrolyzes starch molecules to short chains to glucose. The first enzyme is amylase, amylase liberates “maltodextrin” oligosac-

charides by liquefaction process. The dextrin and oligosaccharides are further hydrolyzed by enzyme such as pullulanase and glucoamylase in a process known as saccharification. Saccharification converts all dextrans to glucose, maltose and isomaltose. The mash is then cooled to 30°C and yeast is added for fermentation [26].

Ethanol production is usually obtained via enzymatic hydrolysis of starch containing crops like corn wheat. Corn ethanol production facilities can be classified into two groups i.e. wet & dry mill processes [25]. Dry mills are usually smaller in size (capacity) and are built primarily to manufacture ethanol only. According to Shapouri et al. [27] modern wet milling plants are able to produce 1 gal ethanol consuming 35150 Btu of thermal energy and 2134 KWh of electricity. If molecular sieves are used the thermal energy input drops to 32150 Btu/gal. The starch grain is prepared for ethanol fermentation by either wet milling or dry grinding as shown in Fig. 5a and b. Wet mill ethanol process produced variety of valuable coproducts such as nutraceuticals, pharmaceuticals, organic acids and solvent. Dry grinding mill process is specially designed for production of ethanol and animal feed.

3.1.1.4. Fermentation process. The term fermentation can generally be defined as the metabolic process in which an organic substrate

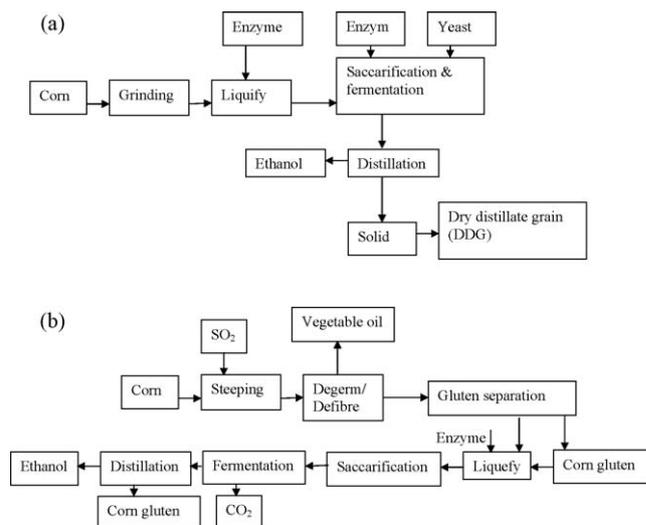
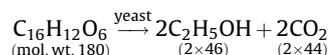


Fig. 5. (a) Dry mill process and (b) Wet mill process.

goes under chemical changes due to activities of enzymes secreted by micro-organisms. There are two basic types of fermentation (a) aerobic and (b) anaerobic depending upon oxygen needed in the process or not. There are thousands of micro-organisms in nature capable of providing fermentative changes. Some of these are capable of producing ethanol from sugar and starch. The micro-organisms employed for ethanol production are classified into three categories viz. yeast (*saccharomyces* species), bacteria (*zymomonas* species), and mold (mycelium). These micro-organisms found in nature and are very selective in their fermentation characteristics, some of these ferment specific to hexoses or pentose, or mixtures of both. Efforts are being made by various researchers to produce ideal micro-organism, which will be able to produce ethanol from any carbohydrate.



Starch is polymer of glucose. Starch cannot be directly fermented to ethanol by conventional fermentation technology. In the process of fermentation, starch broken down glucose molecules once treated with yeast like *saccharomyces cerevial*, *saccharomyces uvarum*, *schizosaccharomyces pombe*, and *kluveromyces* species. Under anaerobic conditions yeasts metabolize glucose to ethanol. Theoretically, the maximum conversion efficiency of glucose to ethanol is 51% on the weight basis, which comes from a stoichiometric calculation of $2 \times (\text{molecular wt of ethanol}) / (\text{molecular wt of glucose}) \times 100 = (2 \times 46) / (180) \times 100 = 51$. However, some of the glucose is used by the yeast for production of cell mass and for metabolic products other than ethanol, thus reducing the conversion efficiency from its theoretical maximum. In practice, between 40 and 48% of glucose is actually converted to ethanol with 46% fermentation efficiency, i.e. 1000 kg of fermentable sugar would produce about 583 lit of pure ethanol (sp gravity at 20 °C = 0.789) [26].

3.1.1.5. Anaerobic digestion of biomass. Anaerobic digestion of solid waste is a process very similar to that used in biogas production. Anaerobic bacteria in the absence of oxygen are used to break down the organic matter of biomass, and during the conversion a mixture of methane and carbon dioxide gases are produced. The typical ratio of gas mixture is 60–70% methane and 30% carbon dioxide. The gas has a heating value 650–750 Btu/ft³. Due to increase cost of energy, the anaerobic digestion of biomass is an attractive alternative for production of fuel and biofertilizer for organic cultivation. Anaerobic digestions in landfills are potential source of methane production from solid waste. Anaerobic digestion of biodegradable portion of the municipal solid waste (mostly biomass and biological waste) produces methane and carbon dioxide in roughly equal amount. These two principal components together with atmospheric nitrogen, oxygen and traces of organic compounds are known as landfill gas (LFG). According to Environmental Protection Agency (EPA), each pound of biodegradable organic waste can produce 10–12 standard cubic feet of gas. Landfill gas is similar to low quality natural gas, in that it requires the removal of the volatile organic contaminants and CO₂ to realize substantial commercial value. The removal of toxic and other contaminants from LFG require efficient separation technology to use it as a substitute for natural gas. The contaminants are toxic vinyl chloride and hydrogen sulphide [26].

The conventional use of land fill gas to energy include electricity generation using internal combustion engine, turbine, micro turbine, direct use in boiler, dryer, kiln, green house and co-generation. The current research of land fill gas focuses on the generation of liquid fuels instead of the gaseous fuel from anaerobic digestion due to the high cost associated for methane purification and collection [26]. Production of methanol as liquid

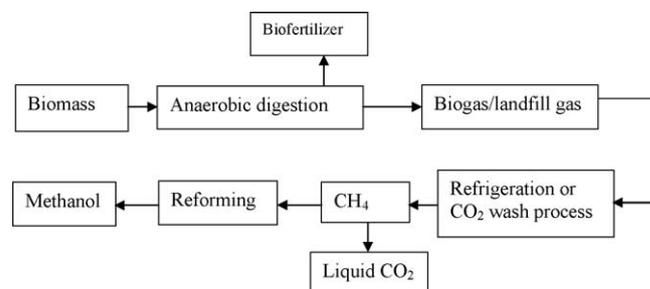


Fig. 6. Anaerobic digestion.

has several advantages. First low sulphur, low ash fuels can be made for commercial use. Second, liquid fuel is much easier to handle, store and transport than gaseous products. By utilizing waste lignocellulosic biomass through anaerobic digestion process will generate liquid fuel and biofertilizer for Agricultural production. The biorefinery concept of anaerobic digestion is shown in Fig. 6.

3.2. Whole-crop biorefinery

A whole-crop biorefinery processes and consumes the whole crop to obtain useful products. Raw materials such as oil seed can be used as feedstock in the unit operations of a whole crop biorefinery as depicted in Fig. 4. In that context, example of jatropha oil seed crop has been discussed. Jatropha seed kernel contains 35–40% oil and 1–1.5 tonnes of oil can be produced per ha [28]. The process of converting biomass into energy is initiated by separation of biomass into different components that are then treated separately. The oil obtained acts as the starting material for biodiesel production or can undergo chemical modification to produce oleochemical products, whereas the de-oil cake fraction after purification can be used as the basic raw materials for the synthesis of valuable chemicals or for gasification. The lignocellulosic biomass produced during the refinery operations can act as the starting material to the lignocellulosic biorefinery for the production of syngas, where syngas can be used as the basic material for the synthesis of fuels and methanol using the Fischer–Tropsch process.

3.2.1. Oleochemicals

Oleochemicals refer to chemicals derived from natural oils and fats of both plant and animal origins. Basically, oleochemicals refer to the fatty acids and glycerol derived from the splitting of the triglyceride structures of oils and fats. However, they also include those derivatives derived from the subsequent modification of the carboxylic acid group of the fatty acids by chemical or biological means, and other compounds obtained from further reactions of these derivatives. Oleochemicals are often categorised into basic oleochemicals such as fatty acids, fatty methyl esters, fatty alcohols, fatty amines and glycerol which are highlighted as bold in schematic, and their further downstream derivatives obtained from further chemical modifications of these basic oleochemicals are highlighted in italics and shown in Fig. 7a and b.

In fact, until the 1980s, almost 95% of natural oils and oils were used in foods and only a small percentage was used in non-food applications such as soap manufacturing and drying oils. It was only after the 1980s that oleochemicals found wide uses in both food and non-food, or technical applications which previously are the domains of “synthetic chemicals” derived from petroleum or better known as petrochemicals. At this moment, oleochemicals are used in the manufacture of such products as foods and specialty fats, soaps and detergents, cosmetics and personal care products, lubricants and greases, drying oil, surface coatings and polymers,

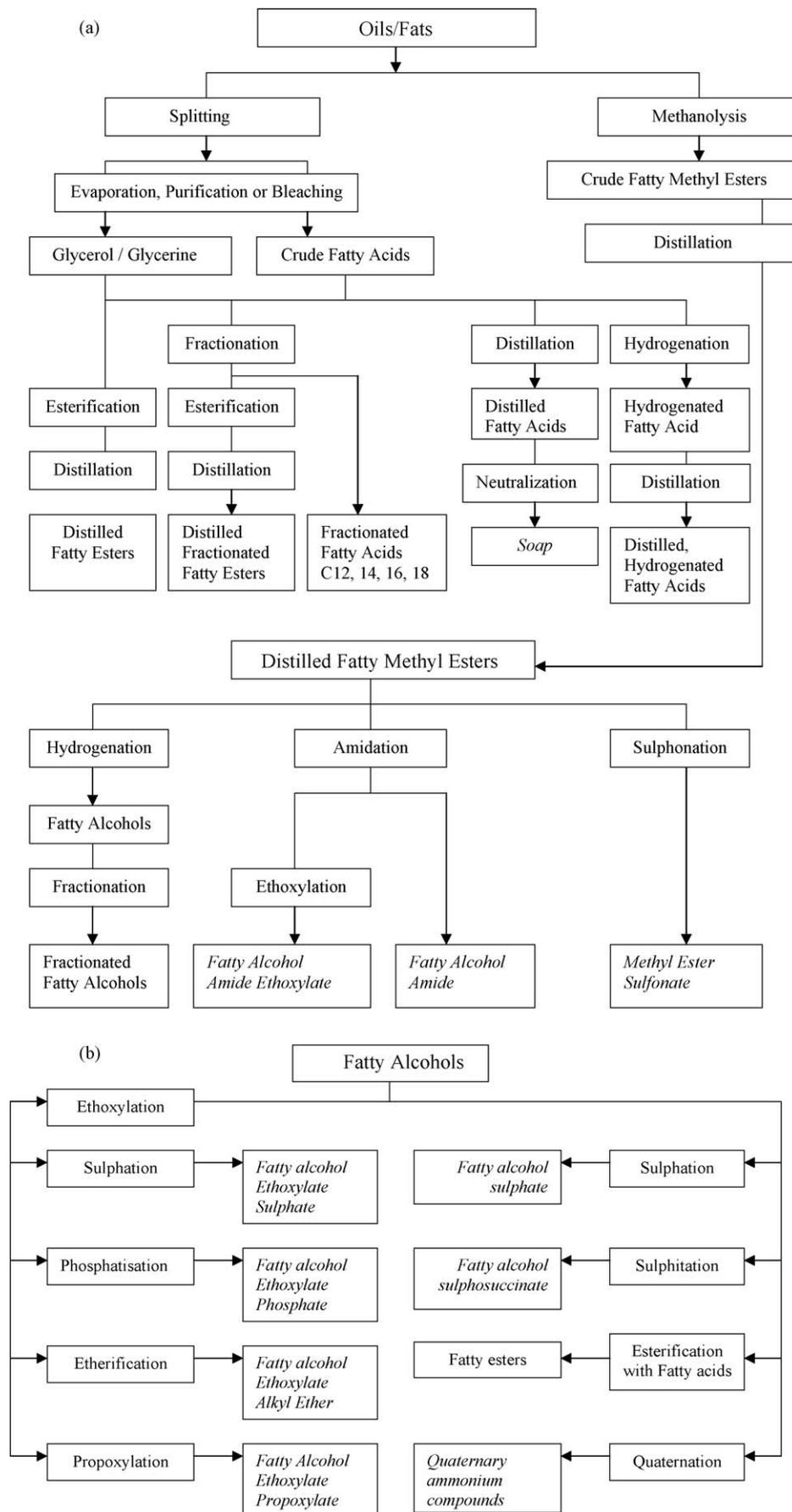


Fig. 7. (a) Basic oleochemicals and downstream oleochemicals and derivatives and (b) basic oleochemicals and downstream oleochemicals and derivatives production flow. Soon [29].

Table 1
Application of oleochemicals.

Industry/Product	Uses
Leather	Softening, dressing, polishing and treating agents
Metal Work and Foundry	Cutting oils, coolants, buffing and polishing compounds
Mining	Surface-active agents for froth floatation of ore and oil-well drilling
Rubber	Vulcanising agents, softeners and mould-release agents
Electronics	Insulation and special-purpose plastic components
Lubricants and Hydraulic Fluids	General and specialty industrial lubricants and biodegradable base oils, hydraulic fluids
Paints and Coatings	Alkyd and other resins, drying oils, varnishes and other protective coatings
Printing and Paper Re-cycling	Printing inks, paper coatings, photographic printing, de-inking surfactants
Plastics	Stabilizers, plasticisers, mould-release agents, lubricants, anti-static agents, antifogging aids, polymerisation emulsifiers
Biofuels	Methyl esters and alcohols
Waxes	Ingredients in waxes and polishes
Soaps & Detergents	Industrial and domestic products, specialty surfactants
Health & Personal Care	Culture media, tableting aids, soaps, shampoos, creams, lotions
Food	Emulsifiers, confectionery and specialty fats for bread, cakes, pastries, margarine, ice-cream and other food products
Animal Feeds	Nutritional supplements

Soon [29].

and biofuels (Table 1). In theory, oleochemicals can replace petrochemicals in all their applications [29]. Why oleochemicals? The reasons are simple First, oleochemicals are derived from renewable resources, as compared to petrochemicals which are obtained from exhaustible or non-renewable petroleum, Secondly, products derived from oleochemicals are more readily biodegradable and hence do not pose a threat to the environment, Thirdly, products derived from petroleum sources use more energy and cause higher emissions of such pollutants as NO_x , SO_2 , CO and hydrocarbons.

3.2.2. De-oil cake

Biomass used for production of biodiesel would generate million tones of residual protein (De-oilcake). The use of protein for non-food applications is currently more limited compared to the utilization fatty acids derivatives. The edible protein can be utilized for production of essential amino acids for animal feeds and human consumption. Some of the nonedible oil seeds cake like jatropha, neem, karanja, etc. would use to produced biopesticides and amino acids for non-food applications. Sanders et al. [30] have reported the application of protein based raw materials for production of 1,2-ethanediamine and 1,4-butanediamine from amino acids. The production of amino acids from de-oil cake would add value to biofuel crops produce in large scale. 1,2-Ethanediamine is produced starting with ethylene by various routes as given in Fig. 8.

1,2-Ethanediamine and 1,4-butanediamine can be synthesized from amino acids such as serine and arginine respectively. Decarboxylation of serine will form ethanolamine, which is converted into diamine by addition of ammonia. Arginine can be hydrolysed to ornithine and urea. Ornithine will form 1,4-butanediamine after carboxylation. Protein based surfactants are the most valuable mild surfactants. Since the structure and properties of the amino acids in the surfactants are similar to the tissue of the skin amino acids, this cause strong affinity and soft feeling on skin. Acyl derivatives from glutamic acid and serine are

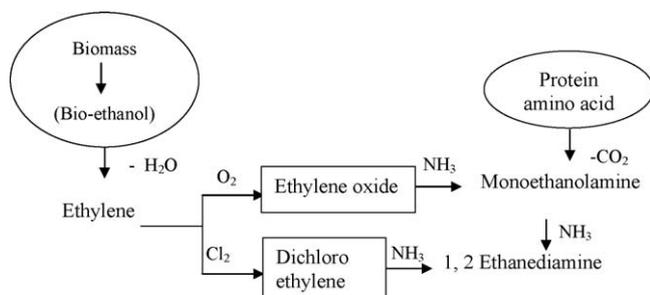


Fig. 8. Production of 1,2-ethanediamine using various routes.

very effective in comparison with conventional surfactants. The production of protein based surfactant involves hydrolysis of protein with sulphuric acid followed by acylation with RCOCl ($\text{R}=\text{C}_{12}\text{--}\text{C}_{18}$) to form acyl amino acid sodium salts which are converted into acylesters of amino acids by esterification with fatty alcohol [30].

4. Second generation biofuels

Second generation biofuels are produced from biomass in a more sustainable fashion, which is truly carbon neutral or even carbon negative in terms of its impact on CO_2 concentrations. In the context of biofuel production, the term 'plant biomass' refers largely to lignocellulosic material as this makes up the majority of the cheap and abundant nonfood materials available from plants [11,31]. At present, the production of such fuels is not cost-effective because there are a number of technical barriers that need to be overcome before their potential can be realized. Plant biomass represents one of the most abundant and underutilized biological resources on the planet, and is seen as a promising source of material for fuels and raw materials. As it is most basic, plant biomass can simply be burnt in order to produce heat and electricity. However, there is great potential in the use of plant biomass to produce liquid biofuels. Plant biomass is comprised mostly of plant cell walls, of which typically 75% is composed of polysaccharides [32]. These polysaccharides represent a valuable pool of potential sugars, and even in traditional food crops such as wheat (*Triticum aestivum*) there is as much sugar tied up in the stems as there is in the starch of the grains. To date, the potential of many crop residues, such as straw and wood shavings, to provide sugar feedstocks for biofuel production has not been realized. However, biofuel production from agricultural by-products could only satisfy a proportion of the increasing demand for liquid fuels. This has generated great interest in making use of dedicated biomass crops as feedstock for biofuel production [22].

Lignocellulosic materials are a collection of feedstocks for advanced biofuels and can be obtained either through hydrolysis and fermentation (i.e. bioethanol) or through gasification (i.e. Fischer-Tropsch bio-diesel, bio-DME and bio-SNG). Typical resources for these fuels are short rotation forestry crops (poplar, willow and eucalyptus), perennial grasses (miscanthus, switch grass and reed canary grass) and residues from the wood industry, forestry and from agriculture. Advanced biofuels, also referred to as 2nd generation biofuels, are carbon-based fuels that are produced by innovative processes mainly using lignocellulosic materials for which commercial utilization is still under development. Bioethanol (advanced) is a substitute of gasoline. It is a full substitute for gasoline in so-called flexi-fuel vehicles. With

hydrolysis, sugars are extracted from lignocellulosic feedstock, after which the sugars are fermented into ethanol. Fischer–Tropsch diesel (FT-diesel) or BTL (Biomass-to-Liquids) is a full substitute of diesel. Lignocellulosic biomass is gasified to produce syngas which is in turn transformed into liquid hydrocarbons, mostly diesel and kerosene. Bio-SNG (Synthetic Natural Gas) is a fuel that can be used in gasoline vehicles with slight adaptations. Lignocellulosic biomass is gasified to produce syngas which is in turn transformed into methane. Bio-DME (Dimethyl Ether) is a fuel that can be used in diesel vehicles with slight adaptations. Lignocellulosic biomass is gasified to produce syngas which is in turn transformed into DME [33].

4.1. Conversion processes for second generation biofuels

There are two main routes available for producing liquid biofuels from biomass; one involves thermochemical processing and the other biochemical processing. Thermochemical processing defines the conversion of biomass into a range of products, by thermal decay and chemical reformation, and essentially involves heating biomass in the presence of different concentrations of oxygen. The clear advantage of thermochemical processing is that it can essentially convert all the organic components of the biomass compared with biochemical processing which focuses mostly on the polysaccharides [11]. This section onwards paper mainly focuses on the conversion processes for lignocellulosic biomass and utilization of combination of technologies for production of other value added chemicals (Fig. 9) and example of some biorefineries based on different feedstocks have been discussed aiming at the integrated utilization of biomass.

4.1.1. Physical conversion

4.1.1.1. Mechanical extraction. Crude vegetable oils are recovered from the oil seeds by applying a mechanical pressure using screw press (expeller). Screw press can be applied in two ways: pre-pressing and full pressing. In pre-pressing, only part of the oil is recovered and the partially de-oiled meal (cake with 18–20% oil) is further treated by solvent extraction. Combined pre-pressing and solvent extraction is commonly applied for oilseeds with high oil

content (30–40%). Full pressing requires 95,000 kPa to squeeze out as much oil as possible, preferably up to 3–5% residual fat for animal materials. Full-pressing can also be carried out in a pre-press and a final press [7].

4.1.1.2. Briquetting of biomass. Agricultural, forestry residues and other waste biomass materials are often difficult to use as biofuels because of their uneven bulky and troublesome characteristics. This drawback can be overcome by means of densification of the residual into compact regular shapes. During densification biomass enclosed in compression chambers presses. There are two major methods of densification, i.e. pressing and maceration. Some time these two processes are combined, in pressing there is a close correlation of an increase in density with an increase in applied pressure in the early stage of compression, but the rate of increase in density fall rapidly as the density of pressed material approaches the density of water. There is no such close correlation of density change and degree of maceration, which may be chopping, grinding, and pulverizing. A coarse chopping of some materials may be as effective as ultrafine grinding. For example tree branches undergo extensive volume reduction when chipped, but fine grinding would provide little, if any, additional reduction in volume [6,7].

4.1.1.3. Distillation. Distillation is the most important method for extracting essential oil and relies on the evaporation of the more volatile constituents of a blend to separate them from the non-volatile parts. Plants are crushed to encourage them to release their oils. The plants are steam distilled, and the essential oils vaporize and rise up with the steam. The vapours are captured, and are allowed to condense back into liquids. A more high tech chemical process is molecular distillation. It is used to produce fragrances that cannot be distilled by conventional methods [7].

4.1.2. Thermo-chemical conversion

Biomass can be converted to energy by mainly two processes. They are either thermo-chemical or biological. The thermo-chemical conversion process includes direct combustion, gasification, liquefaction, and pyrolysis as shown in Fig. 10. When biomass is heated under oxygen deficient conditions, it generates synthesis

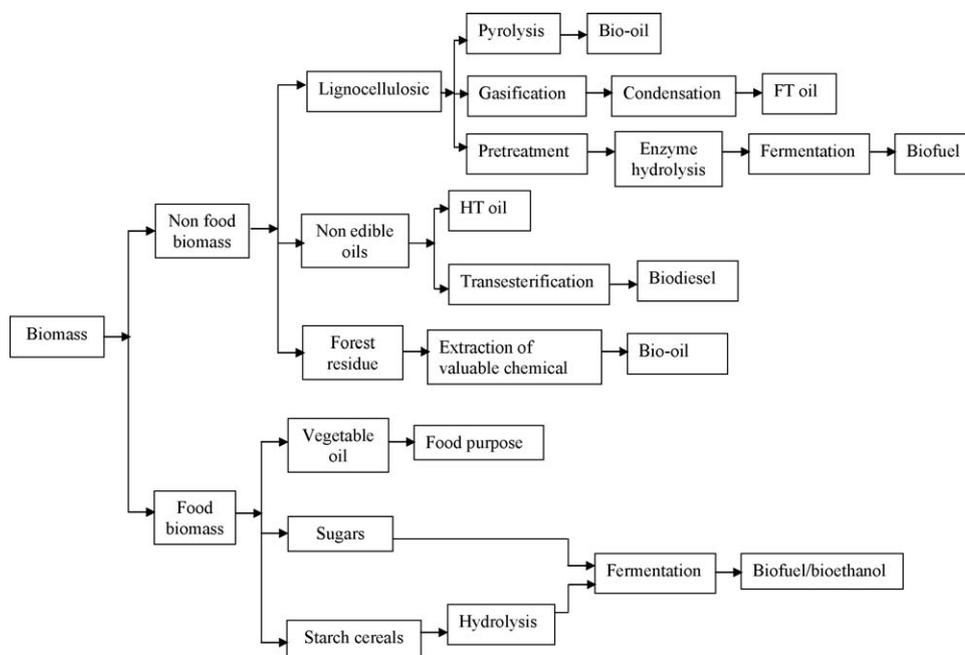


Fig. 9. Second generation biofuel production from biomass.

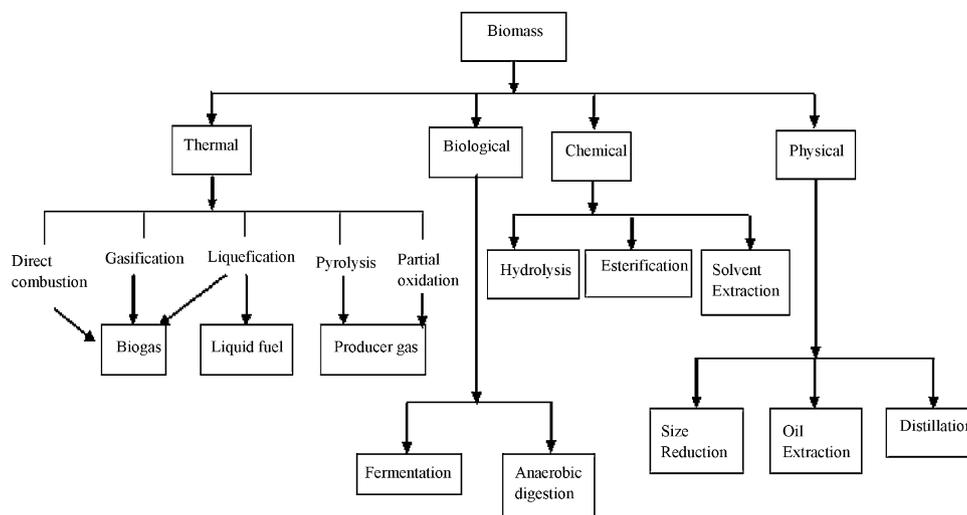


Fig. 10. Thermo-chemical conversion processes.

gas, or syngas, which consists primarily of hydrogen and carbon monoxide. This syngas can be directly burned or further processed for other gaseous or liquid products. In this sense, thermal or chemical conversion of biomass is very similar to that of coal [26].

4.1.2.1. Direct combustion. Combustion is the chemical reaction between a fuel and oxygen which usually takes place in air and is more commonly known as burning. The products are carbon dioxide and water with the release of heat. When the direct combustion of biomass is conducted in a well vented area, biomass burning used for domestic stoves and boilers can be a sound substitute for combustion of conventional fissile fuel. Sulfur emissions (0.05–0.2 wt%) are much lower and the formation of particulate can be controlled at the source [26].

4.1.2.2. Gasification. Generally gasification is not a new technology however its use for the conversion of biomass into a viable fuel has only been investigated for past thirty years. Syngas can be produced from biomass by two routes namely catalytic and noncatalytic. Noncatalytic process requires a very high temperature of operation, as high as 1300 °C, whereas catalytic process can be operated at substantially lower temperature. With more advances in the catalysis, the temperature requirement is expected to go downward further from the current value of about 900 °C [26].

The gasification step involves reacting biomass with air, oxygen, or steam to produce a gaseous mixture of CO, CO₂, H₂, CH₄, and N₂ either known as producer gas or synthesis or syngas, depending on the relative proportions of the component gases [18]. Producer gas is primarily useful as a fuel for stationary power generation, whereas syngas may be, and is presently, used to make a range of fuels and chemical intermediates. For transportation fuels, the main syngas derived routes to fuels are hydrogen by water-gas-shift reaction (WGS) [34], hydrocarbons by Fischer–Tropsch (F-T) synthesis or methanol synthesis followed by further reaction to produce hydrocarbon or oxygenated liquid fuels [33]. The WGS reaction uses CO, H₂O to give H₂ and CO₂. It can be used to upgrade producer gas to syngas by enriching the H₂ content or to produce H₂ as an end product in its own right. F-T synthesis has been used since 1930s to produce hydrocarbon fuels from syngas. The production of methanol from syngas has been practiced since the 1920s [18].

4.1.2.3. Liquefaction. The liquefaction of biomass has been investigated in the presence of solution of alkalis, glycerin, propanol, butanol or direct liquefaction [35]. Liquefaction usually produces water insoluble oils of high viscosity and usually requires solvents,

reducing gases such as CO or H₂ and/or catalysts to be present in addition to biomass [18].

In the field of thermochemical conversion of biomass, lignocellulosic materials can be converted directly to a liquid similar to heavy fuel oils by reacting them with synthesis gas in the presence of suitable catalyst [36]. Aqueous liquefaction of lignocellulosics involves desegregation of the wood ultrastructure, followed by partial depolymerization of the constitutive compounds. In the alkali liquefaction, deoxygenating occurs through decarboxylation from ester formed by hydroxyl group and formate ion derived from carbonate.

Alkali salts such as sodium carbonate and potassium carbonate, can act as catalyst for hydrolysis of macromolecules such as cellulose and hemicellulose into smaller fragments. The heavy oil obtained from the liquefaction process is a viscous tarry lump, which sometimes caused troubles in handling. For this reason, some organic solvents (e.g. propanol, butanol, acetone, methyl ethyl ketone, ethyl acetate) need to be added to the reaction system. All these solvents, except ethyl acetate, may be reproduced from wood during liquefaction. This suggests that the solvent can be recovered for reuse. The oil yield is reported to be higher with the catalytic aqueous liquefaction than with the non-catalytic aqueous liquefaction. The average oil yield is around 31% in the non catalytic process and 63% in the catalytic process [35]. In the liquefaction process, the amount of solid residue increased in proportion to the lignin content. Lignin is a macromolecule, which consists of alkylphenols and has a complex three dimensional structure. It is generally accepted that free phenoxy radicals are formed by thermal decomposition of lignin above 525 K and that the radicals have a random tendency to form solid residue through condensation and polymerization.

Bio-oil obtained from air dried wood by high pressure liquefaction (HPL) result in a complex mixture of volatile organic acids, alcohols, aldehydes, ethers, esters, ketones, and non volatile components. These oils could be upgraded catalytically to yield an organic distillate product which is rich in hydrocarbons and useful chemicals. Compared to bio-oil obtained from the fast pyrolysis method, their yield from HPL process is much lower and highly viscous [35].

4.1.2.4. Pyrolysis. The pyrolysis is thermal degradation of biomass by heat in the absence of oxygen, which results in the production of charcoal (solid), bio-oil (liquid), and fuel gaseous products.

The pyrolysis of biomass has been studied with the final objectives of recovering a biofuel with medium-low calorific

power [35]. Depending on the operating conditions, the pyrolysis process can be divided into three subclasses: (a) Conventional pyrolysis, (b) Fast pyrolysis, and (c) Flash pyrolysis.

4.1.2.4.1. Conventional pyrolysis. Conventional pyrolysis occurs under a slow heating rate (0.1–1 K/s) and residence time is 45–550 s and massive pieces of wood. In the first stage of biomass decomposition which occurs in between 550 and 950 K is called pre-pyrolysis. During this stage, some internal rearrangement such as water elimination, bond breakage, appearance of free radicals, formation of carbonyl, carboxyl and hydroperoxide group take place [37]. The second stage of solid decomposition corresponds to the main pyrolysis process. It proceeds with a high rate and leads to the formation of pyrolysis products. During the third stage, the char decomposes at a very slow rate and it forms carbon rich solid residues.

4.1.2.4.2. Fast pyrolysis. It occurs in the high temperature range of 850–1250 K with fast heating rate (10–200 K/s), short solid residence time (0.5–10 s) and fine particle (<1 mm). The fast pyrolysis is recommended for production of liquid and/or gaseous products. In fast pyrolysis process biomass decomposes to generate vapours, aerosol, and some charcoal like char. After cooling and condensation of vapours and aerosol a dark brown mobile liquid is formed that has heating value that is half that of conventional fuel oil. Fast pyrolysis produced 60–75% of bio-oil, 15–25% solid char and 10–20% non condensed gases depending upon feedstocks [37].

4.1.2.4.3. Flash pyrolysis. It differs strongly from that of conventional pyrolysis, which is performed slowly with massive pieces of wood. It occurs in the temperature range of 1050–1300 K, fast heating rate (>1000 K/s), short residence time (<0.5 s) and very fine particle (<0.2 mm). Bio-oil production from biomass pyrolysis is typically carried out via flash pyrolysis [35] the produced oil can be mixed with the char to produce bioslurry. Bioslurry can be more easily fed to the gasifier (gasifier condition: 26 bars; 927–1227 K) for efficient conversion to syngas. The conversion of biomass to crude oil can have an efficiency of up to 70% for flash pyrolysis process. The so called bio-crude can be used in engines and turbines. Its use as feedstocks for refineries is also being considered [35,38].

4.1.3. Hydrotreating of vegetable oils/green diesel

Vegetable oils are renewable feedstock currently being used for production of biofuels from sustainable biomass resources. The existing technology for producing diesel fuel from plant oils such as rapeseed, soybean, canola and palm oil are largely centered on transesterification of oils with methanol to produce fatty acid methyl esters (FAME) or biodiesel. The future widespread use of biofuels depends on developing new process technologies to produce high quality transportation fuels from biologically derived feedstocks. These new biofuels need to be compatible with the existing fuel and transportation infrastructure to be economically feasible.

Researchers around the world are in pursuit of different processing routes to convert vegetable oils into a high quality diesel fuel or diesel blend stock that would fully compatible with petroleum derived diesel fuel. The isoparaffin-rich diesel known as 'green diesel' is produced from renewable feedstock containing triglycerides and fatty acids by process of catalytic saturation, hydrodeoxygenation, decarboxylation and hydroisomerization. This technology can be widely used for any type of oil feedstock to produce an isoparaffin-rich diesel substitute. This product, referred to as green diesel, is an aromatic and sulfur free diesel fuel having a very high cetane blending value. The cold flow properties of the fuel can be adjusted in the process to meet climate-specific cloud point specifications in either the neat or blended fuel [39]. Table 2 compares the Green diesel fuel properties with petroleum

Table 2
Green diesel fuel properties.

	Petroleum ULSD	Biodiesel (FAME)	Green diesel
% oxygen	0	11	0
Specific gravity	0.84	0.88	0.78
Sulphur (ppm)	<10	<1	<1
Heating value (MJ/kg)	43	38	44
Cloud point (°C)	–5	–5 to +15	–10 to 20
Distillation (°C)	200–350	340–355	265–320
Cetane	40	50–65	70–90
Stability	Good	Marginal	Good

Kalnes et al. [39].

ULSD: is ultra low sulphur diesel.

diesel, and biodiesel. Green diesel has a higher cetane value and good cold flow properties. It is also has excellent storage stability and is completely compatible for blending with the standard mix of petroleum derived diesel fuels. In contrast to fatty acid methyl esters, green diesel properties do not depend on feed origin and process configuration and the fully deoxygenated biofuel is readily blended with diesel fuel.

4.1.4. Bio-oil

Bio-oil/pyrolysis oil is produced by fast pyrolysis process. In this process, organic class of compounds, such as cellulose, hemicellulose, and lignin, etc. are thermally decomposed at moderate temperature (400–600 °C) in absence of oxygen to produce liquid product viz. bio-oil (60–70%), char (13–25%), and gas such as CO, H₂, light hydrocarbons (13–25%). The yield and chemical composition of bio-oil depends upon feed stocks and process condition: particle size of biomass (2–5 mm), residence time (0.1–2 s), and reactor type. In general, reactor types which are presently used are; fluidized bed reactor, circulating fluid bed, fast fluidized bed, etc. (Fig. 11). The bio-oil is a dark brown viscous, corrosive and acidic with distinctive smoky odor used as fuel for boiler, gas turbine, diesel engines, furnaces and stationary engines. Bio-oil has a complex chemical composition contained chemical products of lignocelluloses biomass like aliphatic alcohols/aldehydes, furanoids, pyranoids, benzenoids, fatty acids and high molecular mass hydrocarbons, etc. these constituents are mixed with water (25–45%), which is formed in pyrolysis process to form an emulsion with organic constituents. Therefore a wide range of "Green

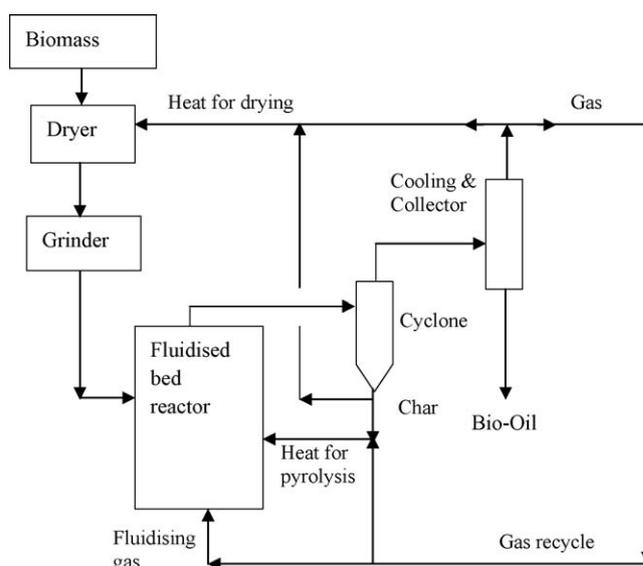
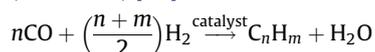


Fig. 11. Fluidized bed fast pyrolysis process.

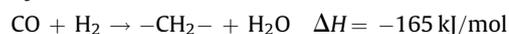
Chemicals” can be extracted from bio-oil by solvent extraction. The Supercritical fluid extraction such as supercritical CO₂ can selectively extract the value added chemicals from bio-oil. These chemical compounds can be utilized for natural resin, food flavors, wood preservatives, slow release fertilizer, pharmaceuticals, etc. [40–45].

4.1.5. FT oil or green motor fuel from biomass

Franz Fisher and Hans Tropsch first studied conversion of syngas (CO + H₂) in to large number of useful organic compounds in 1923. The syngas produced by gasification of biomass can be converted into large number of organic compounds. The process of converting CO and H₂ mixture into liquid fuels or hydrocarbons over transition metal catalyst is known as Fisher-Tropsch oil (FT oil) or Green motor fuel. The FT synthesis processes have flexibility in feed stocks (coal, biomass, natural gas) and the fuel produced by FTS process contains low sulphur. The major drawback of FTS process is the polymerization in the process which yields very high molecular mass waxes which need to be hydrocracked to produce green diesel. Some of the recent publication indicates that the use of FT process technology for biomass conversion to synthetic hydrocarbon may be promising and carbon neutral alternative to conventional fuels. The flow chart for FT process is shown in Fig. 12. Biomass gasification can provide the opportunity to convert biosyngas into green fuels such as H₂ and FT oil. The biomass gasification produces biosyngas, which contains degraded products of biomass such as carbohydrate (cellulose, hemicellulose) and lignin. The gas mixtures consists of carbon monoxide (28–36%), carbon dioxide (22–32%), hydrogen (21–30%), methane (8–11%), benzene/toluene/xylene (0.84–0.96), ethane (0.16–0.22), tar (0.15–0.24) [33]. The FTS reaction is given below.



where n is the average length of hydrocarbon chain and m is the number of hydrogen atom per carbon. All the reactions are exothermic and the product is a mixture of different hydrocarbons in that paraffin and olefins are main parts. In FTS one mole of CO reacts with two mole of H₂ in the presence of catalyst to form a hydrocarbon chain.



The $-\text{CH}_2-$ is the building block for the longer hydrocarbons. The products from FTS are mainly aliphatic straight chain hydrocarbons. Besides the straight chain hydrocarbons, branched hydrocarbons and primary alcohol are also formed in minor quantities. The product distribution obtained from FTS include light hydrocarbon methane (CH₄), ethylene (C₂H₄) and ethane (C₂H₆), LPG (C₃–C₄), propane (C₃), butane (C₄), gasoline (C₅–C₁₂), diesel fuel (C₁₃–C₂₂) and wax (C₂₃–C₃₃). Some raw biomass contained traces of contaminants such as NH₃, H₂S, HCl, dust and alkali in ash. The distribution of products depends upon the

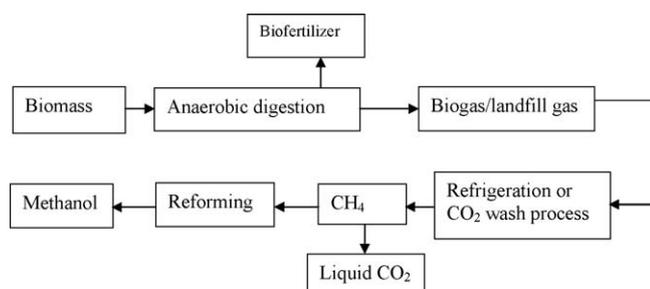


Fig. 12. Biomass based FT synthesis process.

Table 3

Ethanol from renewable lignocellulosic feedstocks.

S. no	Feedstocks	Ethanol yield, lit/tones biomass
1	Cane bagasses	424
2	Corn stover	428
3	Rice straw	416
4	Forest residue	310
5	Saw dust	382

catalyst and process parameters such as temperature, pressure, and residence time [45].

4.1.6. Bioethanol from lignocellulosic biomass

Biological conversion technologies are based on microbial and enzymatic process for producing sugars from biomass such as lignocellulosic, starch, cellulosic. The sugars later can be converted into alcohol and other solvents of interest to fuel and chemicals. For example, yeast based fermentation has shown good yield for ethanol from sugar or starch crops (Table 3). Solid waste has been used to produce methane through anaerobic digestion in fabricated digesters or landfill. The production of ethanol from corn, sugarcane by biochemical means has already been commercially established. It is essential to hydrolyze lignocellulose for biological conversion. Enzymatic hydrolysis of lignocellulosic biomass required some research and developmental work to increase the yield of alcohol.

The conversion of biomass feed stocks to liquid fuels such as ethanol requires a number of basic unit operations including pretreatment, enzyme production, hydrolysis, fermentation and ethanol recovery. Fig. 13 gives details of steps required for the conversion of lignocellulosic biomass to ethanol and utilization of intermediate products for value added chemicals. Biomass ethanol research emphasizes on reduced costs which requires improved cellulose and hemicellulose conversion to sugar, combined xylose and glucose fermentation, lower pretreatment energy requirements, conversion of lignin to value added products, and efficient separation process for alcohol [25,26].

Agricultural residues, forest residue, post harvest processing of Industrial food crops generate enormous amounts of carbohydrate containing lignocellulosic waste [46]. This lignocellulosic biomass consists of three main structural units: cellulose, hemicellulose and lignin. Cellulose is crystalline glucose polymer and hemicellulose is amorphous polymers of xylose, arabinose, and lignin a large poly aromatic compounds. The conversion of complex lignocellulosic biomass to alcohol is more difficult as compared to starch based feedstocks. The conversion of lignocellulosic biomass to alcohol requires three step process i.e. pretreatment of biomass, acid or enzymatic hydrolysis and fermentation/distillation. The pretreatment processes separate xylose and lignin from the crystalline cellulose [47]. The steam explosion process is an efficient pre-processing method for converting lignocellulosic biomass. In this process biomass sample is placed in a pressure

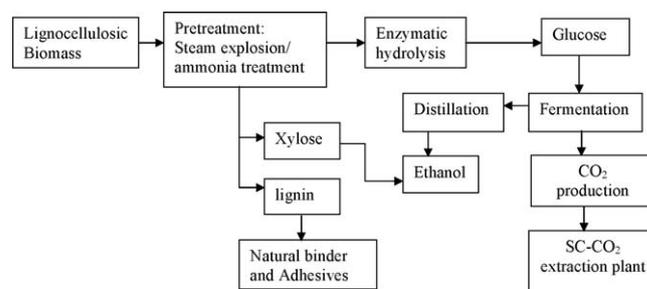


Fig. 13. Conversion of lignocellulosic biomass to ethanol.

vessel (i.e. digester) and vaporized using saturated steam for a short time (20 s to 20 min) at a temperature 473–543 K and high pressure 14–16 bar. The pressure in digester is then dropped quickly by opening the steam and the material is exposed to normal atmospheric pressure to cause explosion which disintegrate lignocellulosic biomass. Different types of devices are available for steam explosion. Steam explosion causes the hemicellulose and lignin from the wood to be decomposed and converted into low molecular weight fractions which can be easily extracted. Therefore most of the water soluble fraction of hemicellulose can be removed by water extraction. At the same time, a part of the low molecular weight fraction of lignin is also extracted. The xylose can be fermented to ethanol and the lignin can be further processed to produce other fuels. The crystalline cellulose remains solid after the pretreatment and later break down to glucose by enzymatic hydrolysis process. The glucose is further fermented to alcohol and the hemicellulose fraction is converted to xylose. The conversion of xylose to ethanol is a difficult process, therefore, pretreatment is necessary to reduce the crystallinity of cellulose to lessen the average polymerization of the cellulose and hemicellulose–lignin sheath that surround the cellulose and to increase available surface area for the enzyme to attack [25].

Ethanol can be blended with gasoline to produce an oxygenated fuel with lower hydrocarbon and green house gas emissions, certain aldehydes are increased, which could cause health issues. Automobiles can be operated on ethanol/gasoline blends from 5% to 25% without any alterations in engine equipments or setting [25]. The fuel properties of alcohol blended gasoline and pure gasoline are given in Table 4. The major engine operation issue with alcohol blended fuels is fuel quality, volatility, octane number, cold start, hot operation, and fuel consumption.

4.1.7. Chemical conversion

4.1.7.1. Chemical hydrolysis. The important specific factors in chemical hydrolysis are surface to volume ratio, acid concentration, temperature, and time. The surface to volume ratio is especially important, in that it also determines the magnitude of the yield of glucose. Hence smaller the particle size the better the hydrolysis in terms of the extent and rate of reaction. With respect to the liquid to solid ratio, the higher the ratio the faster the reaction [48].

4.1.7.2. Solvent extraction. Solvent extraction involves different unit operations: extraction of the oil from the oil seeds using hexane as a solvent; evaporation of the solvent; distillation of the oil–hexane mixture (called miscella); and toasting of the de-oiled meal. In special cases, other solvents can be used: halogenated solvents (mostly dichloromethane), acetone, ethanol or isopropanol. Supercritical extraction can also be performed using CO₂ [7].

Extraction refers to a process in which the desired substance is selectively removed from the raw materials by allowing the desired substance to dissolve into the solvent, and subsequently recovering the substance from the solvent. To remove the particular substance from biomass, extraction and separation are both essential. Typically biomass (wood, wheat straw, aromatic grasses, etc.) contains high

volume of macromolecular compounds (polysaccharide, cellulose, hemicellulose, and lignin) called primary metabolite. The other low volume and high value biochemical molecules like terpenoids, waxes, resins, sterols, and alkaloids are known as secondary metabolites or extractive biomass. In the biorefinery process these chemicals are initially extracted from biomass by using solvent extraction or supercritical fluid extraction. Recently Dewarte et al. [49], Clark et al. [16] reported integrated straw based biorefinery and isolated high value chemicals like waxes, polycosanol, and sterol by using supercritical carbon dioxide. Supercritical fluid extraction can be used for extraction of aromatic woods (cedar wood, sadal wood, pine wood) to isolate extractives. The extracted lignocellulosic biomass is further used for hydrolysis and fermentation for production of biofuels. The other solvent like, ethanol, acetone, methanol, water can be used to isolate desired extractive from biomass [7].

4.1.7.3. Supercritical water conversion of biomass. A supercritical fluid is defined as a substance that is at temperature and pressure conditions which are above its vapour liquid critical point (for water it is 644 K and 22 MPa; for CO₂ it is 304 K and 7.4 MPa). At supercritical conditions a fluid is neither liquid nor gas as it can not be made to boil by decreasing the pressure at constant temperature, and it would not condense by cooling at constant pressure [50].

Supercritical fluid processing of biomass to chemicals represents an alternative path to acid hydrolysis, enzymatic hydrolysis of cellulose to sugars. With acid hydrolysis acid recovery is a costly and polluting issue. Enzymatic saccharification needs pretreatment of lignocellulosic biomass. Supercritical water can quickly convert cellulose to sugar and convert biomass into a mixture of oils, organic acids, alcohol and methane. In supercritical (i.e. 300–644 K; pressure 200–250 bar) and near critical state (523–573 K) acid (H⁺) and base components (OH⁻) of water are separate and dissolve in the biomass. The dissolved supercritical water breaks the bonds of cellulose and hemicellulose rapidly to produce small sugar molecules, glucose, xylose and oligosaccharide [51,52]. These properties make supercritical water a very promising reaction medium without using any catalyst for the conversion of biomass to value added products. The scheme of supercritical water conversion of biomass and integral utilization side streams of the process is shown in Fig. 14. Supercritical water gasification technology has been demonstrated for conversion of cellulose into glucose in the range of 10–20 s and above 45 s pyrolysis start. As temperature increases to 873 K supercritical water becomes strong oxidant and results in complete disintegration of the substrate structure by transfer of oxygen from water to the carbon atoms of the substrate. The hydrogen atom of water is set free and form hydrogen. Supercritical water also breaks the cellulosic bonds and also formed gaseous products. The typical overall reaction for biomass is as follows [53].

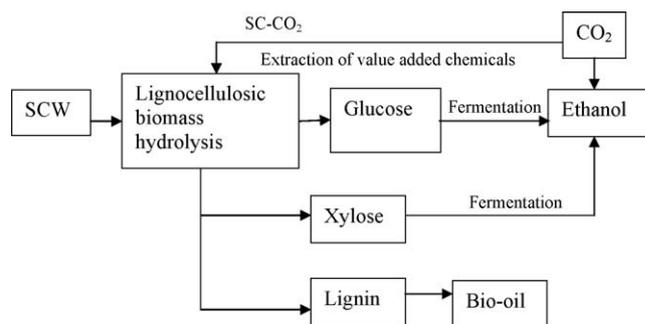
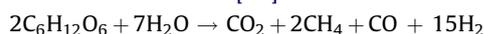


Fig. 14. Supercritical water conversion of biomass.

Table 4
Fuel properties of ethanol, gasoline, blended gasoline.

Property	Ethanol	Gasoline	E ₁₀	E ₂₀
Specific gravity	0.79	0.72–0.75	0.73–0.76	0.74–0.77
Heating value	76000	117000	112900	109000
Vapor pressure	17	59.5	64	63.4
Oxygen content	35	0	3.5	7

Shelley [25].

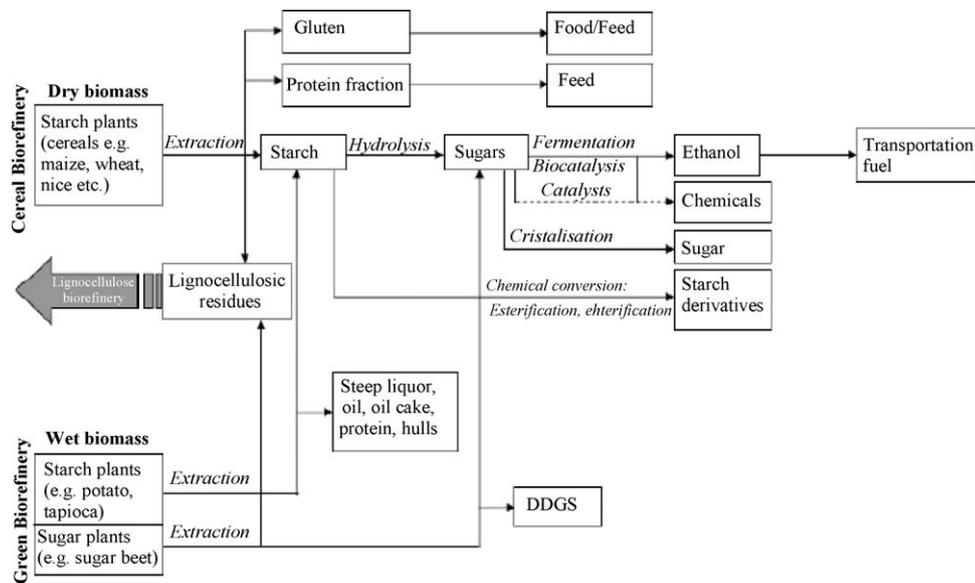


Fig. 15. Green biorefinery. www.biorefinery.euroview.eu [52].

5. Types of biorefinery

5.1. Green biorefinery

A green biorefinery is a multiproduct system which handles its refinery cuts, products, and fractions in accordance with the physiology of the corresponding plant material as described by Kamm and Kamm [21], Fernando et al. [12] and illustrated in Fig. 15. A green biorefinery uses natural wet feedstocks derived from untreated products, such as grass, green plants, or green crops as inputs, which are produced in large quantities in green plants. The first step of the refinery is to treat the green biomass substances in their natural form using wet-fractionation to produce a fiber-rich press cake and a nutrient-rich green juice. The press cake contains cellulose, starch, valuable dyes and

pigments, crude drugs, and other organics, whereas the green juice includes proteins, free amino acids, organic acids, dyes, enzymes, hormones, other organic substances, and minerals. The pressed cake can be also used for the production of green feed pellets, as a raw material for the production of chemicals, such as levulinic acid, and for conversions to syngas and synthetic fuels.

5.2. Forest and lignocellulosic based biorefinery

Lignocellulosic materials contain two types of polysaccharides, cellulose and hemicellulose, bound together by a third component, lignin. LCB consists of three basic chemical fractions, (i) hemicellulose, sugar molecule of mainly pentoses, (ii) cellulose, a glucose polymer, (iii) lignin, polymer of phenols [54]. An overview of potential products of LCB is shown in Fig. 16. In LCB

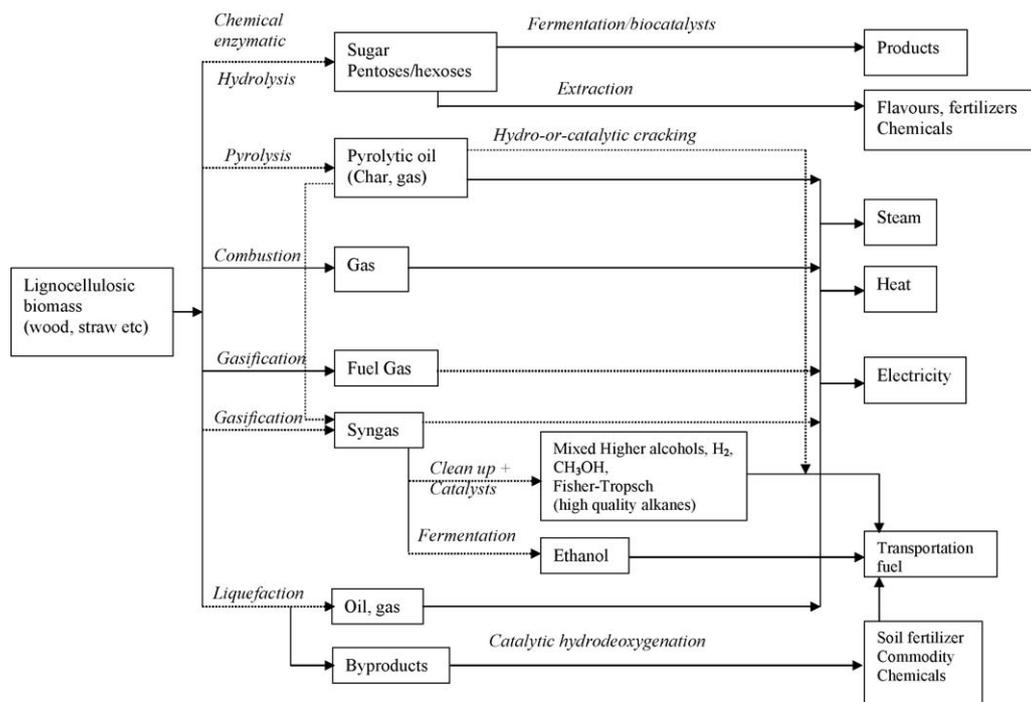


Fig. 16. Forest based and lignocellulosic biorefinery. www.biorefinery.euroview.eu [52].

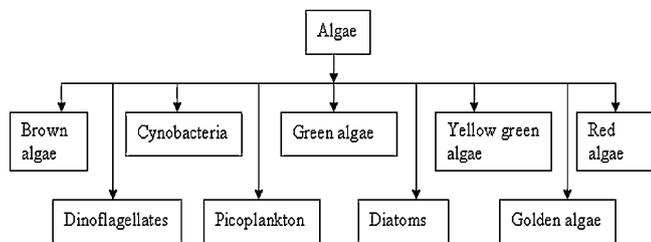


Fig. 17. Classification of algae species.

mainly uses hard fibrous plant materials generated by lumber or municipal waste. In the initial step plant material is cleaned and broken down into three fractions (hemicellulose, cellulose, and lignin) using chemical digestion or enzymatic hydrolysis. Hemicellulose and cellulose can be produced by alkaline (caustic soda) and sulfite (acidic, bisulfite, alkaline, etc.). The sugar polymers (cellulose and hemicellulose) are converted to their component sugars through hydrolysis. In case of hemicellulose, it consists of short, highly branched chains of sugars. It contains five carbon sugars usually D-xylose and arabinose, six carbon sugars and uronic acid. The hydrolysis of cellulose to glucose can be carried out either by enzymatic processing or chemical processing which produces useful products such as ethanol, acetic acid, acetone, butanol, and other fermentation products. Although the hemicellulose and cellulose fractions have numerous uses it is not yet the case for lignin. However, there are still some unsatisfactory parts within the LCB, such as utilization of lignin as fuel, adhesive or binder. It is unsatisfactory because the lignin scaffold contains considerable amounts of mono-aromatic hydrocarbons which, if isolated in an economical way, could add a significant value to the primary processes. Because the primary technologies would generate primary chemicals from which industry could make a wide range of fuels, chemicals, materials, and power. Therefore five stages have been suggested: sugar stage, thermochemical or

syngas stage, biogas stage, carbon rich chains, and plant products. The concept of LCB based on these stages is described in Fig. 16.

5.3. Aquatic or algae-based biorefinery

Algae are photosynthetic microorganisms that convert sunlight, water and carbon dioxide to lipids or triacylglycerol. The lipids may include neutral lipids, polar lipids, wax esters, sterols and hydrocarbons as well phenyl derivatives such as tocopherols, carotenoids, terpenes, quinones, and phenylated pyrole derivatives such as chlorophylls. Algae have high growth rates and tolerance to varying environmental conditions. They can survive and reproduce in low quality high saline water [6]. This feature has allowed algae to be used in wastewater treatment plants for sludge treatment (Gray). In addition, since they have high CO₂ tapping and fixation ability, so the algae can be utilized to reduce carbon dioxide emission from power plants and other industries with high carbon dioxide emission [55]. Algae or cyanobacteria can be used in bioreactors to reduce CO₂ emission from power plants and use the algae biomass for oil extraction and biodiesel production. There are over 40,000 species of algae have been identified and many more yet to be identified, algae are classified in multiple major groupings and its classification is shown in Fig. 17.

Algae synthesize fatty acids principally for esterification of glycerol based membrane lipids which constitutes about 5–20% of their dry cell weight (DCW). Fatty acids include medium chain (C₁₀–C₁₄), long chain (C₁₆–C₁₈) and very long chain (≥C₂₀) species of fatty acid derivatives. Hydrocarbons and other types of neutral lipid are found in algae at a quantity less than 5%. *Bortyococcus braunii* has been shown to produce large quantities of (upto 80% DCW) of very long chain (C₂₃–C₂₀) hydrocarbons, similar to those found in petroleum and thus explored as feedstocks for biofuel and biomaterials. Oil content of some algae species exceeds 80% of the dry weight of algae [56]. Agricultural oil crops such as soybean, rapeseed and oil palm are widely used to produce biodiesel. For

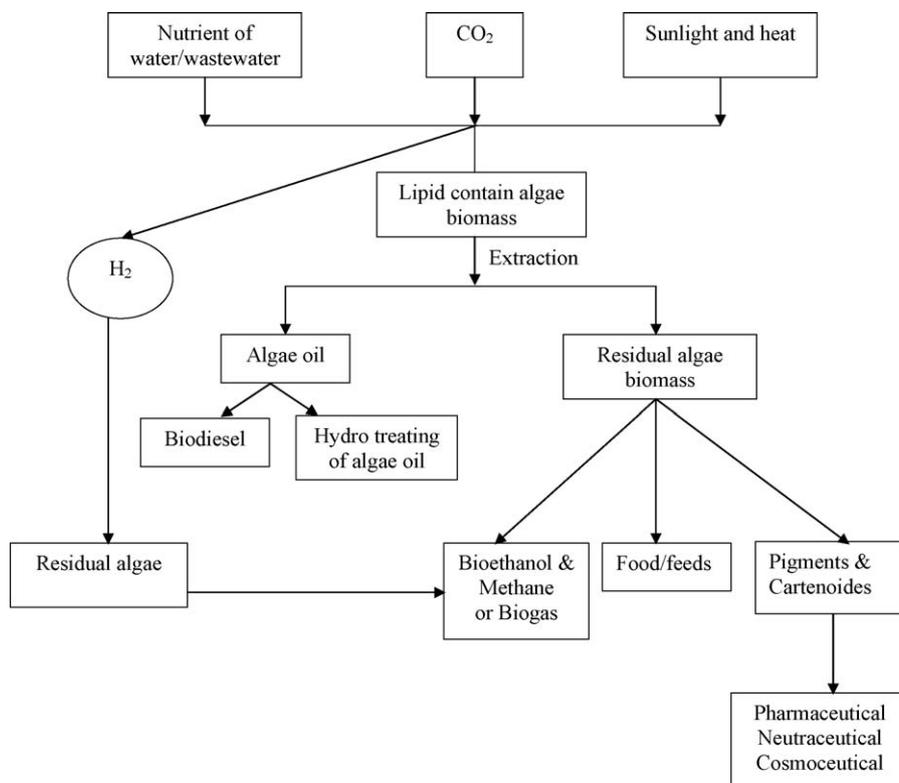


Fig. 18. Algae bio-refinery.

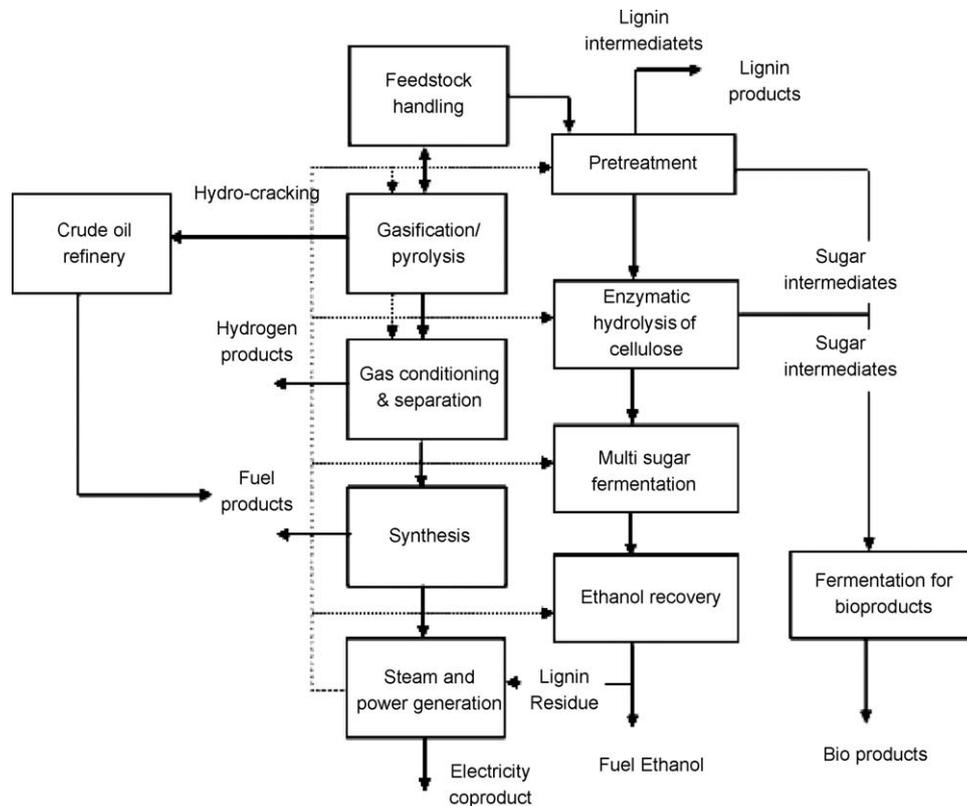


Fig. 19. Schematic of an integrated biorefinery. Fernando et al. [12].

example, palm oil, one of the most productive oil crops yields only 6000 l of oil per hectare, whereas microalgae oil yield per hectare is around 58,700 l/ha [57]. The potential advantages of algae as feedstocks (biofuels and biomaterials) for biorefinery are as follows (Fig. 18).

(1) Algae synthesize and accumulate large quantities of neutral lipids/oil (20–50% DCW), (2) High growth rates (1–3 doublings/day), (3) Thrives in saline/brackish water/coastal sea water, (4) Algae tolerate marginal lands (e.g. desert, arid and semi arid land) that are not suitable for conventional agriculture, (5) Utilize growth nutrients such as nitrogen and phosphorus from variety of wastewater sources (e.g. Agricultural run off, industrial and municipal waste water), (6) Sequester CO₂ from flue gases emitted from fossil fuel fired power plants and other sources there by reducing emissions of a major greenhouse gas, (7) Produced value added co-products or by products (e.g. biopolymers, proteins,

polysaccharides, pigments, animal feed, fertilizer and H₂). (8) Algae can be grown in suitable culture vessel (photo-bioreactor) throughout the year with an annual biomass production.

5.4. Integrated biorefinery

The biorefinery types that have been discussed previously are based on one conversion technology to produce various chemicals. A biorefinery is a capital-intensive project, and when it is based on just one conversion technology, as is the case for the previously described biorefineries, it increases the cost of outputs (or products) generated from such biorefineries. Hence, several conversion technologies (thermochemical, biochemical, etc.) can be combined together to reduce the overall cost, as well as to have more flexibility in product generation and to provide its own power. Fig. 19 provides a schematic of an integrated biorefinery.

Table 5

Physico-chemical properties of bo-oil produced from different biomass.

Properties	Wood	Cereals (wheat)	Rapeseed Crop biomass	Sugar cane bagasses
Density	111–1250	1233	984	1211–1160
Water content % (w/w)	15–30	23.3	<0.05	13.8
pH	2.8–3.8	2.8	3.2	2.7
Elemental analysis (wt% moisture free)				
C	55.3–63.5	58.4	69–72	54.60
H	5.2–7.2	6.0	9.8–10.8	6.45
N	0.07–0.39	0.1	3.3–5.4	0.73
S	0.0–0.05	–	13.1–14.6	<0.10
O	–	–	–	–
Ash	0.03–0.3	0.08	–	0.05
Viscosity (cP)	44–115	50	36	4.1–116.5
HHV (MJ/kg)	22.5–30.2	16.6	35.55–37.85	22.4
Flash point (°C)	56	>106	83	<90

O can be calculated from difference of C, H, N and S.

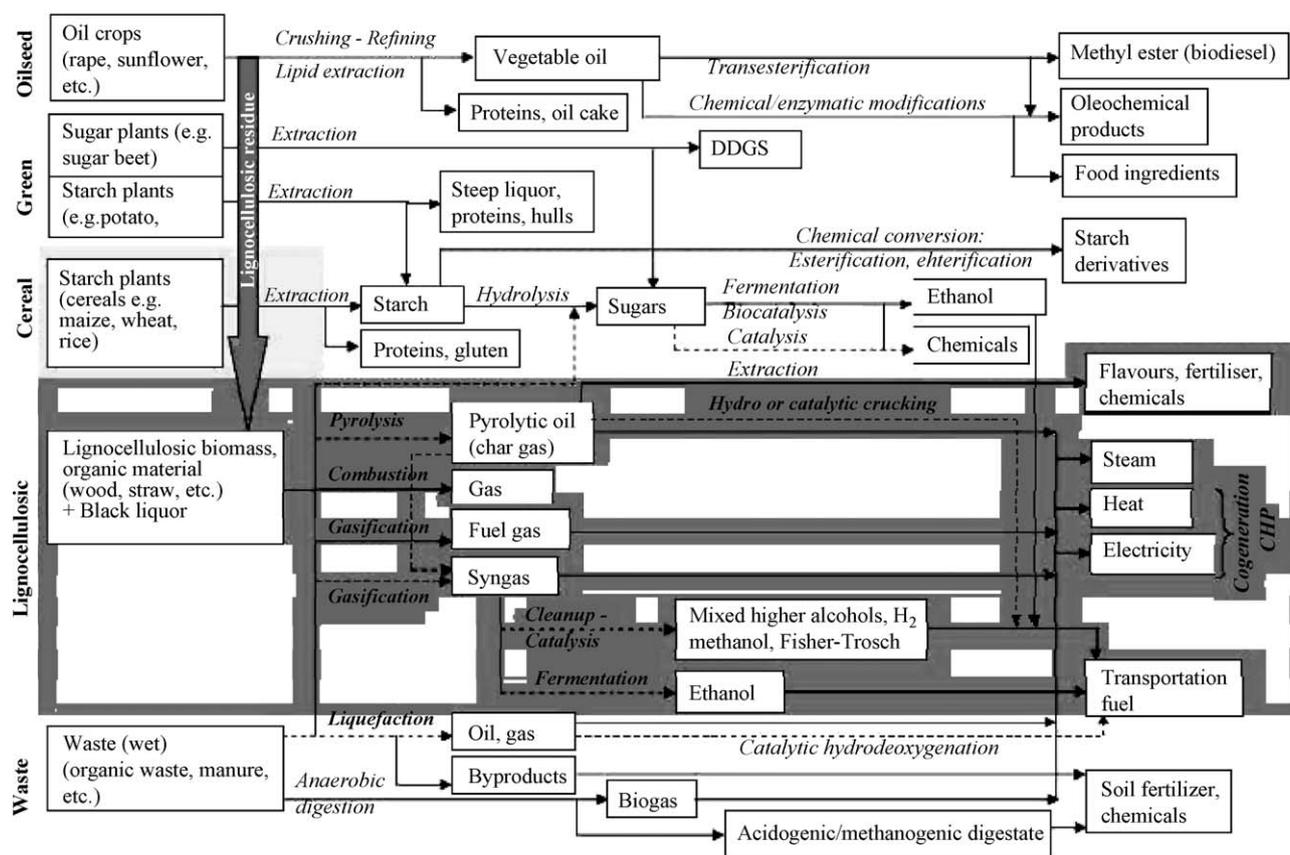


Fig. 20. Integrated biorefinery. www.biorefinery.euroview.eu [52].

Three different platforms, namely: thermochemical, sugar, and nonplatform or existing technologies are integrated. An integrated biorefinery produces various products, which include electricity produced from thermochemical and bioproducts from the combination of sugar and other existing conversion technology platforms.

An emerging concept in the biorefinery arena is conversion of bio-oil, the product from biomass pyrolysis, which could be routed via a conventional petrochemical refinery to generate various chemicals, the typical schematic of the process is shown in Fig. 20. The advantage of this route is that all necessary infrastructures for the separation and purification of products generated are already in place. This concept makes perfect sense since most petroleum refineries are well equipped to handle variable feedstock with the assumption that no two batches of crude oil are the same. Table 5 gives the composition of bio-oil compounds. Bio-oil chemical properties vary with the feedstock but woody biomass typically produces a mixture of 30% water, 30% phenolics, 20% aldehydes and ketones, 15% alcohols, and 10% miscellaneous compounds [58]. A process known as hydrodeoxygenation (HDO) could be applied to replace oxygen by hydrogenation of the raw bio-oils. After several HDO treatment steps the bio-oil could be transformed into a liquid hydrocarbon with properties similar to those of petroleum crude oil. The deoxygenated bio-oils can potentially be refined in existing petroleum refineries, with only minor adjustments to the current petroleum industry refinery infrastructure that is set up for hydrodesulfurization (HDS) process [59].

6. Conclusions

The paper has discussed first and second generation biofuel, concept of biorefineries, different types of biorefineries, and

associated technical challenges. However, growing concerns over first generation biofuels in terms of their impact on food prices and the environment have led to an increasingly bad press in the last year. The unfortunate effect is that biofuel is starting to generate resistance particularly in poor countries with environmental agendas. As the replacement of fossil fuels takes place irrespective of these concerns, the way to avoid the negative effects of producing biofuels from food supplies is to make lignocellulosic-derived fuels available within the shortest possible time (i.e. second generation biofuels). However the immediate use of first generation biofuels involves putting in place logistic changes to use biofuels. This commitment to biofuels in the present will make the transition to the second generation biofuels more economically convenient. But at present the technology to produce these replacement fuels is still being developed. Biorefineries based on lignocellulosics will be able to access a much wider variety of feedstock, including forest biomass. Therefore, there is a need to integrate process operation, reactor and catalyst design to improve the effectiveness of different processes used for bioproducts and biofuels production in a typical biorefinery system. The main objective of the biorefinery is to produce multiple products using combination of technologies. Moreover the commitment of the chemistry, particularly the organic chemistry, needed for the concept of bio-based products and biorefinery systems and to force the combination of the biotechnological and chemical conversion of substances.

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