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Potential Sources of Second and Third Generation Biofuels

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Abstract

Supportable financial and industrial advancement needs impregnable, suitable supplies of energy. The first-generation biofuels seem to be unmaintainable because of the possible stress that their formulation places on food supplies. So, the significant development made to fulfill the economic and technical challenges. Second and third generation biofuels manufacturing will pay more attention to full commercial and economic development. The use of organic waste for the fabrication of biomass also raises sustainability of 3rd generation biofuels as it decreases the emission of greenhouse gas and dumping problems. This review critically evaluates profitable skills and methods to change biomass into beneficial biofuels and bio-products.

Keywords: Biofuels, Energy, Biofuel development, Biomass, bio-products.

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1. Introduction

Energy has become a vital issue for humankind to continue financial development and to maintain high standard of living particularly after the industrial revolution in the late 18th and early 19th century. This world will need 50% more energy in 2030 than today [1-2]. Generally, the transportation sector is the second major energy consuming sector after the manufacturing sector. It is supposed that the transportation sector is responsible for nearly 60% of world's oil demand and will be the largest growing energy consuming sector in the upcoming era. The increase in motorization and industrialization of the earth has led to a sharp increase in the demand of petroleum based fuels [3]. Primary energy sources can be classified as renewable and non-renewable energy sources. The availability of energy from non-renewable sources is inadequate, and more over they imparts some drastic impacts on the environment [4]. The world has challenged with an energy shortage due to depletion of limited resources of fossil fuels [5]. Fossil fuels are non-renewable energy resources. Now a days, over 80% of energy we are using, comes from fossil fuels i.e. natural gas, coal and petroleum [6] of which 58% is used by transport sector [7].

In the 20th century, researchers paid their attention for the progress of natural gas, coal and petroleum based plant to ensure the availability of feed stock which are utilized in production of numerous products such as fuels, fine chemicals, detergents, pesticides, fertilizers, plastics, waxes, asphalt, synthetic fiber etc. to fulfill the increasing demand of the world's population [8]. This energy system is not suitable due to economic, environmental and geopolitical issues [9]. The consumption of fossil fuels is a major cause to raise the amount of CO_2 in the air and also responsible for global warming in current eras. The drastic effects of greenhouse gas discharges on the atmosphere have been observed [10]. Hence, suitable renewable energy will play a significant role in earth's future energy demand [9]. So production of CO_2 free fuels is one of major vital tasks facing our society [11] and supposed to replace fossil fuels. Biofuels obtained from renewable resources may support to reduce burning of fossil fuels and CO_2 emission [8-12]. Biofuels made from biomass would reduce global warming issue because CO_2 emission in atmosphere equals CO_2 consumption by the plants through photosynthesis and therefore does not rise net CO_2 in air [13].

2. Classification of Biofuels

Biofuels are generally categorized as primary and secondary biofuels. Primary biofuels are utilized in an unrefined form, mostly for heating system, food preparation or power generation such as firewood, saw dust, pallets and charcoal etc. Secondary biofuels formed by a series of mechanical or chemical operations of biomass is used mainly in automobiles and numerous manufacturing procedures. Secondary biofuels can be divided as first generation, second generation, and third generation biofuels on the basis of method of the processing used for their production [14] which is elaborated in figure 1.

3. 1st generation biofuels

First generation biofuels are those fuels, which mainly produced from sugars [15], seeds or grains [16] and need a comparatively modest course of development to produce product. Mainly there are three main kinds of first generation biofuels which are biodiesel, biogas and ethanol [17]. Famous first-generation biofuel, ethanol is prepared by agitating sugar obtained from crop foliage and starch present in corn seeds or starchy material; Bioethanol is a substitute of gasoline [17]. It is mainly manufactured from organic based materials (with higher sugar contents) by carrying out fermentation by yeast. Yeasts changes six-carbon sugars to ethanol [14]. Biodiesel is substitute of diesel [17] prepared from vegetable oils of plants by trans-esterification is also famous first-generation biofuels. Trans-esterification can use alkaline, acid or enzymatic catalyzers to produces biodiesel and glycerin [7]. Production of first-generation biofuels production put burden on food supplies [14].

4. Why do we need next generation biofuels?

First generations biofuels are obtained from plant based feedstock [18]. Preparation of biodiesel from edible oil has adverse ecological influence, because it needs arable land for the manufacture of biodiesel. Too much land is required to grow the biodiesel crops for them to fulfill the world's petroleum demand. Use of these feedstocks might cause deforestation in many countries. Moreover, use of biodiesel as an alternative fuel for petroleum-based fuel perhaps leads to uncontrolled destruction to surroundings and wildlife in several counties [19].

5. Second generation biofuels

Second generation biofuels obtained from biomass in an extra supportable way, which is carbonless in terms of its influence on CO_2 concentrations. erm 'plant biomass' discusses mainly to ligno-cellulosic material as this makes up non-edible food materials available from plants [20]. At this time, production of such fuels is not profitable because there are numerous methodological obstacles that must be overcome. Plant biomass mostly made up of plant cell walls, of Znormally 75% is made up of polysaccharides [21]. The production of second-generation biofuel needs much refined processing and production technology. To attain possible energy and financial consequence of second-generation biofuels, additional investigation, progress and application needed on production and transformation skills. Second-generation biofuels produced from ligno-cellulosic material, facilitating in usage of cost effective, non-edible feed-stocks, ensuing a boundary among food and fuel competition [22]. Ligno-cellulosic materials are a group of feedstocks for 2nd generation biofuels and obtained through fermentation, hydrolysis or by gasification. Common resources for these fuels are forestry crops, the perennial grasses and remains from the agriculture and from wood industry [14].

6. Feed stock for 2nd generation biofuels

Crops having low cost and woodland residues, wood wastes, and the organic materials of public solid wastes can be used as 2nd generation ligno-cellulosic feed stocks. Where these types of biomass are accessible, it is possible to produce biofuels from them with no extra-terrestrial necessities or influences on foodstuff and crop production [23].

6.1. Ligno-cellulosic feed stocks

The potential feed stocks for 2nd generation biofuels are mainly the ligno-cellulosic feed stocks and significant components of the ligno-cellulosic feed stocks are hemicellulose and cellulose which can be converted to sugar by a chain of biological and the thermochemical methods [24]. Mainly ligno-cellulosic feed stocks are divided into the following 3 categories i.e.

6.1.1. Agriculture residues

Utilization of agricultural residues may bring about lower general costs in biofuel development as compared to the cost of manufacturing of particularly cultured energy crops, where inputs must be contributed to cultivating, prepare and harvest them. Agriculture deposits, for example, bagasse and remains from production of cereals are feed stocks that may be used to prepare bioethanol. However, just about 15% of remains production would accessible for energy production [25]. Removal of agriculture residues may also be helpful for some crops as it might be helpful to control diseases, pests and also enhance soil temperature which may facilitate seed germination [26]. Crop residues are significant to maintain soil characteristics and increase soil efficiency [27].

6.1.2. Forest residues

Forest residue includes wood obtained from forestland, logging residues from harvest operations and wood dealing mill remains [28].

6.1.3. Herbaceous and woody energy crops

Non-food energy crops (woody energy crops and herbaceous crops) may be a possible source of feed stock for biofuel production. Switch grass and miscanthus are also a good source of feedstock for 2nd generation biofuels because they need low water and nutrients input, and they are also adaptable to low quality land. Some fast-growing woody energy crops are also suitable for biofuel production, i.e. popular, willow and eucalyptus. In short, dictated energy crops as feed stock are best in terms of land requirement, reduce erosion and provide good wildlife habitat. Moreover, additional energy per unit area of land can be attained from these crops but these crops do not fully escape from food verses fuel discussion because extra-terrestrial is required for their production [24].

6.2. Biodiesel feed stocks

Jatropha curcas is an oil seeds species that produced much interest regarding its potential for biodiesel production. Jatropha may be grown in desert climate or marginal soils without big funds in inputs [29]. Its oil may be processed to produce biodiesel and make it useful for rural areas.

6.2.1. Microalgae

Microalgae have ability to produce large quantity of lipids which are adequate for biofuel production. Moreover, they also have the ability to adapted and grow in saline water, wastewater, coastal sea water and non-arable land. Microalgae have ability to produce large amount of oil per unit area of land [30].

6.2.2. Organic waste

Organic waste from recycled cooking oil, paper industry, and animal fats may be used as energy resources. The biodegradable contents present in organic waste may be considered as good source of feed stock for production of biofuel but conversion of organic waste to biofuel give rise to many environmental issues [25].

7. Conversion methods for second generation biofuels

There are two paths available for production of biofuels from biomass; one includes biochemical processing and the other thermochemical processing. Thermochemical processing may be defined as a change of biomass into a variety of products, by thermal deterioration and chemical improvement. It principally includes heating of biomass in the presence of oxygen. Main benefit of thermochemical processing is that it can change all fractions of biomass as compared to biochemical processing mainly concentrate on polysaccharides [17]. Biochemical processing is that in which micro-organisms or enzymes used to convert cellulosic and hemi-cellulosic material of feed stocks to sugars earlier to their fermentation to produce ethanol [23]. The following methods are used to produce lingo-cellulosic biomass free from oil. Produced biomass can be further processed to produce biofuel. Two main conversion methods are shown in figure 2.

7.1. Physical Conversion

7.1.1. Mechanical extraction

Raw plant oils are obtained from oil seeds by using a mechanical compression using an expeller. Screw press may be used in different ways i.e. prepressing and then full pressing. In first, only some of oil obtained and incompletely de-oiled material (material with 18–20% oil) is additional treated by solvent extraction. Pre-pressing is usually applied for oilseeds with higher oil contents (30–40%). Full pressing needs ~95,000 kPa to crush out as much oil as possible, normally up to 3–5% remaining fat for animal supplies. Full-pressing may also be applied in a pre -press & last press [13].

7.1.2. Briquetting of biomass

Agrarian, forestry deposits and other discarded biomass resources are frequently problematic to use as biofuels as of their rough large and troublesome features. This disadvantage can be solved by densification of the remaining into dense regular forms. During densification biomass bounded in compression chambers pressed. Mainly there are two chief approaches of densification available, i.e. maceration and pressing. Sometime these two methods are collectively used [13].

7.1.3. Distillation

Distillation is the utmost significant technique for obtaining essential oil and based on the evaporation of volatile ingredients of a mixture to isolate them from the nonvolatile parts. Vegetation is crushed to discharge their oils. The biomass is steam distilled, and the oils evaporate and rise up with the mist. The vapors are collected and permitted to condense back into the liquors. One of the best chemical processes is molecular distillation which is used to obtained the scents that cannot be extracted by classical methods [13].

7.2. Thermochemical conversion

The thermochemical alteration method includes gasification, direct combustion and liquefaction. When biomass heated in presence of oxygen deficient conditions, it produces syngas, which contain H_2 and CO. This syngas may be burned or processed for other products [17]. Gasification is not a novel term; it is used to convert biomass into biofuel and has been examined for the past 30 years. Syngas may be prepared from biomass by different methods i.e. catalytic and non-catalytic processes. Non-catalytic processes need a very high temperature while catalytic processes may be worked at considerably lower temperatures. Basically, gasification is the thermo-chemical conversion of feedstock to gaseous products through a fractional oxidation method at high temperatures. The ligno-cellulosic structure of biomass is thermally broken into carbon monoxide, hydrogen and carbon dioxide as the major elements of syngas and minor quantities of methane (CH_4) and trace gases [31]. Gasification vessels usually work at high temperatures (800–900°C) irrespective of their kind and shape. Gasification process contains four major steps i.e. drying, pyrolysis, reduction and combustion.

In the drying stage, the feedstock loses its humidity. In pyrolysis, volatile materials are separated in the form of light hydrocarbons, CO and CO_2 and in the form of liquid long-chain hydrocarbons. The nature of tar usually determines by the kind of biomass used as well as the conditions and gasifying agent. The reduction region works as the chief process where the raw materials are totally gasified by using oxygen from the air to form the syngas through a chain of endothermic reactions. At the end in the combustion unit, the remaining material is extra burned to produce more gaseous stuff and the needed heat for the reactions in the reduction region [32]. Resulting gas is mainly beneficial as a fuel for power generation; on other hand syngas may be used to manufacture a wide variety of fuels and chemicals. For carriage fuels, syngas derived paths to fuels are hydrogen by water gas shift reaction, hydrocarbons by Fischer Tropsch synthesis or methanol preparation followed by extra reaction to prepare hydrocarbon / oxygenated fuels. Since 1920s, the preparation of methanol from syngas has been skillful [17]. Liquefaction of biomass has been examined in the presence of solution of glycerin, propanol, alkalis and butanol. Products usually produce water insoluble oils having higher viscosity and generally need solvents, reducing gases such as carbon monoxide or H_2 and/or catalysts in addition to biomass.

In thermochemical transformation of biomass, ligno-cellulosic supplies may be changed to liquid related to heavy fuel oils by reacting them with gas in the presence of appropriate catalyst. Liquefaction of lignocelluloses includes de-segregation of the woody structure, followed by fractional de-polymerization of the constitutive compounds. In the alkali liquefaction, deoxygenating takes place through decarboxylation from ester formed by hydroxyl group and formate ion resulting from carbonate. Alkali salts such as sodium carbonate and potassium carbonate, may act as catalyst for hydrolysis of macro-molecules into small fragments. The oil gets from the liquefaction method is a viscous material, which occasionally produces difficulties in handling. Due to this, some organic solvents (e.g. ethyl acetate, butanol, acetone, propanol, methyl ethyl ketone) prerequisite to be added to the reaction scheme. The normal oil yield is ~31% in the non-catalytic method and 63% in the catalytic method. These oils might be upgraded catalytically to yield an organic product which is enrich in hydrocarbons and valuable to prepare biofuels [17].

7.3. Chemical conversion

The significant issues in chemical hydrolysis are acid concentration, surface to volume ratio, temperature, and time [33]. Solvent extraction involves various steps i.e.

extraction of the oil from the seeds using solvent (hexane); evaporation of the solvent; distillation of the oil hexane blend and heating of the de-oiled material. Other solvents may be used, usually dichloromethane, ethanol, acetone or isopropanol. Supercritical extraction can be done using carbon dioxide. Extraction is a method in which the required material is specifically separated from the raw supplies by permitting the desired material to dissolve into the solvent, and then recovering the material from the solvent. To separate the specific substance from biomass, both separation and extraction are vital. Usually biomass (aromatic grasses, wheat straw, wood etc.) which consist of higher amount of macro-molecular compounds (polysaccharide, hemicellulose, cellulose, and lignin) are called primary metabolite. The other low capacity and high worth biochemical molecules like resins, sterols, terpenoids, waxes and alkaloids are known as secondary metabolites. In the bio-refinery process such chemicals are first removed from biomass by solvent extraction or supercritical fluid extraction. The extracted ligno-cellulosic biomass is additionally used for fermentation and hydrolysis for preparation of biofuels [17]. By acid hydrolysis, acid recovery is expensive and contaminating issues are prominent. In Enzymatic hydrolysis, it needs pre-treatment of the ligno-cellulosic biomass. Supercritical water may rapidly convert the cellulose to sugar and change biomass into a blend of oils, alcohol, methane and the organic acids [17].

7.4. Biochemical conversion

Biochemical conversion skills depend on microbial and enzymatic procedure for manufacturing sugars from biomass (lingo-cellulosic, starch and cellulosic). The sugars then may be changed into alcohol and solvents to oil and chemicals. Preparation of ethanol from maize and sugarcane by biochemical processes has been commercially established. It is vital to hydrolyze ligno-cellulose material for biochemical conversion. Enzymatic hydrolysis of lingo-cellulosic biomass needs investigation and progressive work to enhance yield of alcohol[17]. Cellulose is chief structural constituent of plant cell walls and is therefore resistant to biodegradation in nature. Therefore, the breakdown of lingo-cellulosic biomass to release sugars is costly[34]. The transformation of biomass to fuels such as ethanol needs number of basic unit processes involving pre-treatment, enzyme production, and hydrolysis, fermentation and ethanol recovery. This lingo-cellulosic biomass contains three major operational units: cellulose, hemicellulose and lignin. Cellulose is a crystalline polymer and hemicellulose is an amorphous polymer of arabinose, xylose and lignin is a large poly-aromatic complexes. The transformation of lingo-cellulosic biomass to alcohol needs three step routes i.e. pretreatment of biomass, acid / enzymatic hydrolysis and fermentation or distillation.

The pretreatment methods isolate xylose and lignin from the crystalline cellulose. The mist explosion route is an effective pre-processing technique for changing lingo-cellulosic biomass. In this method biomass sample is inserted in a pressure container and evaporated by using steam for ~20 min at 473–543 K and pressure of 14–16 bar. The pressure in digester is then released quickly by opening the steam and the material is exposed to atmospheric pressure to cause an explosion which disintegrates lingo-cellulosic biomass and changed into low weight chemicals which can be separated. So, water soluble portion of hemicellulose can be separated by water extraction. Simultaneously, a part of the low molecular portion of lignin can be separated. The xylose may be agitated to ethanol and the lignin may be treated to produce other fuels. The cellulose leftovers as solid after the pre-treatment and it may be converted to glucose by enzymatic hydrolysis procedure. Furthermore the glucose fermented to alcohol and the hemicellulose to xylose (Fig. 3) [17].

8. Sustainability challenges

8.1. Food security

It may be relevant for non-food energy crops if grown on land having value for food production, including lingo-cellulose sourced from the global South. Use of agricultural residues would not constitute a direct conflict with food (but questions may arise where biofuel production using residues is linked with 1G feed stock). Residues such as straw can be part of the animal feedstuff mix and thus indirectly linked to the food-chain.

8.2. Large-scale land acquisition

Land chosen as ‘marginal’ or degraded, but appropriate for 2G feedstock, can be relied on by the poor for subsistence. For agricultural remains, the suitable use of land in which the feed stock is cultivated may be relevant.

8.3. Green House Gases (GHG) Balance

If feed stocks, we resourced by deforestation, or by the usage of ‘marginal’ land, a source of food, GHG balance may be questioned. Soil organic carbon content is affected by removal of straw. Net energy balance is relevant given the energy inputs needed to break down lingo-cellulosic material and for transportation of bulky residues. Although, cellulosic ethanol requires fewer fossil fuels for processing heat and electricity than starch-based ethanol.

8.4. Environmental impact

Energy crops may increase biodiversity and water quality because of the reduced requirement for nitrogen fertilizer and pesticide involvements, but slow-growing crops may affect groundwater recharge and require constant access to water[35].

9. Third generation biofuels

First generation biofuels obtained from energy crops such as sugar beet, sugarcane, rapeseed and maize place a huge stress on food markets, lead to water deficiencies and cause deforestation. Second generation biofuels obtained from lingo-cellulosic material, woodland remains and from non-edible crop feed stocks may cause some of the problems discussed earlier. Scientists are now paying attention to microscopic organisms. Hence, on basis of latest scientific facts and technology, third-generation biofuels obtained from microbes and microalgae are studied to be a feasible substitute energy supply is without of main disadvantages related with 1st and 2nd -generation biofuels [36].

9.1. Biofuels from microbes

Current developments have exposed that certain microbial species such as: fungi, yeast and microalgae may be used as possible sources for biofuels as they have ability to bio-synthesize and store huge amounts of fatty acids [37] in their biomass. Microbial oil can be obtained by acid-treated rice waste (straw) hydrolyte in the presence of a microorganism *Trichosporon fermentans*. So, this organism may be used for microbial oil production [38]. Microbial biomass may also be used for biofuels production. In previous study investigators have enhanced the growth medium constituents for culture cultivation and considered the properties of culture environments on microbial biomass and lipid production by *T. fermentans*. The best nitrogen source was peptone, carbon sources were glucose and carbon nitrogen molar ratio were 163 for finest lipid production. The most feasible early pH of the medium and temperature were 6.5 and 25 ^{0}C. Under these conditions, a microbial culture cultivated for 7 days to create a microbial biomass, having higher lipid contents. *T. fermentans* could be cultivated in waste molasses from sugar industry [14]. The microbial lipid including stearic, oleic, palmitic and linoleic acid having unsaturated fatty acids like vegetable oil could be trans-esterified to produce biofuels by base catalyzed reaction.

9.2. Biofuels from algae

Algae are present in all world environments having a large diversity of species living in a wide-ranging environmental conditions [39]. They are simple plants (thallophytes), i.e. stems, roots and leaves deficient, and have chlorophyll as the main photosynthetic pigment. Under normal growth circumstances algae absorbs sunlight and take carbon dioxide from the air and nutrients from the water. Microalgae can manufacture proteins, lipids and carbohydrates in bulk over small periods of time, and the products may be treated to both biofuels and useful co-products [40] but the production of proteins, carbohydrates and lipids may be restricted by accessible sunlight because of diurnal cycles and the periodic variations. Thus limits the capability of marketable manufacture to zones with high solar radiation. Microalgae can assimilate CO_2 from different sources i.e. atmosphere, soluble carbonates and released gases [41]. Under normal growth situations, microalgae fix CO_2 from the air and may stand and use considerably higher amount of CO_2 (up to 150,000 ppmv). Hence, in simple production units, CO_2 passes through the algae growth media from external sources or from soluble carbonates such as sodium carbonate or bicarbonate. The inorganic nutrients essential for algae growth includes, phosphorus, nitrogen and silicon [42]. Algal cells are true small biochemical plants and considered to be extra photo synthetically effective than terrestrial plants as these are actual well-organized CO_2 fixers. The capability of algae to assimilate CO_2 has been planned as a technique of eliminating CO_2 from vent gases from power plants, and thus can be utilized to reduce release of greenhouse gas (GHG). Many algae are exceptionally rich in oil, which can be changed to biodiesel (Fig. 4). There are three different algae production mechanisms, i.e. photo-autotrophic, hetero-trophic and mixo-trophic, follow the natural growth processes.

9.3. Microalgae Cultivation:

From a marketable consideration, a microalgae culture structure needs following potential characteristics: high range yield; more volumetric productivity; cost effective (in sense of investment and maintenance); controlled culture factors (pH, O_2 and temperature); and consistency [43]. Microalgae cultivation is the first stage in the energy manufacture unit. Currently, the cultivation approaches of microalgae are usually using these two techniques: The open pond system and Close photo bioreactors system.

9.3.1. Open pond system

Open pond systems need extremely specific environments because of characteristic risk of contamination and pollution by other alga types and protozoa. The open pond system is the eldest and the simplest method to cultivate microalgae. Generally, microalgae are placed in an open pond with aqua and inorganic nutrients; through natural photosynthesis to make it grow. The open pond is commonly planned in the shape of a channel. It has a blade wheel to mix the algae cells. In the meantime, nutrients are also added in the raceway. Cycle mode is designated for the open pond system, so the fresh stuff can be added from paddle wheel to the pond, and microalgae can be collected in the circulation process [44]. Currently, there are only a few types of microalgae that may adjust to this cultivation atmosphere to grow i.e. spirulina (adaptable to high alkalinity), chlorella (adaptable to nutrient-rich media) and dunaliella (adaptable to nutrient-rich media). The advantages of the open pond system are its simple construction, cost effectiveness and the reliable function.

9.3.2. Close Photo bioreactors System

Photo bioreactors have the capability to grow algae while there are some advantages, such as cleaning power plant flue gases or eliminating nutrients from waste-water. A photo bioreactor is a close bioreactor which combines light source. PBR systems closed, all vital nutrients must be fed into a system that allows algae to propagate and be cultivated. Different types of photo-bioreactors are available e.g. tubular photo-bioreactor, fermentation tank photo-bioreactor, plate photo-bioreactor [45]. Tubular photo-bioreactor system is the most appropriate for both external and internal cultivation. Tubular reactor constructed by utilizing transparent pipes are made up of glass or plastic [46]. Also, the outside light source needs to be made to propagate microalgae in tubes may be vertical, inclined and horizontal. As compared to open pond systems, close photo-bioreactor systems have more suitable culture environments and higher concentration of the microalgae cultivation is easier to be carried out.

9.3.3. Microalgae Production Technology

Microalgae production practice is one of the chief problems of the entire microalgae energy production. It may be classifies to harvesting, oil extraction and energy conversion. Harvesting microalgae and oil extraction has certain problems due to the lesser diameters (3-30 μm) of microalgae cells and their higher water content. So it is problematic to collect the microalgae from the cultivation apparatus [47]. The Energy conversion procedure is also the chief portion of microalgae bio-energy production. Usually, the microalgae harvesting is the two-stage process, involving the:

(1) Bulk harvesting—considered at isolation of biomass from the bulk. The concentration parameters for this process are usually 100–800 times to get 2–7% of entire solid matter. This will be determined by on the early biomass concentration and skills employed, containing flocculation, gravity sedimentation and flotation.

(2) Thickening—the purpose is to concentrate the biomass through methods such as centrifugation, ultrasonic, filtration, aggregation etc. Hence, it is usually a more energy demanding step than bulk harvesting.

So, microalgae should be harvested by certain suitable approaches i.e. centrifugation, membrane filtration, flocculation and froth flotation.

9.3.4. Centrifugation and flocculation

These are the two approaches which are normally used. Centrifugation is the most used harvesting method. Flocculation is one of the well-known chemical tools in microalgae harvesting. Because the sizes of microalgae cells are very small, by using flocculation, microalgae cells are combined into larger size particles. Ferric chloride and Alum are common flocculants [45].

9.3.5. Flotation

Some algae certainly float on the surface of the water, as the lipid contents of microalgae increase. Though flotation has been stated as a possible harvesting technique, there is limited proof of its practical or financial feasibility. Flotation does not need any addition of substances.

9.3.6. Filtration

Filtration is that technique of harvesting microalga that has been verified to be the inexpensive as compared to other harvesting techniques. There are numerous forms of filtration, such as microfiltration, dead end filtration, ultra filtration, pressure filtration, the tangential flow filtration (TFF) and vacuum filtration [48]. Normally, filtration comprises running the liquid with algae, passes through sieves on which algae accumulate and let the medium pass through the filter.

9.3.7. Drying processes

The harvested biomass material is fresh and must be treated quickly after harvest; drying is normally used to improve feasibility. Techniques that have been used for drying include low-pressure shelf spray drying, sun drying, drum drying, and freeze drying [49].

9.3.8. Microalgae oil extraction

After drying microalgae oil remains in the microalgae cell. The main point of oil extraction is to destroy the cell membrane and cell wall, and then allow the oil to discharge from the microalgae cells. Microalgae oil can be obtained by numerous methods. Enzymatic Extraction, Chemical cool press method, and Supercritical Fluid Extraction are the common methods used in the microalgae oil extraction process [50].

9.4. Energy conversion from microalgae to bioenergy

The working basis of microalgae energy conversion is that materials are changed to biofuel energy by utilizing chemical or biological approaches. Two main energy conversion methods are used in the laboratory experiments or in industrial production units i.e. thermochemical conversion and biochemical conversions [51].

9.5. Thermochemical Conversion

Thermochemical conversion is a method in which we use chemical approaches to convert biomass into biofuel under heating conditions. It consists of gasification, pyrolysis and liquefaction (Fig. 5).

9.5.1. Gasification

Gasification refers to fractional, non-catalytic oxidation reactions at elevated temperature conditions (about 800-900 ^{0}C) in which solid biomass is converted to the gas fuels. The chief products comprise of carbon monoxide, hydrogen, ammonia and methane. A gasifying agent, for example steam, air or oxygen-enriched air is frequently fed at same time into container. The composition and quality of the product gas is closely related to feedstock, reaction conditions and gasifying agent. Moreover, these gases can be utilized for synthesis of chemicals, electricity production and production of fuels. At this time, in microalgae energy transformation investigation, catalytic gasification low at temperature has been started [9]. In this technique, biogas is taken out from microalgae with nitrogen cycling. Nitrogen present in the microalgae may be transformed into ammonia in gasification method and recovered solution comprises of the ammonia, nitrogen nutrient reclaimed to cultivate microalgae. Without drying, the microalgae containing higher moisture contents can be gasified to form ethanol. The high moisture containing microalgae can be gasified to the methanol without drying.

9.5.2. Pyrolysis

Commonly Pyrolysis is a decomposition reaction at the elevated temperature in the absence of oxygen. In microalgae energy conversion method pyrolysis refers to the transformation of biomass to biofuel. Biomass is combusted in the absence of oxygen approximately at 500 ^{0}C. As a result, oil fraction, hydrocarbon-rich gas mixture, and high carbon content residue are produced. Pyrolysis is supposed to continue through multi-stage process i.e. dehydration followed by degradation, slow stage in which char formation, decomposition and volatilization occur [40]. In the fast pyrolysis method, in the presence of catalyst, elevated temperature and short gas residence time, the biomass decomposed into the series of short chain molecules and then all the gases will be liquefied to produce biofuel directly. As compared to the fast pyrolysis method, slow pyrolysis process has long gas residence time and low heating rate. As a result, it decreases the oil yield and alters the characteristics of biofuel.

9.5.3. Liquefaction

The liquefaction of biomass is usually done in an aqueous solution of alkali or its salt at 575 K and 10 MPa by utilizing stainless steel autoclave. Nitrogen is fed into the autoclave to purify residual gas. Dichloromethane is commonly used to isolate water from microalgae and oil fraction. Function of liquefaction is transformation of microalgae raw materials into biofuel. It is thought hydrothermal liquefaction method found to more significant option for production of bio-diesel from algae [52].

9.6. Biochemical conversion

Biochemical conversion means a method in which biomass and the microbial metabolism are utilized to produce biofuel. Commonly two biochemical transformation approaches may be utilized in the microalgae energy production i.e. fermentation and trans-esterification.

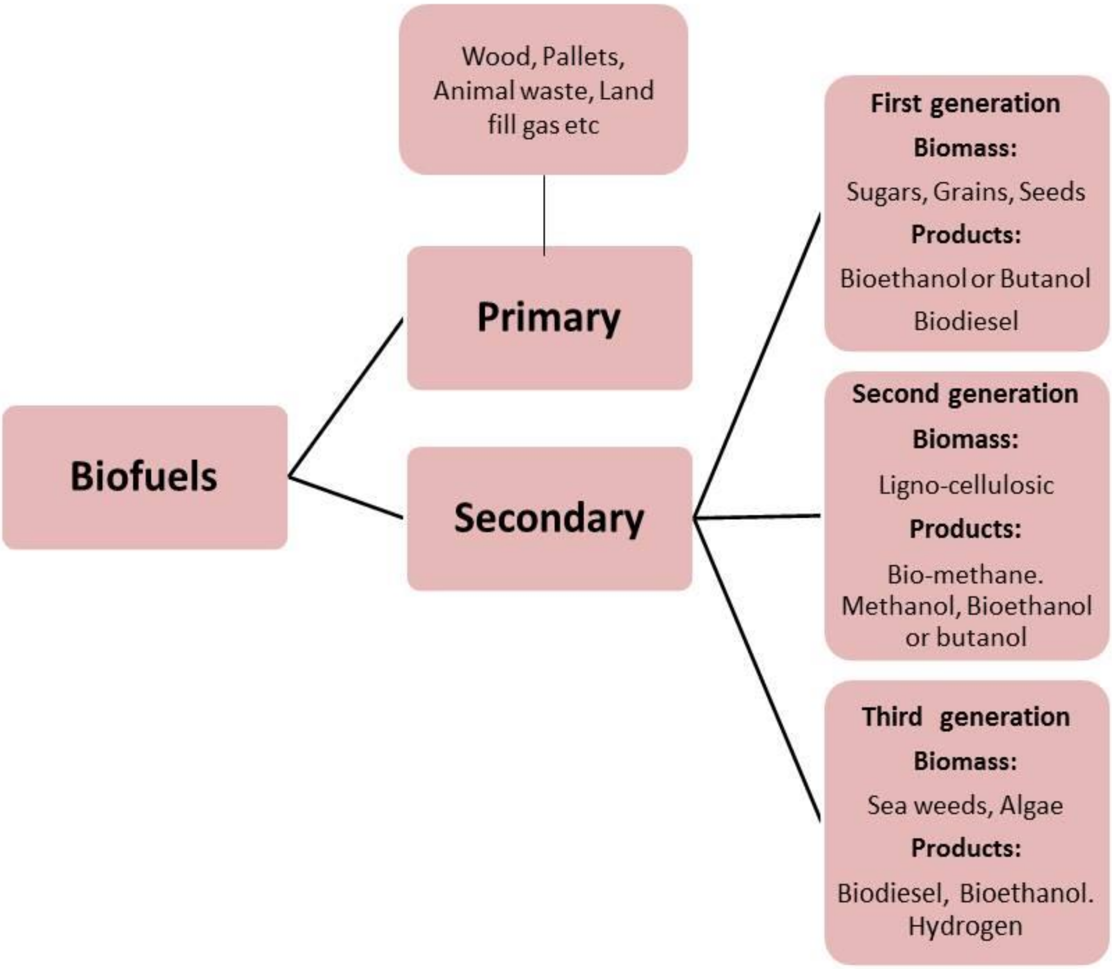

Figure 1. Classification of biofuels

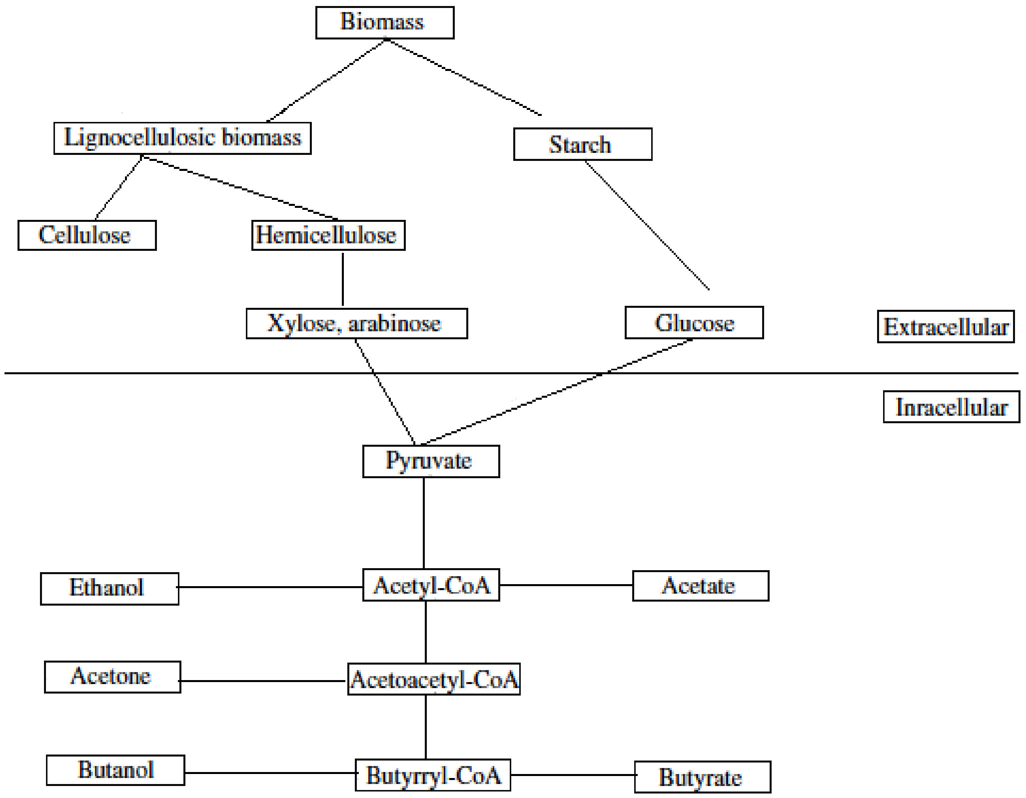

Figure 2. Conversion of biomass through biochemical and thermochemical routes

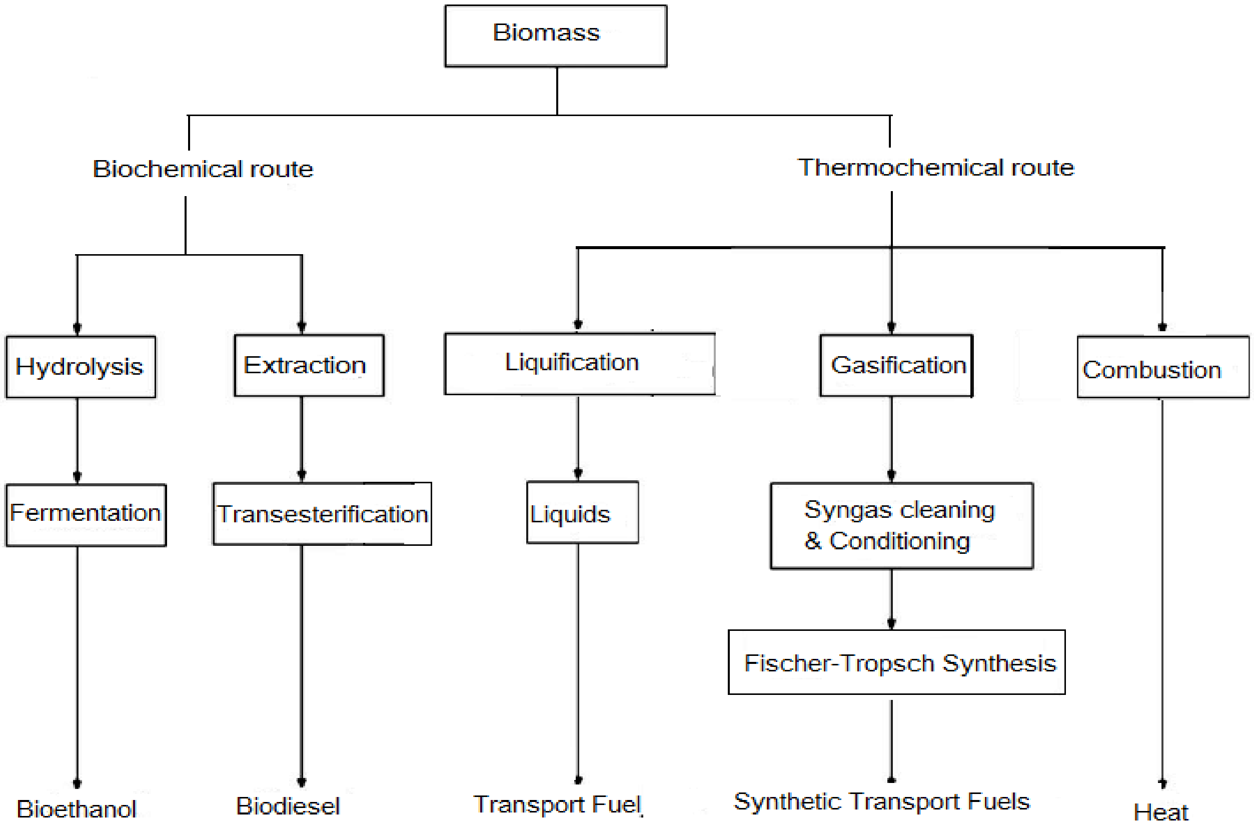

Figure 3. Production of various chemicals from biomass

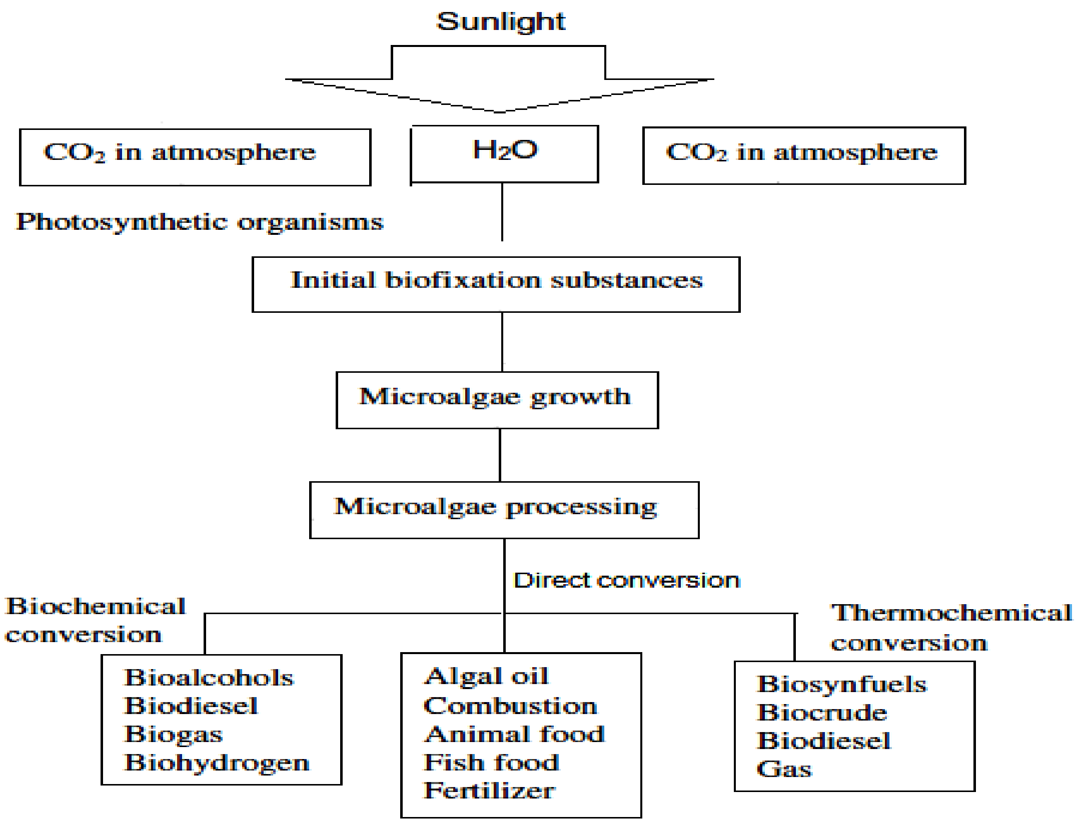

Figure 4. Third generation biofuels production from microalgae

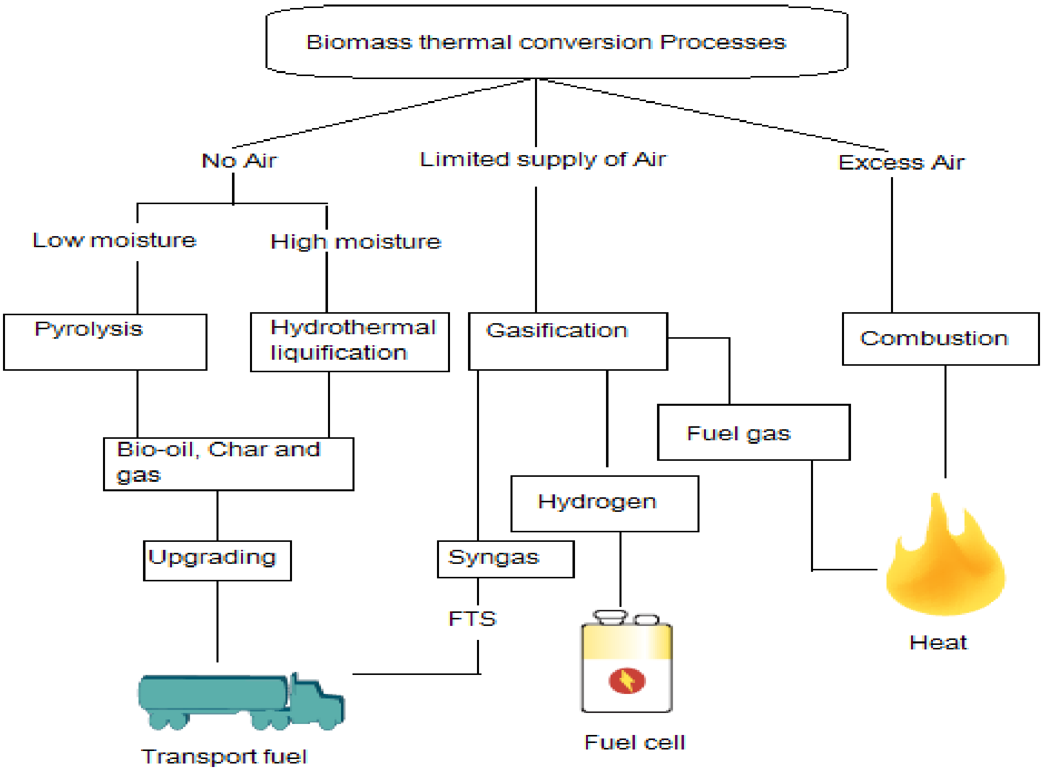

Figure 5. Thermal conversion of biomass

9.6.1. Fermentation

Fermentation is broadly used in producing bioethanol from starch and sugar crops. Microalgae has enough starch, which may be changed to sugar. The conversion process may contain of following steps, initially, starch is isolated from the microalgae by mechanical or enzymatic action and when the microalgae cells initiate to degrade, *Saccharomycess cerevisiae* is fed into the raw microalgae for fermentation. Gluco-amylase enzyme transforms the starch into D-glucose. The enzymatic hydrolysis is done which followed by fermentation, distillation and dehydration to produce bio-ethanol [9].

$$C12H22O11 \rightarrow C6H12O6 + C6H12O6$$

$$C6H12O6 + yeast \rightarrow 2C2H5OH + 2CO2 \uparrow$$

At last, ethanol isolated to be distilled. Carbon dioxide may be collected and utilized for microalgae cultivation again.

9.7. Trans-esterification

Trans-esterification is a conversation reaction in which an ester reacts with an alcohol to form new ester and an alcohol in the presence of catalyst (acid, a base or an enzyme) [53-58]. Trans-esterification may be used to prepare biofuel from the microalgae. First of all oil from the microalgae is isolated and then water is removed from the oil at elevated temperature up to 120 ^{0}C in 5-10 min. In second step, mixing process takes place in which sodium hydroxide; the oil and methanol are mixed and cooled. Then this mixture is fed into a catalyst tank for stirring. The resulting product is sodium meth-oxide [50]. The solution will be separated and cooled in third step. The separation process takes 15-60 min approx. At end, methyl ester floating on top layer, and glycerol collected at bottom. Then methyl ester washed and dried (biodiesel).

10. Conclusions

Bioenergy is becoming a part of the world's energy. To fulfill the desired goals, the continuous sources of all kinds of biomass should be increased. Though the production of first-generation biofuels in advanced countries with modern technologies, accessible infrastructure, it is criticized because of its Fuel or food debates. Besides, the modern biofuels obtained from algal biomass and lignocellulosic increase the availability of biofuels by reducing greenhouse gas emission and less land requirement. Recently, second generation biofuel production technologies are comparatively mature, with a small number of industrial units and third generation technologies are still under development and scientific research. In spite of its characteristic as a biofuel supply, many challenges have obstructed the progress of algal biofuel skill to marketable sustainability that could permit for utilization and production. They involve: (1) Balance requirements of species selection (2) development of methods for single species farming, CO_2 diffusion losses and evaporation reduction (3) managing advanced photosynthetic productivity.

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