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Lignocelluloses Feedstock Biorefinery as Petrorefinery Substitutes

Hongbin Cheng and Lei Wang

Additional information is available at the end of the chapter

1. Introduction

1.1. Lignocelluloses feedstock (LCF) biorefinery

1.1.1. Background

The material needs from our society are reaching the crisis point, as the demand for resources will soon exceed the capacity of the present fossil resource based infrastructure [1]. Currently, fossil-based energy resources, such as petroleum, coal, and natural gas, are responsible for about three quarters of the primary energy consumption in our world. While decreasing crude-oil reserves, enhanced demand for fuels worldwide, increased climate concerns about the use of fossil-based energy carriers, and political commitment, the focus has recently turned to develop the utilization of renewable energy resources [2]. Gullón *et al.* [3] described the variety of problems on present social, economic and technological situation, which including: the fear for a shortening of the supplies of basic resources, as the population growth; the increasing *per capita* demands of the developing economies for goods and energy, derived from the increasing purchase power of the population; environmental challenges, especially those related to effects of greenhouse gas emissions (emphasis on CO_2) on the global climate; the national security issues surrounding reliance on imported oil [4].

On our market, nowadays, there are more than 2500 different oil-based products. The petroleum crisis of the 1970s resulted in a shift from total reliance on fossil resources and simultaneously triggered research into biomass based technologies. As a result of the oil crisis, renewable resources became a popular phrase [5]. Currently, the most of energy requirements in the world are still met by fossil fuels. The limited deposits of these fossil fuels coupled with environmental problems have prompted people to look for sustainable resources as alternatives to meet the increasing energy demand. Bio-energy production has

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the advantage of forming smaller amounts of greenhouse gases compared to the conversion of fossil fuels, as the carbon dioxide generated during the energy conversion is consumed during subsequent biomass re-growth [6]. However, simply providing sustainable and non-polluting energy will not be enough. In our life, clothes, shelter, tools, medications and so on are all, to a greater or lesser degree, dependent on organic carbon. As fossil-based resources will be replaced, new sources of organic carbon have be found or alternate applications and processing of existing sources must be developed. The challenge is to find replacements not only for current usage, but also for the even future greater energy consumption, with a likely concomitant increase in biomass demand for manufacturing [7].

1.1.2. What is biorefinery?

The core aim for biorefineries is to produce both high-volume liquid fuels and high-value chemicals. As petroleum refinery uses petroleum as the major input and processes it into many different products, the term 'biorefinery' has been coined to describe the processing complexes that will use biomass as feedstocks to produce a wide spectrum of chemicals, fuels and bio-based materials, that can be used as industrial intermediates or sold directly to consumers [1, 8, 9]. Biorefineries have been considered as the key for access to an integrated production of chemicals, materials, goods, fuels and energy of the future [10]. As oil prices continue to rise and biorefining technology matures, biorefineries are playing an increasingly major role in the global economic system, with the potential to ultimately replace petroleum refineries as the world's principal method of fuel generation.

1.1.3. Lignocelluloses feedstock (LCF) biorefinery

The largest organic carbon reservoir in our world is the biomass - plants and algae. Each year, plants fix approximately 90 billion tons of CO_2, most of this as wood [11]. Lignocelluloses are the natural combination of cellulose, hemicelluloses and lignin. It's the raw material for potential conversion to energy fuels and chemical feedstock for manufacturing. LCF biorefinery has been drfined as one of the so-called phase-III biorefinery concepts which are characterized by the ability to use a variety of resources by different routes to generate multiple products [12].

A LCF biorefinery uses lignocellulosic biomass, including forestry residue, agricultural residue, yard waste, wood products, animal wastes, etc. Initially, plant material is cleaned and broken down into the three main fractions (hemicellulose, cellulose, and lignin) by chemical digestion or enzymatic hydrolysis. Hemicellulose and cellulose can be produced by alkaline and acid. Lignin can also be further broken down with enzymes. The hemicellulose and cellulose are sugar polymers, which can be converted to their component sugars through hydrolysis. A hemicellulose is a polymer that contains five-carbon sugars (usually D-xylose and L-arabinose), six-carbon sugars (D-galactose, D-glucose, and D-mannose), and uronic acid. Cellulose is a polymer of only glucose. The hydrolysis process of hemicelluloses and cellulose result in the aforementioned sugars [13].

The LCF Biorefinery is a promising alternative due to the abundance and variety of available raw materials and the good position of the conversion products on the market [14]. Its profitability is also dependent on the technology employed to alter the structure of lignocellulosic biomass in order to produce high value co-products from its three main fractions *i.e.* cellulose, hemicellulose, and lignin [15].

Currently the main feedstock for biorefineries is still based on starch. The practiced technologies in fuel ethanol industry are primarily based on the fermentation of sugars derived from starch and sugar crops, which are quite mature with little possibility of process improvements. However, using starch and sugar crops to produce ethanol also has been questioned since it draws its feedstock from a food stream. Lignocellulosic biomass is a more promising renewable resource as it is available in large quantities and does not compete with food or feed. Lignocellulosic biomass is a renewable resource that stores energy from sunlight in its chemical bonds, with great potentials for the production of affordable fuel ethanol [16, 17]. Its main obstacle for a major breakthrough is the high production costs for bioenergy products.

On the other hand, lignocellulosic biomass-derived products can significantly reduce green house gas emissions, compared to fossil-based products. Also, many common petrochemicals could be obtained with lower green house gas emissions from bio-based feedstocks. The maturity and economics of the conversion processes and logistics is a major challenge for lignocellulosic biomass [18].

1.1.4. The main goal of Biorefinery

With, implementing innovative, environmentally sound and cost-effective production technologies for a variety of products, the integrated biorefinery is increasing the availability and use of bioenergy and bio-based products. The main objective of a biorefinery is to produce high-value low volume and low-value high-volume products by a series of producing processes. The processes are designed to maximize the valued products while minimizing the waste streams by converting low-value high-volume intermediates into energy. The high-value products can enhance the profitability, and the high-volume fuels will help to meet the global energy demand. The power produced from a biorefinery can also help to reduce the overall cost. Figure 1 shows the elements of a biorefinery, in which biomass is used to produce various useful products such as fuel, power, and chemicals by biological and chemical conversion processes [13].

Traditionally, the matured biorefinery pathways include bioconversion (aerobic and anaerobic digestion) and chemical conversion (bio-pulping). There are two most promising emerging biorefinery platforms. One is the sugar platform and the other is the thermo-chemical platform (syngas platform). In sugar biorefineries platform, biomass will be broken down into different types of component sugars for fermentation or other biological processing into various fuels and chemicals. In thermo-chemical biorefineries platform, biomass will be synthesized hydrogen and carbon monoxide or pyrolysis oil, the various components of which could be directly used as fuel [19].
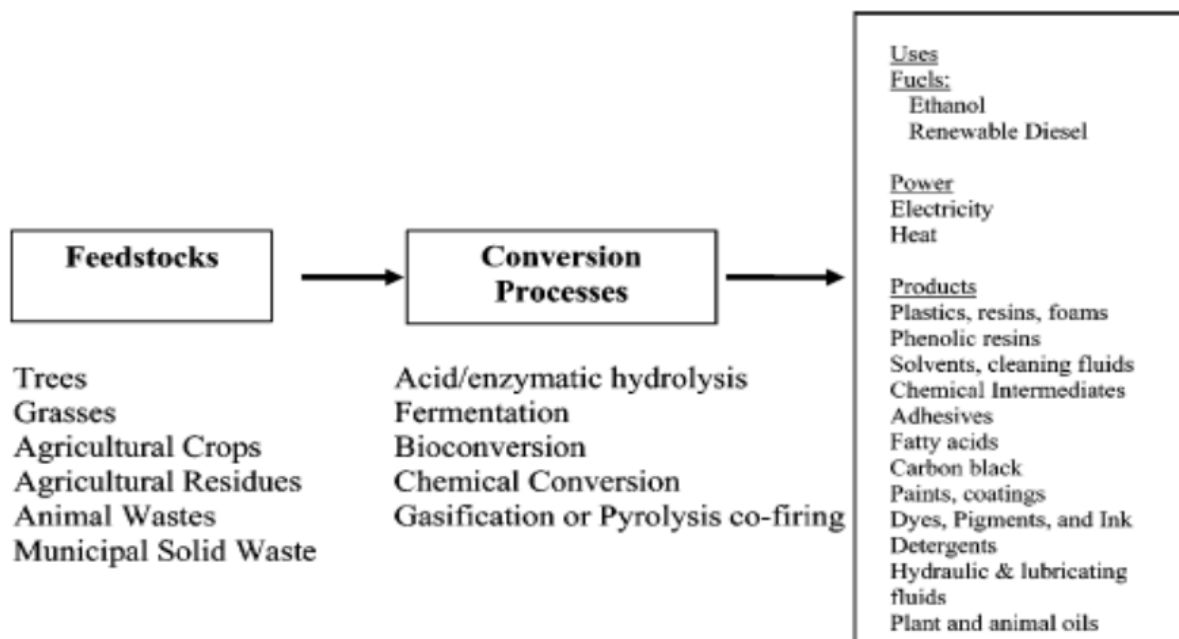
Figure 1. Simple procedure for three-step biomass-process-products [13]

1.1.5. Disadvantages

It is very important to increase the reaction rates, as slow reactions rates is one of the main disadvantages for biological conversions in biorefinery processes. Another disadvantage is the often low product concentrations, which means the high product recovery costs with existing technology. The lower yields of targeted products is often found in some multiple products systems [20]. Therefore the biorefinery processes to become an actual alternative to fossil fuels and petroleum-derived products, biorefinery processes must be competitive and cost-effective [21].

2. Biofuels

As an important category of bioenergy, biofuel is a type of fuel which is biologically derived from biomass. The biofuels, which include liquid, solid biofuels and various biogases, can replace the conventional petroleum or petroleum derived products. Many biological reactions involved in biofuels production are at mild conditions, can offer relatively high products yields and generally result in low levels of contamination to the environment. The modern application of biological transformations, known as biotechnology, is also an evolving field that has great promise for substantial improvements and significant cost reductions. In this section, several liquid and gases biofuels are introduced *e.g.* (1) bioethanol, biobutanol, and biodiesel which can replace the gasoline used as transportation fuels; and (2) biogas, which is produced from anaerobic digestion of biomass as a substitute for natural gas either for industrial applications or for transportation.
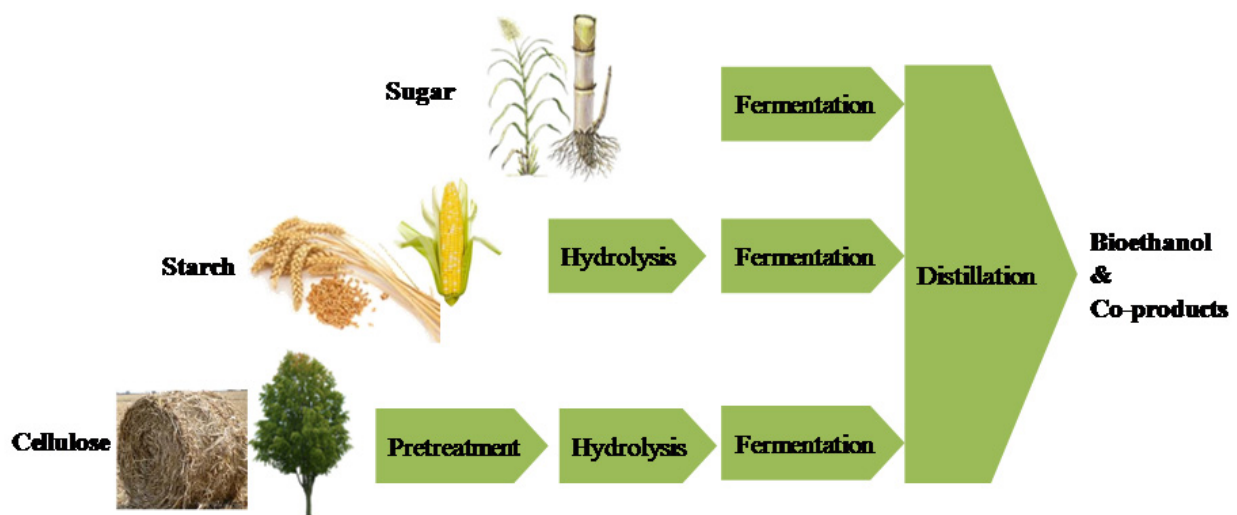
2.1. Bioethanol

Bioethanol is a promising transport fuel alternative to gasoline because it has higher oxygen content and no sulphur or nitrogen when compared with gasoline [22]. Currently, the blends E5 and E10 that consist of 5% (v/v) and 10% (v/v) ethanol respectively, have a widespread usage since these blends can supply the existing vehicular fleet without major changes to engines. High bioethanol blends (E100, E95 and E85) require modified or dedicated vehicles.

Bioethanol can be produced from three types of raw materials: sugars (from sugarcane, sugar beet, molasses, and fruits), starch (from corn, cassava, potatoes, and root crops), and cellulose (from wood, agricultural residues, waste sulphite liquor from pulp and paper mills). Among the three main types of raw materials, cellulose contained in lignocellulosic biomass represents the most abundant global source of biomass, which can be utilised for bioethanol production [23]. There are also two approaches for producing bioethanol from lignocellulosic biomass through (1) Biochemical (2) Thermochemical processes.

2.1.1. Biochemical production of bioethanol

Figure 2 illustrates the high level technologies for producing bioethanol from these various biomass feedstocks. Typically, the common steps for biologically producing bioethanol from different feedstocks are fermentation and distillation. For the first generation (1G) bioethanol production, the sugar extracted from sugar-rich crops and that from starch digestion by amylases or acids is directly fermented to bioethanol. To convert lignocellulosic biomass into second generation (2G) bioethanol, an additional step of pre-treatment is usually required.

Figure 2. Technologies required producing bioethanol from biomass. [24]

A wide variety of lignocellulosic feedstocks are potentially available for bioethanol production such as wood, grass, agricultural waste and MSW (municipal solid waste). Their physical structures and chemical compositions are different; therefore technologies applied for bioethanol production can be diverse. In addition to the main product bioethanol, co-

products are also usually produced, such as heat and electricity generated by burning lignin-rich residue from fermentation and also, potentially, a wide range of high value-added chemicals like acetic acid, furfural and hemicellulose sugar syrup and the low molecular weight lignin.

General technologies required for biologically producing 2G bioethanol include (1) pre-treatment, (2) enzymatic hydrolysis, (3) fermentation, and (4) distillation.

Pre-treatment is applied to enhance the accessibility of enzyme to biomass by increasing available biomass particle surface area for enzyme to attack. This can be achieved by partially removing lignin and/or hemicellulose, changing the structure of biomass fibres to decrease cellulose crystallinity and its degree of polymerization. The current available pre-treatment methods can be classified as mechanical, chemical and biological. Table1 summarised some typical pre-treatment methods and their characterisations. Pre-treatment has been viewed as the most expensive step in the biologically production of bioethanol. Therefore, it is important to assess the economic feasibility of the pre-treatment method in addition to its technology performance. More information about each pre-treatment method can be found in Section 5.

Enzymatic hydrolysis is carried out under mild conditions with potentially high sugar yields and relatively low maintenance costs. Nevertheless, major challenges for cost-effective commercialisation remain, such as the high cost of enzymes, the slow rate of enzymatic reaction and potential inhibition by sugar degradation products from pre-treatments [48]. In enzymatic hydrolysis, cellulose is hydrolysed by a suite of enzymes, including cellulase and β-glucosidase crudely purified from lignocellulose-degrading fungi such as *Trichoderma reesi*, *Trichoderma viride* and *Aspergillus niger*. Cellulase refers to a class of enzymes including endocellulase breaking internal bonds of cellulose, exocellulase cleaving from the free ends of chains produced by endocellulase to form cellobiose (a dimer of glucose), and cellobiase (β-glucosidase) then hydrolysing cellobiose to produce glucose monomers. In addition, most of cellulase mixtures contain hemicellulase that facilitates hemicellulose hydrolysis to assist with the overall effectiveness of enzymatic hydrolysis.

After the enzymatic hydrolysis, sugar monomers can then be fermented to ethanol by micro-organisms (*e.g. Saccharomyces cerevisiae* and *Zymomonas mobilis*). Fermentation has been commercialised in brewery and food manufacturing for centuries and itself is not a complex and expensive process. The challenges regarding fermentation for the bioethanol industry are: (1) to convert pentose (C5 sugar) which cannot be fermented by the conventional yeast efficiently, and (2) to prevent inhibition caused by sugar degradation products from pre-treatments. Research has shown the feasibility of construction and application of genetically engineered yeasts capable of converting both pentose and hexose to ethanol [49]. Further potential lies in using bacteria with the metabolic pathways necessary to ferment all sugars available from lignocellulosic biomass. *Z. mobilis* has shown to be capable of metabolising 95% of glucose, 80% of xylose and 40% of other sugars in corn stover hydrolysate [50]. Metabolic engineered *Geobacillus thermoglucosidasius* has demonstrated an ethanol yield of over 90% of theoretical at temperatures in excess of 60°C [51].

Pre-treatment method	Process and conditions	Possible changes in biomass	Disadvantages	Reference
Steam explosion	No agent temperature:160-260°C,20-50 bar , 2-5 minutes	Dissolve hemicelluloses Low sugar degradation	Partially degrade hemicellulose	[25-27]
Ammonia fibre explosion (AFEX)	Ammonia as agent, 65-90°C, 0.5-3 hours	Change biomass physical structure Enhancing hemicelluloses hydrolysis	Limited effects on soft and hardwood	[28, 29]
SO_2/H_2SO_4 explosion	SO_2 as agent, 160-220°C, < 2 minutes	Dissolve hemicelluloses effectively for hardwood and agricultural residues	Degradation of hemicelluloses, less effective for softwood	[30, 31]
CO_2 explosion	CO_2 as agent, 35°C, 56.2 bar, 10-60 minutes	Interrupt crystalline structure of cellulose	Inefficient for softwood and high capital cost	[32, 33]
Hot liquid water	Water as agent, 190-230°C, 45 seconds-4 minutes	Effectively dissolve hemicelluloses Very low degradation	Water recycling prohibitively expensive	[34-36]
Dilute acid	H_2SO_4 as agent , over 160°C, 2-10 minutes	Effectively dissolve hemicelluloses	Needs neutralisation, significant formation of fermentation inhibitors	[37-39]
Alkaline	NaOH/ $Ca(OH)_2$ /Ammonia as agent, 70-120°C, 20-60 minutes	Removal of lignin Low hemicelluloses degradation	Costs of reagents and wastewater treatment are high	[40-42]
Oxidation	$Ca(OH)_2+O_2/H_2O_2$ as agent, 140°C, 3 hours	Removal of lignin Low hemicelluloses degradation	Costs of reagents and wastewater treatment are high	[43, 44]
Organic solvent	Ethanol as agent, 140-200°C, 30-150 minutes	Removal of lignin	Cost of solvent recovery is high	[45, 46]
Ionic liquid	Ionic liquid as agent, 120°C, 22 hours	Remove of lignin and hemicellulose	Costs of reagents and long treatment time	[47]

Table 1. Chemical pre-treatment methods for lignocellulosic biomass.

Bioconversion process configurations, including Separate Hydrolysis and Fermentation (SHF), Simultaneously Saccharification and Fermentation (SSF), Simultaneously Saccharification and Co-Fermentation (SSCF), and Consolidated Bioprocessing (CBP). The SHF has many advantages, such as allowing both enzyme and micro-organisms to operate at their optimum conditions. Also, any accidental failure of enzymatic hydrolysis and fermentation would not affect the other steps. Alternatively the enzymatic hydrolysis may also be combined with fermentation and can thus be carried out simultaneously in a same reactor - this being known as the simultaneous saccharification and fermentation (SSF). During enzymatic hydrolysis, the cellulases are strongly inhibited by hydrolysis products: glucose and short cellulose chains ('end-point' inhibition). SSF can overcome this inhibition by fermenting the glucose to ethanol as soon as it appears in solution. However, ethanol itself inhibits the action of fermenting micro-organisms and cellulase although ethanol accumulation is less inhibitory than high concentrations of hydrolysis products [52]. Nevertheless, SSF operating at the compromised temperature (37-40 °C) has some drawbacks caused by the different optimal temperatures for the action of cellulases (45-50°C) and the growth of microorganisms (typically 28-35°C). One method to overcome this disadvantage is the utilisation of thermo-tolerant fermenting organisms. SSCF is a promising SSF process where the micro-organism co-ferment pentose and hexose to bioethanol. CBP currently becomes the focus of most research efforts to date; it integrates cellulase production, cellulose hydrolysis and fermentation in one step by using an engineered strain [53]. Many studies have been reported in CBP technologies developments recently [54-56].

Nevertheless, other significant efforts are also required to enable future integrated biorefinery. They include (1) promising process designs to integrate energy consumption and minimise the water footprint (2) producing a range of high value added by products, *e.g.* power, chemicals, and lignin-derived products *etc*.

2.1.2. Thermo-chemical production of bioethanol

The thermo-chemical bioethanol production refers to a series of processes including biomass indirect gasification, alcohol synthesis and alcohol separation as shown in Figure 3.

The biomass is processed and dried by flue gas before being fed to biomass gasifier. The biomass is chemically converted to a mixture of syngas components (*i.e.* CO, CH_4, CO and H_2 *etc*), tars, and a solid char which is the fixed carbon residual from the biomass. The heat required for endothermic gasification reactions is supplied by circulating hot synthetic olivine 'sand' between the gasifier and combustor. The solid char and 'sand' from the gasifier are separated by cyclones and then sent to a char combustor where the char is oxidised by oxygen injected. The heat released from the oxidation of the char reheats the 'sand' over 980 °C. The hot 'sand' is then sent to the gasifier to provide heat required by gasification reactions. The ash from the char combustor and sand particles captured are sent to landfill after being cooled and moistened. The tar produced in the gasifier is reformed to CO and H_2 with the presence of catalyst in a bubbling fluidized bed reactor. The syngas

generated in the biomass gasifier goes through a cooling and clean-up process to remove CO_2 and H_2S. During this process, the tar is reformed in an isothermal fluidized bed reactor and the catalyst is regenerated. The cleaned syngas is then converted to alcohols in a fixed bed reactor. The produced alcohol stream is depressurised in preparation of dehydration and separation afterwards. The evolved syngas in alcohol stream is recycled to the Gas Cleanup & Conditioning section. Finally, the alcohol mix is separated to methanol, ethanol and other higher molecular weight alcohols. The heat required for the gasifier and reformer operations and electricity for internal power requirements is provided by a conventional steam cycle. The steam cycle produces steam by recovering heat from the hot process streams throughout the plant.
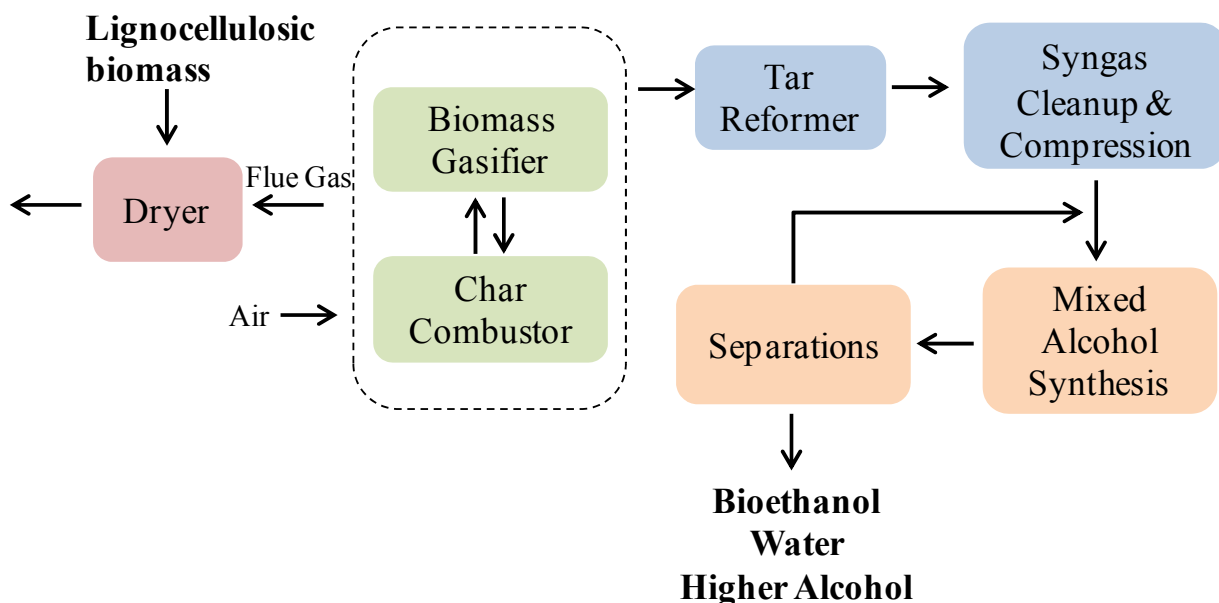
Figure 3. The schematic of a thermo-chemical cellulosic ethanol production process [57]

To compare these two approaches (biochemical *vs.* thermo-chemical) for producing bioethanol from economic point of view, process simulation and economic analysis are usually performed to calculate the minimum ethanol selling price (MESP) calculated from the discounted cash flow method. The MESP is defined as the selling price of bioethanol that makes the net present value of the biomass to bioethanol process equal to zero with a certain discounted cash flow rate with in a return period over the life of the plant [37]. In other words, it refers to the ethanol price at the break-even point which means annual costs and income are equal at this price. Several studies suggested that the estimated prices for 2G bioethanol produced biochemically is in the range of 2.16 to 4.44 USD $/gallon, depending on the type of biomass feedstock, technologies applied and the reference year based on [37, 58-61]. On the other hand, NREL (National Renewable Energy Laboratory) reported a relatively low MESP for bioethanol produced thermo-chemically as 1.07 USD $/gallon. Nevertheless, raw materials cost (including biomass feedstock and catalyst or enzyme) is the main contributor to the MESP. For example, the cost of corn stover accounts for 40% and 43% of the MESP for bioethanol biochemically and thermo-chemically produced respectively [37, 57].

From environmentally point of view, a comparative LCA study showed that biochemical approach offers a slightly better performance on greenhouse gas emission and fossil fuel consumption impact categories, but the thermo-chemical pathway has significantly less water consumption [62].
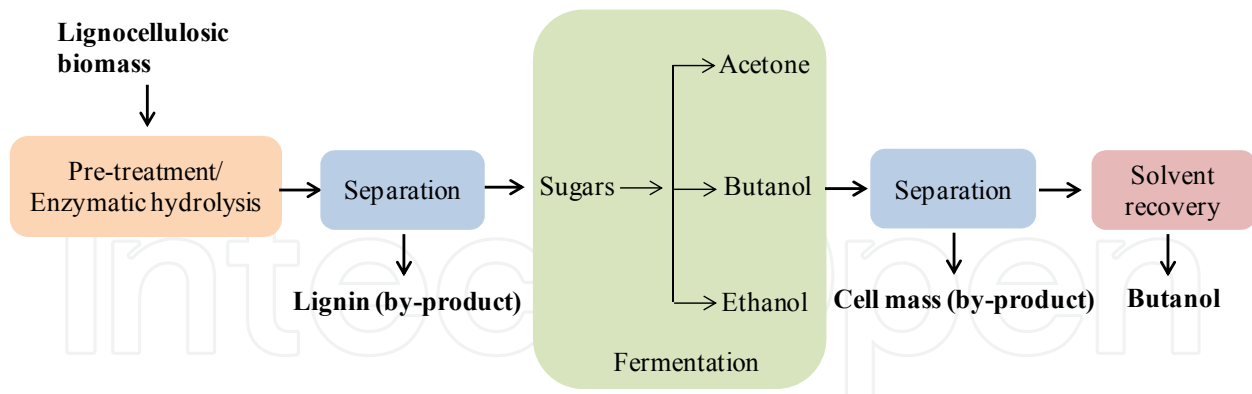
2.2. Butanol

Butanol is another attention attracted alternative fuel to gasoline besides ethanol because of its properties with respect to gasoline blending, distribution and refuelling, and end use in existing vehicles. For instance, butanol has relatively high energy content which is 30% higher than ethanol and is closer to gasoline. Additionally, butanol has low vapor pressure, low sensitivity to water and it is less volatile, and less flammable when compared with other liquid fuels [63]. Therefore butanol can be handled conventionally in the existing petroleum infrastructure, including transport *via* pipeline. It also can be blended, at any ratio, with either gasoline or diesel fuel at existing refineries, thus avoiding the capital investment associated with plant revamps and the need for major operational, *etc*.

Similarly to bioethanol, butanol can be biochemically produced from both agricultural crops and lignocellulosic biomass using *Clostridium acetobutylicum* or *C. beijerinckii* to ferment lignocellulosic hydrolysate sugars (hexoses and pentoses) to butanol. Traditionally, sugar-rich agricultural crops such as corn, cane molasses and whey permeate have been successfully used as feedstocks in the commercial production of butanol for decades. However, the cost for these food crops rises significantly nowadays; therefore, lignocellulosic biomass becomes more popular as substrates for butanol production. In similar ways of producing bioethanol, pre-treatments are required prior to enzymatic hydrolysis (using cellulase and cellobiose). However, one of technology challenges is the inhibition caused by by-products in pre-treatments such as furfural, HMF, acetic acid, and ferulic acid generated in dilute acid pre-treatments *etc*. Among these by-products, ferulic and ǫ-coumaric acids were found can significantly inhibit fermentation but furfural and HMW were surprisingly stimulating to the cell culture [64].

The resulted lignocellulosic hydrolysate is then fermented by microorganisms *via* Acetone-butanol-ethanol (ABE) fermentation (Figure 4). The main challenge in the ABE fermentation is the product butanol itself is toxic to the fermenting microorganisms. In order to overcome this drawback, focused research efforts are to (1) improve the fermentation strategies to minimise the level of inhibitors accumulated such as simultaneously removing butanol and (2) to develop or genetically improve butanol – producing cultures.

However, biobutanol has several potential shortcomings. It is more toxic to humans and animals in the short term than ethanol or gasoline (although some components of gasoline, such as benzene, are more toxic and/or carcinogenic). And it is not clear whether butanol will degrade the materials commonly used in automobiles that can come into contact with motor fuels; building evidence suggests that it will not cause problems, but there has been no definitive testing on the wide range of potentially affected polymers and metals [65].

Figure 4. Phases of ABE fermentation for producing butanol

Additionally, butanol is reported cannot deliver a better economic feasibility and a more sustainable environmental performance when compared with bioethanol under the current level of technology [66]. The relatively low yield of solvents out of glucose (mixture of acetone, ethanol and butanol), which is in the range of 33% - 45% (wt), is the main cause for the high cost of butanol. This economic study argued that butanol perhaps can be sold as chemicals rather than transport fuel unless the technology would be improved to make butanol production economically competitive with bioethanol.
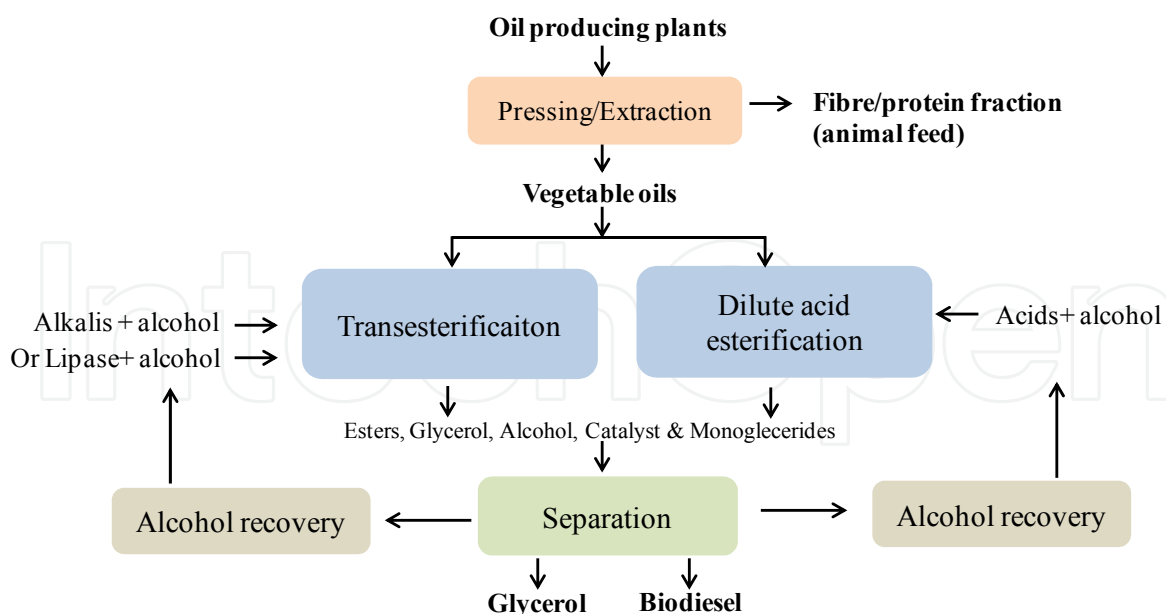
2.3. Biodiesel

Biodiesel refers to a liquid fuel alternative to petroleum diesel which can be used alone or blended with petroleum diesel. Similarly to bioethanol blends, blends of 20% biodiesel (B20) or lower can be used in diesel equipment without or with only minor modifications. Biodiesel can be produced from animal fat or oil from plants such as soybean and *Jatropha*, or from microalgae and fungi.

2.3.1. Biodiesel from vegetable oil

Conventionally, the biodiesel is produced from vegetable oil with the presence of alcohol/alkaline/acid catalyst. This process is known as transesterificaiton or alcoholysis as shown in Figure 5 [67].

The vegetable oil is converted to esters and glycerol by reacting with an alcohol which can be ethanol, methanol or butanol. During this reaction, catalysts (*e.g.* alkalis, acids or enzymes) are required to improve the reaction rate and yield. Alkalis including NaOH, KOH and carbonates *etc*. are usually used as catalyst when feedstock containing less than 4% fatty acids. Acids, which are normally used when feedstocks contain more than 4% free fatty acids, include sulfuric acid, hydrochloric acid and sulphonic acids *etc*. Lipase, an enzyme that catalyses the hydrolysis of fats, can be used as a biocatalyst [68].

Figure 5. The schematic of biodiesel production [67]

A review by Ma and Hanna [69] summarized the parameters significantly influencing the rate of transesterificaiton reaction which include temperature, ratio of alcohol to oil, type of catalyst and catalyst concentration. The ester yield is increased by rising the transesterificaiton temperature; however, it will increase the risk of forming methanol bubbles when the temperature is close to methanol's boiling point. The ratio of alcohol to oil depends on the type of catalyst used which is approximately 6:1 for alkali catalyst and 30:1 for acid catalyst [70]. Enzyme used as a catalyst is becoming more attractive nowadays because it tolerates free fatty acid and water contents in the oil to avoid soap formation and thus results in an easier purification of biodiesel and glycerol [68]. However, the relatively high price of enzyme catalyst makes its utilization in the commercial production of biodiesel challenging.

Nowadays, 90% of U.S. biodiesel is made from soybean oil. The price relationship between vegetable oils and petroleum diesel is key influential factor to the profitability of biodiesel industry. Because of the increasing price of vegetable oils, biodiesel industry is suffering uncomfortable situations [71]. As a result, alternative non-food feedstocks and the associated technologies are becoming the focused research in biodiesel area.

Jatropha curcas is an agro-forestry crop growing in tropical and sub-tropical countries, such as India, Sahara Africa, South East Asia and China. This crop grows rapidly and takes 2-3 years to reach maturity with economic yields [72]. Lu *et al.* reported a higher than 98% biodiesel yield by a pre-esterification using solid acid followed by a transesterificaiton using KOH [73]. A high yield of 98% (wt) is also reported by Shah *et al.* [74] which is obtained from *Jatropha* oil using *Pseudomonas cepacia* lipase. Kumari *et al.* [75] also documented a relatively high yield of 94% (wt) biodiesel yield from *Jatropha* oil using lipase from *Enterobacter aerogene.* They also reported negligible loss in lipase activity even after repeated use for several cycles.

2.3.2. Biodiesel from microalgae

Due to biodiesel produced from oil crops, waste cooking oil and animal fat cannot meet the high demand for renewable transport fuels, another biomass feedstock microalgae becomes attractive. This is because (1) microalgae are sunlight-driven cells, (2) grow rapidly with biomass double time of 24 hours, (3) require less high quality land used compared to other feedstock, (4) many are exceedingly rich in oil and (5) biodiesel produced from microalgae is 'carbon neutral' [76] (see Figure 6). However, several challenges need to be tackled in order to produce biodiesel from microalgae commercially. Scott *et al.* [77] provides a comprehensive review discussing these challenges and potential tackles.
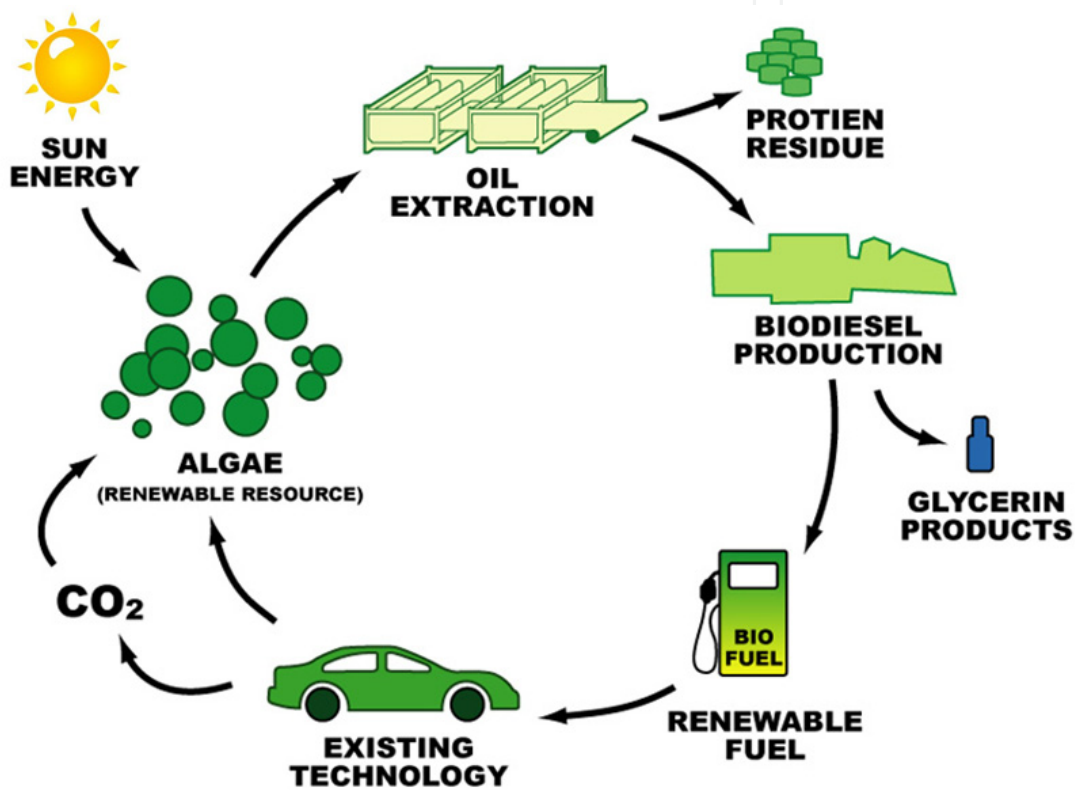
Figure 6. Life cycle of biodiesel produced from microalgae

There are estimated 300 000 species in algal strain. After screening, typical species including *Botryococcus braunii*, *Nannochloropsis sp.*, *Neochloris oleoabundans*, *Nitzschia sp.*, and *Schizochytrium sp.* have up to 77% (dry wt) oil content [76]. Microalgal biomass is produced with the presence of light, fed carbon dioxide and essential inorganic elements including nitrogen (N), phosphorus (P), iron and in some cases silicon. Biomass is then harvested and extracted to obtain oil for biodiesel production using transesterificaiton with methanol. Nutrients and spent biomass are recycled in the downstream process.

Factors involved in these phases are all important to be considered and optimized to maximize the biomass yield and minimize the production cost. First of all, the light level needs to be manipulated to deliver an optimal light to all of the algae cells within the culture. The excess light level not only can results in less efficient use of absorbed light

energy but also can cause biochemical damage to the photosynthetic machinery [77]. Secondly, though minimal nutrients requirement can be estimated according to the approximate molecular formula of microalgae which is $CO_{0.48} H_{1.83} N_{0.11} P_{0.01}$[78], nutrients such as phosphorous must be supplied in excess. In order to minimise the nutrient cost, sea water supplement with commercial nitrate and phosphate fertilisers can be used for growing microalgae [76]. Thirdly, the choice of facility (open raceway ponds or closed photobioreactor) is important since the scale-up of biomass production is largely depending on the surface area rather than volume because light only penetrate a few centimeters [77]. The former raceway pond is an open-top close loop recirculation channel with a typical depth of 0.3 m. It is relatively cheap to build and has been operated with extensive experience for decades. However, the drawbacks for this type of facility are (1) it is difficult to avoid microbial contamination, (2) it requires for extensive areas of land for ht raceways and substantial cost regarding harvesting, and (3) it has poorly mixed therefore has optically dark zone [76, 77]. The photobioreactor a tubular reactors consists of an array of glass or plastic transparent tubes. It requires a large amount of energy for pumping and compressing air for sparging culture [77].

The biomass broth from production phase is harvested and processed to remove water and residual nutrients which are recycled. The concentrated biomass paste is then extracted to obtain oil and lipids using water and extraction solvent (*e.g.* hexane) [79]. It is difficult to release lipids from microalgae intracellular location using an energy-efficient way because of the large amount of solvent required. Also it is key to avoid significant contamination by other cellular components such as DNA [77].

The efforts in academic research and industrial commercialization of biodiesel production from microalgae include: (1) integration of production process such as energy integration, water and nutrient recycling; (2) improvement of microalgae biology *via* genetic and metabolic engineering such as enhancing their photosynthetic efficiency, increasing biomass yield and oil content and improving temperature tolerance to reduce cost associated with cooling; (3) improving photobioreactors regarding their capacity and operational ability [76].

2.4. Biogas from anaerobic digestion

Anaerobic digestion (AD) has been used to treat biodegradable solid waste such as MSW, industrial waste and sewage sludge over decades. Biogas containing methane and carbon dioxide is the main product form AD digester. Generally, biogas is collected in the gas tank and they can be directly exported to national gas grid or sent to combustion in the CHP system to generate electricity (with a yield in the range of $0.7 – 2.0$ kwh/m^3 biogas) and heat.

AD process is a dynamic complex system involving microbiological, biochemical, and physical-chemical processes though which the biodegradable waste are turned into biogas. Among biological waste treatment methods, AD has been identified as the most environmentally sustainable option for treating biowaste since it offers a unique technology which enables not only diverting biodegradable from landfill but also producing bio-energy and potential by-products such as a beneficial soil conditioner [80].

AD systems generally have four classifications [80]:

- Mesophilic (30 - 40 °C) or thermophilic (50 - 65°C) according to temperature
- Wet digestion (< 15% dry solid) or dry digestion (between 20% - 40% dry solid) according to the solid content in feedstock
- Single step (one vessel) or multiple step digestions (normally two-step digestion i.e. hydrolysis and methanogenesis)
- Batch digestion (loading feedstock in the beginning and remove products at the end of process) or continuous digestion (loading feedstock and withdraw products continuously)

Generally, five trophic groups are considered to be relevant to the process such as hydrolysing bacteria, acidogenic bacteria, acetogenic bacteria, aceticlastic and hydrogentrophic methanogens. They are involved in a series of digestion steps which are described as following and in Figure 7 [81] :

1. Carbohydrates, lipids, proteins *etc.* are broken down through hydrolysis to sugars, long – chain fatty acids and amino acids by extracellular enzymes released by hydrolytic bacteria;
2. Then these molecules are converted into volatile fatty acids, alcohols, CO_2 and H_2 in acidogenesis step;
3. These molecules are then further converted by acetogenic bacteria mainly into acetic acid, H_2 and CO_2;
4. Finally, all these intermediate products are turned into CH_4, CO_2 and water in the last step where methanogenic bacteria are involved. Three biochemical pathways are used by methanogens to produce methane gas:

   a. Acetotrophic methanogenesis: $4\ CH_3COOH \rightarrow 4\ CO_2 + 4\ CH_4$

   b. Hydrogenotrophic methanogenesis: $CO_2 + 4\ H_2 \rightarrow CH_4 + 2\ H_2O$

   c. Methylotrophic methanogenesis: $4\ CH_3OH + 6\ H_2 \rightarrow 3\ CH_4 + 2\ H_2O$
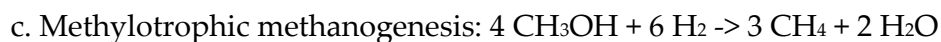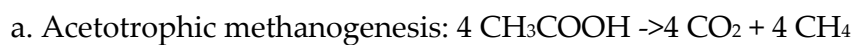
Due to for different substances, biological consortia and digestion conditions, the overall biogas yield and methane content will vary. Typically, the methane content of biogas is in the range of 40-70 % (v/v) [82].

Several key factors influence the Ad performance. They include pH, temperature, organic loading rate (OLR), the ratio of inoculum to substance (I/S) and the presence of inhibitory substances. Generally, mesophilic AD (35 - 37 °C) is more preferred than thermophilic AD (50 - 60°C) since the latter one offers less methane yield and it is more sensitive to environment change [81]. The pH range suggested for AD process is in the range of 6.8 -7.2 [80]. In addition, anaerobic digestion requires attention to the loading of nutrients for bacteria including carbon and nitrogen. The proper ratio of these two components (C/N) depends on the digestibility of the carbon and nitrogen sources between 20: 1 and 30:1. Other nutrients such as S, Mg, K, P, Ca, Fe, Zn, Al, Ni, Co, Cu and vitamin B12 are necessary [80]. However, these components are generally contained in the Organic Fraction of MSW (OFMSW) while they are added in the laboratory scale AD systems.
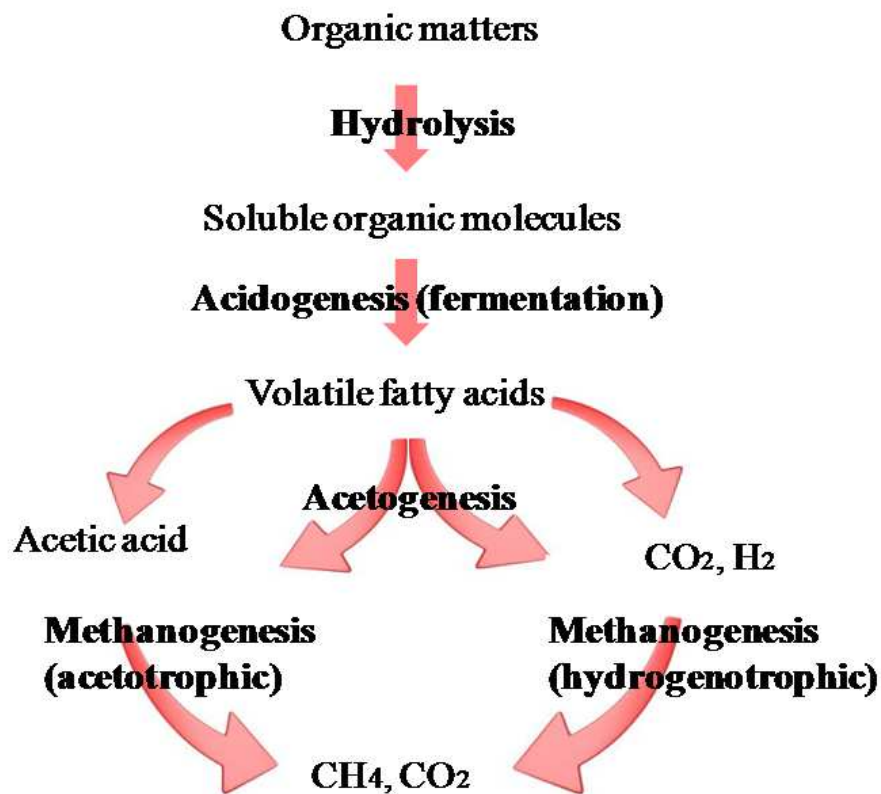
Figure 7. Anaerobic digestion biochemical conversion pathways

Regarding the AD process operation, I/S ratio is considered as one the most important parameter. It is suggested to be approx 1 by Raposo *et al.*[83] who found that biogas production was inversely proportional to the I/S ratio in the range of 1 to 3. two stage AD is more preferred because it provides optimum environmental conditions for each bacteria group, offers accelerated digestion rates, better stability and thus increased methane yield [80]. Another process parameter is retention time which includes hydraulic retention time and solid retention time. The former refers to the mean time that any portion of liquid feed remains in a digestion system; the latter is defined as the mean time for any portion of solid feed or microbal biomass remains in the digester. These two retention times are the same in a single stage digester; while in a two stage digestion system the longer solid retention time is, the higher degradation rates and biogas yields are obtained [80]. In addition to the above process parameters discussed, the organics loading rate (OLR) is also critical which is measured as volatile solid (VS) or chemical oxygen demand (COD) of feed to a unit volume of digester per unit time [80]. The range for OLR is suggested in the range of 6 - 9.7 kg VS/day/m^3 which is varied with the biodegradability of feedstock and AD systems [81].

Furthermore, the quality of OFMSW treated in biogas plants is also crucial for balanced performance of the biogas process, the technical feasibility of process and the use of residual/effluent as agricultural soil conditioner. Therefore, the costs associated with waste collection, sorting and pre-treatment should be considered [84].

Currently, most of MSW in the U.S. are sent to composting as an alternative to landfill. This is because it is more difficult to treat OFMSW than treating wastewater or manure. In addition, the AD of OFMSW requires a large amount of investment and technological experience as well as a higher capital and operating cost than compositing and landfilling [82]. The relatively low gate fees for landfill in the U.S. and relatively low energy prices make AD difficult to be commercialized in the U.S compared to those in Europe [82]. However, in the UK, there is currently very little waste treatment using AD apart from the use of AD to treat sewage sludge and wastewaters [85].

However, LCA studies have shown that AD of MSW reduces environmental impacts and is more cost - effective (in Europe) on a whole system basis than composting or landfilling options [86, 87].

3. Commodity chemicals and materials

Today, only a small numbers of chemicals are produced from lignocellulosic feedstocks via fermentation. Much less attention has been given to biomass as a feedstock for organic chemicals, while there has been a strong political and technical focus on using biomass to produce transportation fuels. However, replacement of petroleum-derived chemicals with those from biomass will play a key role in sustaining the growth of the chemical industry [88]. One way to replace petroleum is through biological conversion of lignocellulosic resources into products now derived from petroleum. The current developments especially in fermentation technologies, membrane technologies and genetic manipulation open new possibilities for the biotechnological production of market relevant chemicals from renewable resources [5].

In lignocellulosic feedstocks biorefinery processes, the sugars or some of the fermentation products can be chemically converted into a variety of chemicals, which could be used to form biological materials, such as protein polymers, xantham gum, and polyhydroxybutyrate. The lignin as remaining fraction from lignocellulosic feedstocks, could be converted through hydrogenation processes into materials, such as phenols, aromatics, and olefins, or simply burned as a boiler fuel for cost efficiency of the overall process. Currently, conventional chemicals include acetaldehyde, acetic acid, acetone, n-butanol, ethylene, and isopropanol can simply be derived from LCF. Appropriate organisms could then convert the sugars into the desirable products and co-products for this process. The advantage to such products is that the market is already established, and minimal effort is required to integrate these products into existing markets. However, co-product markets might be limited, and caution must be taken in considering their impact on overall economics, especially for large-scale implementation. A sequence of processes comparable to those employed for cellulosic ethanol production would be used to pre-treat the lignocellulosic biomass to open its structure for the weight of the feedstock. Therefore, lignocellulosic biomass might be expected as the low cost of raw materials could be converted to a variety of commodity chemicals and materials [20].

3.1. Present promising commodity chemicals and materials from LCF biorefinery

3.1.1. Lactic acid

Lactic acid represents a chemical with a small world market, and the market for traditional applications of lactic acid is estimated to be growing at about 3–5% annually. New products based on lactic acid may increase the world market share significantly, which includes the use of derivatives such as ethyl esters to replace hazardous solvents like chlorinated hydrocarbon solvents in certain industrial applications. In theory, one mole of glucose results in almost two moles of lactic acid. The recovery process for lactic acid is much more sophisticated than that of the ethanol fermentations, involving various precipitations, chromatographic and distillation steps [5].

Lactic acid can be converted to methyl lactate, lactide, and polylactic acid (PLA) by fermentation [89]. The PLA is a biodegradable polymer used as environmentally friendly biodegradable plastic, which can be the replacement for polyethylene terephthalates (PETs) [90]. Recently, attempts have been made to produce PLA homopolymer and its copolymer by direct fermentation by metabolically engineered [91], shows a great potential for utilizing lignocellulosic feedstock for the key biodegradable polymers. Efforts are also under way to develop efficient processes for converting biologically produced lactic and hydroxypropionic acids to methacrylic and acrylic acids [88].

Lactic acid can be produced either chemically or by microbial fermentation. A major disadvantage for chemical synthesis is the racemic mixture of lactic acid. Microbial fermentation offers both utilization of renewable carbohydrates and production of pure L- or D-lactic acid depending on the strain selected. Currently, most of lactic acid production is produced mainly from corn starch. However, the use of lignocellulosic feedstock for lactic acid production appears to be more attractive because they do not impact the food chain for humans. But the process for converting lignocellulosic feedstock into lactic acid is not cost efficient due to the high cost of cellulase enzymes involved in cellulose hydrolysis [92, 93]. In addition, the main bottleneck during the hydrolysis of lignocellulosic feedstock by cellulases is the inhibition on cellulase by glucose and cellobiose, which remarkably slows down the rate of lignocellulosic feedstock hydrolysis [94]. Economic improvements on the process are mainly focused on increasing the lactic acid tolerance, reducing the requirements for complex and cost intensive growth supplements and products recovery [95].

3.1.2. Acetone–butanol–ethanol (ABE)

An acetone – butanol – ethanol blend (in a ratio of 3-6-1) may serve as an excellent car fuel, which can be easily mixed not only with petrol but also with diesel. ABE as a fuel additive has the advantage of a similar heat of combustion to hydrocarbons, and perfect miscibility with hydrocarbons, even when water is present. The fermentative production of ABE used to be the second largest industrial fermentation after ethanol production [5]. Product inhibition caused principally by butanol is the main problem that hindering commercial development of the fermentation process. One way to overcome this inhibition problem

would be to couple the fermentation process to a continuous product removal technique, so that inhibitory product concentrations are never reached. However, even with continuous product removal, product formation in these systems does not proceed indefinitely, because of the inhibition caused by the accumulation of mineral salts in the reactor [96]. Due to the shortage of raw materials, namely corn and molasses, and to decreasing prices of oil, ABE fermentation is not profitable when compared to the production of these solvents from petroleum. During the 1950s and 1960s, ABE fermentation was replaced by petroleum chemical plants.

Currently, the production of mixtures of acetone, butanol and ethanol (ABE) by sugars derived from lignocellulosic feedstocks continues to receive attention because of its potential commercial significance. The traditional fermentative production of acetone– butanol– ethanol is batch anaerobic bacteria fermentation with Clostridia. The substrate consists of molasses, and phosphate and nitrogen sources. Instead of molasses other sugar sources like sugar from lignocellulosic feedstock can also serve as a raw material for fermentation [97].

3.2. Xylan

As one of main polysaccharides in lignocellulosic biomass, xylan has a variety of applications in our everyday life and affects our well-being. For example, (1) xylans are important functional ingredients in baked products [98]; (2) xylans can be potentially used for producing hydrogels as biodegradable coatings and also encapsulation matrices in many industrial applications; (3) xyl, the main constituent from xylans, can be converted to xylitol which is used as a natural food sweetener and a sugar substitute [99]; (4) xylans can be used for clarification of juices and improvement in the consistency of beer [100]; (5) xylans are also important for livestock industry as they are critical factors for silage digestibility; (6) xylans are major constituents in non-nutritional animal feed [101]; (7) xylans can be converted to sugars and then further to fuels and chemicals; (8) enzymes that degrade xylan can facilitate paper pulping and biobleaching of pulp [100].

Xylans, the main component in hemicellulose, are heteropolysaccharides with homopolymeric backbone chains of 1,4 linked β-d-xylopyranose units. In addition to xylose, xylans may also contain arabinose, glucuronic acid or its 4-O- methyl ether, acetic, ferulic, and p-coumaric acids. Xylans can be categorized as linear homoxylan, arabinoxylan, glucuronoxylan, and glucuronoarabinoxylan. Depends on the different sources of xylan (i.e. soft- and hard- wood, grasses, and cereals), the composition of xylans differs [100].

Hemicellulose can be derived via chemical treatment or enzymatic hydrolysis. As discussed in Section 2.1.1, several pre-treatments listed in Table 1 are available to fractionate, solubilize and hydrolyze and separate hemicellulose from cellulose and lignin components. Generally, hemicelluloses are solublized by either high temperature and short residence time (270°C, 1 min) or lower temperature and longer residence time (190 °C, 10 min) [102]. However, some of chemical treatment result in hemicellulose degradation by-products such as furfural and

5-hydroxymethyl furfural (HMF) which are inhibitors for microorganisms involved in downstream fermentation if applicable.

Biodegradation of xylan requires enzymes including endo-β-1,4-xylanase, β-xylosidase, and several accessory enzymes, such as α-L-arabinofuranosidase, α-glucuronidase, acetylxylan esterase, ferulic acid esterase, and *p*-coumaric acid esterase, which are necessary for hydrolyzing various substituted xylans. The endo-xylanase attacks the main chains of xylans while β-xylosidase breaks xylooligosaccharides to monomeric sugar xylose. The α-arabinofuranosidase and α-glucuronidase remove the arabinose and 4-*O*-methyl glucuronic acid substituents from the xylan backbone [100]. The esterases hydrolyze the ester linkages between xylose units of the xylan and acetic acid (acetylxylan esterase) or between arabinose side chain residues and phenolic acids , for example ferulic acid (ferulic acid esterase) and *p*-coumaric acid (*p*-coumaric acid esterase) [100].

Hemicellulose hydrolysates from lignocellulosic biomass either obtained by chemical treatment or enzymatic hydrolysis are attractive feedstock for producing bioethanol, 2,3-butanediol or xylitol. Other value added products from hemicellulose hydrolysate include (1) ferulic acid, and (2) lactic acid which can be used in the food, pharmaceutical, and cosmetic industries [100].

3.3. Other main chemicals and materials from lignocellulosic feedstock

Acetic acid, at present, most demand of the commercial acetic acid is met synthetically. The production involves fermentation by a species of Acetobacter, which converts ethanol to acetic acid with a small final concentrations percentage (4–6%), using almost exclusively for vinegar production. In commercial practice, the actual yield roughly 75–80% of the theoretical yield [5].

Ferulic acid, as a precursor for numerous aromatic chemicals used in the chemistry industry, can be produced from lignocellulosic feedstock [88].

Levulinic Acid, Formic Acid and Furfural, their biorefinery process usually involves the use of dilute acid as a catalyst but it differs from other dilute-acid lignocellulosic-fractionating processes in that free monomer sugars are not the product. Instead, these monosaccharides are converted into the platform chemicals levulinic acid and furfural as the final products by multiple acid-catalysed reactions [103].

3.4. Opportunities and challenges

New products from lignocellulosic feedstock including new adhesives, biodegradable plastics, degradable surfactants, and various plastics and polymers could also be derived through the unique biotechnologies. The products with desirable properties that are not easily matched by petrochemical processing are particularly promising targets. Therefore, less price pressure would exist initially for such new products. However, to have a substantial impact on petroleum consumption, it is necessary to ensure that large markets have to be eventually resulted [20].

Even today, the potential of microorganisms for the production of bulk chemicals is far from being fully exploited. The cost of feedstocks still remains one of the crucial points if biotechnological processes are to succeed. The transition of industrial chemical production from petrochemical to biomass feedstock faces real hurdles. Biorefinery processes do not require the high pressures and temperatures compared with most non-biological chemical processes, thus have the potential to reduce costs. However, current non-biological chemical processes (often continuous, and well integrated) for production of commodity chemicals have become highly efficient by evolved through considerable investment. Therefore biorefinery processes for production of commodity chemicals must rapidly approach similar levels of efficiency and productivity. Nevertheless, available technologies, economic opportunities, and environmental imperatives make the use of lignocellulosic feedstock and biorefinery for industrial chemical production not only feasible but highly attractive from multiple perspectives [88].

Simple criteria have been devised to allow rapid screening of potential chemicals and materials from lignocellulosic feedstock for their economic merit. We now need to identify products that have economic potential and improve the technology to a point where these technologies can be applied in a cost-effective way [20].

4. Fractionation of lignocellulosic feedstock

4.1. Definition

Conversion of lignocellulosic materials to higher value products requires fractionation of the material into its components: lignin, cellulose, and hemicellulose, which convert to fuels, and chemicals for the production of most of our synthetic plastics, fibres, and rubbers is technically feasible. Liquefaction of LCF might serve as feedstocks for cracking to chemicals in the similar way that crude oil is presently used. Currently commercial products of LCF fractionation include levulinic acid, xylitol, and alcohols [104]. The ultimate goal of LCF fractionation is the efficient conversion of lignocellulose materials into multiple streams that contain value-added compounds in concentrations that make purification, utilization, and/or recovery economically feasible [15].

Fractionation of LCF is being developed as a means to improve the overall biomass utilization. Hemicellulose when separated from the LCF may find broader use for chemicals, fuel, and food application. The lignin separated in the process can be used as a fuel [105]. Unlike the lignin generated from pulping process, lignin fractionated from biomass by our approach is relatively clean, free of sulphur or sodium.

Fractionation of lignocellulosic materials is very difficult to accomplish efficiently, because of their complex composition and structure [106, 107]. However, fractionation of lignocellulosic materials is essential for some important applications, for example, paper-making, and in their conversion into basic chemical feedstocks or liquid fuels.

Figure 8 shows that fractionation of lignocellulosic biomass into its three major components, cellulose, hemicelluloses and lignin. It has been proposed as the first step of LCF refining to

high value-added products [108]. Achieving high fractionation yields and maintaining the integrity of the macromolecular fractionation products are of major importance regarding the effectiveness of the whole refining process [109].
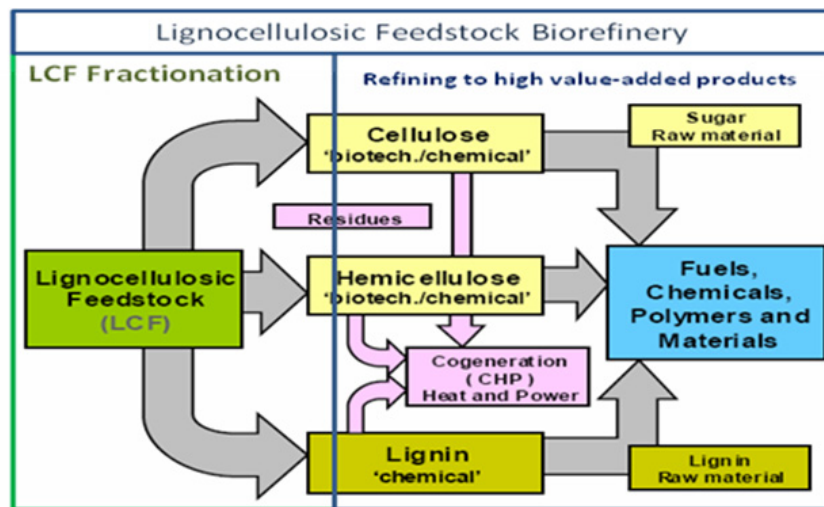
Figure 8. Lignocellulosic Feedstock Biorefinery [110]

4.2. Organosolv fractionation

The organosolv process is a unique and promising LCF fractionation. Using organosolv, lignocellulosic biomass can be converted into cellulosic fibres, hemicellulose sugars and low molecular weight lignin fractions in one-step fractionation [111-113]. Organosolv fractionation is the process to using organic solvents or their aqueous solutions to remove or decompose the network of lignin from lignocellulosic feedstocks with varying simultaneous hemicellulose solubilisation [114]. In this process, an organic or aqueous organic solvent mixture with or without an acid or alkali catalysts is used to dissolve the lignin and part of the hemicellulose, leaving reactive cellulose in the solid phase [106, 115-117]. Usually, the presence of catalyst can increase the solubilisation of hemicellulose and the digestibility of substrate is also further enhanced [118]. Comparing to other chemical pre-treatments the main advantage of organosolv process is that relatively pure, low molecular weight lignin is recovered as a by-product [119]. Organic solvents are always easy to recover by distillation and recycled for fractionation; the chemical recovery in organosolv fractionation processes can separate lignin as a solid material and carbohydrates as syrup, both of which can be used as chemical feedstocks [112, 120, 121]. A variety of organic solvents have been used in the organosolv process such as ethanol, methanol, acetone, ethylene glycol, triethylene glycol, tetrahydrofurfuryl alcohol, glycerol, aqueous phenol, aqueous n-butanol, esters, ketones, organic acids, *etc* [117, 119, 122]. For economic reasons, among all possible solvents, the use of low-molecular-weight alcohols with lower boiling points such as ethanol and methanol has been favoured [123].

Organic solvents are costly and their use requires high-pressure equipment due to their high volatility. The applied solvents should be separated from the system is necessary because

the residual solvents may be inhibitors to enzymatic hydrolysis and fermentation [106], and they should be recycled to reduce operational costs. Otherwise organic solvents are always expensive, so it should be recovered as much as possible, but this causes increase of energy consumption.

The organosolv fractionation seems more feasible for biorefinery of lignocellulosic biomass, as it considers the utilization of all the biomass components. However, there are inherent drawbacks to the organosolv fractionation. In order to avoid the re-precipitation of dissolved lignin, the fractionated solids have to be washed with organic solvent previous water washing, the cumbersome washing processes means more cost. In addition, organosolv fractionation must be performed under extremely tight and efficient control due to the volatility of organic solvents. No digester leaks can be tolerated because of inherent fire and explosion hazard [121]. Its successful commercialization will depend on the development of high-value co-products from lignin and hemicelluloses [124].

4.3. Ionic liquids fractionation

The ionic liquids (ILs) is a group of promising green solvents for the efficient fractionation of lignocellulosic materials. This technology has been used for delignification of lignocellulosic materials in paper-making [125]. Moreover, by fractionating lignocelluloses with ionic liquids it is possible to extract cellulose cleanly, which establishes a platform for the development of cellulose composites and derivatives.

ILs are liquid salts exist at relatively low temperatures (often at room temperature), which typically composed of large organic cations and small inorganic anions. By adjusting the anion and the alkyl constituents of the cation, ILs' solvent properties can be varied. The solvent properties include chemical and thermal stability, non-flammability, low vapour pressures and a tendency to remain liquid in a wide range of temperatures [126]. ILs are called "green" solvents, as no toxic or explosive gases are formed.

Most ILs are nonflammable and recyclable solvents with very low volatility and high thermal stability. Carbohydrates and lignin can be simultaneously dissolved in ILs, and the intricate network of non-covalent interactions between biomass polymers of cellulose, hemicellulose, and lignin is effectively disrupted while minimizing formation of degradation products [127-129].

ILs can dissolve large amounts of cellulose at considerable mild conditions and feasibility of recovering nearly 100% of the used ILs to their initial purity makes them attractive [130]. ILs as cellulose solvents, comparing with regular volatile organic solvents of biodegradability, possesses several advantages including low toxicity, broad selection of anion and cation combinations, low hydrophobicity, low viscosity, enhanced electrochemical stability, thermal stability, high reaction rates, low volatility with potentially minimal environmental impact, and non-flammable property.

However, ILs fractionation using ionic liquids faces many challenges in putting these potential applications into industrial scale., for example, the high cost of ILs, regeneration requirement [16]. Their toxicity toward enzymes and microorganisms must also be established before ILs can be considered as a real option for LCF pre-treatment [129].

Other main challenges are the recovery of ionic liquids and the recovery of hemi-cellulose and lignin from the ionic liquids after extraction of cellulose [126].

4.4. Liquid hot water (LHW) fractionation

Liquid hot water fractionation does not employ any catalyst or chemicals. Pressure is utilized to maintain water in the liquid state at elevated temperatures (160–240 °C) and provoke alterations in the structure of the lignocelluloses [131-133]. LCF in LHW undergoes high temperature cooking in water with high pressure. LHW pre-treatment has been reported to have the potential to enhance cellulose digestibility, sugar extraction, and pentose recovery, with the advantage of producing hydrolysates containing little or no inhibitor of sugar fermentation [134].

Water is an abundant, non-toxic, environmentally benign and inexpensive solvent. LHW is the part range of sub-critical water that near its critical point (374 °C, 22.1 MPa), Sub-critical water (SCW) possesses marvellous properties which are very different from that of ambient liquid water [135-138]. In SCW, dielectric constant, surface tension, and viscosity decrease dramatically with increasing temperature, which enhances the solubility of organic compounds. Sub-critical water is more like non-polar organic solvent (similar with acetone), thus it can substitute for some of organic solvents, and become a clean medium for chemical reactions. SCW is a tunable reaction medium for conducting ionic/free radical reactions, and an effective medium for energy and mass transfer. The ionic product of SCW is larger by three orders of magnitude than that of ambient water, which means concentrations of hydrogen and hydroxide ions are much higher. Therefore, in addition to the increase in kinetic rates with temperature, both acid and base catalyses by water are enhanced in SCW, which can be a solvent or reactant participated in chemical reaction. And without any pollution, hydrolysis in SCW is an environment-friendly technology

The objective of the liquid hot water is to solubilise mainly the hemicellulose to make the cellulose more accessible and to avoid the formation of inhibitors. By keeping the pH between 4 and 7 the autocatalytic formation of fermentation inhibitors are avoided during the fractionation [34, 139, 140]. If catalytic degradation of sugars occurs it results in a series of reactions that are difficult to control and result in undesirable side products.

The slurry generated after pre-treatment can be filtered to obtain two fractions: one solid cellulose-enriched fraction and a liquid fraction rich in hemicellulose derived sugars [34]. Lignin is partially depolymerised and solubilised as well during hot water fractionation but complete delignification is not possible using hot water alone, because of the re-condensation of soluble components originating from lignin.

Water under high pressure can penetrate into the LCF, hydrate cellulose, and remove hemicellulose and part of lignin. The major advantages are no addition of chemicals and no requirement of corrosion-resistant materials for hydrolysis reactors in this process. Liquid hot water pre-treatments are attractive from no catalyst requirement and low-corrosion potential. Liquid hot water has the major advantage that the solubilised hemicellulose and lignin products are present in lower concentrations, due to higher water input and subsequently concentration of degradation products like furfural and the condensation and precipitation of lignin compounds is reduced. However, water demanding in the process and energetic requirement are higher and it is not developed at commercial scale [141].

4.5. Combined technology for LCF fractionation

The efficiency of lignocelluloses utilization can be significantly improved by fractionation [40]. Fractionation of lignocellulosic materials may be achieved by various physical, chemical and biological methods. Combination of different methods may lead to more efficient fractionation processes of lignocellulosic materials [5].

The most promising combined technology for LCF fractionation is the combination of liquid hot water (LHW) with the assisted technologies, which usually are performed before or during the LHW fractionation, including steam explosion, CO2 explosion, Ammonia fibre explosion (AFEX), acid or alkaline pre-treatment, High energy radiation pre-treatment, Wet oxidation and Ozonolysis *etc*.

4.5.1. Combination with steam explosion

Steam explosion is the most widely employed physical-chemical pre-treatment for lignocellulosic biomass. It is a hydrothermal pre-treatment in which the biomass is subjected to pressurised steam for a period of time ranging from seconds to several minutes, and then the pressure is suddenly reduced and makes the materials undergo an explosive decompression. The treatment leads to the disruption of the structure of the material due to the rapid expansion of the water vaporized inside it. The temperatures involved are higher than, or close to, the glass transition temperature of hemicellulose, lignin and cellulose impregnated with water [142, 143], so that the internal cohesion of lignocelluloses is weakened and disaggregation and defibration of the material are facilitated. This pre-treatment combines mechanical forces and chemical effects due to the hydrolysis (auto-hydrolysis) of acetyl groups present in hemicelluloses.

Hydrolytic treatments of lignocellulosic biomass by saturated steam, with (un-catalyzed) and without (catalyzed) addition of small amounts of mineral acids, have been widely studied as a method to weaken the lignocellulosic structure and increase its chemical reactivity and enzyme accessibility [144, 145].

Un-catalyzed steam-explosion is one of only a very limited number of cost-effective pre-treatment technologies that have been advanced to pilot scale demonstration and commercialized application [16]. Autohydrolysis takes place when high temperatures

promote the formation of acetic acid from acetyl groups; furthermore, water can also act as an acid at high temperatures. The mechanical effects are caused because the pressure is suddenly reduced and fibres are separated owing to the explosive decompression. In combination with the partial hemicellulose hydrolysis and solubilisation, the lignin is redistributed and to some extent removed from the material [146]. Catalyzed steam-explosion is very similar to un-catalyzed steam-explosion on their action modes, except that some acidic chemicals (gases and liquids), primarily including SO_2, H_2SO_4, CO_2, oxalic acid, etc. are used as catalysts to impregnate the LCF prior to steam-explosion, to improve recovering both cellulose and hemicellulose fractions [147]. It is recognized as one of the most cost-effective pre-treatment processes [148, 149]. Compared to un-catalyzed steam explosion, catalyzed steam-explosion has more complete hemicellulose removal leading to more increased enzymatic digestibility of LCF with less generation of inhibitory compounds [150]. A steam-explosion/separation process offers several attractive features when compared to the alternative hydrolysis and pulping processes. These include the potential for significantly lower environmental impact, lower capital investment, more potential for energy efficiency, less hazardous process chemicals and conditions [151]. Steam-explosion allows the recovery of all constitutive LCF components without the destructive degradation of any one component in favour of any other [152]. The process is generally followed by fractionation steps in order to separate the various components.

4.5.2. Combination with CO₂ explosion

Carbon dioxide explosion can also be used for lignocellulosic biomass pre-treatment. The method is based on the utilization of CO_2 as a supercritical fluid, which refers to a fluid that is in a gaseous form but is compressed at temperatures above its critical point to a liquid like density. Supercritical carbon dioxide has been used as an extraction solvent for non-extractive purposes, due to some advantages such as availability at relatively low cost, non-toxicity, non- flammability, easy recovery after extraction, and environmental friendly [153]. Besides a liquid-like solvating power, supercritical carbon dioxide displays gas-like mass transfer properties [154].

Supercritical pre-treatment conditions can effectively increase substrate digestibility by removing lignin. Addition of co-solvents such ethanol can improve delignification. Supercritical carbon dioxide has been mostly used as an extraction solvent but it is being considered for non-extractive purposes due to its many advantages [155]. CO_2 molecules are comparable in size to water and ammonia and they can penetrate in the same way the small pores of lignocelluloses. This mechanism is facilitated by high pressure. After CO2 explosive, pressure released, disruption of cellulose and hemicellulose structure is observed and consequently accessible surface area of the substrate to enzymatic attack increases [141].

4.5.3. Combination with ammonia fibre explosion (AFEX)

Similar to steam explosion, AFEX is one of the alkaline physical-chemical pre-treatment processes. Here the biomass is exposed to liquid ammonia under high pressure for a period

time, and then the pressure is suddenly released, resulting in a rapid expansion of the ammonia gas that causes swelling and physical disruption of LCF fibres and partial decrystallization of cellulose. This swift reduction of pressure opens up the structure of lignocellulosic biomass leading to increased digestibility of biomass.

One of the main advantages of AFEX pre-treatment is no formation of some types of inhibitory by-products, which are produced during the other pre-treatment methods, such as furans in steam explosion pre-treatment.

AFEX has been studied for decreasing cellulose crystallinity and disrupt lignin–carbohydrates linkages [156]. Ammonia recovery and recycle is feasible despite of its high volatility [157] but the associated complexity and costs of ammonia recovery may be significant regarding industrial scale using of the AFEX pre-treatment [34, 158].

There are some disadvantages in using the AFEX process compared to some other processes. AFEX simultaneously de-lignify and solubilize some hemicellulose while decrystallizing cellulose, but does not significantly solubilize hemicellulose as acid and acid-catalyzed steam-explosion pre-treatments [159-161]. The AFEX produces only a pre-treated solid fraction, while steam explosion produces a slurry that can be separated in a solid and a liquid fractions [15]. Furthermore, ammonia must be recycled after the pre-treatment to reduce the cost and protect the environment [106, 158].

4.5.4. Combination with acid or alkaline treatment

A way to improve the effect of LHW fractionation is to add an external acid or alkali, which can catalyze the solubilisation of the hemicellulose, reduce the optimal pre-treatment temperature and gives a better enzymatic hydrolysable substrate [162-164].

Acid pre-treatments can be performed with concentrated or diluted acid. However utilization of concentrated acid is less attractive for ethanol production due to the formation of inhibiting compounds, and high acid concentration (e.g. 30-70%) in the concentrated-acid process makes it extremely corrosive and dangerous [165, 166]. Diluted acid pre-treatment appears as more favourable method for industrial applications and have been studied for fractionation wide range of lignocellulosic feedstocks, including softwood, hardwood, herbaceous crops, agricultural residues, wastepaper, and municipal solid waste. It performed well on most biomass materials, mainly xylan, but also converting solubilised hemicellulose to fermentable sugars. Of all acid-based pre-treatment methods, sulphuric acid has been most extensively studied since it is inexpensive and effective. Organic acids such as fumaric or maleic acids are appearing as alternatives to pre-treat LCF for fractionation. Organic acids also can pre-treat lignocellulosic materials with high efficiency although fumaric acid was less effective than maleic acid. Furthermore, less amount of furfural was formed in the maleic and fumaric acid pre-treatments than with sulphuric acid [167]. Phosphoric acid, hydrochloric acid and nitric acid have also been tested [34].

Alkali pre-treatment refers to remove lignin and a part of the hemicellulose, by use of alkaline solutions such as NaOH and Ca(OH)2, and efficiently increase the accessibility of

enzyme to the cellulose. Alkali pre-treatment can be used at room temperature and times ranging from seconds to days. It is reported to cause less sugar degradation than acid pre-treatment. It is basically a delignification process, in which a significant amount of hemicellulose is solubilised as well. Alkaline pre-treatment of lignocellulosic materials causes swelling, increasing the internal surface of cellulose and decreasing the degree of polymerization and crystallinity, which provokes lignin structure disruption, and separation of structural linkages between lignin and carbohydrates [117]. In general, alkaline pre-treatment is more effective on hardwood, herbaceous crops, and agricultural residues with low lignin content than on softwood with high lignin content [168]. Alkali pre-treatment was shown to be more effective on agricultural residues than on wood materials [169]. Addition of an oxidant agent (oxygen/H_2O_2) to alkaline pre-treatment (NaOH/Ca(OH)$_2$) can favour lignin removal to improve the performance [170].

4.5.5. Combination with ammonia and carbon dioxide solution

The aim of combination is to enhance alkaline or acidic intensity of liquid hot water by ammonia or carbon dioxide for lignocelluloses fractionation.

Ammonia is an extremely important widely used bulk chemical. The polarity of Ammonia molecules and their ability to form hydrogen bonds explains to some extent the high solubility of ammonia in water. In aqueous solution, ammonia acts as a base, acquiring hydrogen ions from H2O to yield ammonium and hydroxide ions.

$$NH_3(aq) + H_2O(l) \approx NH_4^+(aq) + OH^-(aq)$$

The production of hydroxide ions when ammonia dissolved in water gives aqueous solutions of ammonia the characteristics of alkaline properties.

Carbon dioxide can be considered as an ideal solvent for the treatment of natural products, because of the relatively low critical pressure (73.8 atm) and critical temperature (31.1 °C), it. In contrast with organic solvent, Super-critical carbon dioxide is non-toxic, non-flammable, non corrosive, cheap and readily available in large quantities with high purity [171].

Carbon dioxide dissolves in water becomes acidic due to the formation and dissociation of carbonic acid:

$$CO_2 + H_2O \approx H_2CO_3 \approx H^+ + HCO_3^-$$

Over the temperature range 25-70 °C and pressure range 70-200 atm, the pH of solution ranged between 2.80 and 2.95, and increases with increasing temperature and decreases with increasing pressure [172]. It was shown that in the presence of water, supercritical CO_2 can efficiently improve the enzymatic digestibility of lignocellulosic materials [32].

4.5.6. Combination with high energy radiation treatment

Digestibility of lignocellulosic materials can be enhanced by the application of high energy radiation methods, such as microwave heating [173-175] and ultrasound [176, 177]. The

treatments can cause hydrolysis of hemicellulose, and partial depolymerization of lignin, the increase of specific surface area, decrease of the degrees of polymerization and crystallinity of cellulose.

Microwave treatment is a physical-chemical process involving both thermal and non-thermal effects. Treatments can be carried out by immersing the biomass in dilute chemical reagents and exposing the slurry to microwave radiation for a period of time [178]. The treatment of ultrasound on lignocellulosic biomass have been used for extracting hemicelluloses, cellulose and lignin [179]. Some researchers have also shown that saccharification of cellulose is enhanced efficiently by ultrasonic pre-treatment [180]. The efficiency of ultrasound in the treatment of vegetal materials has been already proved [181]. The well known benefits from ultrasounds, such as swelling of vegetal cells and fragmentation due to the cavitational effect associated to the ultrasonic treatment. Furthermore, mechanical impacts produced by the collapse of cavitation bubbles, give an important benefit of opening up the solid substrates surface for enzymatic hydrolysis [180].

However, the high energy radiation methods are usually energy-intensive and prohibitively expensive; appear to be strongly substrate-specific. The current estimation of overall cost from high energy radiation techniques looks too high, lack commercial appeal.

4.5.7. Combination with oxidative treatment

Wet oxidation

Wet oxidation is an oxidative pre-treatment method which employs oxygen or air as catalyst, and can be operated at relatively low temperatures and short reaction times [182]. It is an exothermic process, therefore self-supporting with respect to heat while the reaction is started [183]. Wet oxidation of the hemicellulose fraction is a balance between solubilisation and degradation. Wet oxidation has been proven to be an efficient method for separating the cellulosic fraction from lignin and hemicellulose [184], and also been widely used for ethanol production followed by SSF [185]. Wet oxidation pre-treatment mainly causes the formation of acids from hydrolytic processes, as well as oxidative reactions. The hemicelluloses are extensively cleaved to monomer sugars, cellulose is partly degraded, and the lignins undergo both cleavage and oxidation in wet oxidation pre-treatment. Therefore lignin produced by wet oxidation cannot be used as a fuel [186]. In general, low formation of inhibitors and efficient removal of lignin can be achieved with wet oxidation pre-treatment.

Ozonolysis

Ozone is a powerful oxidant that shows high delignification efficiency [106]. This method can effectively degrade lignin and part of hemicellulose. The pre-treatment is usually carried out at room temperature, and does not lead to inhibitory compounds [187]. It is usually performed at room temperature and normal pressure and does not lead to the formation of inhibitory compounds that can affect the subsequent hydrolysis and fermentation. However, ozonolysis might be expensive since a large amount of ozone is required, which can make the process economically unviable [106].

5. Other bioconversion technologies

5.1. Landfill gas (LFG) production

As discussed in Section 2.4, anaerobic digester is a suitable waste treatment method to deal with wastewater, sewage sludge and animal mature since the high solid content of other types waste would challenge the anaerobic digester operation technologies. Currently most of biodegradable waste is sent to landfill where landfill gas (LFG) is generated.

Because the wastes sent to landfill include not only biodegradable components but also other hazard wastes, the LFG produced contains approx 40 - 60% methane, CO_2, and varying amounts of nitrogen, oxygen, water vapour, volatile organics (VOC), H_2S and other contaminates (also known as non-methane organic compounds NMOCs). Some other inorganic contaminants, for example, heavy metals are found present in the LFG. Therefore, the direct release of the landfill gas to atmosphere will cause serious greenhouse gas emissions and pollutions. LFG produced from landfill site has to be monitored and managed appropriately. The general LFG managing options are: flaring (burn without energy recovery), boiler (produces heat), internal combustion (producing electricity), gas turbine (producing electricity), fuel cell (producing electricity), convert the methane to methyl alcohol, or sent to natural gas lines after cleaning process [188].

5.2. Biopulping and wood utilization

Biopulping, also known as biological pulping, refers a type of industrial biotechnology using fungus to convert wood chips to paper pulp. This technology has the potential to improve the quality of paper pulp, reduce energy consumption and environmental impacts when compare with the traditional chemical pulping technologies [189].

The aim of pulping is to extract cellulose from plant material. The traditional approaches are mechanical and chemical pulping. The former method is generally accomplished by refining grinding or thermo-mechanical pulping. The latter way is to dissolve lignin from the cellulose and hemicellulose fibers via chemical treatment, such as kraft pulping in which wood chips are cooled in a solution containing sodium hydroxide and sodium sulfide [190]. These traditional pulping technologies have several drawbacks: (1) high energy demand; (2) low cellulose yield, especially from chemical pulping due to partial degradation of cellulose; (3) potential hazards chemicals emitted to the environment [189].

Lignin is a complex polymer which serves as a structural component of higher plants and is highly resistant towards chemical degradation [191]. White-rot and brown-rot fungi are two classifications of wood-rotting basidiomycetes. White-rot basidimycetes have been reported enable to, selectively or simultaneously with cellulose, degrade lignin in different types of wood [191, 192]. Brown-rot basidiomycetes, which grow mainly on softwood, can degrade wood polysaccharides but cause only a partial modification of lignin. Besides white- and brown- rot basidimycetes, some scomycetes so-called soft-rot fungi which can degrade wood under extreme environmental conditions such as high or low water potential that prohibit the activity of other fungi [191].

The fungal treatment process fits in a paper mill operation well. After wood is debarked, chipped and screened, wood chips are briefly steamed to reduce natural chip microorganisms, cooled with air, and inoculated with the biopulping fungus for 1 to 4 weeks prior to further processing. The biopulping has been indicated as a technology technologically feasible and economically beneficial [193].

This biological treatment of wood using fungi has also been studied and used as a pre-treatment approach prior to enzymatic hydrolysis for biofuel production [194-196]. However, more research are required to understand the mechanism of wood degradation, structural changes of wood cell wall caused by these wood decay fungus and to improve the treatment technologies [197, 198].

6. Conclusions

The concept of 'biorefinery' has emerged since the potential of lignocellulosic based products substituting fossil fuel derived products has been discovered. Biorefienries may play a major role in tackling climate change by reducing the demand on fossil fuel energy and providing sustainable energy, chemicals and materials, potentially aiding energy security, and creating opportunities and market. This paper reviewed a wide range of such lignocellulosic derived products and current available biorefinery technologies. Some of these technologies have been or being close to the industrialization and others are still at the early stage of development. However, more research efforts are required to improve the technologies and integrate the biorefinery system in order to achieve the maximum outputs and to make biorefinery work at scale.

Author details

Hongbin Cheng[*]
Department of Process Engineering, Stellenbosch University, South Africa
New China Times Technology Ltd, China

Lei Wang[*]
Department of Life Science, Imperial College London, UK
New China Times Technology Ltd, China

7. References

[1] Clark, J.H., *Green chemistry for the second generation biorefinery—sustainable chemical manufacturing based on biomass.* Journal of Chemical Technology & Biotechnology, 2007. 82(7): p. 603-609.

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[*] The two authors contribute equally to this study

[2] Stöcker, M., *Biofuels and Biomass-To-Liquid Fuels in the Biorefinery: Catalytic Conversion of Lignocellulosic Biomass using Porous Materials.* Angewandte Chemie International Edition, 2008. 47(48): p. 9200-9211.

[3] Gullón, P., et al., *Selected Process Alternatives for Biomass Refining: A Review.* The Open Agricultrure Journal 2010. 4: p. 135-144.

[4] Kelley, S.S., *Lignocellulosic Biorefineries: Reality, Hype, or Something in Between?*, in *Materials, Chemicals, and Energy from Forest Biomass.* 2007, American Chemical Society. p. 31-47.

[5] Danner, H. and R. Braun, *ChemInform Abstract: Biotechnology for the Production of Commodity Chemicals from Biomass.* ChemInform, 2000. 31(6): p. no-no.

[6] Chheda, J.N., G.W. Huber, and J.A. Dumesic, *Liquid-Phase Catalytic Processing of Biomass-Derived Oxygenated Hydrocarbons to Fuels and Chemicals.* Angewandte Chemie International Edition, 2007. 46(38): p. 7164-7183.

[7] Rowlands, W.N., A. Masters, and T. Maschmeyer, *The Biorefinery—Challenges, Opportunities, and an Australian Perspective.* Bulletin of Science, Technology & Society, 2008. 28(2): p. 149-158.

[8] Sanders, J.P.M., B. Annevelink, and D.A.v.d. Hoeven, *The development of biocommodities and the role of North West European ports in biomass chains.* Biofuels Bioproducts and Biorefining, 2009. 3(3): p. 395-409.

[9] Kamm, B., *Production of Platform Chemicals and Synthesis Gas from Biomass.* Angewandte Chemie International Edition, 2007. 46(27): p. 5056-5058.

[10] Kamm, B., P. Schönicke, and M. Kamm, *Biorefining of Green Biomass – Technical and Energetic Considerations.* CLEAN – Soil, Air, Water, 2009. 37(1): p. 27-30.

[11] Li, L., S. Lu, and V. Chiang, *A Genomic and Molecular View of Wood Formation.* Critical Reviews in Plant Sciences, 2006. 25(3): p. 215-233.

[12] Kamm, B., et al., *Biorefinery Systems – An Overview*, in *Biorefineries-Industrial Processes and Products*. 2008, Wiley-VCH Verlag GmbH. p. 1-40.

[13] Fernando, S., et al., *Biorefineries: Current Status, Challenges, and Future Direction.* Energy & Fuels, 2006. 20(4): p. 1727-1737.

[14] Kamm, B. and M. Kamm, *Biorefinery - Systems.* Chemical and Biochemical Engineering Quarterly, 2004. 18(1): p. 1-6.

[15] Mosier, N., et al., *Features of promising technologies for pretreatment of lignocellulosic biomass.* Bioresource Technology, 2005. 96(6): p. 673-686.

[16] Zheng, Y., Z. Pan, and R. Zhang, *Overview of biomass pretreatment for cellulosic ethanol production.* International Journal of Agricultural and Biological Engineering, 2009. 2(3): p. 51-68.

[17] McKendry, P., *Energy production from biomass (part 1): overview of biomass.* Bioresource Technology, 2002. 83(1): p. 37-46.

[18] Kristian, M. and M. Hurme, *Lignocellulosic biorefinery economic evaluation.* Cellulose Chemistry and Technology, 2011. 45(7-8): p. 443-454.

[19] Lynn, W., *Biomass Energy Data Book: Edition 1.* 2006.

[20] Wyman, C. and B. Goodman, *Biotechnology for production of fuels, chemicals, and materials from biomass.* Applied Biochemistry and Biotechnology, 1993. 39-40(1): p. 41-59.

[21] García, A., et al., *Biorefining of lignocellulosic residues using ethanol organosolv process.* Chemical Engineering Transactions, 2009. 18: p. 911-916.

[22] Puppan, D., *Environmental evaluation of biofuels.* Periodica Polytechnica Ser. Soc. Man. Sci., 2002. 10(1): p. 95-116.

[23] Lin, Y. and S. Tanaka, *Ethanol fermentation from biomass resources: current state and prospects.* Applied Microbiology and Biotechnology, 2006. 69(6): p. 627-642.

[24] Slade, R.B., *Prospects for cellulosic ethanol supply-chains in Europe: a techno-economic and environmental assessment*, in *Centre for Process Systems Engineering and Centre for Environmental Policy*. 2009, Univiersity of London. p. 170.

[25] Josefsson, T., H. Lennholm, and G. Gellerstedt, *Steam Explosion of Aspen Wood. Characterisation of Reaction Products.* Holzforschung, 2002. 56(3): p. 289-297.

[26] Ballesteros, I., et al., *Effect of chip size on steam explosion pretreatment of softwood.* Applied Biochemistry and Biotechnology, 2000. 84-86(1): p. 97-110.

[27] Ruiz, E., et al., *Evaluation of steam explosion pre-treatment for enzymatic hydrolysis of sunflower stalks.* Enzyme and Microbial Technology, 2008. 42(2): p. 160-166.

[28] Holtzapple, M., et al., *Pretreatment of lignocellulosic municipal solid waste by ammonia fiber explosion (AFEX).* Applied Biochemistry and Biotechnology, 1992. 34-35(1): p. 5-21.

[29] Alizadeh, H., et al., *Pretreatment of switchgrass by ammonia fiber explosion (AFEX).* Applied Biochemistry and Biotechnology, 2005. 124(1): p. 1133-1141.

[30] Tengborg, C., et al., *Comparison of SO_2 and H_2SO_4 impregnation of softwood prior to steam pretreatment on ethanol production.* Applied Biochemistry and Biotechnology, 1998. 70-72(1): p. 3-15.

[31] Öhgren, K., M. Galbe, and G. Zacchi, *Optimization of Steam Pretreatment of SO_2;-Impregnated Corn Stover for Fuel Ethanol Production*, in *Twenty-Sixth Symposium on Biotechnology for Fuels and Chemicals*, B.H. Davison, et al., Editors. 2005, Humana Press. p. 1055-1067.

[32] Kim, K.H. and J. Hong, *Supercritical CO2 pretreatment of lignocellulose enhances enzymatic cellulose hydrolysis.* Bioresource Technology, 2001. 77(2): p. 139-144.

[33] Zheng, Y., H.M. Lin, and G.T. Tsao, *Pretreatment for Cellulose Hydrolysis by Carbon Dioxide Explosion.* Biotechnology Progress, 1998. 14(6): p. 890-896.

[34] Mosier, N., et al., *Optimization of pH controlled liquid hot water pretreatment of corn stover.* Bioresource Technology, 2005. 96(18): p. 1986-1993.

[35] Laser, M., et al., *A comparison of liquid hot water and steam pretreatments of sugar cane bagasse for bioconversion to ethanol.* Bioresource Technology, 2002. 81(1): p. 33-44.

[36] Allen, S.G., et al., *A Comparison between Hot Liquid Water and Steam Fractionation of Corn Fiber.* Industrial & Engineering Chemistry Research, 2001. 40(13): p. 2934-2941.

[37] Aden, A., Ruth, M., Ibsen, K., Jechura, J., Neeves, K., Sheehan, J., Wallace, B., Montague, L., Slayton, A., Lukas, J, *Lignocellulosic Biomass to Ethanol Process Design and Economics Utilizing Co-Current Dilute Acid Prehydrolysis and Enzymatic Hydrolysis for Corn Stover*. 2002, National Renewable Energy Laboratory (NREL). p. 95. NREL/TP-510-32438.

[38] Torget, R., M.E. Himmel, and K. Grohmann, *Dilute sulfuric acid pretreatment of hardwood bark.* Bioresource Technology, 1991. 35(3): p. 239-246.

[39] Schell, D.J., et al., *Dilute-sulfuric acid pretreatment of corn stover in pilot-scale reactor - Investigation of yields, kinetics, and enzymatic digestibilities of solids.* Applied Biochemistry and Biotechnology, 2003. 105: p. 69-85.

[40] Kim, T.H. and Y.Y. Lee, *Fractionation of corn stover by hot-water and aqueous ammonia treatment.* Bioresource Technology, 2006. 97(2): p. 224-232.

[41] Vaccarino, C., et al., *Effect of SO2, NaOH and Na2CO3 pretreatments on the degradability and cellulase digestibility of grape marc.* Biological Wastes, 1987. 20(2): p. 79-88.

[42] Chander Kuhad, R., et al., *Fed batch enzymatic saccharification of newspaper cellulosics improves the sugar content in the hydrolysates and eventually the ethanol fermentation by Saccharomyces cerevisiae.* Biomass and Bioenergy, 2010. 34(8): p. 1189-1194.

[43] Sierra, R., L.A. Garcia, and M.T. Holtzapple, *Selectivity and delignification kinetics for oxidative short-term lime pretreatment of poplar wood. Part I: Constant-pressure.* Biotechnology Progress, 2011. 27(4): p. 976-985.

[44] Chang, V., et al., *Oxidative lime pretreatment of high-lignin biomass.* Applied Biochemistry and Biotechnology, 2001. 94(1): p. 1-28.

[45] Pasquini, D., et al., *Extraction of lignin from sugar cane bagasse and Pinus taeda wood chips using ethanol–water mixtures and carbon dioxide at high pressures.* The Journal of Supercritical Fluids, 2005. 36(1): p. 31-39.

[46] Hallac, B.B., et al., *Effect of Ethanol Organosolv Pretreatment on Enzymatic Hydrolysis of Buddleja davidii Stem Biomass.* Industrial & Engineering Chemistry Research, 2010. 49(4): p. 1467-1472.

[47] Brandt, A., et al., *Ionic liquid pretreatment of lignocellulosic biomass with ionic liquid-water mixtures.* Green Chemistry, 2011. 13(9): p. 2489-2499.

[48] Hamelinck, C.N., G.v. Hooijdonk, and A.P.C. Faaij, *Ethanol from lignocellulosic biomass: techno-economic performance in short-, middle- and long-term.* Biomass and Bioenergy, 2005. 28(4): p. 384-410.

[49] Sedlak, M. and N. Ho, *Production of ethanol from cellulosic biomass hydrolysates using genetically engineered saccharomyces yeast capable of cofermenting glucose and xylose.* Applied biochemistry and biotechnology, 2004. 114(1): p. 403-416.

[50] Humbird, D. and A. Aden, *Biochemical Production of Ethanol from Corn Stover: 2008 State of Technology Model.* 2009, National Renewable Energy Laboratory (NREL). NREL/TP-510-46214.

[51] Cripps, R.E., et al., *Metabolic engineering of Geobacillus thermoglucosidasius for high yield ethanol production.* Metabolic Engineering, 2009. 11(6): p. 398-408.

[52] Bezerra, R. and A. Dias, *Enzymatic kinetic of cellulose hydrolysis: Inhibition by ethanol and cellobiose.* Applied Biochemistry and Biotechnology, 2005. 126(1): p. 49-59.

[53] Lynd, L.R., et al., *Consolidated bioprocessing of cellulosic biomass: an update.* Current Opinion in Biotechnology, 2005. 16: p. 577-583.

[54] van Zyl, W., et al., *Consolidated Bioprocessing for Bioethanol Production Using Biofuels*, L. Olsson, Editor. 2007, Springer Berlin / Heidelberg. p. 205-235.

[55] Jin, M., et al., *Consolidated bioprocessing (CBP) performance of Clostridium phytofermentans on AFEX-treated corn stover for ethanol production.* Biotechnology and Bioengineering, 2011. 108(6): p. 1290-1297.

[56] Olson, D.G., et al., *Recent progress in consolidated bioprocessing.* Current Opinion in Biotechnology, (0).

[57] Phillips, S., et al., *Thermochemical Ethanol via Indirect Gasification and Mixed Alcohol Synthesis of Lignocellulosic Biomass.* 2007, National Renewable Energy Laboratory (NREL). NREL/TP-510-41168.

[58] Dutta, A., et al., *An economic comparison of different fermentation configurations to convert corn stover to ethanol using Z. mobilis and Saccharomyces.* Biotechnology Progress, 2010. 26(1): p. 64-72.

[59] Stephenson, A.L., et al., *The environmental and economic sustainability of potential bioethanol from willow in the UK.* Bioresource Technology, 2010. 101(24): p. 9612-9623.

[60] Sassner, P., M. Galbe, and G. Zacchi, *Techno-economic evaluation of bioethanol production from three different lignocellulosic materials.* Biomass and Bioenergy, 2008. 32(5): p. 422-430.

[61] Wang, L., et al., *Technology performance and economic feasibility of bioethanol production from various waste papers.* Energy & Environmental Science 2012. 5(2): p. 5717-5730.

[62] Mu, D., et al., *Comparative Life Cycle Assessment of Lignocellulosic Ethanol Production: Biochemical Versus Thermochemical Conversion.* Environmental Management, 2010. 46(4): p. 565-578.

[63] Qureshi, N. and T.C. Ezeji, *Butanol, 'a superior biofuel' production from agricultural residues (renewable biomass): recent progress in technology.* Biofuels, Bioproducts and Biorefining, 2008. 2(4): p. 319-330.

[64] Ezeji, T., N. Qureshi, and H.P. Blaschek, *Butanol production from agricultural residues: Impact of degradation products on Clostridium beijerinckii growth and butanol fermentation.* Biotechnology and Bioengineering, 2007. 97(6): p. 1460-1469.

[65] Cascone, R., *Biobutanol – a replacement for bioethanol?* Chemical Engineering Progressing, 2008. 104: p. S4-S9.

[66] Pfromm, P.H., et al., *Bio-butanol vs. bio-ethanol: A technical and economic assessment for corn and switchgrass fermented by yeast or Clostridium acetobutylicum.* Biomass and Bioenergy, 2010. 34(4): p. 515-524.

[67] Shereena, K.M. and T. Thangaraj, *Biodiesel: an alternative fuel produced from vegetable oils by transesterification.* Electronic Journal of Biology, 2009. 5(3): p. 67-74.

[68] Zabeti, M., W.M.A. Wan Daud, and M.K. Aroua, *Activity of solid catalysts for biodiesel production: A review.* Fuel Processing Technology, 2009. 90(6): p. 770-777.

[69] Ma, F. and M.A. Hanna, *Biodiesel production: a review.* Bioresource Technology, 1999. 70(1): p. 1-15.

[70] Marchetti, J.M., V.U. Miguel, and A.F. Errazu, *Possible methods for biodiesel production.* Renewable and Sustainable Energy Reviews, 2007. 11(6): p. 1300-1311.

[71] Schnepf, R., *Agriculture-Based Biofuels: Overview and Emerging Issues.* 2010, Congressional Research Service. R41282.

[72] Tamalampudi, S., et al., *Enzymatic production of biodiesel from Jatropha oil: A comparative study of immobilized-whole cell and commercial lipases as a biocatalyst.* Biochemical Engineering Journal, 2008. 39(1): p. 185-189.

[73] Lu, H., et al., *Production of biodiesel from Jatropha curcas L. oil.* Computers & Chemical Engineering, 2009. 33(5): p. 1091-1096.

[74] Shah, S. and M.N. Gupta, *Lipase catalyzed preparation of biodiesel from Jatropha oil in a solvent free system.* Process Biochemistry, 2007. 42(3): p. 409-414.

[75] Kumari, A., et al., *Enzymatic transesterification of Jatropha oil.* Biotechnology for Biofuels, 2009. 2(1): p. 1.

[76] Chisti, Y., *Biodiesel from microalgae.* Biotechnology Advances, 2007. 25: p. 294-306.

[77] Scott, S.A., et al., *Biodiesel from algae: challenges and prospects.* Current Opinion in Biotechnology, 2010. 21(3): p. 277-286.

[78] Grobbelaar, J., *Turbulence in mass algal cultures and the role of light/dark fluctuations.* Journal of Applied Phycology, 1994. 6(3): p. 331-335.

[79] Chisti, Y., *Biodiesel from microalgae beats bioethanol.* Trends in Biotechnology, 2008. 26(3): p. 126-131.

[80] Monson, K.D., et al., *Anaerobic digestion of biodegrabale municiple solid wastes: A review.* 2007, University of Glamorgan

[81] Trzcinski, A.P., *Anaerobic membrane bioreactor technology for solid waste stabilization,* in *Chemical Engineering and Chemical Technology.* 2009, Imperial College London: London.

[82] Rapport, J., et al., *Current anaerobic digestion technologies used for treatment of municipal organic solid waste.* 2008, Department of Biological and Agricultural Engineering, University of California Davis, CA

[83] Raposo, F., et al., *Influence of inoculum to substrate ratio on the biochemical methane potential of maize in batch tests.* Process Biochemistry, 2006. 41(6): p. 1444-1450.

[84] Hartmann, H., H.B. Moller, and B.K. Ahring, *Efficiency of the anaerobic treatment of the organic fraction of municipal solid waste: collection and pretreatment.* Waste Management & Research, 2004. 22: p. 35-41.

[85] WRAP, *Anaerobic digestate.* 2008, Waste & Resources Action Programme (WRAP)

[86] Edelmann, W., K. Schleiss, and A. Joss, *Ecological, energetic and economic comparison of anaerobic digestion with different competing technologies to treat biogenic wastes.* Water Science and Technology, 2000. 4(3): p. 263-273.

[87] Edelmann, W., U. Baier, and H. Engeli, *Environmental aspects of the anaerobic digestion of the organic fraction of municipal solid wastes and of solid agricultural wastes.* Water Science and Technology, 2004. 52(1-2): p. 203-208.

[88] Dodds, D.R. and R.A. Gross, *Chemicals from Biomass.* Science, 2007. 318(5854): p. 1250-1251.

[89] Carlson, T.L. and E.M. Peters. 2006. Patent application US2006/094093 A1.

[90] Lorenz, P. and H. Zinke, *White biotechnology: differences in US and EU approaches?* Trends in Biotechnology, 2005. 23(12): p. 570-574.

[91] Jung, Y.K., et al., *Metabolic engineering of Escherichia coli for the production of polylactic acid and its copolymers.* Biotechnology and Bioengineering, 2010. 105(1): p. 161-171.

[92] Wyman, C.E., et al., *Coordinated development of leading biomass pretreatment technologies.* Bioresource Technology, 2005. 96(18): p. 1959-1966.

[93] Yáñez, R., et al., *Production of D(−)-lactic acid from cellulose by simultaneous saccharification and fermentation using <i>Lactobacillus coryniformis</i> subsp. <i>torquens</i>.* Biotechnology Letters, 2003. 25(14): p. 1161-1164.

[94] Adsul, M.G., et al., *Development of biocatalysts for production of commodity chemicals from lignocellulosic biomass.* Bioresource Technology, 2011. 102(6): p. 4304-4312.

[95] Danner, H., et al., *Bacillus stearothermophilus for thermophilic production of l-lactic acid.* Applied Biochemistry and Biotechnology, 1998. 70-72(1): p. 895-903.

[96] Maddox, I.S., N. Qureshi, and K. Roberts-Thomson, *Production of acetone-butanol-ethanol from concentrated substrate using clostridium acetobutylicum in an integrated fermentation-product removal process.* Process Biochemistry, 1995. 30(3): p. 209-215.

[97] Jones, D.T. and D.R. Woods, *Acetone-butanol fermentation revisited.* Microbiology and Moclecular Biology Reviews, 1986. 50(4): p. 484-524.

[98] Faik, A., *Xylan biosysthesis: News from the grass.* Plant Physiology, 2010. 153: p. 396-402.

[99] Granström, T., K. Izumori, and M. Leisola, *A rare sugar xylitol. Part II: biotechnological production and future applications of xylitol.* Applied Microbiology and Biotechnology, 2007. 74(2): p. 273-276.

[100] Saha, B., *Hemicellulose bioconversion.* Journal of Industrial Microbiology & Biotechnology, 2003. 30(5): p. 279-291.

[101] Choct, M. and G. Annison, *Anti-nutritive activity of wheat pentosans in broiler diets.* British Poultry Science, 1990. 31(4): p. 811-821.

[102] Duff, S.J.B. and W.D. Murray, *Bioconversion of forest products industry waste cellulosics to fuel ethanol: a review.* Bioresource Technology, 1996. 55: p. 1-33.

[103] Hayes, D.J., et al., *The Biofine Process – Production of Levulinic Acid, Furfural, and Formic Acid from Lignocellulosic Feedstocks*, in *Biorefineries-Industrial Processes and Products*. 2008, Wiley-VCH Verlag GmbH. p. 139-164.

[104] Fatih Demirbas, M., *Biorefineries for biofuel upgrading: A critical review.* Applied Energy, 2009. 86, Supplement 1(0): p. S151-S161.

[105] Saddler, J.N., *Bioconversion of Forest and Agricultural Plant Residues.* Biotechnology in agriculture. 1993: CABI, Wallingford, UK.

[106] Sun, Y. and J.Y. Cheng, *Hydrolysis of lignocellulosic materials for ethanol production: a review.* Bioresource Technology, 2002. 83(1): p. 1-11.

[107] Zhu, S., et al., *FED-BATCH SIMULTANEOUS SACCHARIFICATION AND FERMENTATION OF MICROWAVE/ACID/ALKALI/H2O2 PRETREATED RICE STRAW FOR PRODUCTION OF ETHANOL.* Chemical Engineering Communications, 2006. 193(5): p. 639-648.

[108] Koukios, E.G. and G.N. Valkanas, *Process for chemical separation of the three main components of lignocellulosic biomass.* Industrial & Engineering Chemistry Product Research and Development, 1982. 21(2): p. 309-314.

[109] Koukios, E.G., *Biomass refining: a non-waste approach.*, in *Economics and Ecosystem Management*, D.O. Hall, N. Myers, and N.S. Margaris, Editors. 1985, Dr W. Junk Publishers: Dordrecht, The Netherlands. p. 233-244.

[110] Kamm, B., P.R. Gruber, and M. Kamm, *Biorefineries – Industrial Processes and Products*, in *Ullmann's Encyclopedia of Industrial Chemistry*. 2000, Wiley-VCH Verlag GmbH & Co. KGaA.

[111] Kleinert, T.N., *Organosolv pulping with aqueous alcohol.* Tappi Journal, 1974. 57: p. 99-102.

[112] Lora, J.H. and S. Aziz, *Organosolv pulping — a versatile approach to wood refining.* Tappi Journal, 1985. 68(6): p. 94-97.

[113] Sarkanen, K.V., *Chemistry of solvent pulping.* Tappi Journal, 1990: p. 215-219.

[114] Pan, X., et al., *Bioconversion of hybrid poplar to ethanol and co-products using an organosolv fractionation process: Optimization of process yields.* Biotechnology and Bioengineering, 2006. 94(5): p. 851-861.

[115] Pan, X., et al., *Effect of organosolv ethanol pretreatment variables on physical characteristics of hybrid poplar substrates.* Applied Biochemistry and Biotechnology, 2007. 137-140(1): p. 367-377.

[116] Pan, X., et al., *The bioconversion of mountain pine beetle-killed lodgepole pine to fuel ethanol using the organosolv process.* Biotechnology and Bioengineering, 2008. 101(1): p. 39-48.

[117] Taherzadeh, M.J. and K. Karimi, *Pretreatment of lignocellulosic wastes to improve ethanol and biogas production: A review.* International Journal of Molecular Sciences, 2008. 9(9): p. 1621-1651.

[118] Chum, H.L., et al., *Organosolv pretreatment for enzymatic hydrolysis of poplars: I. Enzyme hydrolysis of cellulosic residues.* Biotechnology Bioengineering, 1988. 31(7).

[119] Zhao, X., K. Cheng, and D. Liu, *Organosolv pretreatment of lignocellulosic biomass for enzymatic hydrolysis.* Applied Microbiology and Biotechnology, 2009. 82(5): p. 815-827.

[120] Johansson, A., O. Aaltonen, and P. Ylinen, *Organosolv pulping — methods and pulp properties.* Biomass, 1987. 13(1): p. 45-65.

[121] Aziz, S. and K.V. Sarkanen, *Organosolv pulping—a review.* Tappi Journal, 1989. 72: p. 169-175.

[122] Thring, R.W., E. Chornet, and R.P. Overend, *Recovery of a solvolytic lignin: Effects of spent liquor/acid volume ratio, acid concentration and temperature.* Biomass, 1990. 23(4): p. 289-305.

[123] Sidiras, D. and E. Koukios, *Simulation of acid-catalysed organosolv fractionation of wheat straw.* Bioresource Technology, 2004. 94(1): p. 91-98.

[124] Zhu, J.Y. and X.J. Pan, *Woody biomass pretreatment for cellulosic ethanol production: Technology and energy consumption evaluation.* Bioresource Technology, 2010. 101(13): p. 4992-5002.

[125] Myllymaki, V. and R. Aksela. 2005. Dissolution and delignification of lignocellulosic materials with ionic liquid solvent under microwave irradiation. WO patent 2005/017001

[126] Hayes, D.J., *An examination of biorefining processes, catalysts and challenges.* Catalysis Today, 2009. 145(1–2): p. 138-151.

[127] Dadi, A.P., S. Varanasi, and C.A. Schall, *Enhancement of cellulose saccharification kinetics using an ionic liquid pretreatment step.* Biotechnology and Bioengineering, 2006. 95(5): p. 904-910.

[128] Zhu, S., *Use of ionic liquids for the efficient utilization of lignocellulosic materials.* Journal of Chemical Technology & Biotechnology, 2008. 83(6): p. 777-779.

[129] Reichert, W.M., et al., *Derivatization of chitin in room temperature ionic liquids*, in *222 ACS National Meeting.* 2001: Chicago, IL, United States.

[130] Heinze, T., K. Schwikal, and S. Barthel, *Ionic Liquids as Reaction Medium in Cellulose Functionalization.* Macromolecular Bioscience, 2005. 5(6): p. 520-525.

[131] Dien, B.S., et al., *Enzymatic saccharification of hot-water pretreated corn fiber for production of monosaccharides.* Enzyme and Microbial Technology, 2006. 39(5): p. 1137-1144.

[132] Negro, M., et al., *Hydrothermal pretreatment conditions to enhance ethanol production from poplar biomass.* Applied Biochemistry and Biotechnology, 2003. 105(1): p. 87-100.

[133] Rogalinski, T., T. Ingram, and G. Brunner, *Hydrolysis of lignocellulosic biomass in water under elevated temperatures and pressures.* The Journal of Supercritical Fluids, 2008. 47(1): p. 54-63.

[134] van Walsum, G., et al., *Conversion of lignocellulosics pretreated with liquid hot water to ethanol.* Applied Biochemistry and Biotechnology, 1996. 57-58(1): p. 157-170.

[135] Franck, E.U., *Fluids at high pressures and temperatures.* Chemical thermodynamics, 1987. 19: p. 225-242.

[136] Shaw, R.W., et al., *Supercritical water. A medium for chemistry.* Chemical Engineering News, 1991. 23: p. 26-39.

[137] Savage, P.E., et al., *Reactions at supercritical conditions: {A}pplications and fundamentals.* AIChE Journal, 1995. 41(7): p. 1723-1778.

[138] Katritzky, A.R., et al., *Reactions in High-Temperature Aqueous Media.* Chemical Reviews, 2001. 101(4): p. 837-892.

[139] Kohlmann, K.L., et al., *Enhanced Enzyme Activities on Hydrated Lignocellulosic Substrates*, in *Enzymatic Degradation of Insoluble Carbohydrates*. 1996, American Chemical Society. p. 237-255.

[140] Weil, J., et al., *Continuous pH monitoring during pretreatment of yellow poplar wood sawdust by pressure cooking in water.* Applied Biochemistry and Biotechnology, 1998. 70-72(1): p. 99-111.

[141] Alvira, P., et al., *Pretreatment technologies for an efficient bioethanol production process based on enzymatic hydrolysis: A review.* Bioresource Technology, 2010. 101(13): p. 4851-4861.

[142] Goring, D.A.I., *Thermal softening of lignin, hemicelluloses and cellulose.* 1963: Pulp and Paper Research Institute of Canada.

[143] Overend, R.P., E. Chornet, and J.A. Gascoigne, *Fractionation of Lignocellulosics by Steam-Aqueous Pretreatments [and Discussion].* Philosophical Transactions of the Royal Society of London. Series A, Mathematical and Physical Sciences, 1987. 321(1561): p. 523-536.

[144] Mason, W.H. 1929. Apparatus and process of explosion defibration of lignocellulosic material. U.S. Patent No. 1655618

[145] Montane, D., et al., *Application of steam explosion to the fractionation and rapid vapor-phase alkaline pulping of wheat straw.* Biomass and Bioenergy, 1998. 14(3): p. 261-276.

[146] Pan, X., et al., *Strategies to enhance the enzymatic hydrolysis of pretreated softwood with high residual lignin content.* Applied Biochemistry and Biotechnology, 2005. 121-124: p. 1069-1079.

[147] Eklund, R., M. Galbe, and G. Zacchi, *The influence of SO2 and H2SO4 impregnation of willow prior to steam pretreatment.* Bioresource Technology, 1995. 52(3): p. 225-229.

[148] Fein, J.E., D. Potts, and D. Good, *Development of an optimal wood-to-fuel ethanol process utilizing best available technology.* Energy Biomass and Waste, 1991. 15(745-765).

[149] Ropars, M., et al., *Large-scale enzymatic hydrolysis of agricultural lignocellulosic biomass. Part 1: Pretreatment procedures.* Bioresource Technology, 1992. 42(3): p. 197-204.

[150] Morjanoff, P.J. and P.P. Gray, *Optimization of steam explosion as method for increasing susceptibility of sugarcane bagasse to enzymatic saccharification.* Biotechnology Bioengineering, 1987. 29(6): p. 733-741.

[151] Focher, B., A. Marzetti, and V. Crescenzi, *Steam Explosion Techniques, Fundamentals and Industrial Applications.* 1991, Gordon and Breach Publishers: Philadelphia. p. 412.

[152] Avellar, B.K. and W.G. Glasser, *Steam-assisted biomass fractionation. I. Process considerations and economic evaluation.* Biomass and Bioenergy, 1998. 14(3): p. 205-218.

[153] Zheng, Y. and G.T. Tsao, *Avicel hydrolysis by cellulase enzyme in supercritical CO2.* Biotechnology Letters, 1996. 18(4): p. 451-454.

[154] Zheng, Y., et al., *Supercritical carbon dioxide explosion as a pretreatment for cellulose hydrolysis.* Biotechnology Letters, 1995. 17(8): p. 845-850.

[155] Schacht, C., C. Zetzl, and G. Brunner, *From plant materials to ethanol by means of supercritical fluid technology.* The Journal of Supercritical Fluids, 2008. 46(3): p. 299-321.

[156] Laureano-Perez, L., et al., *Understanding Factors that Limit Enzymatic Hydrolysis of Biomass*

[157] *nty-Sixth Symposium on Biotechnology for Fuels and Chemicals*, B.H. Davison, et al., Editors. 2005, Humana Press. p. 1081-1099.

[158] Teymouri, F., et al., *Optimization of the ammonia fiber explosion (AFEX) treatment parameters for enzymatic hydrolysis of corn stover.* Bioresource Technology, 2005. 96(18): p. 2014-2018.

[159] Eggeman, T. and R.T. Elander, *Process and economic analysis of pretreatment technologies.* Bioresource Technology, 2005. 96(18): p. 2019-2025.

[160] Ghosh, S., et al., *Pilot-scale gasification of municipal solid wastes by high-rate and two-phase anaerobic digestion (TPAD).* Water Science and Technology 2000. 41(3): p. 101-110.

[161] Beccari, M., et al., *Enhancement of anaerobic treatability of olive oil mill effluents by addition of Ca(OH)2 and bentonite without intermediate solid/liquid separation.* Water Science and Technology, 2001. 43(11): p. 275-282.

[162] Tanaka, S., et al., *Effects of thermochemical pretreatment on the anaerobic digestion of waste activated sludge.* Water Science and Technology, 1997. 35(8): p. 209-215.

[163] Brownell, H.H., E.K.C. Yu, and J.N. Saddler, *Steam-explosion pretreatment of wood: Effect of chip size, acid, moisture content and pressure drop.* Biotechnology and Bioengineering, 1986. 28(6): p. 792-801.

[164] Gregg, D. and J. Saddler, *A techno-economic assessment of the pretreatment and fractionation steps of a biomass-to-ethanol process.* Applied Biochemistry and Biotechnology, 1996. 57-58(1): p. 711-727.

[165] Chang, V.S., et al., *Simultaneous saccharification and fermentation of lime-treated biomass.* Biotechnology Letters, 2001. 23(16): p. 1327-1333.

[166] Sun, X.F., et al., *Characteristics of degraded cellulose obtained from steam-exploded wheat straw.* Carbohydrate Research, 2005. 340(1): p. 97-106.

[167] Jones, J.L. and K.T. Semrau, *Wood hydrolysis for ethanol production — previous experience and the economics of selected processes.* Biomass, 1984. 5(2): p. 109-135.

[168] Kootstra, A.M.J., et al., *Comparison of dilute mineral and organic acid pretreatment for enzymatic hydrolysis of wheat straw.* Biochemical Engineering Journal, 2009. 46(2): p. 126-131.

[169] Bjerre, A.B., et al., *Pretreatment of wheat straw using combined wet oxidation and alkaline hydrolysis resulting in convertible cellulose and hemicellulose.* Biotechnology and Bioengineering, 1996. 49(5): p. 568-577.

[170] Kumar, P., et al., *Methods for Pretreatment of Lignocellulosic Biomass for Efficient Hydrolysis and Biofuel Production.* Industrial & Engineering Chemistry Research, 2009. 48(8): p. 3713-3729.

[171] Carvalheiro, F., L.C. Duarte, and F.M. Gírio, *Hemicellulose biorefineries: a review on biomass pretreatments.* Scientific & Industrial Research, 2008. 67: p. 849-864.

[172] Molero Gómez, A., C. Pereyra López, and E. Martinez de la Ossa, *Recovery of grape seed oil by liquid and supercritical carbon dioxide extraction: a comparison with conventional solvent extraction.* The Chemical Engineering Journal and the Biochemical Engineering Journal, 1996. 61(3): p. 227-231.

[173] Toews, K.L., et al., *pH-Defining Equilibrium between Water and Supercritical CO2. Influence on SFE of Organics and Metal Chelates.* Analytical Chemistry, 1995. 67(22): p. 4040-4043.

[174] Intanakul, P., M. Krairiksh, and P. Kitchaiya, *Enhancement of Enzymatic Hydrolysis of Lignocellulosic Wastes by Microwave Pretreatment Under Atmospheric Pressure.* Journal of Wood Chemistry and Technology, 2003. 23(2): p. 217-225.

[175] Saha, B.C., A. Biswas, and M.A. Cotta, *Microwave Pretreatment, Enzymatic Saccharification and Fermentation of Wheat Straw to Ethanol.* Journal of Biobased Materials and Bioenergy, 2008. 2(3): p. 210-217.

[176] Ma, H., et al., *Enhanced enzymatic saccharification of rice straw by microwave pretreatment.* Bioresource Technology, 2009. 100(3): p. 1279-1284.

[177] Imai, M., K. Ikari, and I. Suzuki, *High-performance hydrolysis of cellulose using mixed cellulase species and ultrasonication pretreatment.* Biochemical Engineering Journal, 2004. 17(2): p. 79-83.

[178] Nitayavardhana, S., et al., *Ultrasound pretreatment of cassava chip slurry to enhance sugar release for subsequent ethanol production.* Biotechnology and Bioengineering, 2008. 101(3): p. 487-496.

[179] Keshwani, D.R., *Microwave Pretreatment of Switchgrass for Bioethanol Production.* 2009, North Carolina State University.

[180] Sun, R.C. and J. Tomkinson, *Characterization of hemicelluloses obtained by classical and ultrasonically assisted extractions from wheat straw.* Carbohydrate Polymers, 2002. 50(3): p. 263-271.

[181] Yachmenev, V., et al., *Acceleration of the enzymatic hydrolysis of corn stover and sugar cane bagasse celluloses by low intensity uniform ultrasound.* Biobased Material Bioenergy, 2009. 3: p. 25-31.

[182] Vinatoru, M.e.a., *Ultrasonically assisted extraction of bioactive principles from plants and their constituents*, in *Advances in Sonochemistry*, T.J. Mason, Editor. 1999, JAI Press. p. 209-248.

[183] Palonen, H., et al., *Evaluation of wet oxidation pretreatment for enzymatic hydrolysis of softwood.* Applied Biochemistry and Biotechnology, 2004. 117(1): p. 1-17.

[184] Schmidt, A.S. and A.B. Thomsen, *Optimization of wet oxidation pretreatment of wheat straw.* Bioresource Technology, 1998. 64(2): p. 139-151.

[185] Chum, H.L., et al., *Evaluation of pretreatments of biomass for enzymatic hydrolysis of cellulose.* 1985, Solar Energy Research Institute: Golden, Colorado. p. 64

[186] Martín, C., et al., *Wet oxidation pretreatment, enzymatic hydrolysis and simultaneous saccharification and fermentation of clover–ryegrass mixtures.* Bioresource Technology, 2008. 99(18): p. 8777-8782.

[187] Galbe, M. and G. Zacchi, *A review of the production of ethanol from softwood.* Appl Microbiol Biotechnol, 2002. 59: p. 618 - 628.

[188] Vidal, P., *Ozonolysis of Lignin – Improvement of in vitro digestibility of poplar sawdust.* Biomass, 1988. 16(1): p. 1-17.

[189] Energy Information Administration, *Chapter 10 Growth of the Landfill Gas Industry*, in *Renewable Energy Annual 1996.* 1997.DOE/EIA-0603(96)

[190] Breen, A. and F.L. Singleton, *Fungi in lignocellulose breakdown and biopulping.* Current Opinion in Biotechnology, 1999. 10(3): p. 252-258.

[191] Hischier, R., *Life Cycle Inventories of Packaging and Graphical Papers*, in *Ecoinvent Report No.11.* 2007, Swiss Centre for Life Cycle Inventories: Dübendorf

[192] Martínez, Á.T., et al., *Biodegradation of lignocellulosics: microbial, chemical, and enzymatic aspects of the fungal attack of lignin.* International micorbiology, 2005. 8: p. 195-204.

[193] Maijala, P., et al., *Biomechanical pulping of softwood with enzymes and white-rot fungus Physisporinus rivulosus.* Enzyme and Microbial Technology, 2008. 43(2): p. 169-177.

[194] Shukla, O.P., U.N. Rai, and S.V. Subramanyam. *Biopulping and Biobleaching: An Energy and envioronment Saving Technology for Indian Pulp and Paper Industry.* 2004 [cited 2012 April]; Available from: http://isebindia.com/01_04/04-04-3.html.

[195] Ray, M.J., et al., *Brown rot fungal early stage decay mechanism as a biological pretreatment for softwood biomass in biofuel production.* Biomass and Bioenergy, 2010. 34(8): p. 1257-1262.

[196] Wan, C. and Y. Li, *Fungal pretreatment of lignocellulosic biomass.* Biotechnology Advances, (0).

[197] Yu, H., et al., *The effect of biological pretreatment with the selective white-rot fungus Echinodontium taxodii on enzymatic hydrolysis of softwoods and hardwoods.* Bioresource Technology, 2009. 100(21): p. 5170-5175.

[198] Monrroy, M., et al., *Structural change in wood by brown rot fungi and effect on enzymatic hydrolysis.* Enzyme and Microbial Technology, 2011. 49(5): p. 472-477.