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Production of Biofuel using Biomass as a Sustainable Biological Resource

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Abstract: Biomass feedstock has received great interest to be used as an alternative and renewable source of energy. Lignocellulosic biomass has significant potential to contribute to the biofuel production to decrease green house gas emission and global warming. Researchers with a tremendous enthusiasm have pursued biofuel development using biomass feedstocks over the past decades. Emerging first generation and second generation of biofuels introduced promising renewable energy resources by utilization of sustainable and abundant biomass sources as raw materials. In this study, biomass-based transportation biofuels and biochemical processes for the production of first generation and second generation of biofuels are discussed.

Key words: Biomass, first generation biofuels, second generation biofuels, green house gas

INTRODUCTION

Sustainable globalization demands expanded fuel feedstocks. In the twentieth century main studies were concentrated on the development of cheaply use of fossil fuels for heat, electricity (industrial, commercial and residential), transportation fuels and chemicals including pharmaceuticals, detergents, synthetic fiber, plastics, pesticides, fertilizers, lubricants, solvent, waxes, coke, asphalt to meet the growing demand of the population (Bender, 2000; Demirbas, 2006; Scott *et al.*, 2010). The transportation sector, moreover, requires considerable supplies of liquid transportation fuel which accounts for a major part of oil reserves. Currently, the fossil resources are not considered as sustainable resources so that it is predicted that oil reserves are relatively depleted by 2025 (Greene *et al.*, 2006). The vast combustion of fossil fuels over the past century has brought serious concerns for most nations in the world due to environmental impact of CO₂ emission on the atmosphere contributing global warming. It has been realized that the green house emission from widespread utilization of fossil fuels has a deleterious effect on climate temperature. Consequently, there is a growing trend towards exploiting alternative, renewable and environmentally friendly fuels which are cost-wise competitive with fossil fuels (Vasudevan *et al.*, 2010).

Plant biomass, agricultural residues and forest wastes have received much attention as feedstock for the

production of fuels which are known as biofuels. Biofuels could help decrease global demands for fossil fuels resulting reduction of greenhouse gas emission and environmental warming (Goh *et al.*, 2010). This review study is aimed at highlighting biomass resources, different type of biofuel (first and second generation of biofuels) and biotechnological process used for biofuels production.

Biomass: Biomass is known as an organic, non-fossil material with a biological origin including plants, agricultural residues, forest wastes, microbial cells and municipal wastes derived from biological sources all which represent a potential sustainable energy source (Wu *et al.*, 2010). Agro-industrial residues obtained in food bioprocess constitute the large sources of biomass such as palm kernel cake produced in palm oil industry (Abdeshahian *et al.*, 2010a). The total amount of biomass produced on the Earth is approximated 100 billion tones organic dry matter of land biomass annually and 50 billion tones of aquatic biomass (Naik *et al.*, 2010).

Lignocellulose is the most plentiful renewable biomass which forms approximately half of the plant matter produced by photosynthesis indicating a vast sustainable organic resource in soil.

Lignocellulose is composed of three types of biopolymers namely, cellulose, hemicellulose and lignin that are strongly linked by non-covalent forces and by covalent crosslinkages with a relatively low content of

monosaccharides, starch, protein, or oils. Only a small part of the lignocellulosic substances obtained in agriculture or forestry is used as food, feed, industrial raw materials and energy resources, the rest being considered waste recycled to the Earth system (Sanchez, 2009).

Lignocellulose is a potential feedstock for the production of biofuels, industrial enzymes, animal feed, biofertilizers, biopesticide and biopromoter products. Lignocellulosic raw materials are also used in the paper industry (Tangerdy and Szakacs, 2003). Lignocellulosic raw materials are also used in the production of industrial enzymes (Abdeshahian *et al.*, 2010b).

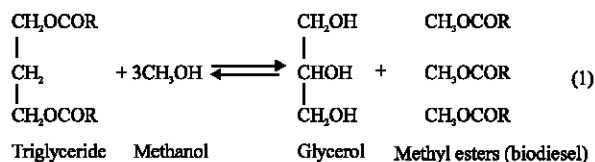
Plant biomass has been realized as a major non-fossil resource of energy due to sustainable development of plant biomass for biotechnological applications, positive effect on global warming with the mitigation of atmospheric CO₂ and making independency to fossil fuel energy (Demirbas, 2007). In the sector of bioenergy production plant biomass has been known for decades as one of the most potentially renewable energy sources that could be utilized for the production of biofuels. Moreover, plant biomass can contribute to provide approximate 14% the total world's energy demand representing a key role for global economy (Zhao *et al.*, 2009).

Biofuel: The term of biofuel refers to liquid fuels and blending components produced from renewable biological products (biomass) for using preliminary in the transport sector (Wu *et al.*, 2010). Biofuels are considered as a favorite, green alternative to fossil sources of energy offering several advantages including compatibility used in transportation infrastructure, contribution to mitigating carbon dioxide emissions, sustainability in production, plant biomass-based origin, security of supply and development of rural economy (Reijnders, 2006; Yan and Lin, 2009). Biotechnological efforts in 21st century have been aimed at finding industrial feedstock and green processes for the production of biofuels and bioproducts using renewable biomass sources (Stevens and Verhe, 2004).

FIRST GENERATION OF BIOFUELS

The first generation of biofuels refers to the fuels produced from edible feedstock including carbohydrate derived from corn, wheat, sugarcane and sugar beet, as well as oil-seed component produced from plants such as palm oil and soybean oil (Moore, 2008). There are three main types of biofuels in this category which are commercially used in transportation infrastructure with the large production around the world. These fuels include biodiesel (bio-esters), ethanol and biogas.

Biodiesel: Biodiesel is an alternative diesel which is produced by transesterification of vegetable oil, residual oil and fats. Transesterification is a reversible reaction in which vegetable oil and animal fat are mixed with methanol in the presence of a liquid catalyst to produce methyl esters known as biodiesel and glycerol which is a valuable co-product. As shown in Eq. 1, in transesterification process triglyceride and methanol are reactants. This process is catalyzed by a liquid acid or a liquid base:



However, transesterification is hampered in the case of a high content of free fatty acids in oil which leads to a decrease in methyl esters quantity due to saponification reaction. The use of solid catalyst can catalyze the simultaneous transesterification of triglyceride and esterification of high free fatty acid existing in oil. The transesterification process occurs between triglyceride and methanol while esterification process occurs between high free fatty acid and methanol in each which the final product is methyl esters (Kulkarni *et al.*, 2006; Meher *et al.*, 2006).

Carbohydrate sources used in ethanol production: A large number of carbohydrate based feedstocks are used for the production of ethanol through fermentation process. Three main groups of carbohydrate sources used in this process are:

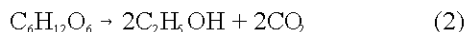
- **Agricultural crops containing sugar:** Sugar cane, wheat, beet root, fruits, palm juice
- **Agricultural crops containing starch:** Grain (wheat, barley, rice, corn and sweet sorghum) and root plants like potato and cassava
- **Cellulosic biomass:** Wood and wood waste, cedar, pine, agricultural residues and fibers

Agricultural food sources like corn, wheat, barley, sweet sorghum form grain alcohol whereas the alcohol obtained from lignocellulosic biomass is called biomass ethanol or bioethanol (Minteer, 2006).

The conversion of starch feedstocks to ethanol: Starch components consist of a long polymeric chain of glucose. It is not possible to directly convert starch feedstocks to ethanol by conventional fermentation technology. The polymeric structure of starch is first broken down into

simple molecules of glucose and other oligosaccharides. In this process, a mash contained 15-20% starch concentration is produced by grinding starch substances and mixing with distilled water. The mash is then heated at or more than its boiling point and subsequently processed with two enzyme preparation. The first enzyme is amylase which releases maltodextrin oligosaccharides by liquefaction process. The second enzymes are pullulanase and glucoamylase which hydrolyze the dextrin and oligosaccharide to produce glucose, maltose and isomaltose. The process of second enzyme reaction is known saccharification. The mash is then cooled to 30°C to be treated by yeast in fermentation process (Lee *et al.*, 2007).

Fermentation process is a next stage of ethanol production. Fermentation process refers to biochemical processes in which organic substances are metabolized by microorganisms producing enzymes (Abdeshahian *et al.*, 2009). Fermentation process can be performed in aerobic or anaerobic conditions. In the production of ethanol simple sugar (hexoses and pentoses) are fermented in anaerobic conditions by microorganisms including yeast (*Saccharomyces* species), bacteria (*Zymomonas* species) and mold (mycelium). These microorganisms live in natural environment and very specific for fermentation of hexoses or pentoses or mixture of them. Different yeasts are used in ethanol production under anaerobic conditions such as *Saccharomyces cerevial*, *Saccharomyces uvarum*, *Shiozosaccharomyces pombe* and *Kluyveromyces* species. In anaerobic conditions yeasts hydrolyze glucose to ethanol with an efficiency conversion of 51% on the weight basis. In practice, 40-48% of glucose is converted to ethanol with 46% fermentation efficiency because of partly consumption of glucose for the production of cell components and metabolic products other than ethanol production (Lee *et al.*, 2007). The Eq. 2 shows the general anaerobic conversion of glucose to ethanol:



The ethanol produced from starch grain like corn is generally categorized into two processes, namely dry mill and wet mill. Dry mills have small size processed for manufacturing ethanol and animal feed. Wet mills are utilized for the production of ethanol and a variety of high value co-products such as nutraceuticals, pharmaceuticals, organic acids and solvent (Shapouri *et al.*, 1995; Minter, 2006).

Biogas production: Anaerobic biodegradation of solid biomass leads to the production of biogas. In this process

anaerobic bacteria digest organic matter of biomass to produce a mixture of methane and carbon dioxide gases with a typical ratio of 60-70% methane and 30% carbon dioxide. The gas has a heating value of 650-750 British thermal units (Btu) per cubic feet of gas (1 Btu = 1055 Joule). Anaerobic biodegradation of municipal solid waste (mainly biomass and biological waste) in landfills produce methane and carbon dioxide in approximate equal volume. These two basic gas together other gas of atmosphere (nitrogen and oxygen) and a slight amount of organic compounds form landfill gas (LFG).

However, LFG contains unfavorable contaminants including toxic vinyl chloride and hydrogen sulphide. Thus, LFG requires the efficient technology for removal of contaminants and carbon dioxide to be used as a substitute for natural gas (Lee *et al.*, 2007). The main use of LFG is the production of energy as electricity using internal combustion engine, turbine, micro turbine as well as direct use in boiler, dryer, kiln and green house. The high cost of methane refinery has led to new trend of landfill gas utilization toward the production of methanol (Lee *et al.*, 2007). The advantages of methanol as liquid fuel are low production of sulphur and ash in commercial use and much simpler handle, transportation and store of methanol than gas products.

SECOND GENERATION OF BIOFUELS

Second generations of biofuels are produced from non-edible sources specifically lignocellulosic biomass. The combustion of these biofuels releases low volume of carbon dioxide into the atmosphere mitigating green house gas (Goh *et al.*, 2010). In a commercial aspect, the cost of these biofuels potentially comparable with standard petrol and diesel, hence they are cost-effective for road transport.

Plant biomass is a promising feedstock for the production of 2nd generation biofuels. In this time, the production of 2nd generation biofuels is not cost-effective because of technological bottlenecks which need to be overcome before they can potentially be used (Pauly and Keegstra, 2008; Wu *et al.*, 2010).

CONVERSION PROCESSES FOR SECOND GENERATION BIOFUELS

Physical conversion

Mechanical extraction: In this method crude vegetable oil is obtained from oil seeds by screw press (expeller) using mechanical pressure. Screw press works in two ways of pre-pressing and full pressing. In pre-pressing, only a part of the oil is separated from seeds and the remained cake with 18 to 20% oil is further processed by solvent

extraction. Oilseeds with high oil content (30-40%) are processed in combined pre-pressing and solvent extraction methods. Full pressing includes the imposition of 95000 kPa to extract most of oil content. Full-pressing can also be carried out by an initial pre-pressing and a final press (Stevens and Verhe, 2004).

Briquetting of biomass: Agricultural residues, forestry waste and other plant biomass materials have a rough bulky shape. This drawback can be alleviated by densification of residuals into compact regular shapes. In densification biomass is placed in a press chamber. Densification is performed in two methods of pressing and maceration. In pressing method an increase in density with an increase of used pressure in the early stage of compression is applied, but the rate of increase in density falls rapidly as the density of pressed materials reaches close to the density of water, however, there is no close correlation between density change and degree of maceration of materials which may be chopping, grinding and pulverizing. A coarse chopping of some materials may be as effective as ultrafine grinding. Thus, in chopping process the volume of tree branches chipped is extensively reduced, while fine grinding provides a reduction in volume that is not considerable higher than chopping method (Kitani and Hall, 1989; Stevens and Verhe, 2004).

Distillation: The evaporation of volatile components of a mixture to separate them from non-volatile parts is called distillation. This process is a main method for recovery of plant oil. Plants are crushed before distillation to extract the oil easier. Plants are then steamed and the important oils vaporize, move up with steam and condensed to be come liquid. An advanced technology is molecular distillation. This method is utilized for production of fragrances which are difficult to be distilled in conventional method (Stevens and Verhe, 2004).

THERMO-CHEMICAL CONVERSION

Direct combustion: Combustion (burning) is the chemical reaction between a fuel and oxygen. As a consequence, carbon dioxide and water are released with the production of heat. In direct combustion plant biomass are used as a substitute of fossil fuels in combustion reaction. Advantages of direct combustions are lower sulfur emission (0.05-0.2 w.t. %) and the better control of particulate formation in the source (Lee *et al.*, 2007).

Gasification: Gasification is a technology for the conversion of biomass to sustainable fuels. Gasification

step includes reacting biomass with oxygen and/or steam to produce a gaseous blend of CO and H₂ with various amounts of CO₂, CH₄, N₂ and other gases under elevated temperature which depending on the proportion of gaseous constituents are called producer gas or synthesis gas (Syngas) (Rowlands *et al.*, 2008; Wu *et al.*, 2010).

Gasification can be performed by two routes, namely catalytic and non-catalytic method. In non-catalytic method a very high temperature as high as 1300 °C is required, while catalytic process can be operated at lower temperature (900 °C) and even lower than that with using high technology (Lee *et al.*, 2007). Producer gas is mainly used for stationary power generation, whereas syngas is currently applied for the production of transportation fuels and chemical intermediates. The chemical reaction routes for the fuel production using syngas are hydrogen production by Water-Gas-Shift reaction (WGS), hydrocarbon production by Fischer-Tropsch (F-T) synthesis and methanol synthesis (Balat, 2006; Van Steen and Claeys, 2008). In WGS reaction, the chemical reaction of CO and H₂O results in H₂ and CO₂. This process can be used to enhance producer gas to syngas by enriching the H₂ component or production of H₂ as an end product. F-T synthesis is utilized for the production of hydrocarbon from syngas. The production of methanol from syngas has been carried out since 1920s (Rowlands *et al.*, 2008).

Hydrogen as a biogas can also be produced in biological processes (Alshiyab *et al.*, 2008a). In the process of biohydrogen production biomass is fermented in anaerobic conditions to produce hydrogen by microorganisms such as *Rhodobacter sphaeroides* and *Clostridium acetobutylicum* (Alshiyab *et al.*, 2008b; Jaapar *et al.*, 2009).

Liquefaction: Liquefaction of biomass is usually performed in the presence of a solution of alkalis, glycerin, propanol, butanol or direct liquefaction (Demirbas, 2004). In liquefaction water insoluble oil with high viscosity is produced using solvents for decreasing gases such as CO and H₂. In this method catalyst is added to biomass (Rowlands *et al.*, 2008). Lignocellulosic biomass can also be converted to a liquid like heavy fuel oils by reacting lignocellulosic substances with prepared gases using suitable catalyst.

Aqueous liquefaction includes desegregation of wood ultrastructure and subsequent partial depolymerization of structural components. Alkali liquefaction involves deoxygenation through decarboxylation from ester produced by hydroxyl group and formate ion derived from carbonate. Alkali salts (e.g., sodium carbonate and potassium carbonate), can

work as catalyst for hydrolysis of cellulose and hemicelluloses to release smaller components.

The heavy oil produced from liquefaction has a high viscosity and tarry property which may not be handled easily; therefore, organic solvents such as propanol, butanol, acetone, methyl ethyl ketone and ethyl acetate are added to reaction system. These solvents except ethyl acetate, can be recovered during wood liquefaction. Catalytic aqueous liquefaction produces higher oil yield (63%) than that in non-catalytic (31%) (Demirbas, 2004).

High Pressure Liquefaction (HPL) process can be used to produce bio-oil containing a complex blend of volatile organic acids, alcohols, aldehydes, ethers, esters, ketones and non volatile compounds. These oils can be enhanced by using catalyst to produce an organic distilled product which is enriched with hydrocarbons and valuable chemicals (Demirbas, 2004).

Pyrolysis: Heating biomass in anaerobic conditions results in the production of solid charcoal, liquid bio-oil and fuel gases. This process is called pyrolysis. Pyrolysis can be categorized into three groups depending on environment conditions, namely conventional pyrolysis, fast pyrolysis and flash pyrolysis.

Conventional pyrolysis involves heating wood biomass in a slow rate (0.1-1 Kelvin/second) for a range time of 45-550 sec. This process is divided into three stages. In the first stage biomass degradation occurs at a temperature range of 550-950 K which is known as pre-pyrolysis. The second stage is the main stage of pyrolysis in which a high rate of temperature is used. In this stage the pyrolysis products are produced. In the third stage char formed is heated at a very slow rate and it results in carbon rich solid residues (Shafizadeh, 1982).

Fast pyrolysis consists of heating the biomass at a high temperature range of 850-1250 K with a heating rate 10-200 K sec⁻¹, short time of heating (0.5-10 sec) and a particle size less than 1 mm. The fast pyrolysis is used for the production of liquid or gaseous products. In this process biomass decomposes to produce vapors, aerosol and some charcoal similar to char. Cooling and condensation of vapors and aerosol results in a dark brown liquid which its heating value is half of that in conventional fuel oil. Depending on raw material used in fast pyrolysis, 60-75% bio-oil, 15-25% solid char and 10-20% non condensed gaseous products can be obtained (Shafizadeh, 1982).

Flash pyrolysis represents the pyrolysis process in which operating conditions are a temperature range of 1050-1300 K, a heating rate higher than 1000 K sec⁻¹, residence time less than 0.5 sec and a particle size less than 0.2 mm. Flash pyrolysis is used for the production of

bio-oil which can be mixed with the char to produce bioslurry. Bioslurry can be easily used in gasifier conditions (pressure of 26 bars and temperature range of 927-1227 K) to produce syngas. Biomass can be converted to crude oil in flash pyrolysis with efficiency up to 70%. There is a type of fuel called bio-crude which can be used in engine and turbine. Furthermore, bio-crude is capable of using as feedstock in refineries (Demirbas, 2004; Mohan *et al.*, 2006).

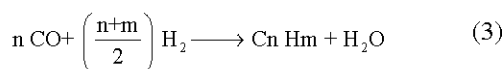
Production of green diesel fuel using vegetable oils: As previously discussed, oil derived from plants such as rapeseed, soybean, canola and palm tree are widely used in the production of fatty acid methyl ester (biodiesel). Energy biotechnology has made huge efforts to present biofuels which are compatible with fossil fuels with an economical feasibility. Isoparaffin-rich diesel called green diesel is a new product of biodiesel that is produced from renewable plant oils comprising triglycerides and fatty acids processed under catalytic saturation, hydrodeoxygenation, decarboxylation and hydroisomerization. Isoparaffin-rich diesel is an aromatic and sulfur free diesel fuel with a very high cetan blending value. Green diesel fuel is capable of adjusting to any environmental climate; it is used as neat or blended fuel. Any type of feedstock oil can be converted to this product. Compared to petroleum based diesel fuel and fatty acid methyl ester (biodiesel), green diesel represents a high cetan value, good cold flow property and high storage stability (Kalnes *et al.*, 2007). Green diesel also is satisfactorily compatible for blending with existing diesel fuels derived from fossil feedstocks.

Bio-oil production using pyrolysis process: Bio-oil is a fuel oil that is produced in fast pyrolysis process by heating biomass feedstock in anaerobic conditions. During this process the lignocellulosic substances are thermally degraded to produce liquid bio-oil (60-70%), char (30-35%) and gas such as CO, H₂ and volatile hydrocarbons (13-25%) under operating conditions of 2-5 mm particle size and heating time of 0.1-2 sec. The amount of bio-oil produced and the chemical content of bio-oil is varied depending upon the feedstock composition, operating conditions and bioreactor type. Physically bio-oil is a dark brown, viscous, corrosive and acidic liquid with a specific smoky odor. Bio-oil is usually used as fuel for boiler, gas turbine, diesel engines, furnaces and stationary engines. Chemical content of bio-oil is generally includes chemicals derived from lignocellulose compounds such as aliphatic alcohols/aldehydes, furanoids, pyranoids, benzenoids, fatty acids and high molecular mass hydrocarbons. These chemicals are mixed

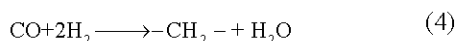
with water formed in pyrolysis to produce an emulsion. Some value added chemicals can be obtained from biofuels which are used for the production of natural resin, food flavors, wood preservatives, slow release fertilizer and pharmaceuticals (Ates and Isikday, 2008; Elliott, 2007; Ozbay *et al.*, 2006; Rout *et al.*, 2009; Scott *et al.*, 1993).

Production of FT oil (green motor fuel): Syngas (CO and H₂ mixture) obtained in gasification of biomass can be processed for the production of liquid fuels and hydrocarbonic compounds using transition metal catalyst. This process refers as Fisher-Tropsch synthesis (FTS). The liquid fuels obtained in FTS process are called FT oil or green motor fuel. The feedstocks used for FTS are coal, biomass and natural gas. The gasification of lignocellulosic biomass produces biosyngas which consists of carbon monoxide (28-36%), carbon dioxide (22-32%), benzene/toluene/xylene (0.84-0.96%), ethan (0.16-0.22%), hydrogen (21-30%), methane (8-11%) and tar (0.15-0.24%) (Balat, 2006).

The general chemical reaction of FTS is shown in Eq. 3:



where n is the average length of hydrocarbon chain and m is the number of hydrogen atom per carbon. As shown in Eq. 4, one mole CO reacts with two mole H₂ in the presence of catalyst to form a hydrocarbon chain:



The -CH₂- is a unit for building longer chains. Most of the products formed in FTS are aliphatic straight chain with a low amount of branched hydrocarbon. Main hydrocarbon products in FTS are olefin and paraffin, other hydrocarbons include methane (CH₄), ethylene (C₂H₄), ethane (C₂H₆), propane (C₃), butane (C₄), gasoline (C₅-C₁₂), diesel fuel (C₁₃-C₂₂) and wax (C₂₃-C₃₃). The proportion of products depends on operating condition like the temperature, pressure and the type of catalyst used. The range of temperature and pressure used for FTS are 202-352°C and 15-40 bar, respectively. Cobalt and iron are the main catalyst for FTS process (Chew and Bhatia, 2008; Rout *et al.*, 2009).

Production of bioethanol from renewable lignocellulosic feedstock: Biotechnological process for bioethanol production is based on microbial and enzymatic reaction

for sugar synthesis from biomass feedstock like lignocellulosic substances and starch. Sugar obtained is then converted to alcohol and other fuels as well as chemicals by fermentation process. The pathway for conversion of lignocellulosic biomass to ethanol requires different operating units including pretreatment, enzyme production, hydrolysis, fermentation and ethanol recovery. Biotechnological efforts have focused on reducing cost of conversion process of lignocellulosic biomass to liquid fuels and chemicals by means of integrated xylose and glucose fermentation, reduced energy needed for pretreatment, bioprocess of lignin to valuable products and well-established process for recovery of alcohol (Lee *et al.*, 2007; Minter, 2006). Main lignocellulosic resources for the production of liquid fuel are agricultural residues, agro-industrial wastes, forest residues and post harvest materials of food crops which generate a rich source of carbohydrate (Huber and Corma, 2007).

As discussed previously, the lignocellulosic biomass is constructed from three main parts including cellulose, hemicellulose and lignin. Cellulose is a crystalline polymer of glucose. Hemicellulose is an amorphous polymer of xylose, mannose and arabinose while lignin is a large polyaromatic compounds. The conversion of lignocellulosic biomass to alcohol consists of pretreatment of biomass, hydrolysis by acid or enzyme, fermentation process and distillation. The pre-treatment process is used for separation of xylose and lignin from crystalline cellulose.

One of the important pre-treatment methods is steam explosion process. In this method lignocellulosic biomass is exposed to a high pressure of saturated steam inside a vessel for a short residence time of 20 sec to 20 min at a temperature range of 473-543 K and pressure 14-16 bar. The pressure in vessel is then quickly dropped to atmospheric pressure to make explosion. Steam explosion causes disintegration of hemicellulose and lignin in biomass structure which is subsequently converted to low molecular weight components. A large part of water soluble components is removed by water extraction. At the same time steam explosion reduce crystallinity of cellulose to lessen the polymerization of cellulose and hemicelluloses-lignin compound which in turn increases the accessibility area for enzyme reaction. In pre-treatment process low molecular weight fraction of hemicelluloses form xylose and solid cellulose is converted to glucose through enzymatic process. Glucose and xylose are processed in fermentation process to produce ethanol. Ethanol can be mixed with gasoline for the production of an oxygenated fuel with the lower hydrocarbon and green house emission (Minter, 2006).

CHEMICAL HYDROLYSIS

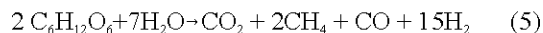
There are a number of important factors affecting chemical conversion of biomass to biofuel. These factors include the ratio of surface to volume, the concentration of acid used, temperature and time. Among these factors, the surface to volume ratio is of great importance because of its determinant effect on the yield of glucose. The smaller particle size, therefore, has a better hydrolysis process. With consideration of the ratio of liquid to solid, a higher ratio causes chemical reaction rate more quickly (Jensen *et al.*, 2008).

Solvent extraction process: Extraction is defined as the process of separation of a desired substance from the raw feedstock by dissolving the desired materials into a suitable solvent and subsequent recovery of substance from solvent. Solvent extraction needs to different operating parts including the extraction of oil from oil seeds, evaporation of solvent, distillation of the mixture of oil and solvent and heating of meal residue. Different types of solvent are used in separation process such as hexane (for extraction of seed oil), dichloromethane, acetone, ethanol and isopropanol. The extracted lignocellulos biomass can be used in hydrolysis and fermentation process for the production of biofuels (Stevens and Verhe, 2004).

Supercritical fluid processing: Supercritical fluid refers to a substance in conditions which its temperature and pressure are above the critical point of these variables in vapor liquid status. At supercritical conditions a substance is not liquid or gas and reduced pressure at constant temperature doesn't cause it to boil as it cannot be condensed by cooling at constant pressure (Saka *et al.*, 2006). Supercritical fluid process can be used for the extraction of aromatic woods (cedar wood, sadal wood, pine wood) to separate extractive biomass.

Supercritical fluid processing can be used as a substitute for acid hydrolysis or enzymatic hydrolysis since acid recovery in acid hydrolysis is expensive and is a polluting methods and enzymatic hydrolysis needs to the pretreatment of biomass. In supercritical conditions (temperature 300-644 K and pressure 200-250 bar) acid and base components (H^+ and OH^-) of water are released and dissolved in biomass. The dissolved acidic and basic components of water break the bonds of cellulose and hemicelluloses to simple molecules of sugar i.e. glucose, xylose and oligosaccharides (Sasaki *et al.*, 1998). Supercritical fluid gasification technology has been used for the hydrolyzing cellulose to glucose in residence time 10-20 sec and above 45 sec pyrolysis start. When temperature increases to 873 K, the complete

disintegration of biomass structure occurs by transfer of oxygen from water to carbon atoms of the biomass. The hydrogen atom of water forms hydrogen. The general reaction for this process is shown in Eq. 5:



where $C_6H_{12}O_6$ represents the molecule of biomass (Loppinet-Serani *et al.*, 2008).

CONCLUSION

The concerns to the depletion of fossil fuels sources followed by global warming due to increasing CO_2 emission (green house gas) as well as soared price of petroleum and subsequent rapid drop over past decades has kindled worldwide interest for the development of renewable energy resources as an alternative for unsustainable fossil fuels resources. Global efforts have employed biomass as potentially sustainable fuel feedstocks for the generation of energy with reducing green house gas and dependency to fossil resources. In this regard, the first generation of biofuel source provided a reliable substitute for fossil fuel sources. However, the controversy of food demand versus biofuel consumption caused that energy biotechnology introduces the second generation of biofuel sources which are mainly plant biomass feedstocks. The conversion of lignocellulosic biomass to liquid fuels is a costly process which demands more scientific studies for finding biotechnological processing of plant biomass to form liquid biofuels with a cost-effective green process.

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