

Hawaii Renewable Energy Development Venture Technology Assessment Biomass Conversion Technology

1. Overview - Issues and Enabling Technology Needs

1.1 Fermentation based ethanol production.

Ethanol can be produced by the fermentation of sugars by yeast. Sugar based ethanol production is established technology and has been practiced for thousands of years as an ingredient in beer, wine, and other spirits. At industrial scales, sugars are derived directly from sugar bearing plants (e.g. sugarcane) or indirectly from plant starches (e.g. corn). The cellulose and hemicellulose components of plant fiber can also be processed to provide a source of sugar for fermentation. This latter technology is currently at the pilot plant stage of development. In the U.S. outside of the beverage industry, ethanol is most commonly produced by fermenting milled corn using either wet or dry methods (Anon, 2002; Shleser, 1994).

In the dry milling method, dry corn kernels are ground into a meal, which is mixed with enzymes and water and cooked to liquefy the mixture into a "mash." A second set of enzymes is added to convert starches in the mash to dextrose in a process called saccharification. Yeast then is added to ferment the sugars into ethanol over a 48-50 hour period. The fermented mash, known as "beer," is distilled to extract ethanol at about 96% purity. Additional dehydration results in pure ethanol.

The wet milling method adds a soaking step before grinding, enabling the mechanical separation of corn kernels into individual components. The separate components then can be used to produce a wider variety of higher valued products than the dry milling process. The wet milling process normally requires greater capital outlay and is more costly than the dry milling process. The theoretical yield of ethanol is 124 gallons per ton of corn grain. Typical yields are ~95 gallons ethanol per ton corn.

Production of ethanol from sugarcane or other sugar bearing plants involves extracting the sugars and fermenting them directly. Sugarcane processing facilities can be designed to split the extracted juices between sugar and ethanol production. Molasses contains sugars that are economically unrecoverable in the manufacture of raw sugar and is sold as a byproduct by Hawaii's producers, some of it locally as a cattle feed supplement. The sugars present in molasses can be fermented to produce ethanol and this is the basis for rum production. A yield of ~150 gallons of ethanol per ton of fermentable sugars can be expected from these sources and this translates to ~70 gallons per ton of molasses.

Ethanol from biomass fiber via fermentation pathways has seen continued development. Fiber is composed of cellulose, hemicellulose, and lignin. The

first two components are polysaccharides that can be broken down or hydrolyzed into simple sugars such as glucose that can subsequently be fermented into ethanol. Hydrolysis can be accomplished using dilute acid solutions, enzymes, or a staged combination of the two. Pretreatment of fiber to make the chemical linkages between the substituent sugars more amenable to hydrolysis is the focus of ongoing research. Ethanol from fiber is widely viewed as the process that will ultimately provide plentiful supplies of fuel but has yet to be realized at a commercial scale.

1.2 Pyrolysis

Pyrolysis, is a process in which biomass is heated rapidly to ~600°C in the absence of oxygen. The biomass feedstock decomposes and when the products are brought to ambient conditions, the result is a mixture of solid char, permanent gases, and liquid phase. Pyrolysis processes are designed to maximize the production of the liquid called bio-oil or pyrolysis oil. The yield of bio-oil from wood and paper range from 60 to 80% (weight) and 75 to 93% (weight), respectively, correlating with cellulose content of the biomass material. Char and permanent gases account for 4 to 30% and 2 to 20%, respectively, of the initial feedstock mass. The composition of bio-oil is approximately 20-25% water, 25-30% water insoluble pyrolytic lignin, 5-12% organic acids, 5-10% non-polar hydrocarbons, 5-10% anhydrosugars, and 10-25% other oxygenated compounds (Anon, 2001; Oasmaa and Peacocke, 2001; Oasmaa *et al.*, 1997). Bio-oil has a heating value of ~7,500 BTU per lb, similar to that of most solid biomass fuels at 10 to 12% moisture. As a liquid fuel, bio-oil has an energy density of ~75,500 BTU per gallon, about 55% of the value for fuel oil. A summary of bio-oil characteristics for Ensyn's RPT™ Process is provided in Table 1 for a variety of feedstocks.

Commercial pyrolysis units are available from two Canadian companies, Ensyn Corporation of Ottawa and DynaMotive Energy Systems Corporation of Vancouver. Pyrolysis oils have commercial markets, mainly as liquid smoke that is applied to meat products. Red Arrow International LLC of Manitowoc, Wisconsin, is perhaps the best-known company marketing this product. Bio-oil may also be used as a chemical intermediate that can be fractionated into its chemical constituents and sold to chemical markets, although this is not currently practiced commercially. Energy products show potential but have seen limited implementation at commercial scales (Freel and Graham, 2000). Red Arrow uses bio-oil to satisfy 6 MW_{th} of industrial energy demand at their manufacturing facility. Bio-oil has also been co-fired with coal in a grate-fired, utility boiler in Wisconsin near Red Arrow's manufacturing facility. Minor modifications were performed on the boiler to allow injection of steam-atomized bio-oil in the over-fire area above the grate. The bio-oil accounted for 5% of the total fuel energy input and emission and performance evaluations concluded that there were no noticeable changes compared to coal.

Table 1. Typical bio-oil yield and quality from Ensyn RTP™ Process

Feedstock	Wood	Bark	Bagasse	Corn Fiber	Mixed Paper
Typical Product Yields ¹ (weight %)					
Bio-Oil	71-80	60-67	75-81	71-76	71-93
Char	12-20	16-28	12-14	7-14	4-20
Gas	5-12	8-17	5-10	10-17	2-12
Bio-Oil Higher Heating Value					
BTU per lb	6,800-8,400	7,780-8,900	7,670-8,350	7,100-8,250	6,700-8,000
BTU per gal	75,500	81,500	79,500	73,500	74,000

¹ Yields are on an ash-free basis

With additional processing bio-oil can be used in combustion turbines. In boilers, bio-oil does not provide energy advantages over firing biomass directly, as any gain in efficiency is more than offset by the energy expended to produce the bio-oil. The potential advantage of bio-oil in steam boiler applications is that it generally has a greater energy density (BTU per ft³) than the parent biomass material that can be useful if it is necessary to transport fuel from point of production to point of use. There are clear advantages for using bio-oil in combustion turbines and other power generation systems that have higher conversion efficiency than steam-based units and cannot use biomass directly. The use of bio-oil in higher efficiency units will need to address technical challenges. The composition and fuel properties of bio-oil differ considerably from commonly used petroleum-based fuels for which most conversion technologies were developed. Depending on the feedstock and the type of fast pyrolysis method employed, bio-oil composition may also vary significantly. These differences should be taken into consideration in the selection of bio-oil-fired power generation units (Anon, 2001; Anon, 2001a).

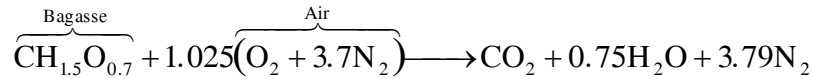
Bio-oil may also be upgraded to produce clean transportation fuels using unit operations typically found in an oil refinery. This pathway for bioenergy development could potentially take advantage of existing refinery conversion infrastructure and the products would be compatible with distribution equipment. Hydro-processing would remove oxygen from the bio-oils compounds using high pressure hydrogen in the presence of catalyst to produce hydrocarbon compounds (Huber, 2007).

1.3 Gasification

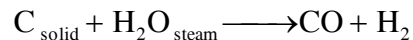
Gasification is the partial oxidation of a solid fuel to form a combustible gas. Generally, the goal of a gasification process is to simultaneously maximize the solid fuel carbon conversion and the heating value of the product gas. Air and steam are commonly used oxidizers when electricity is the desired end product. Oxygen can also be used but the additional expense required to produce a concentrated oxygen stream for the process limits this option to applications

where the product gas is to be used to synthesize higher-valued chemical compounds such as methanol.

The composition of biomass varies depending on the species and local growing and harvesting conditions. Nonetheless, on a dry mass basis, biomass typically contains about 48% carbon, 6% hydrogen, and 42% oxygen with the remainder composed of inorganic elements. The fraction of each component varies depending on the type of biomass. Wood for example typically has very little (~0.5%) inorganic material whereas grass species may have ~5%. When subjected to proximate analysis, biomass typically contains ~80% volatile matter and 15% fixed carbon. The volatile matter is classified as the amount of fuel mass which is driven off as a gas when a sample is heated in an inert environment. Complete oxidation using air to produce carbon dioxide and water follows the reaction;



This reaction defines a stoichiometric air-fuel ratio of ~5.6 (mass basis) for bagasse combustion, neglecting the mass of ash in the fuel. Boilers are often operated with rates of excess air from 30% to 100% of stoichiometric, (air-fuel ratios of 7.3 to 11.3 (mass basis)), to ensure complete combustion and control temperature. Air blown gasifiers typically operate at about 30% of stoichiometric air (air-fuel ratio of 1.7 (mass basis)) and produce gas composed of CO₂, CO, H₂, H₂O, CH₄, N₂, and higher hydrocarbon compounds. The mixture of these components will vary depending on the gasifier technology employed. Air blown gasifiers are directly heated in that some portion of the fuel reacts with the oxygen and provides the heat required to volatilize or gasify the remainder. Steam may also be fed to an air-blown gasifier to moderate temperatures near the air injection point and to improve carbon conversion and gas quality by increasing the rate of the reaction:



Product gas from air blown gasifiers has a higher heating value in the range of 100 to 135 BTU per ft³ [1]. A typical gas composition is shown in Table 2. A typical dry gas yield for an air-blown gasification system is ~32 dry ft³ per lb of dry fuel. Note that this includes the nitrogen input from the fluidizing air.

Most of the development efforts currently under way that seek to match biomass gasifiers to combustion turbines have selected bubbling or circulating fluidized bed technologies for the gasification reactor. Schematics of these two types are shown in Figure 2. Fluidized beds contain fine, inert particles of sand or alumina that have been selected for size, density and thermal characteristics. As gas is forced through the bed from below with increasing velocity, a point is reached when the frictional force between particle and gas counterbalances the weight of the particle. This is the point of minimum

fluidization, and increases in gas flow rate beyond this point result in bubbling and channeling of the fluid through the bed media. Bubbling fluidized beds are operated in this regime.

Table 2. Typical gas composition from pressurized air blown biomass gasifier

Gas Component	Air Blown	Steam Blown
H ₂	9	22.2
CO	14.1	43.2
CH ₄	9	15.8
CO ₂	19.2	13.5
N ₂	47.4	
Higher Hydrocarbons	1.3	5.5

As shown in Figure 1 (a), the bubbling fluidized bed reactor design includes a larger diameter section at the top, called the disengagement zone, which reduces the flow velocity allowing unreacted fuel and bed particles to return to the lower section of the reactor. Continued increases in gas flowrate beyond minimum fluidization velocity reach a point where the terminal velocity of char and bed particles is exceeded and particles become entrained in the gas flow. Circulating fluidized beds are operated in this manner and particles exiting from the top of the reactor are separated from the gas flow in a cyclone and returned to the bed. In both types of fluidized beds, the inert particles are initially heated at start-up and then serve as an ignition source and thermal energy carrier at steady state conditions. Table 3 provides a comparison of bubbling and circulating fluidized bed characteristics.

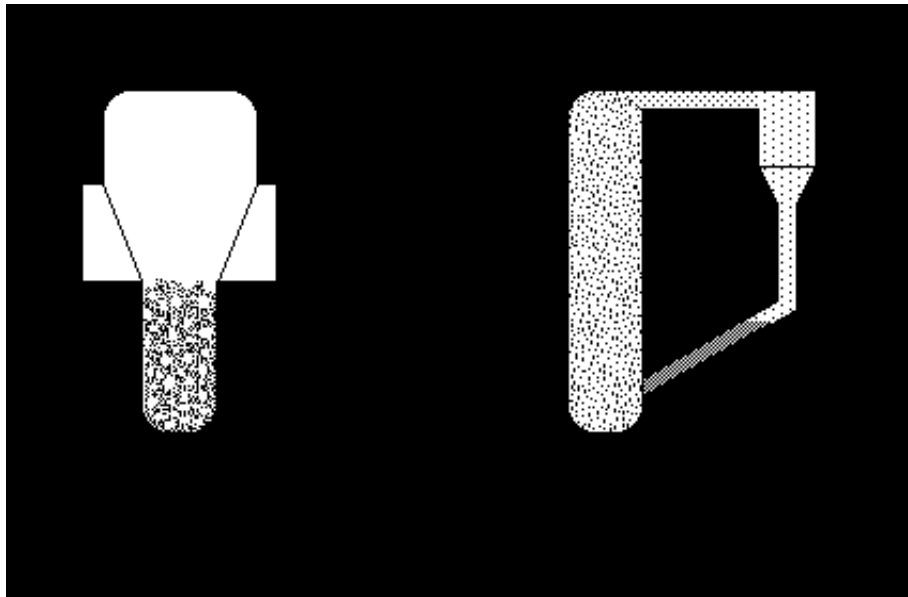
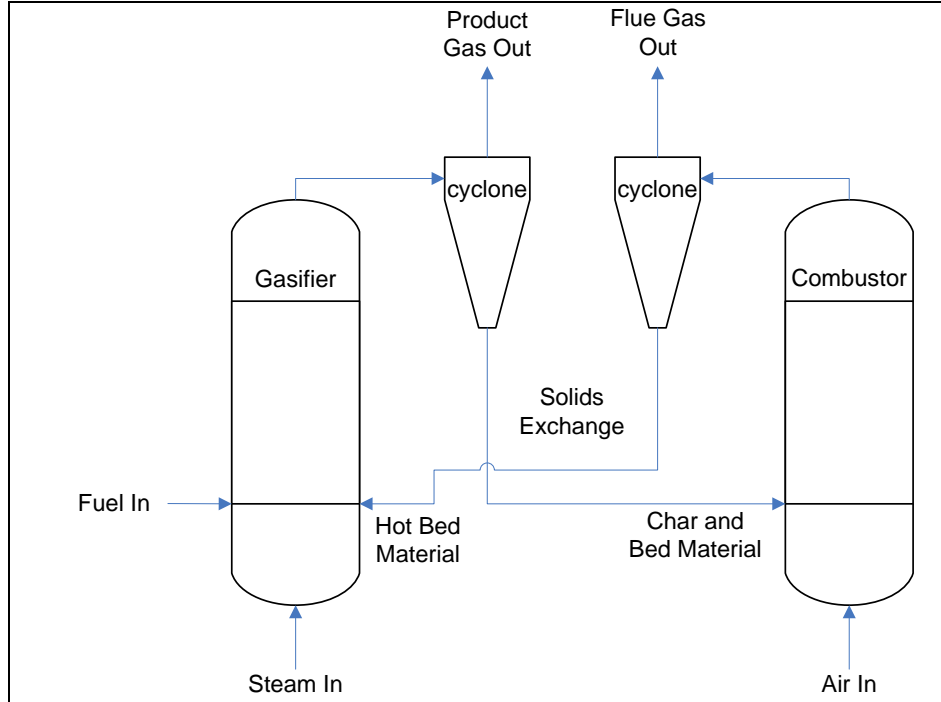


Figure 2: Schematics of bubbling (a) and circulating (b) fluidized bed gasifiers.

Table 3. Comparison of circulating and bubbling fluidized beds [2].

	Circulating Fluidized Bed	Bubbling Fluidized Bed
Gas Solid Reaction	Suitable for rapid reactions. Recirculation of small particles is crucial.	Yields a uniform product gas. Large bubble size may result in gas bypass through bed.
In-Bed Temperature Distribution	Temperature gradients in direction of solid flow; may be minimized by sufficient circulation of solids.	Exhibits a nearly uniform temperature distribution throughout the reactor.
Particles	Size of fuel particles determined by minimum transport velocity. High velocities may result in equipment erosion.	Ability to accept a wide range of fuel particle sizes including fines.
Heat Exchange and Transport	Heat exchange less efficient than bubbling fluidized bed, but high heat transport rates possible due to high heat capacity of bed material.	Provides high rates of heat transfer between inert material, fuel, and gas.
Conversion	High conversion possible.	High conversion possible.

Indirectly heated fluidized bed gasifier technology has also been developed. One variant of this is shown in Figure 3. Fuel is fed to a circulating fluidized bed gasifier containing hot bed material that uses low pressure steam as the fluidizing agent. Without oxygen present, the fuel is pyrolyzed and the volatiles react with steam producing a combustible gas. Pyrolysis is the thermal decomposition of fuel to form a mixture of gases when heated in the general temperature range from 200 to 600°C. With no oxygen present and limited amounts of heat, carbon conversion from solid to gas is incomplete, resulting in a mixture of char and bed material being entrained from the gasifier. This mixture of solids is separated from the product gas in a cyclone and directed to a second circulating fluidized bed that is blown with air and operated as a combustor, yielding a stream of flue gas and hot bed material. A second cyclone disengages the hot solids and they are returned to the gasifier to provide the heat required for fuel pyrolysis and reactions between fuel volatiles and steam. This system effectively decouples the gasification reactions from the combustion reactions, yielding product gas with a small amount of nitrogen compared to an air blown gasifier and a heating value of ~400 BTU/ft³. Typical gas composition for an indirectly heated gasifier is shown in Table 1 and dry gas yields for this process are ~12 ft³ of dry gas per lb of dry biomass (Bain *et al.*, 1997).



q Figure 3: Schematic of indirectly heated fluidized bed gasifier.

1.3.1 Gasification for Power Generation

In a biomass integrated gasifier, combined cycle (BIGCC) application, the product gas would be fired in a combustion turbine to generate electricity in a topping cycle. The hot exhaust products are directed through a heat recovery steam generator (HRSG) and steam raised in this manner is used in a steam turbine to generate additional electricity in a bottoming cycle and to satisfy motive and thermal requirements at the installation. The use of a gas turbine requires the fuel gas and combustion air stream to be pressurized, typically to a minimum of 300 psi, depending on the design of the machine. Two configurations have been developed for meeting these requirements while integrating the gasifier with the power block. The first involves pressurizing the gasifier, maintaining pressure through gas conditioning equipment, and feeding the conditioned product stream to the combustor of the gas turbine. The second approach is to operate the gasifier and gas conditioning equipment at nominally atmospheric pressure, then compress the product gas to satisfy turbine requirements. The former approach is shown schematically in Figure 4. To date, no known BIGCC units are operating commercially.

Smaller scale biomass gasification power projects (5 kW to 5 MW) using reciprocating engines are under commercial development in the U.S., India, and Europe.

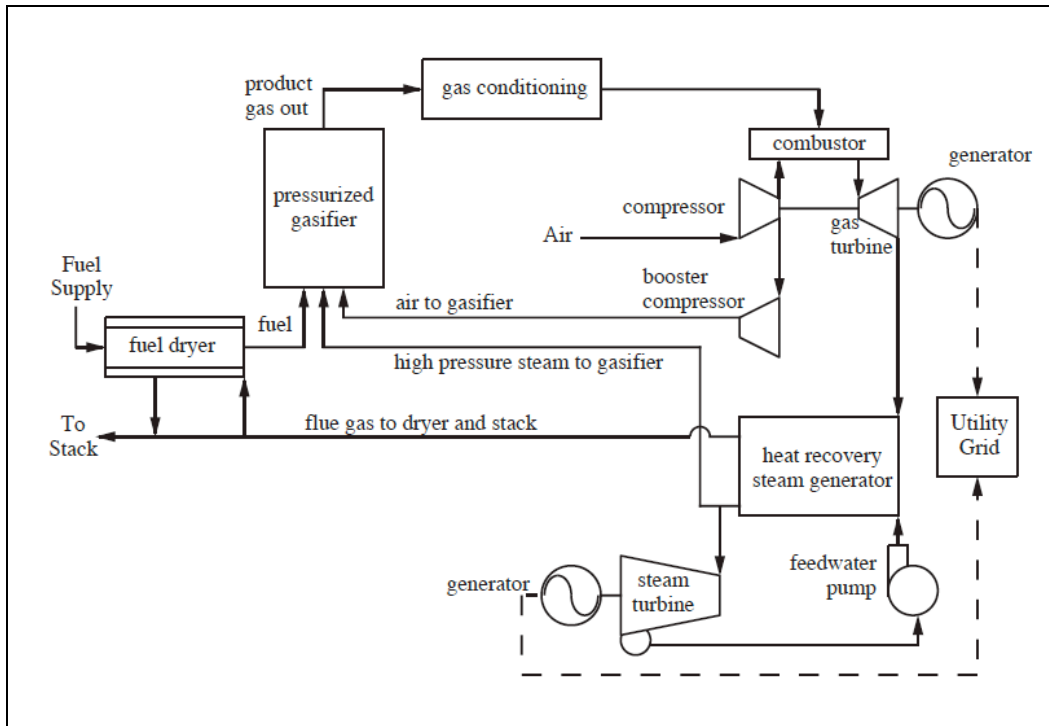


Figure 4: Schematic of pressurized biomass integrated gasifier combined cycle power system.

1.3.2 Gasification for Synthesis of Fuels and Chemicals

A variety of fuels and chemicals can be synthesized from gas rich in hydrogen and carbon monoxide commonly called syngas. Syngas containing a prescribed ratio of these two building block molecules is passed over a catalyst at specified conditions of temperature and pressure to synthesize target compounds. The basic concept of a catalyst reaction is that (1) the reactants (H_2 and CO) adsorb on the catalyst surface, (2) the reactants are rearranged in the adsorbed state to produce the desired product, and (3) the product is desorbed from the catalyst surface. Note that the catalyst is not consumed in the reaction. Hydrogen is also produced from the purification of syngas. The most common energy resource used for syngas production is natural gas (primarily methane) but it can be produced from any hydrocarbon material or biomass. A recent report by the National Renewable Energy Laboratory reviewed possible fuel and chemical products that might be produced from biomass via gasification and included hydrogen, Fischer Tropsch liquids, ammonia, methanol, dimethyl ether (DME), acetic acid, formaldehyde, methyl tert-butyl ether (MTBE), ethanol, and mixed higher alcohols. Their review concluded that the best product to pursue were hydrogen and methanol and that ethanol from syngas could potentially be cost competitive but needed to be demonstrated at larger scales.

Most of the hydrogen produced in Hawaii is generated from crude oil in the refining process. Current hydrogen use in Hawaii is mainly limited to use in the refineries, as a coolant in large turbo generators, and in small volume, specialty

chemical applications. Hydrogen does not represent a large, near-term market that could be entered from production via biomass.

Ethanol, methanol, and dimethyl ether (a methanol derivative) all have potential for entry into local transportation, power generation, or fuel gas markets. Ethanol has immediate local markets as a transportation fuel in the state-mandated E10 gasoline blend, provided it can be produced and sold at a price that is competitive with imported ethanol. Methanol is a commodity chemical, one of the top 10 chemicals produced globally. It can be used directly as a fuel in spark ignited engines or blended with gasoline. Methanol has been used in the past as a ground transportation fuel in several demonstration programs, e.g., in California and in Hawaii, but is not widely used commercially as a primary fuel today because of its higher cost (relative to gasoline), toxicity, and corrosiveness. Methanol is more corrosive than most other fuels, thus requires special storage and delivery equipment. Methanol will dissolve many of the gasketing and fuel-delivery materials used in gasoline engines (Owen and Coley, 1995). DME can be derived from methanol. It is primarily used as an intermediate in the chemical industry and as a propellant for aerosol cans. DME is a liquid at modest pressures and can be used as a cooking fuel, thereby having potential as a locally-produced, biofuel replacement for LPG. DME also has potential as a diesel fuel substitute, having a cetane number comparable to diesel fuel. Use in diesel engines would require modification to the fuel delivery system.

1.4 Direct Combustion of Biomass

Direct combustion of biomass for power generation has a long history in Hawaii. Sugar companies have used bagasse as fuel to generate steam for mechanical, thermal, and electrical power. At present, no power plant in the state is operated using a dedicated fuel supply system, i.e. biomass grown only for fuel production. Conventional biomass power generation units combust the fuel in a water wall boiler, raising steam that is used in a turbogenerator to produce electricity. Units are necessarily limited in size by the supply of fuel that can be economically delivered to the plant with transportation costs serving as a major factor. Biomass power plants developed in the 1980's in California using urban wood waste and agricultural residues were typically sized at 25 MW. Larger facilities (~50 MW) exist such as the McNeill Generating Station in Burlington, Vermont, fueled with waste wood from the forest industries and Okeelanta Power in South Bay, Florida, fueled with bagasse and waste wood. Hawaiian Commercial & Sugar (HC&S) on Maui typically produces 29 MW of electricity to satisfy internal demand and exports ~10 MW to Maui Electric Co. In addition to the bagasse produced from sugar milling, HC&S uses coal as a supplemental fuel for periods when the mill is not operating or is at reduced processing capacity (Jakeway, 2006).

Direct combustion, steam-based, biomass power plants are a mature technology. Modern units include grate fired and fluidized bed units. The later boiler units installed at sugar mills in Hawaii were grate fired units operating at pressures of 450 to 900 psi. Many of the biomass power plants installed in

California in the last 25 years were fluidized bed combustors selected for their tolerance of a wide range of fuels.

1.5 Biodiesel Production

Biodiesel can be produced from vegetable oils, animal fats, or recycled restaurant grease. Converting cooking oil and restaurant grease to biodiesel eliminates the need to dispose of these wastes, and creates a commercial product that reduces air emissions and decreases the nation's dependence on imported fossil fuels (Sheehan *et al.*, 1998; Mittelbach, 1996; Anon, 2003b; Tyson, 2001).

Biodiesel has properties similar to those of petroleum-based diesel fuel with several notable exceptions. Biodiesel is virtually free of sulfur, ring molecules, and aromatics often associated with its fossil counterpart (Sheehan *et al.*, 1998; Mittelbach, 1996). Biodiesel also has slightly lower energy density than petroleum diesel.

Biodiesel is composed of fatty acid methyl esters, derived from medium length (C16-C18) fatty acid chains. Biodiesel is produced by esterification of these fatty acids, which are found in vegetable and animal fats. Oil reacts with ethanol or methanol and a lye catalyst in a process called transesterification, to produce biodiesel (Sheehan *et al.*, 1998; Tyson, 2001). The major byproduct of the transesterification process is glycerin, which is separated from the biodiesel fuel. Glycerin that is not removed in the separation step can cause problems with filter plugging, injector deposition, and cold weather operation, and can build-up in storage and fueling systems. Maximum levels of both free glycerin and total glycerin are stipulated in ASTM standard D6751, Standard Specification for Biodiesel Fuel (B100) Blend Stock for Distillate Fuels.

Use of biodiesel and biodiesel blends is becoming increasingly common, especially in government vehicles, bus fleets, and commercial fleets. To a large extent, this increase has been in response to the EPA Act of 1992, which required fleets to purchase alternative fuel vehicles (AFV). In 1998, the act was amended to allow fleet operators to meet one-half of the AFV requirement by using fuel blends that contain at least 20% biodiesel. Fleet operators obtain one fuel credit for every 450 gallons of neat biodiesel purchased. Each fuel credit counts as one AFV purchased (Tyson, 2001; Anon, 1992).

Biodiesel use has also increased as a result of growing public awareness and greater availability of the fuel. Biodiesel should become increasingly competitive as petroleum supplies dwindle and the technology for producing biodiesel improves. Although generally more expensive, the price of biodiesel has, at times, approached that of petroleum diesel.

Biodiesel, its use, and effect on diesel engines have been researched extensively, though mainly for transportation applications. Most studies report that biodiesel performs comparably to diesel fuel. Operators report no noticeable changes in vehicle performance. Tests have also shown that

replacing diesel fuel with biodiesel dramatically reduces particulate matter, carbon monoxide, and net carbon dioxide emissions, and eliminates sulfur emissions. On the down side, biodiesel usually is more costly, has a slightly lower energy density, and produces higher NO_x emissions than diesel fuel (Lue *et al.*, 2001; Yamane and Shimamoto, 2001; Graboski *et al.*, 1999).

1.6 Biofuels Technology Summary

The biofuel technologies from the preceding sections are presented in Table 4 to summarize their readiness for commercial application. Each is characterized as pilot scale, demonstration scale, or mature commercial. Pilot scale systems simulate the important parameters of a full scale unit and are used to systematically investigate operating conditions. Feedstock throughput depends on the technology employed, e.g. gasification pilot plants have typically been 5 to 10 dry ton per day units. Demonstration scale units are typically 10 times larger than pilot scale and are constructed to (1) verify the operability of the unit and its subcomponents at near commercial scale in a long duration (~1000 hour) test program(s) and (2) collect engineering and cost data that can be used in the design of commercial units. Demonstration scale tests may yield commercial product but the intent of the program is to verify/validate the technology. Mature, commercial technologies are those that have been successfully demonstrated and are offered by suppliers as turn-key units.

Table 4. Characterization of the development status of biomass conversion technologies

	Pilot	Demonstration	Commercial	Appropriate for HI?
Ethanol from Biochemical Route				
Sugar			X	Y
Starch			X	Y
Fiber ¹	X	x		Y
Gasification				
Heat			X	Y
Power	X	X		Y
Synfuels	X	X		Y
Pyrolysis				
Bio-oil production			X	Y
Charcoal production		X	X	Y
Bio-oil production for fuels	X			Y
Combustion			X	Y
Transesterification			X	Y
¹ Demonstration projects for cellulosic ethanol production currently underway				
² Pyrolysis for bio-oil production as food ingredient is at commercial scale but use of bio-oil for energy other than combustion applications remains at pilot scale				

All of the bioenergy technologies reviewed in this section have potential application in Hawaii but all are not expected to be commercial. The utility of the technologies will depend on completion of technology development for those that are not yet fully commercial and the availability of suitable, cost competitive, sugar, starch, fiber, and oil feedstock resources. Questions of appropriate scale for the technologies will also need to be addressed and will evolve as fossil fuel supplies dwindle and efficiency and conservation serve to reduce energy product demand. A concomitant enhanced appreciation for energy security and economic benefits derived from local production of bioenergy products can be expected to foster policy support.

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