

Biofuels from Municipal Wastes-
Background Discussion Paper
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Introduction

The California Biomass Forum on 28 March in Sacramento is sponsored by the California Integrated Waste Management Board. The day's theme is "Producing biofuels from solid waste: research and commercialization strategies for upgrading solid waste residuals to fuels and chemicals" Breakout sessions associated with this *Biofuels from Municipal Solid Wastes Forum* are intended to provide the Board with public comment regarding future agency research and commercialization activities in this area. This background paper was developed to serve as a discussion starting point.

Despite large gains in waste reduction and diversion since enactment of AB 939 in 1989, California landfilled 42 million tons of MSW and used 3 million tons of green alternative daily cover. The biomass fraction of the disposal stream represents a significant resource for renewable energy (including electricity and biofuels). The disposed biomass is also responsible for the majority of green house gas emissions and nearly all of the methane emissions from California landfills.¹

To reduce environmental impacts from landfills in the long term, biodegradable components either separately or in combination with other organic constituents in the disposed waste stream could be diverted and utilized. Fuels and energy recovery could be a large market for these resources.

The forum discussions can help inform the Board and attendees on research needs, information gaps, and pathways to commercialization of biofuels from the municipal waste stream.

¹ Landfill methane emissions account for 1.7% of California greenhouse gas emissions (on a CO₂ equivalent basis). Landfills emit about 30% of the state's methane emissions. Enteric fermentation and manure management for California livestock account for 45% of the state's methane emissions. Small amounts of methane emissions occur from vehicle use and other landfill related operations.

See latest GHG inventory by the California Energy Commission (Report CEC-600-2006-013-SF)
<http://www.energy.ca.gov/2006publications/CEC-600-2006-013/CEC-600-2006-013-SF.PDF>

Resource Potentials

Disposal Stream

A large amount of material is disposed in California landfills. In 2005, 42 million tons of MSW and 4.7 million tons of alternative daily cover (ADC) were buried in California landfills (3 million tons of the ADC was green waste). Of this material in landfills, some 26.7 million tons are of biological origin (biogenic), 5.9 million tons are plastics and textiles (the latter assumed to be all synthetic textiles), and the remaining 14.1 million tons are mineral and other inorganic material (glass, metal, non-wood construction/demolition waste and inorganic ADC) (Figure 1 and Table 1).²

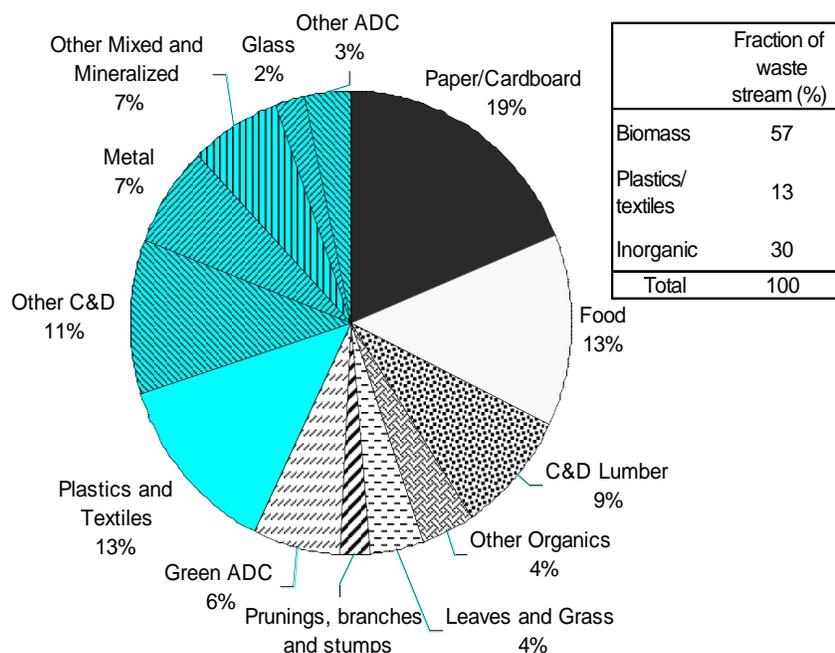


Figure 1. California landfilled waste stream by material type.³

The potential energy from MSW and ADC annually landfilled in California is also quite large. Primary energy of the disposed stream is about 0.4 Quads per year which is equivalent to the energy in 70 million barrels of crude oil. Even including efficiency differences in converting waste to commercially valuable energy compared with oil, the resource still constitutes a significant development potential for the state in helping to improve overall sustainability (Table 1, Figure 2).

² CIWMB Disposal Reporting System (2006) <http://www.ciwmb.ca.gov/lgcentral/DRS/Reports/Statewide/ADCMatTyp.asp>

³ adapted from Cascadia Consulting Group. (2004). "Statewide waste characterization study." Contractor's report to CIWMB. Publication #340-04-005. Available at; <http://www.ciwmb.ca.gov/Publications/default.asp?pubid=1097>

Table 1 California annual disposed waste characterization (wet basis) and potential energy.⁴

Component	Landfilled ^a (Million tons)	% of Total	Moisture ^b (%wb)	Landfilled (Million tons dry)	HHV ^b (Btu/dry lb.)	Primary Energy by Component	
						(Quad) ^c	(million barrels oil equiv.) ^d
Paper/Cardboard	8.8	18.9	10	7.9	7,640	0.121	21
Food	6.1	13.2	70	1.8	6,020	0.022	4
C&D Lumber	4.0	8.7	12	3.5	8,310	0.059	10
Other Organics	1.8	4.0	4	1.8	3,810	0.014	2
Leaves and Grass	1.8	3.8	60	0.7	6,450	0.009	2
Prunings, branches and stumps	1.1	2.3	40	0.7	8,170	0.011	2
Green ADC	3.0	6.4	40	1.8	8,170	0.029	5
Biomass Total	26.7	57.3		18.3		0.27	47
Plastics and Textiles	5.9	12.6	3.3	5.7	12,340	0.140	25
Other C&D	5.0	10.8	-	5.0	-	-	-
Metal	3.2	6.9	-	3.2	-	-	-
Other Mixed and Mineralized	3.2	6.8	-	3.2	-	-	-
Glass	1.0	2.1	-	1.0	-	-	-
Other ADC	1.6	3.4	-	1.6	-	-	-
Totals	46.6	100.0		38		0.41	71

a) California waste stream composite data (<http://www.ciwmb.ca.gov/WasteChar/Study1999/OverTabl.htm>) & California Solid Waste Generation and Diversion (<http://www.ciwmb.ca.gov/Igcentral/Rates/Diversion/RateTable.htm>)

b) Adapted from Tchobanoglous, G., Theisen, H. and Vigil, S.(1993),"Integrated Solid Waste Management", Chapter 4, McGraw-Hill, New York & Themelis, N. J., Kim, Y. H., and Brady, M. H. (2002). "Energy recovery from New York City municipal solid wastes." Waste Management & Research, 20(3), 223-233.

c) 1 Quad = 10¹⁵ Btu. US primary energy use is about 100 Quads, World primary energy use is about 500 Quads.

d) Meant to indicate primary energy in MSW in terms of equivalent barrels of oil. This does not mean that MSW energy can be converted into liquid fuels with same yield and efficiencies as from crude oil.

While paper and cardboard account for about 20 % of the disposed stream by mass, these constituents in combination contain nearly 30% of the total potentially recoverable energy and 45% of the energy in biomass. Food waste accounts for about 13% of the landfill stream and represents about 6% of potential energy. Plastics and textiles make up about 13% of disposal but represent 35% of the energy.

Liquid Fuel Potential from Lignocellulosic Portion of Disposal

The potential ethanol as well as liquid hydrocarbons such as those produced by Fischer Tropsch (FT) or other catalytic synthesis from the lignocellulosic portion of landfilled biomass is estimated to be equivalent to about 300 million gallons of gasoline (Table 3).⁵ The analysis assumes half of the mixed paper in the landfill stream and about 40% of the wood and green wastes can be economically recovered for fuel production. Ethanol yield and FT liquid yields are assumed to be 70 and 50 gallons per dry ton of feedstock respectively.

⁴ Adapted from Williams, R. B. (2006). "Biomass in Solid Waste in California: Utilization and Policy." California Biomass Collaborative. University of California, Davis. *CEC PIER Contract 500-01-016*.

⁵ Ethanol has a heat of combustion about two-thirds that of gasoline. The equivalent number of gallons of gasoline is therefore about a third less than the actual number of gallons of ethanol.

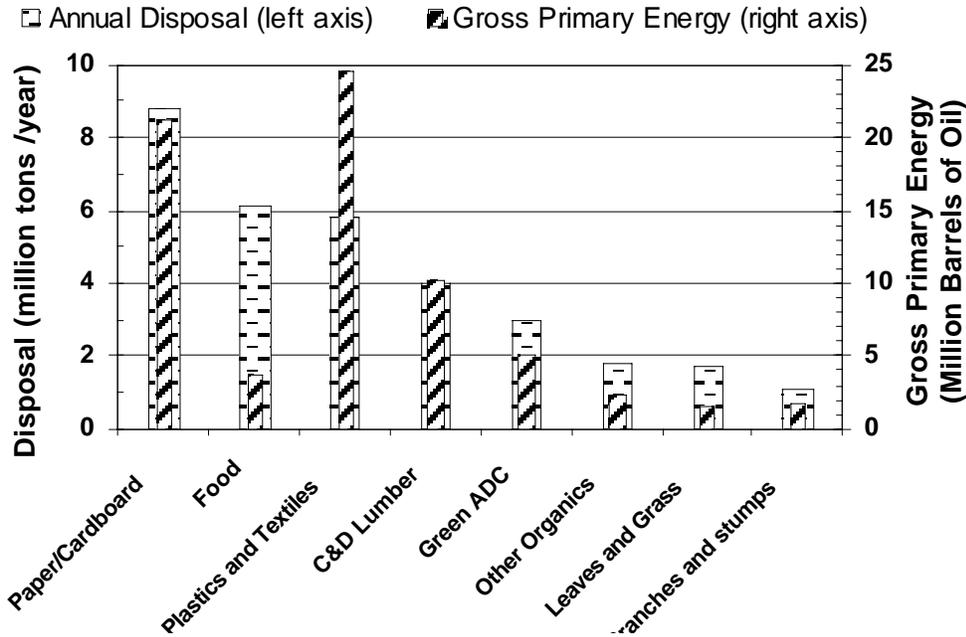


Figure 2. Annual disposal amounts of waste stream components and associated energy contents (2005 disposal data).

Technical and economical recovery rates may be higher or lower than assumed here, but solid waste nonetheless represents a significant energy potential.⁶

Table 3. Estimates of ethanol or liquid hydrocarbon potential from the lignocellulosic fraction of the California landfill stream.

Ethanol Scenario	Gross Biomass (million BDT)	Tech. Avail. Factor	Technical Annual amount (million BDT)	Ethanol yield (gal/dry ton)	Potential Ethanol	
					(million gallons/y)	(million gallons gasoline equivalent)
Landfilled mixed paper/cardboard	7.9	0.5	3.97	70	278	185
Landfilled wood & green (+ ADC)	6.7	0.4	2.68	70	188	125
Totals					466	310
-Alternative Scenario -						
Conversion to Fischer-Tropsch Liquids (hydrocarbons)				FT Liquid yield (gal/dry ton)	(million gallons gasoline equivalent)	
Landfilled mixed paper/cardboard	7.9	0.5	3.97	50	198	
Landfilled wood & green (+ ADC)	6.7	0.4	2.68	50	134	
Total					333	

Projected Landfill Disposal

Landfill disposal amounts have been increasing since 1996 while per-capita disposal has remained more or less constant at around 2200 pounds per person per year (Figure 3).

⁶ This analysis applies only to the current waste stream going to landfill (including green ADC). CIWMB estimates that approximately 8 million tons of MSW material go each year to compost or solid fuel combustion facilities and only about 31% (4.8 million tons/year) of waste paper is diverted (1997 data, see <http://www.ciwmb.ca.gov/Paper/>). The amount of urban wood waste or construction and demolition (C&D) lumber estimated to be currently consumed in power production facilities is 1.7 million tons per year.

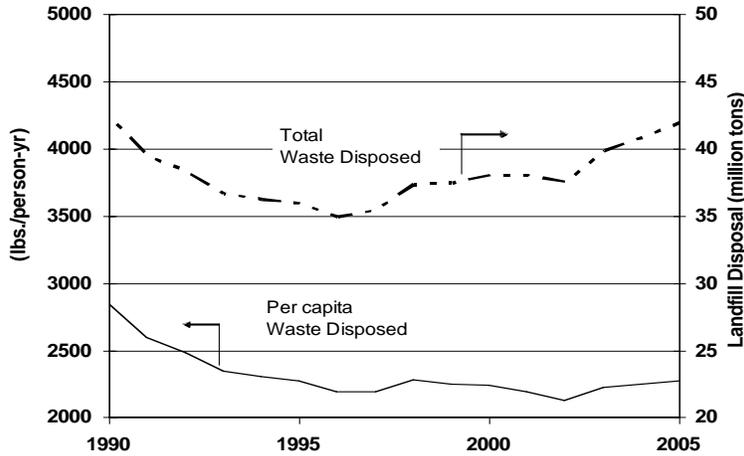


Figure 3. Landfill and per-capita disposal since 1990 in California (excludes ADC).

Assuming business as usual (i.e., constant per capita disposal), and high and low state population projections presented by Hanak and Baldassare (2005),⁷ landfill disposal may range from 55 to nearly 70 million tons per year by 2050 (Figure 4).

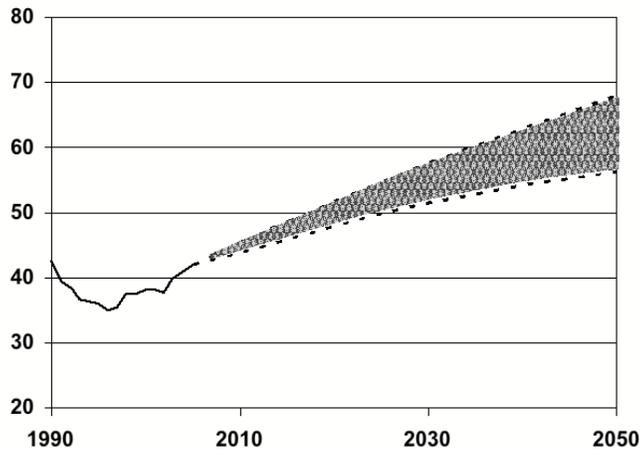


Figure 4. Historical and projected annual landfill disposal.

Waste-in-Place and LFG

Current as well as future landfill gas (LFG) production depends on the amount of waste-in-place (WIP) in existing landfills as well as future disposal.

The California Integrated Waste Management Board estimates there are about 1.2 billion tons of WIP at 365 California landfills (active and closed) each having 10,000 tons or greater including biodegradable ADC. Some 146 of these landfills are active and account for more than 60% of the state's total WIP.⁸

Current (2005) gross landfill methane production has been estimated at about 85 billion standard cubic feet per year (BCF y⁻¹) with increasing amounts in the future as landfilling continues (Figure 5). Total

⁷ Hanak, E. & Baldassare, M. (2005). "California 2025 - Taking on the future." Public Policy Institute of California. http://www.ppic.org/content/pubs/report/R_605MB1R.pdf

⁸ Walker, S., Compilation of landfill waste-in-place (WIP) and landfill gas-to-energy information. November 30 Memorandum to Howard Levinson, 2005.

LFG volume (including the CO₂) is about 170 BCF y⁻¹. The methane production from landfills in the state is about 3% of current natural gas consumption (2,572 BCF/y in 2004).⁹

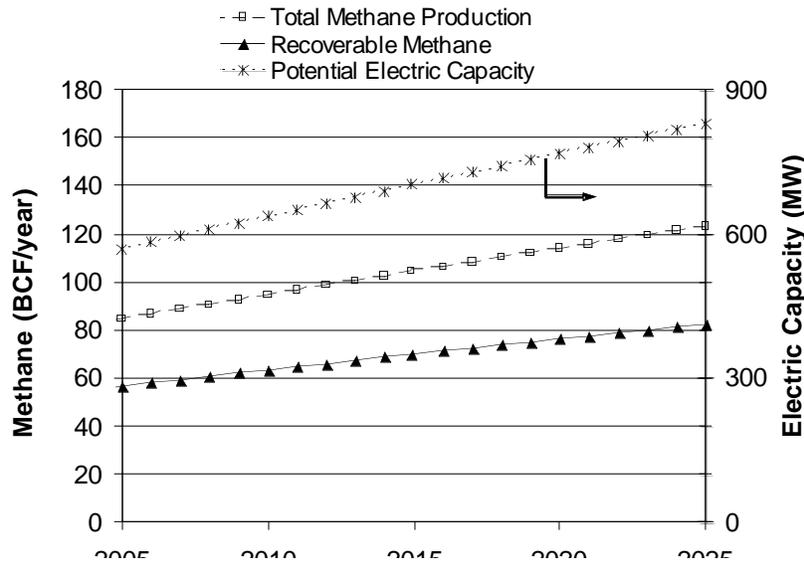


Figure 5. LFG methane and electricity generation potential from conventional landfills in California.¹⁰

Waste fats, oils, and grease

About 6.5 million tons of rendered animal fats and oils and waste restaurant grease (yellow and trap) are produced annually in the US.^{11,12} The majority is used for animal feed, soaps, lubricants and fatty acids. About 20% is exported for similar uses. The 6.5 million tons of fats, oils, and grease (FOG), represent a potential 1.7 billion gallons of biodiesel. An estimate for restaurant waste yellow and trap grease in California can be made using per capita waste grease estimates. Wiltsee (1999) estimated about 20 pounds of restaurant waste oils are generated per person per year in metropolitan areas.¹³ Assuming 25 million Californians living in metropolitan areas, some 250,000 tons of restaurant waste oils are produced per year representing about 65 million gallons of biodiesel potential if feedstock is diverted from existing feed markets and water treatment plants.

⁹ Williams, R.B., et al., (2006). *An Assessment of Biomass Resources in California -Draft Report*. 2006 California Biomass Collaborative.

¹⁰ Adapted from Jenkins, B. M. (2005). "Biomass in California: Challenges, opportunities, and potential for sustainable management and development." *CEC-500-2005-160*, California Biomass Collaborative.

¹¹ Swisher, K. (2006). "Market Report 2005." In: *Render (April)*.

¹² Tyson, K. S., Bozell, J., Wallace, R., Petersen, E., and Moens, L. (2004). "Biomass oil analysis: Research needs and recommendations." *NREL/TP-510-34796*.

¹³ Wiltsee, G. (1999). "Urban Waste Grease Resource Assessment." *NREL/SR-570-26141*, Appel Consultants, Inc., Valencia, CA.

Conversion Pathways

Energy conversion of organic materials can proceed along three main pathways—thermochemical, biochemical, and physicochemical. Currently, all three pathways are utilized to varying degrees with fossil fuel feedstocks.

Thermochemical conversion processes include combustion, gasification, and pyrolysis. Biochemical conversion processes include aerobic conversion (i.e., composting), anaerobic decomposition or digestion (which occurs in landfills and controlled reactors or digesters) and anaerobic fermentation (for example, the conversion of sugars from hydrolyzed cellulose and hemicellulose by ethanol producing yeasts and recombinant bacteria). Physicochemical conversion involves the physical and chemical synthesis of products from feedstocks (for example, biodiesel).

Biochemical conversion proceeds at lower temperatures and lower reaction rates. Higher moisture feedstocks are generally good candidates for biochemical processes. Thermochemical conversion is characterized by higher temperatures and faster conversion rates. It is best suited for lower moisture feedstocks. For biomass feedstocks, the lignin fraction currently can not be converted biochemically, although research is investigating lignin fermentation processes. On the other hand, thermochemical routes can convert all of the organic portion of suitable feedstocks. The inorganic fraction (ash) of a feedstock does not contribute significantly to the energy products but does participate in important ways including fouling of high temperature equipment, increased nutrient (e.g. K and P) loading in facility waste water treatment and disposal, and in some cases by providing marketable co-products or adding disposal cost. Inorganic constituents may also be catalytic for some of the conversion reactions.

Pathways to Biofuels

Biofuels are fuel products produced from biomass. In the general sense, biofuel refers to an energy source or carrier that is derived from ‘recently’ living material.¹⁴ The biofuel can be solid (i.e., wood, crops and their residues, portions of municipal wastes, etc.), liquid (raw plant oils, waste cooking oils, as well as refined biodiesel, ethanol other alcohols, pyrolysis oils, and biobased liquid hydrocarbons), and gaseous (biomethane, biogas, landfill gas, hydrogen derived from biomass). In the US, biofuel commonly means transportation fuels derived from biomass even though the applications for biofuels extend well beyond the transportation sector. This paper primarily uses the ‘transportation fuel’ inference for biofuel.

Biochemical conversion

The principal near-term biofuels produced from biochemical routes are biogas (including landfill gas) and ethanol (sometimes referred to as bioethanol). Biobutanol and other fermented alcohols are being investigated and could become important biofuels.

Anaerobic Digestion

Anaerobic digestion (AD) is a fermentation technique that operates without free oxygen and results in a biogas containing mostly methane and carbon dioxide but frequently carrying impurities such as moisture, H₂S, ammonia, siloxane, and particulate matter. Anaerobic digestion occurs in manure lagoons (covered or not), and is the principal process occurring in landfills.

¹⁴ There is some debate as to how ‘recently’ living the material needs to be to be considered biomass. There is no debate that fossil fuels (coal, natural gas, petroleum, tar sands, oil shale, etc.) are not biomass.

Biomethane from upgraded biogas is the principal biofuel from AD processes. The other common application for biogas is electricity generation. Hydrogen can be manufactured by reforming the methane.

AD systems are employed in many waste water treatment facilities for sludge degradation and stabilization, used in engineered anaerobic digesters to treat high-strength industrial and food processing waste waters prior to disposal, and to treat the biodegradable fraction of solid waste prior to landfilling in order to reduce future methane and leachate emissions (Figures 6 and 7). The latter has developed as part of the European Union (EU) strategy to reduce greenhouse gas emissions.

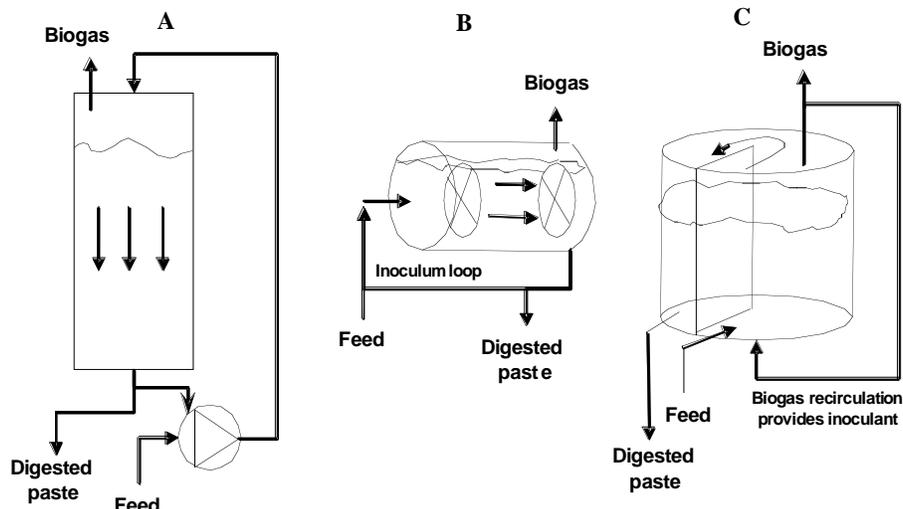


Figure 6. High solids single stage plug flow digester designs (A – Dranco, B – Kompogas, C- Valorga).¹⁵

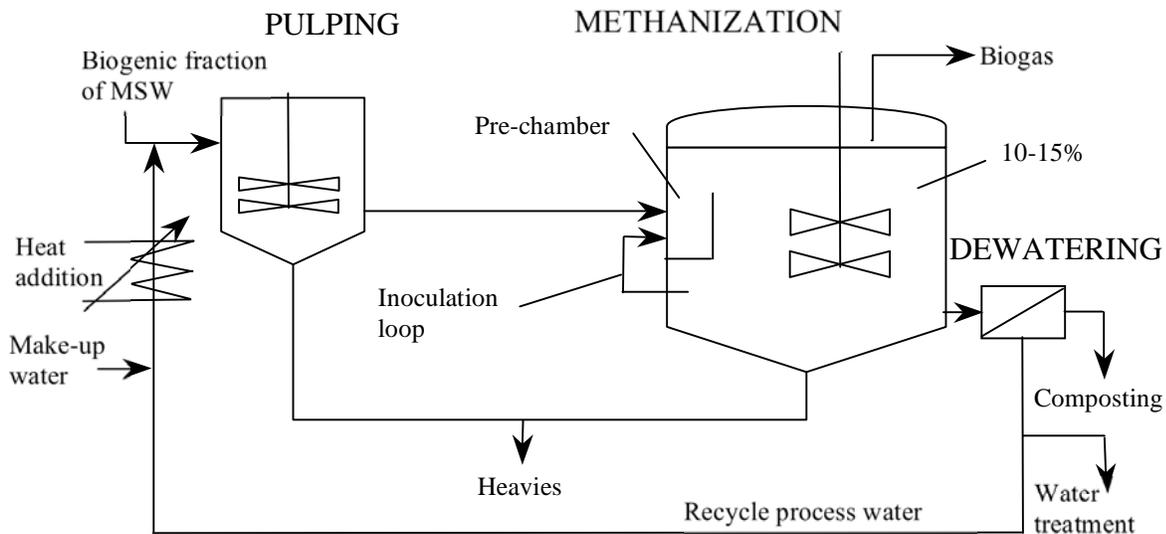


Figure 7. Schematic of a typical single-stage low solids digester.¹⁶

¹⁵ Adapted from Mata-Alvarez, J., Ed. (2003). Biomethanization of the organic fraction of municipal solid wastes. London, IWA Publishing.

¹⁶ Ibid.

Upgrading Biogas and landfill gas to biomethane

Biogas upgrading principally refers to removal of the CO₂ from the biogas to increase energy density and decrease needed storage volumes of finished product.¹⁷ Moisture, sulfur compounds, organo-silicon compounds (siloxanes) and other impurities in biogas or LFG are usually removed as well to meet gas quality specifications, and because they can cause problems in gas handling equipment and damage engines and emissions controls. Biomethane from upgraded biogas or landfill gas can be compressed or liquefied and used as a fuel in compressed natural gas (CNG) or liquefied natural gas (LNG) vehicles.

Processes available for separating CO₂ from the methane in biogas include adsorption methods such as scrubbing with water, Selexol (polyethylene glycol ether), and amines, pressure swing absorption (PSA), membrane separation, and cryogenic separation.¹⁸

Energy for upgrading, principally as electricity, represents about 5-10% of the energy in the original biogas.^{19, 20} Depending on capacity, costs of upgrading can range from about \$3.50 to \$15 per thousand cubic feet of upgraded gas, or roughly \$3.50-15.00/MMBtu.^{21,22}

Hydrogen

Hydrogen can be used in piston engines either pure or mixed with CNG or in fuel cell vehicles. For widespread use of hydrogen as a transportation fuel, several hurdles must be overcome including hydrogen distribution infrastructure, economic on-vehicle storage systems, and economic and reliable fuel cell vehicles. Estimates for when hydrogen fuel will become commonly used vary.

Hydrogen can be produced by reforming biomethane (including from LFG) or directly from biological processes. Potential biological processes for direct hydrogen production include biophotolysis of water by algae, dark and photo-fermentive and two stage dark/photo fermentive production under conditions similar to the acidogenic stage in anaerobic digestion.^{23,24}

Advantages of biohydrogen include sourcing from 'low cost' and renewable organic feedstocks. The major problems are the low rates and yields of hydrogen formation, requiring large reactor volumes.²⁵

¹⁷ Depending on landfill age and LFG collection technique, CH₄ content of LFG varies from as high as 60% to a low 25% (with the balance primarily CO₂ but also N₂, O₂, sulfides, etc.). For more highly engineered digesters, methane content can vary from about 50% to as high as 70%, depending on the feedstock.

¹⁸ Hagen, M., Jensen, J. K., Jonsson, O., Polman, E., Myken, A., and Dahl, A. (2001). "Adding gas from biomass to the gas grid." Report SGC 118, Swedish Gas Center.

¹⁹ Berglund, M., and Borjesson, P. (2006). "Assessment of energy performance in the life-cycle of biogas production." *Biomass & Bioenergy*, 30(3), 254-266.

²⁰ Persson, M. (2003). "Evaluation of upgrading techniques for biogas," Lund University, Lund, Sweden.

²¹ Ibid.

²² Krich, K., Rutledge, B., Salour, D., Augenstein, D., Benemann, J., and Batmale, J. P. (2005). "Biomethane from Dairy Waste- A sourcebook for the production and use of renewable natural gas in California." USDA Rural Development and Western United Dairymen.

²³ California Biomass Collaborative (2006). "A Roadmap for the Development of Biomass in California" University of California, Davis. CEC-500-2006-095-D

²⁴ Hawkes, F.R., Dinsdale, R., Hawkes, D.L., & Hussy, I. (2002), "Sustainable fermentative hydrogen production: challenges for process optimisation." *International Journal of Hydrogen Energy*, 27, 1339-1347.

²⁵ CBC Roadmap (2006). Op. Cit.

Hydrolysis with fermentation to alcohols (or fermentation to liquid)²⁶

Fermentation is generally used industrially to convert substrates such as glucose to ethanol for use in beverage, fuel, and chemical applications and to other chemicals (e.g., lactic acid used in producing renewable plastics) and products (e.g., enzymes for detergents).

Fermentation of starch and sugar based feedstocks (i.e., corn and sugar cane) into ethanol is fully commercial but not yet for cellulosic biomass because of the expense and difficulty in breaking down (hydrolyzing) the materials into fermentable sugars.

Cellulosic feedstocks, including the majority of the organic fraction of MSW, need hydrolysis pretreatment (acid, enzymatic, or hydrothermal hydrolysis) to depolymerize cellulose and hemicellulose to simple sugars needed by the yeast and bacteria for the fermentation process. Lignin in biomass is refractory to fermentation and as a byproduct is typically considered for use as boiler fuel or as a feedstock for thermochemical conversion to other fuels and products. Hydrolysis of lignocellulosic feedstocks is the subject of intense research.

Ethanol

Cellulosic ethanol processes can be differentiated primarily by the method of hydrolysis employed. Hydrolysis pretreatment methods that have been investigated the most are acid processes, enzymatic hydrolysis, and steam explosion. With the possible exception of acid recycling and recovery, acid processes are technologically mature, but enzymatic processes are projected to have a significant cost advantage once improved.²⁷ Steam explosion yields less sugar and releases more material that inhibits fermentation.

After hydrolysis, the sugars can undergo microbial fermentation producing ethanol and CO₂.²⁸ Ethanol inhibits microbial growth, essentially halting the process when ethanol concentration is near 12%. Ethanol must be separated from the fermentation broth and concentrated by conventional distillation technology and dehydrated to yield fuel grade anhydrous ethanol. Wet-ethanol fuels (ethanol-water mixtures that reduce the need for full distillation and dehydration) are being investigated. The remaining liquid broth is recycled or sent to a wastewater treatment facility for appropriate management (see figure 8).

²⁶ Adapted from Hackett, C., Williams, R. B., Durbin, T. D., Welch, W., Pence, J., Aldas, R., Jenkins, B. M., and Salour, D. (2004). "Evaluation of conversion technology processes and products -Draft Final Report." University of California.

²⁷ Lynd, L., R., "Overview and Evaluation of Fuel Ethanol from Cellulosic Biomass: Technology, Economics, the Environment, and Policy." *Annual Review of Energy and the Environment*, Vol. 21, 1996, pp. 403-465.

²⁸ A variety of microorganisms, generally bacteria, yeast, or fungi, ferment carbohydrates to ethanol under anaerobic conditions.

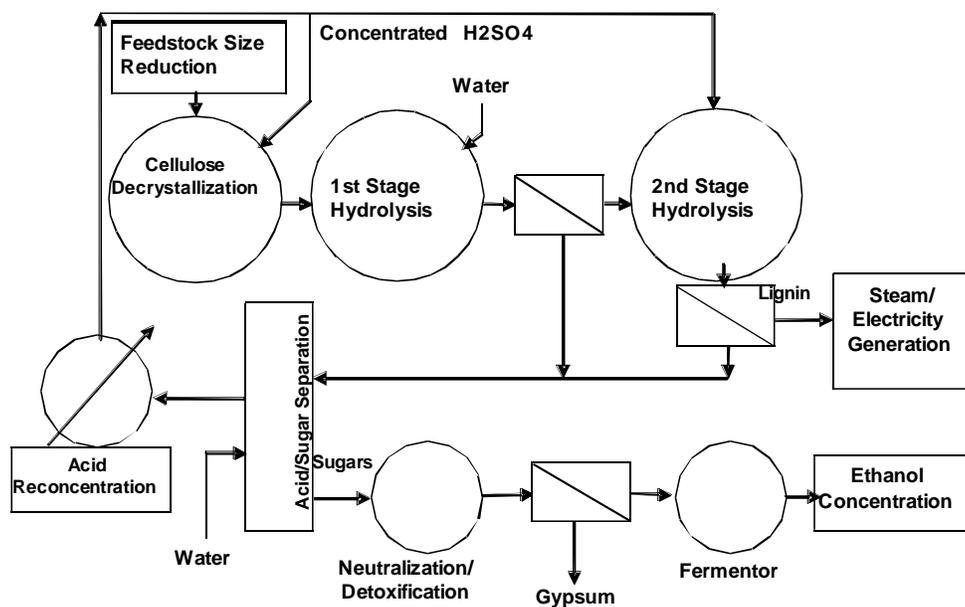


Figure 8. Schematic of concentrated acid hydrolysis fermentation.²⁹

Butanol

Butanol is a four-carbon alcohol that can be obtained by fermentation from the same feedstocks used in ethanol fermentation. Some properties of butanol are superior to ethanol for fuel—butanol has more energy/gallon than ethanol, it does not absorb water easily which unlike ethanol may allow it to be transported via gasoline pipeline, and butanol-gasoline blends have lower vapor pressure than ethanol-gasoline blends which is important in reducing evaporative hydrocarbon emissions. BP and Dupont are cooperating on research for production of fuel butanol from cellulosic feedstocks.³⁰

Traditionally, butanol is fermented from *Clostridium acetobutylicum* via the so called ABE (acetone-butanol-ethanol) fermentation. ABE fermentation yields 3 parts acetone, 6 parts butanol, and 1 part ethanol (3:6:1). However, butanol from ABE fermentation is less economic than ethanol essentially because the fermentation is impeded by low concentrations of the products (end-product inhibition) requiring larger process stream volumes, reactors, and tanks.^{31,32} Recent work using a different fermentation route may improve butanol yield and reduce cost.³³

Mixed Alcohols (MixAlco process)

The “MixAlco Process” developed by Holtzapple and colleagues at Texas A&M University (TAMU) is an alternative biochemical route to mixed alcohols.

²⁹ Adapted from <http://www.ott.doe.gov/biofuels/concentrated.html>

³⁰ BP Dupont reference

³¹ Jesse, T. W., Ezeji, T. C., Qureshi, N., and Blaschek, H. P. (2002). "Production of butanol from starch-based waste packing peanuts and agricultural waste." *Journal of Industrial Microbiology & Biotechnology*, 29(3), 117-123.

³² Ezeji, T. C., Karcher, P. M., Qureshi, N., and Blaschek, H. P. (2005). "Improving performance of a gas stripping-based recovery system to remove butanol from *Clostridium beijerinckii* fermentation." *Bioprocess and Biosystems Engineering*, 27(3), 207-214.

³³ Ramey, D., and Yang, S.-T. (2004). "Production of butyric acid and butanol from biomass." Environmental Energy Inc., DOE Contract FG02-00ER86106.

Biomass feedstock is mixed with water and pretreated with hydrated lime ($\text{Ca}(\text{OH})_2$) followed by fermentation using acid forming microbes which form carboxylic acids. This is followed by addition of calcium carbonate (CaCO_3) which neutralizes the solution and forms dilute carboxylate salts. The salts are then dried and sent to a heated reactor where they are converted to ketones (e.g., acetone), releasing calcium carbonate. Finally, the ketones are hydrogenated to mixed alcohols, predominately propanol, butanol and pentanol (Figure 9).³⁴

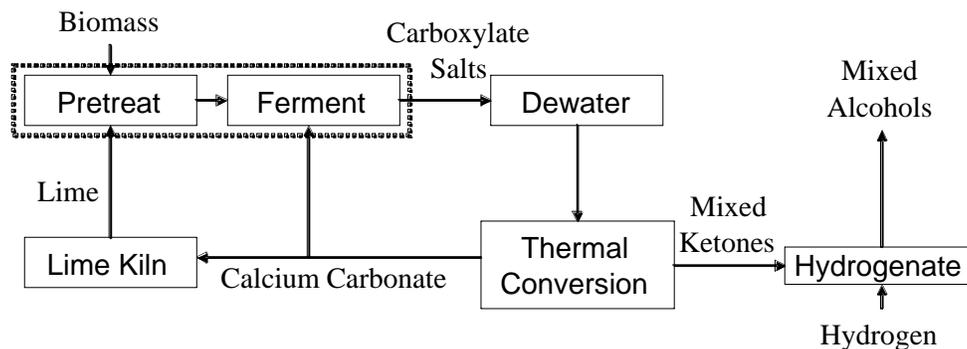


Figure 9. Schematic of the MixAlco process (source Holtzapple et al. (1999))

Individual sub processes of the MixAlco process exist as lab and pilot scale projects at TAMU. The fermentation stage is relatively slow (140 day solids retention time and 14 day liquid retention time) which requires a large reactor volume. To keep costs low, the fermentation stage is envisioned as a covered and lined in-ground lagoon or landfill with recirculating hydrated lime solution. Hydrogen needs to be added at a rate of about 0.17 pounds per gallon of alcohol (or 2.6% of final weight). In a full scale system, mixed alcohol production is estimated to be about 60 gallons per dry ton of post-sorted feedstock.³⁵

Thermochemical conversion

Thermochemical conversion processes include combustion, gasification, and pyrolysis. Potential biofuels from thermochemical routes include, ethanol, methanol, mixed alcohols, Fischer-Tropsch (FT) liquids,³⁶ other renewable gasolines and diesels, pyrolysis oils, and others. Direct electricity production can also be used for transportation through plug-in hybrids and battery-electric vehicles.

³⁴ Holtzapple, M. T., Davison, R. R., Ross, M. K., Aldrett-Lee, S., Nagwani, M., Lee, C. M., Lee, C., Adelson, S., Kaar, W., Gaskin, D., Shirage, H., Chang, N. S., Chang, V. S., and Loescher, M. E. (1999). "Biomass conversion to mixed alcohol fuels using the MixAlco process." *Applied Biochemistry and Biotechnology*, 77-9, 609-631.

³⁵ Holtzapple et al., (1999). Op Cit. And Holtzapple Lecture April 2006
<http://engineering.tamu.edu/research/lectures/>

³⁶ Fischer-Tropsch synthesis is a process for producing mainly straight-chain hydrocarbons (C_xH_y) from a synthesis gas rich in CO and H_2 usually employing catalysts. The synthesis gas must have very low tar and particulate matter. Biomass derived synthesis gas for FT liquid production is still developmental due to gas cleaning issues. (See Boerrigter, H. and H. den Uil (2002). Green Diesel from Biomass via Fischer-Tropsch synthesis: New Insights in Gas Cleaning and Process Design. Pyrolysis and Gasification of Biomass and Waste, Expert Meeting, Strasbourg, France.)

Combustion

Combustion means oxidation of the fuel for the production of heat at elevated temperatures without generating useful intermediate fuel gases, liquids, or solids. Combustion normally employs excess oxidizer (air) to ensure maximum fuel conversion. Products of combustion processes include heat, oxidized species (e.g. CO₂, H₂O), products of incomplete combustion (e.g. CO and hydrocarbons), other reaction products (most as pollutants), and ash. Electricity can be produced using boilers and steam-driven engines and turbogenerators, or through organic Rankine, Brayton (gas turbine), and combined cycles.

Gasification

Gasification typically refers to conversion via partial oxidation using substoichiometric (insufficient) air or oxygen or by indirect heating to produce fuel gases (synthesis gas, producer gas). The product, or synthesis gas, is principally CO, H₂, methane, and lighter hydrocarbons, but depending on the process used, the product gas can contain significant amounts of CO₂ and N₂, the latter mostly from air. Gasification processes also produce liquids (tars, oils, and other condensates) and solids (char, ash) from solid feedstocks. The combustion of gasification-derived fuel gases generates the same categories of products as direct combustion of solids, but pollution control and conversion efficiencies may be improved.

Electricity and heat can be produced by burning the synthesis gas in a steam boiler and turbine plant, a gas turbine or an internal combustion or stirling engine generator, or synthesis gases can be reacted to fuel products and other chemicals.

Biomass to Liquids (BTL)

Biofuels produced via gasification routes include direct gasoline and diesel substitutes made from gas-to-liquid processes (i.e., the Fischer-Tropsch [FT] process), methanol, ethanol, mixed alcohols, and hydrogen (see Figure 10). Gas-to-liquids technologies are utilized commercially using natural gas or stranded natural gas as feedstock. Coal was used extensively by Germany in WWII and is still used in the Sasol (South Africa) facilities for gasoline and diesel fuel synthesis (coal-to-liquids or CTL) along with a wide variety of other products. For biomass feedstocks, the process is still being developed. Gas cleaning, catalyst durability and selectivity, feedstock preparation and handling, and production costs are the primary issues needing investigation.

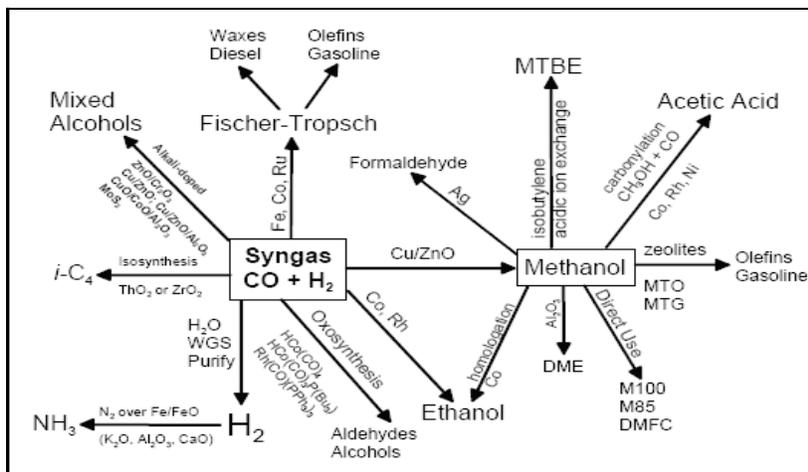


Figure 10. Diagram of potential syngas processing and product routes. ³⁷

³⁷ From Spath, P. L., and Dayton, D. C. (2003). "Preliminary Screening-Technical and economic assessment of synthesis gas to fuels and chemicals with emphasis on the potential for biomass-derived syngas." NREL/TP-510-34929, NREL, Golden, CO.

In a BTL process, feedstock undergoes a pretreatment or selection (sizing, drying, sorting) and then is gasified in a reactor. The gas product (CO, H₂, light hydrocarbons, tars, particulate material, and other) undergoes extensive clean up to remove catalyst poisons and other undesirable components. This is followed by gas processing/reforming where the H₂:CO ratio is adjusted before entering the FT synthesis reactor. The FT or liquid synthesis reactor contains catalyst material and operates at elevated pressure and temperature forming hydrocarbon compounds or alcohols from the synthesis gas. The liquids can be further refined to the desired end product (Figure 11).

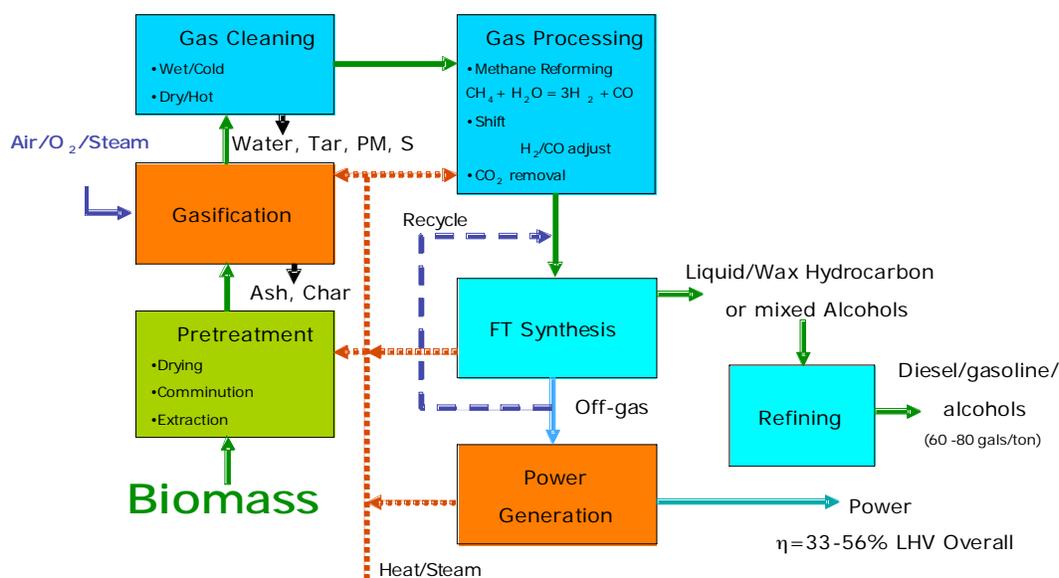


Figure 11. Block diagram of biomass to liquids Fischer Tropsch process.³⁸

Hybrid Thermo-biochemical routes

An anaerobic bacterium capable of converting CO and H₂ to a mixture of acetate and ethanol was isolated in 1987 (*Clostridium Ljungdahllii*)^{39,40} by Gaddy and colleagues at the University of Arkansas. They investigated syngas fermentations using this microbe and developed bioreactors to metabolize CO and H₂ for ethanol production.^{41,42,43,44} The process is now in the process of commercialization by BRI (Figure

³⁸ Source: BM Jenkins (2006). "Overview of thermochemical biorefining." Biobased Industry Outlook Conference. 28-29 August, Ames, Iowa

³⁹ Klasson, K., Ackerson, M., Clausen, E., and Gaddy, J. (1992). "Bioconversion of synthesis gas into liquid or gaseous fuels." *Enzym. Microb. Technol.*, 14, 602-608.

⁴⁰ Tanner, R. S., Miller, L. M., and Yang, D. (1993). "Clostridium Ljungdahllii Sp-nov, an acetogenic species in Clostridial ribosomal - RNA homology group -I." *International Journal of Systematic Bacteriology*, 43(2), 232-236. See abstract at; <http://ijs.sgmjournals.org/cgi/content/abstract/43/2/232>

⁴¹ Phillips, J. R., Clausen, E. C., and Gaddy, J. L. (1994). "Synthesis Gas as Substrate for the Biological Production of Fuels and Chemicals." *Applied Biochemistry and Biotechnology*, 45-6, 145-157.

⁴² Vega, J. L., Prieto, S., Elmore, B. B., Clausen, E. C., and Gaddy, J. L. (1989). "The Biological Production of Ethanol from Synthesis Gas." *Applied Biochemistry and Biotechnology*, 20-1, 781-797.

⁴³ Gaddy, J. L., and Clausen, E. C. (1993). "Production of Ethanol from Biomass by Gasification Fermentation." *Abstracts of Papers of the American Chemical Society*, 206, 25-FUEL.

⁴⁴ Klasson, K. T., Ackerson, M. D., Clausen, E. C., and Gaddy, J. L. (1991). "Bioreactor design for synthesis gas fermentations." *Fuel*, 70(5), 605-614.

12). A research group at Oklahoma State University is also investigating biological conversion of synthesis gas.^{45,46,47}

The process is similar to the BTL process described above except that the synthesis gas is injected into a bioreactor where the desired fuel products are produced by fermentation. A dilute solution of product (i.e., ethanol) is extracted from the bioreactor and undergoes distillation followed by molecular sieve (MS)_dehydration to final fuel grade ethanol.

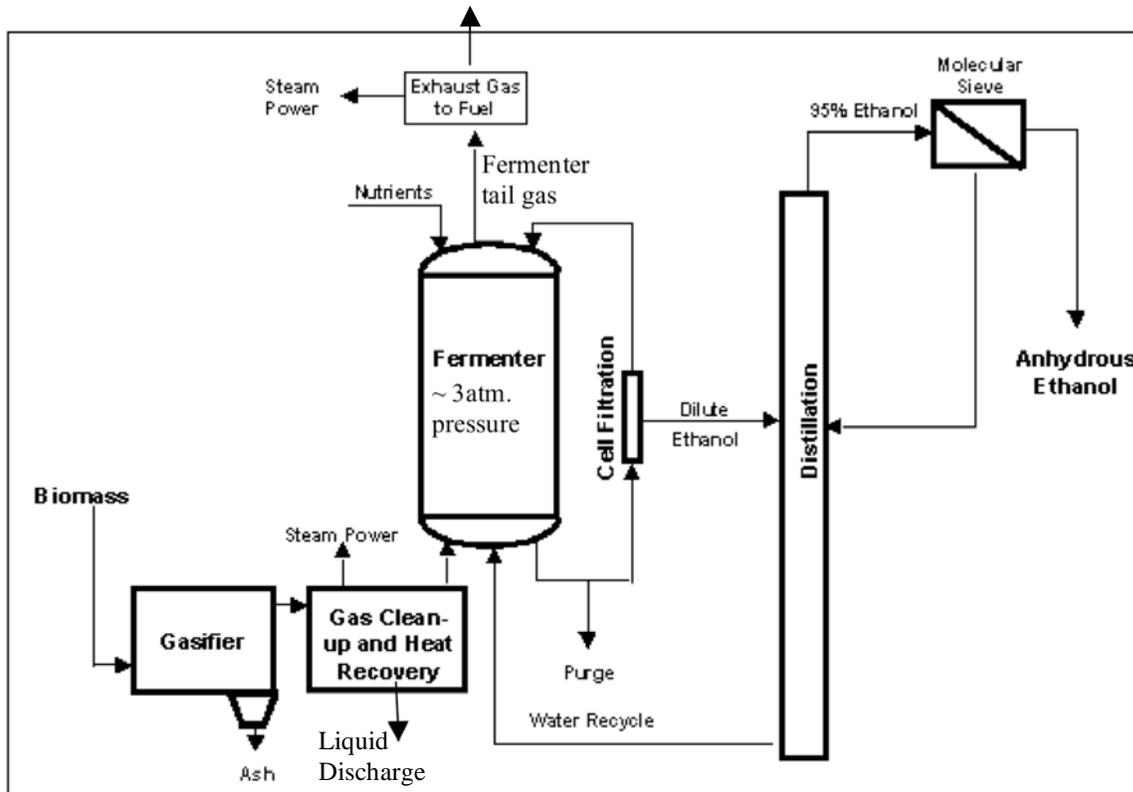


Figure 12. Gasification-to-bioreactor fermentation process schematic (BRI process).⁴⁸

Pyrolysis

Pyrolysis means the thermal degradation of a material usually without the addition of any air or oxygen. The process is similar to gasification but generally optimized for the production of fuel liquids or pyrolysis oils (sometimes called bio-oils if biomass feedstock is used). Pyrolysis also produces gases and a solid char product.

⁴⁵ Rajagopalan, S., P. Datar, R., and Lewis, R. S. (2002). "Formation of ethanol from carbon monoxide via a new microbial catalyst." *Biomass and Bioenergy*, 23(6), 487-493.

⁴⁶ Ahmed, A., Cateni, B. G., Huhnke, R. L., and Lewis, R. S. (2006). "Effects of biomass-generated producer gas constituents on cell growth, product distribution and hydrogenase activity of *Clostridium carboxidivorans* P7(T)." *Biomass & Bioenergy*, 30(7), 665-672.

⁴⁷ Datar, R. P., Shenkman, R. M., Cateni, B. G., Huhnke, R. L., and Lewis, R. S. (2004). "Fermentation of biomass-generated producer gas to ethanol." *Biotechnology and Bioengineering*, 86(5), 587-594.

⁴⁸ Source: BRI, <http://www.brienergy.com/>

Pyrolysis liquids can be used straight (e.g. as boiler fuel and in some stationary engines) or refined for higher quality uses such as motor fuels, chemicals, adhesives, and other products. Direct pyrolysis liquids may be toxic, corrosive, and oxidatively unstable.

A commonly proposed model for bio-oil production with upgrading entails distributed or regional pyrolysis facilities that convert biomass feedstocks into a relatively energy-dense liquid which would then be more efficiently transported to a central facility for the upgrading or refining operation (Figure 13).

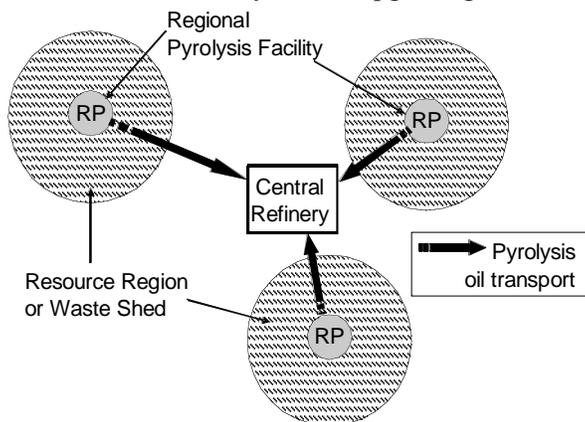


Figure 13. Concept of regional pyrolysis facilities with transport of bio-oils to a central refinery.⁴⁹

Hydrothermal Processing

This class of technology is related to pyrolysis in that it degrades (or depolymerizes) biomass in the absence of air or oxygen. Hydrothermal processing, also called hydrothermal upgrading (HTU) or thermal depolymerization reacts the feedstock in a liquid water slurry under moderate pressure and temperatures producing products similar to those from pyrolysis.

Physicochemical conversion

This pathway involves the physical and chemical synthesis of products from feedstocks and is primarily associated with the transformation of fresh or used vegetable oils, animal fats, greases, tallow, and other suitable feedstocks into liquid fuels or biodiesel.

Biodiesel from waste fats, oils, and greases (FOG)

Biodiesel is produced by the transesterification of triglyceride molecules in lipids into mono-alkyl esters (triglycerides are the main component of vegetable oils and animal fats and are composed of three fatty acids with a glycerol backbone). This is done by reacting an alcohol with the oil in the presence of an alkaline catalyst (sodium or potassium hydroxide – lye) creating the ester (biodiesel) and glycerol as a co-product.⁵⁰ Methanol is usually used but ethanol is also suitable. Both can be produced from biomass as renewable feedstocks to the process.

⁴⁹ Adapted from: Raffelt, K., Henrich, E., Koegel, A., Stahl, R., Steinhardt, J., and Weirich, F. (2004). "Stable slurries from biomass pyrolysis products for entrained flow gasification." In: 2nd World Conference and Technology Exhibition on Biomass for Energy, Industry and Climate Protection., Rome, Italy.

⁵⁰ Other names used for biodiesel include FAME (fatty acid methyl ester), FAEE (fatty acid ethyl ester), RME (rape-oil methyl ester), SME (soy-oil methyl ester).

Biodiesel production from unused or virgin vegetable oils is a facile technique and can yield high quality fuel as long as best practices are followed.

It is more difficult or complex to make high quality biodiesel at reasonable yields from waste oils and fats because they contain high concentrations of free fatty acids (FFA). FFA will form soap in the alkaline catalyzed main triglyceride reaction reducing yield and making final glycerol removal and washing difficult. Water in the waste oil is also undesirable. Good quality raw vegetable oil feedstocks for biodiesel have FFA concentrations below 0.1 %.

Restaurant waste oils, rendered animal fats, and “trap grease” (grease trapped from kitchen waste water before entering sewer lines) have high FFA content. So called yellow grease has FFA content between about 1.5% and 15%. Brown grease, with cooked or burnt suspended solids and water, may have FFA content as high as 40%. Trap grease FFA content can range from 40% to 100% and contains large amounts of water and solids.^{51,52}

After a cleaning and drying step, high FFA feedstocks undergo a pretreatment step in which the FFA are reacted with the alcohol and acid catalyst to form esters and water. The esters along with the triglycerides then go through the base catalyzed transesterification step described earlier. Final steps include washing, alcohol and catalyst recovery and glycerin separation (Figure 14).

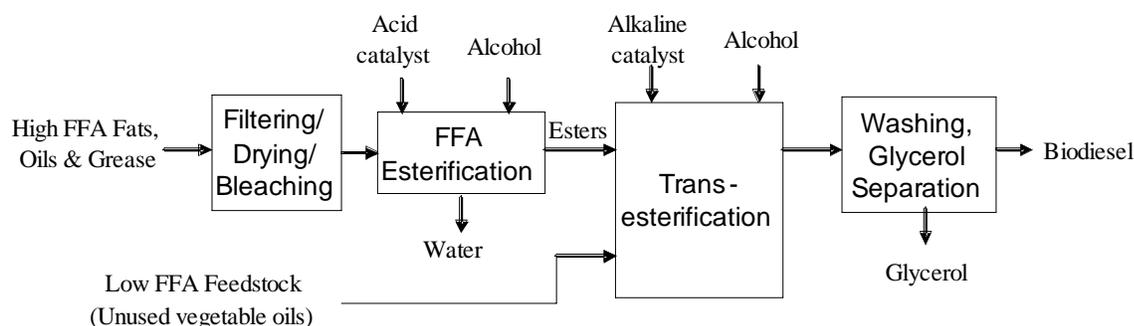


Figure 14. Principle steps in mono-alkyl ester biodiesel production.

Municipal waste to fuels facilities- commercial or operating demonstrations

At present, municipal wastes are not utilized extensively for biofuels. Globally, electricity and heat are the primary form of energy recovered from municipal waste, including solid waste combustion and the use of LFG. In parts of Europe, upgraded biogas from digesters and landfills contributes a few percent of urban transit or taxi fuel energy at a handful of urban centers (for example, Sweden). There is one facility in Germany that produces methanol and synthetic natural gas from gasification that consumes mostly coal and petroleum coke with minor amounts of biosolids and other municipal wastes as co-feeds. In the US and California, facilities making fuels from municipal wastes (and portions thereof) include several upgrading LFG to biomethane, and many biodiesel facilities using waste fats, oils, and grease feedstocks.

⁵¹ Tyson, K. S., Bozell, J., Wallace, R., Petersen, E., and Moens, L. (2004). "Biomass oil analysis: Research needs and recommendations." *NREL/TP-510-34796*.

⁵² Canakci, M., and Van Gerpen, J. (2001). "Biodiesel production from oils and fats with high free fatty acids." *Transactions of the Asae*, 44(6), 1429-1436.

*LFG to biofuels in California*⁵³

The Puente Hills landfill in Los Angeles County has successfully operated a LFG to compressed natural gas (CNG) facility for about 13 years. The capacity is about 1000 gallons of gasoline equivalent per day and serves mostly LA County Sanitation District owned vehicles.

The Bowerman landfill in Orange County recently completed installation of a plant that will convert LFG to liquid methane for nearby LNG markets. The plant is undergoing commissioning but is sized to produce 5,000 gallons of LNG per day. If successful, additional capacity can be added. In addition, the Kiefer landfill in Sacramento County is reportedly undergoing contract negotiations with same energy technology company for an LNG facility. The CIWMB has a solicitation for a 10,000 gallons per day LNG facility using LFG as feedstock. A pilot LFG-to-CNG facility has been built at the Sonoma County Central landfill. It is sized to fuel about 6 CNG transit buses.

*Biodiesel from waste oils and grease*⁵⁴

Enterprises that currently convert waste cooking oils and/or rendering products into biodiesel in California include:⁵⁵

- the Naval Research Facility at Port Hueneme in Ventura County,
- SoCal Biofuels in Anaheim,
- Energy Alternative Solutions, Inc. in Gonzales,
- Yokayo Biofuels, Ukiah
- Imperial Western Products, Coachella

Those investigating feasibility and or planning to produce biodiesel from FOG include;

- the East Bay Municipal Utilities District, Oakland,
- and the San Francisco PUC
- Blue Sky Biofuels, Oakland (investigating co-feeding virgin oils with waste fats)

This list is not necessarily comprehensive. A project proposal from the San Francisco PUC with Metcalf & Eddy recently was recommended funding by the CEC PIER to demonstrate biofuel production from recovered brown grease.⁵⁶ The Naval facility at Port Hueneme has operated a pilot facility since 2004 using waste oils from dining facilities on the base and is nearing completion on a larger production unit. There are numerous technology providers, including those handling high FFA lipids.⁵⁷

Digester Biogas upgrading for fuels

Biogas from municipal and agricultural wastes as well as purpose grown crops is utilized extensively in Europe (Figure 15).^{58,59,60} The biogas is primarily used for heat and power production though there is a

⁵³ Allen Dusault, Scott Walker, Jeff Pierce, (March, 2006). Personal Communication.

⁵⁴ Joerg Blischke (Metcalf&Eddy), Dan Dalton (SoCalBiofuels), Kurt Buehler (Naval Facilities Engineering), and Sunny Beaver (Yokayo Biofuels) (2006). Personal Communication- March.

⁵⁵ Mention of a specific company, brand, or trade name does not constitute an endorsement by the University of California, the California Integrated Waste Management Board, the California Energy Commission, or the State of California.

⁵⁶ See Notice of Proposed Awards: http://www.energy.ca.gov/contracts/BIOFUELS-PIER_NOPA.PDF

⁵⁷ For example, see Tyson, K.S., Bozell, J., Wallace, R., Petersen, E., & Moens, L. (2004). Biomass oil analysis: Research needs and recommendations, Rep. No. NREL/TP-510-34796.

⁵⁸ De Baere, L. (2006) Will anaerobic digestion of solid waste survive in the future? *Water Science and Technology*, **53**, 187-194.

⁵⁹ Williams, R.B., Jenkins, B.M., & Nguyen, D. (2003). Solid Waste Conversion- A review and database of current and emerging technologies. Final Report. CIWMB interagency agreement IWM-C0172.

small market for municipal transit and taxi services that use upgraded biogas for fuel or injection to the natural gas grid.

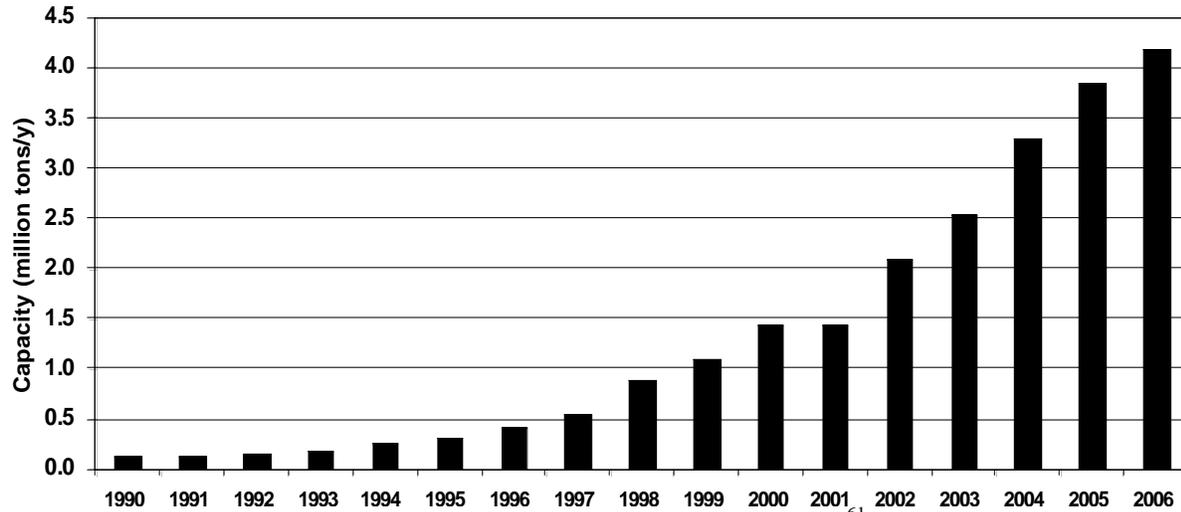


Figure 15. Growth of solid waste anaerobic digester capacity in Europe.⁶¹

Pacific Gas and Electric Company has recently expressed interest in purchasing pipeline quality biomethane from animal and potentially from food wastes, but not from LFG. At least two companies are proposing to supply biomethane. Sempra/SoCal Gas is investigating feasibility of digester gas for pipeline injection and has contracted with a Swedish engineering firm for assistance. Hilmar Cheese and Western United Dairymen have received an award from US EPA to do an engineering study for a potential biogas upgrading and fueling facility at the cheese factory for fueling milk transport trucks.

A pilot scale anaerobic-phased-solids (APS) digester at UC Davis is currently being commissioned. The facility is designed for high-solids feedstocks and will accept food and green wastes as well as other feedstocks for testing purposes. It can be operated so as to co-produce hydrogen and methane and may be equipped with gas upgrading components in the future for biomethane production.

Some technology providers for municipal waste digester systems include:

- Kompogas (Switzerland)
- Arrow Bio (Israel)
- DRANCO (Belgium)
- Vallorga (France)
- BTA (Germany)
- Biopercolat (Germany)
- CiTec (Finland)
- Linde-KCA (Germany)
- OnSite Power (California)

⁶⁰ Hackett, C., Williams, R.B., Durbin, T.D., Welch, W., Pence, J., Aldas, R., Jenkins, B.M., & Salour, D. (2004). Evaluation of conversion technology processes and products -Draft Final Report. University of California.

⁶¹ De Baere, L. (2006). Op Cit.

Facilities in California using AD for treatment of food processing wastes include:

- Valley Fig (Fresno, CA)
- Sierra Nevada Brewery (Chico, CA)
- Joseph Gallo Farms (Atwater, CA)
- Hilmar Cheese (Hilmar, CA)
- Inland Empire Utility Agency (Chino, CA)

Ethanol

Despite the large amount of cellulosic material in the solid waste stream, there are no known operating ethanol facilities that use municipal wastes for feedstock. Several companies report having produced ethanol in laboratory and pilot facilities (e.g., BRI, Masada, BlueFire/Arkenol, Genahol/Waste-to-Energy). Two of the recent (February 2007) DOE cellulosic biorefinery awards propose to use municipal wastes as feedstock: 1) BlueFire Ethanol with an acid hydrolysis process, and 2) Alico which will use the BRI syngas fermentation technology.

Companies known to have interest in ethanol production from MSW feedstocks or components sorted from MSW are listed below by technology type:

Acid hydrolysis followed by fermentation

- BlueFire Ethanol (previously Arkenol)
- Masada Oxynol
- Genahol/Waste-to-Energy

Hydrolysis-fermentation to carboxylates-hydrogenate to alcohols

- MATHenol (the MixAlco process)

Gasification followed by syngas fermentation

- BRI

Gasification followed by chemical catalytic conversion of syngas to alcohols

- Range Fuels (potentially urban wood wastes)
- Genahol/Waste-to-Energy

The US DOE recently announced funding awards for six commercial scale cellulosic ethanol refineries. Over the next four years, the DOE expects to grant \$385 million in the facilities with industry and investment partners adding \$1.2 billion (Table 4).⁶²

⁶² USDOE (2007) Press Release, <http://www.energy.gov/news/4827.htm>

Table 4. DOE cellulosic biorefinery commercialization awards

Company	Proposed Location	Method	Proposed Feedstocks	Proposed Capacity (million gallons per year)
Abengoa Bioenergy	Kansas	Combined Thermo- and Biochemical	Stover, straws, switchgrass, other	11.4
Alico (BRI technology)	Florida	Combined Thermo- and Biochemical	Yard, wood, food processing wastes	7
BlueFire	California	Biochemical (Concentrated Acid- followed by Fermentation)	Sorted green and wood waste	19
Broin	South Dakota	Enzymatic hydrolysis followed by fermentation	Corn fiber and stover	31 (lignocellulosic) 94 (from corn)
Iogen	Idaho	Enzymatic hydrolysis followed by fermentation	Stover, straws, switchgrass	18
Range Fuels	Georgia	Gasification w/ catalytic upgrading of syngas	Purpose grown trees and forest wood wastes	10

Discussion Topics

Numerous challenges and potentials face commercialization of technologies producing biofuels from wastes. These range from demonstrating technical and economic performance at full scale to reducing overall life cycle impacts, among other aspects. The previous discussion has highlighted a number of technologies and applications. In developing future policies and regulations, public input is sought on critical research areas remaining, standards and best practices for implementing technologies, and ways to promote commercialization of systems leading to enhanced overall sustainability of waste management.

Potential discussion topics are listed in following table but the list should not be considered entirely comprehensive. Other topics can be added as desired for Board consideration.

Suggested discussion topics during breakout sessions

Issue	Alcohols	Gasolines/Diesels	Biogas
Pathways to Commercialization			
Policies Affecting MSW conversion to fuels			
Policies Affecting use and market for biofuels			
Financing			
Siting			
Regulation Issues and needs			
Other			
Research/Information Needs			
Improve knowledge of technical resource recovery factors			
What is real world performance of technologies/systems?			
What are emissions from conversion to fuels? [Include in LCA]			
What key improvements/breakthroughs are needed?			
Fuels quality/performance /emissions questions need answered			
What are estimated costs of biofuels from MSW?			
Life-Cycle Environmental Impacts (including carbon and GHG)			
Market Impacts			
Other			