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Authors

Valkenburg, C Norbeck, J N Park, C S

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Availability Assessment of Carbonaceous Biomass in California as a Feedstock for Thermo-chemical Conversion to Synthetic Liquid Fuels

Corinne Valkenburg¹, Dr. Joseph M. Norbeck^{1, 2}, Dr. Chan Seung Park¹ ¹University of California, Riverside Bourns College of Engineering Department of Chemical and Environmental Engineering and the Center for Environmental Research and Technology (CE-CERT) 1084 Columbia Ave. Riverside, Ca. 92507 Phone: 951-781-5748, Fax: 951-781-5790

²University of California, Riverside Environmental Research Institute University Office Bldg. Room 236, Riverside, Ca. 92521 Phone: 951-827-2525, Fax: 951-827-4483

Abstract

The United States currently imports 60% of its transportation fuel. Meanwhile, millions of tons of carbonaceous waste are deposited in U.S. landfills every day. Much of this waste could be converted into synthetic liquid fuels and other commodity chemicals using CE-CERT technology. One of the goals of CE-CERT's waste conversion research program is to determine the potential of waste or residual biomass materials for conversion into valuable forms of energy including electricity, process heat and synthetic diesel (or liquid) fuel. There are several factors pertinent to successful "waste" utilization, comprising a thorough assessment of available resources, beneficial use of the end product(s), an adequate market to derive revenue and a process technology that can attract investment. This study provides a preliminary assessment of biomass resources available in California and its potential impact on the state's petroleum market. It is concluded that agricultural residues, forestry residues combined with livestock manure and municipal solid waste streams produced in California could potentially displace 148% of the state's diesel fuel market or 22% of total U.S. petroleum consumption.

Introduction

The necessary transition from fossil fuels to renewable resources is being addressed by many technologies currently under development. An important part of this development is an assessment of available feedstocks. This is the purpose of the following study. Using the information, practical encashment areas can be created whereby available resources may be utilized to their fullest potential, while minimizing the cost of transportation/delivery of feedstock. This particular study focuses on technology in the development stage at University of California, Riverside's Bourns College of Engineering Center for Environmental Research and Technology (CE-CERT). The potential impact of using California's biomass resources is based on conversion as observed utilizing the CE-CERT thermo-chemical conversion process (hereby referred to as CE-CERT process/technology).

CE-CERT Technology

A general schematic of the CE-CERT process for a woody feedstock is shown in Figure 1.



Figure 1. General Process schematic illustrating the path of entering carbon stream.

The first reactor receives aqueous biomass slurry and subjects it to high-pressure steam and heat. Here the carbonaceous material undergoes steam pyrolysis (SPR) and hydrogasification (HGR). The products at this point are methane, carbon dioxide and char. Modeling efforts for a woody feedstock using Aspen® software and an equilibrium model (minimization of Gibbs free energy) indicate that 70% of the feed carbon becomes CH_4 , 10% CO_2 and 20% converts to char within the SPR/HGR¹. Note that char may then be utilized to produce heat and/or electricity. Methane and steam are then treated in the steam-methane reformer (SMR) to yield synthesis gas (CO and H₂). Synthesis gas is polymerized to yield high-molecular weight liquids and waxes in the Fischer-Tropsch reactor (FTR). Conversion efficiency to F-T products in the FTR is assumed to be 90%². The overall conversion efficiency of carbon from a woody feedstock into F-T products is then estimated at 63% using CE-CERT technology. This conversion efficiency was imposed upon each of the available feedstocks to estimate product yields from California biomass.

Availability Assessment Methods

Much of the information required to construct an availability assessment is found in annual publications generated by the National Agricultural Statistics Survey (NASS), the U.S. Department of Energy (DOE) and the U.S. EPA. Elemental compositions of biomass materials obtained by the Energy research Centre of the Netherlands (ECN) as given by Phyllis³ were employed to estimate total carbon masses.

Potential biomass inventory in California is divided into four categories: agricultural residues (field & seed (FS), vegetable & melon (VM), fruit & nut (FN)), forestry residues, animal manures and MSW. Note that no quantification of "secondary"

¹ Z.A. Zainal, R.Ali, C.H. Lean, D.N. Seetharamu. Prediction of performance of a downdraft gasifier using equilibrium modeling for different biomass materials. Energy Conversion and Management 42 (2001) 1499-1515.

² The remaining 10% of the carbon is assumed to be methane-slip.

³ http://www.ecn.nl/phyllis/

processing residues is given in this assessment. This report covers only residues resulting from the harvest or routine maintenance of a field. Further investigation of secondary processing facilities as well as other waste streams will yield another large volume of energy-rich residue in the form of nut hulls, cotton gin trash, mash (distillers' grain or other fermentation byproducts such as lignin), vegetable matter, and tires.

Further assumptions regarding certain waste streams must be considered to ensure sustainability. For example: in the case of FS crops, assuming only 70% of all residues produced are available for conversion technologies is imperative to soil health. Note that the harvest indexes⁴ for each crop evolve as they are engineered to give us more food and less waste until some critical plant mass required to sustain the crop is reached. At this point the HI remains constant. Thus, current HIs determined at the UC Agronomy Research & Information Center at UC Davis⁵ were used to determine the total mass of plant matter left after harvest for as many FS crops as possible. Similarly masses of residues from VM, FN operations (based on producing acreage) and animal manures (based on animal classification) have been published⁶. It is then assumed that 70% of the residue is available for biomass conversion technologies, animal feed and bedding, etc.

The true mass of sustainably harvested residue (SHR) is highly region-specific. Since the amount of residue required to retain appropriate soil conditions (eg. nonerodibility, carbon, nitrogen, potassium and water levels, infiltrability or porosity) is a function of topography, soil texture and local rainfall as well as the quality of residue, a value should be determined for each region (eg. county, farm, etc.). This task could be accomplished using the latest GIS technology (for highly accurate soil mapping, field and crop characteristics), local precipitation rates and estimations of the quality of local residue. This may even be done by the farmer himself/herself and maintained in an updatable database.

FS crops include cereal crops (grains), corn and cotton. These crops covered over 1,575,000 of the acres harvested in California in 2003. Residues available from these fields consist mostly of straws that are easily bailed, transported and stored. Implementation of cooperative organizations is strongly recommended in this category, as pick-up timing for these residues is crucial. Straws must have a moisture content of approximately 13-15% to be bailed. This means that pick-up (residue harvest) may have to occur within days of harvesting the food crop. In addition, residues not left behind for soil health must be removed beforehand if farmer is to reuse the field. Cooperative organizations could protect the farmer in these scheduling requirements. From an industrial perspective, co-ops would see to uniformity in feedstock preparation and handling, thereby ensuring quality feedstock for conversion.

FN orchards comprised more than 2,334,000 acres of California in 2003. These orchards require routine maintenance making clippings, leaves and stems available for collection. At harvest, the entire nut (along with any twigs/debris) is picked up and hauled either to a hulling plant or to a hulling/shelling plant. These factories then produce a "secondary" crop residue. Many hulling/shelling operations incinerate this "waste" to supplement their energy sources. CE-CERT technology presents an opportunity for extremely valuable use of their already recognized fuel. Further research is required to

⁴ Harvest index = merchantable mass/total above ground mass

⁵ Telephone/email communications with Steve Temple, Kent Brittan, James E. Hill and Steve Kaffka.

⁶ Agricultural residue yields and manure production rates adapted from Knutson and Miller, 1982.

determine the <u>total</u> amount of available FN crop residues, including secondary processing waste streams. VM crops are the smallest segment of California's agriculture, covering over 889,000 acres in 2003. Like FN crops, VM crops involve secondary processing, the waste from which may also be utilized by the CE-CERT process for conversion.

By far, the greatest potential source of residue in California is her 18 National Forests. Conservation measures are currently in place, requiring the mechanical removal of at least 20 million bone-dry tons of timberland each year. Forestry residue estimates include only available timber harvesting and processing residues generated based on published waste generation rates and recoverability, measures of economic activity and trends in virgin wood use in specific markets⁷.

Availability of MSW is assumed to be only the mass of materials currently entering landfills. A generalized distribution of materials entering the landfill⁸ is assumed to determine the total mass of carbon involved in this category.

Energy Balance Methods and Assumptions

Several assumptions were made to determine an overall energy balance between the actual field and the barrel of F-T products because agricultural residues are generally not harvested. Many (thorough) studies of this nature have been performed for corn-toethanol and they provided a good place to begin this investigation. Here it is assumed that the food producer incurs energetic costs due to irrigation, herbicides, pesticides, electricity, labor, seeds, drying/processing of food products and machinery. Energetic costs incurred by the CE-CERT process include the harvesting and transport of residues to a facility centralized within a 50-mile radius encashment area.

Harvesting energy was determined using calorific values and specific volumes of gasoline and diesel fuels utilized in corn farming as cited in literature⁹. Note that these values are given for the entire farming operation and are not limited to harvesting operations. It is assumed that gasoline and diesel fuels have a density of 760 kg/m³ and 840 kg/m³ respectively. Heavy-duty diesel trucks (class 6-8) are assumed to achieve a mileage of 6.5 dge^{10,11}. An average load is then assumed to be 70,000 lbs (32 Mg). One 50-mile round trip (100 mi total) is assumed to obtain residues and transport them to a centralized facility.

Results and Discussion

Data for California's major crops produced in 2003 is given in Tables 1-3. Table 4 gives potential forestry residues. As aforementioned, some timberland may not be accessible. Additional uses for timber are conventionally recognized. A conservative estimate of availability is assumed (lower limit) to account for logistics and other alternative uses. Table 5 shows California's annual manure production based on livestock category and 2003 data. Table 6 gives California's currently landfilled municipal solid waste stream; also 2003 data.

⁷ McKeever, D. and Falk, R. "Inventories of Woody Residues and Solid Wood Waste in the U.S., 2002",

[&]quot;Woody Residues and Solid Waste Wood Available for Recovery in the U.S., 2002" USDA Forest Service Forest Products Laboratory Madison, Wisconsin USA.

⁸ Find reference for CE-CERT's waste stream distribution determination

⁹ Berthaiaume et al., 2001., Patzek, 2004., Pimentel, 2003., Shapouri et al., 2002., Wang et al., 1997.

¹⁰ dge = diesel gallon equivalent, therefore 6.5 dge amounts to $4.46 (10^{-5})$ mi/kJ.

¹¹ California Clean Fuels Market Assessment 2001.

Tables 7-9 show potential production of F-T products based on chemical reaction stoichiometry and overall carbon conversion efficiency of the CE-CERT process. Note that CO_2 yield is included in the tables. This will be important in determining a complete emissions inventory and life cycle analysis of the CE-CERT process.

Further studies should include economic assessment. This is a non-trivial task given the logistics involved. Minimization of transportation costs can be achieved by forming 40-50 mile-radius encashment areas. Detailed distribution of California's biomass resources is beyond the scope of this assessment. The top five producing counties of MSW, agricultural and forestry residues in 2003 are shown in Figure 2.

Results of the overall energy balance performed for agricultural residues are shown in Tables 10 and 11. Total harvested area includes FS, FN and VM crops only.

Harvested Mass (per ha)	Total Crop Yield on dry basis (Mg/ha)	Harvest Index, HI (crop mass/total mass) _{dry}	Residue (Mg/ha)	Total Mass of Residue (Mg/a)	Total Mass of sustainably harvested Residue (Mg/a)
158 bushels	3.03	0.40	4.54	106,679	74,676
395 bushels	8.73	0.50	8.74	601,066	420,746
64.2 tons	1.42	0.50	1.42	203,965	142,775
3264.3 lbs	1.29	0.30	3.01	662,931	464,052
2945.5 lbs	1.16	0.30	2.71	163,543	114,480
17.3 tons	13.81	0.40	20.71	9,136,956	6,395,869
8.6 tons	6.87	0.40	10.36	2,011,807	1,408,265
198 bushels	2.69	0.40	4.02	57,000	39,900
17050.4 lbs	6.81	0.50	6.81	19,280	13,496
19150.8 lbs	7.64	0.50	7.64	1,416,847	991,793
15567.7 lbs	6.21	0.50	6.21	105,620	73,934
222 bushels	4.96	0.40	7.46	30,175	21,123
44.5 tons	35.53	0.40	53.26	172,441	120,708
173.5 bushels	4.16	0.40	6.23	1,223,120	856,184
Total:	104		143	15,911,428	11,137,999

 Table 1. California's Sustainably Harvested Field and Seed Crop Residues

Residue	Bearing Acres (1000 acres)	Yield per acre (tons)	Conversion Factor (BDT/Acre)	Total Residue per annum (1000 Mg)
Almond	530.0	1,920 lbs	1.3	624.9
Apple	29.0	12.05	2.2	57.9
Apricot	18.0	4.28	2.0	32.7
Avocado	59.0	3.61	1.5	80.3
Cherry	25.0	2.21	0.4	9.1
Date	4.8	4.04	1.0	4.4
Fig	13.0	3.58	2.2	25.9
Grape	803.0	7.42	2.0	1,456.6
Grapefruit	15.4	818 cartons	1.0	14.0
Kiwi	4.5	5.27	2.0	8.2
Lemon	49.5	914 cartons	1.0	44.9
Olive	36.0	3.28	1.5	49.0
Orange	194.5	560 cartons	1.0	176.4
Peach	67.8	12.80	2.0	123.0
Pear	18.3	16.70	2.3	38.2
Pistachio	88.0	0.66	1.0	79.8
Plum	36.0	5.89	1.5	49.0
Prune	72.0	7.93	1.0	65.3
Total:	2,334			2,939

Table 2. California's Available Fruit and Nut Orchard Residues

Table 3. California's Major Vegetable and Melon Crop Residues

Residue	Harvested Acres (1000 acres)	Conversion Factor (BDT/Acre)	Total Residue per annum (1000 Mg)
Artichoke	8.0	1.7	12
Asparagus	35.3	2.2	70
Cantaloupe	56.8	1.2	62
Cucumber	4.7	1.7	7
Honeydew	21.0	1.2	23
Lettuce	228.0	1.0	207
Potato	43.1	1.2	47
Squash	480.0	1.2	522
Watermelon	12.5	1.2	14
Total:	889		964

Forestry Timberland Residues	mBDT (per year)	mMg/annum
Upper Limit:	105.4	96.7
Lower Limit:	21.9	20.1

Table 4. Upper and Lower limits of California's Forestry Residue Availability

Livestock	Number	Production (Kg dry matter animal ⁻¹ day ⁻¹)	Biomass (Mg day ⁻¹)	Biomass (Mg a⁻¹)
Beef Cattle	720,000	4.1	2,952.0	1,077,480.0
Dairy Cattle	1,700,000	5.9	10,030.0	3,660,950.0
Chickens (layers)	20,831,000	0.04	833.2	304,132.6
Chickens (broilers)	237,300,000	0.02	4,746.0	1,732,290.0
Turkeys	17,300,000	0.1	1,730.0	631,450.0
Swine	135,000	0.5	67.5	24,637.5
Sheep/lambs	680,000	-	-	-
Total (Mg a ⁻¹):				7,430,940.1

Table 5. California's Livestock Manure Production

Table 6. California's Municipal Solid Waste Stream

Municipal Solid Waste Streams currently landfilled	Landfilled (m BDT a ⁻¹)	Landfilled (m Mg a ⁻¹)
Paper/Cardboard	10.2	9.2514
Food	1.8	1.6326
Leaves and Grass	1.2	1.0884
Other Organics	2.5	2.2675
C&D Lumber	1.6	1.4512
Purnings, trimmings, branches and stumps	0.5	0.4535
All non-Film Plastic	1.9	1.7233
Film Plastic	1.5	1.3605
Textiles	0.7	0.6349
Other C&D	2.5	2.2675
Metal	2.3	2.0861
Other Mixed and Mineralized	2	1.814
Glass	1.1	0.9977
Total:	21.9000	19.8633

Table 7.	Potential	Yield of F-T	Products from	California's Agricu	Itural and Forestry
			Residues		

Available Mass	Mass C	Mass C	Mass C ₁₆ H ₃₄	Mass CO ₂	Mass C ₁₆ H ₃₄	Mass CO₂	Volume C ₁₆ H ₃₄	Volume C ₁₆ H ₃₄
(Mg a ⁻¹)	(Mg a ⁻¹)	(m moles a ⁻¹)	(m moles a ⁻¹)	(m moles a ⁻¹)	(Mg a ⁻¹)	(Mg a ⁻¹)	(m ³ a ⁻¹)	(bbl yr ⁻¹)
39,927,027.6	19,164,973.3	1,597,081.1	41,067.8	554,089.4	9,281,322.8	26,596,289.4	7,935,531.0	49,912,978.3

Table 8. Potential Yield of F-T Products from California's Livestock Manure

Available Mass	Mass C	Mass C	Mass C ₁₆ H ₃₄	Mass CO ₂	Mass C ₁₆ H ₃₄	Mass CO₂	Volume C ₁₆ H ₃₄	Volume C ₁₆ H ₃₄
(Mg a ⁻¹)	(Mg a ⁻¹)	(m moles a ⁻¹)	(m moles a ⁻¹)	(m moles a ⁻¹)	(Mg a ⁻¹)	(Mg a⁻¹)	(m ³ a ⁻¹)	(bbl yr ⁻¹)
7,430,940.1	2,972,376.0	247,698.0	6,369.4	85,936.0	1,439,479.3	4,124,930.0	1,230,754.8	7,741,213.0

Table 9. Potential Yield of F-T Products from California's MSW Stream

Available Mass	Mass C	Mass C	Mass C ₁₆ H ₃₄	Mass CO ₂	Mass C ₁₆ H ₃₄	Mass CO₂	Volume C ₁₆ H ₃₄	Volume C ₁₆ H ₃₄
(Mg a ⁻¹)	(Mg a ⁻¹)	(m moles a ⁻¹)	(m moles a ⁻¹)	(m moles a ⁻¹)	(Mg a ⁻¹)	(Mg a ⁻¹)	(m ³ a ⁻¹)	(bbl yr ⁻¹)
69,184,141.6	33,208,388.0	2,767,365.7	71,160.8	960,106.5	16,082,347.9	46,085,109.9	13,750,407.5	86,487,443.8



Figure 2. Counties producing the greatest amount of biomass in 2003.

Total Harvested Area (ha)	Liters of Gasoline Used	Liters of Diesel Used	Total Energy Consumed as Gasoline (MJ)	Total Energy Consumed as Diesel (MJ)
2,879,302	1.04E+08	2.29E+08	4.14E+09	9.30E+09

Table 10. Energy Consumed on Crop Field

 Table 11. Energy Consumed during Transportation

Total Residue Mass (Mg)	Total Truck Loads (#)	Total Truck Loads for one encashment area (#)	Energy for one 100-mi Trip (MJ)	Total Energy for Truck Loads of one Encashment Area (MJ)	Total Energy for all Truck Loads (MJ)
15,365,394	480,169	339,231	2,242	760,461,261	1,076,404,788

Net energy generation is then the difference between the energetic content of the F-T products¹² and energy costs incurred during harvesting and transportation. Assuming F-T products have the same energy density as diesel no.2, agricultural residues had the potential to yield $1.16 (10^{11})$ MJ in 2003. The energy required to produce one gallon of F-T products is 18 MJ. Thus 12.4% of the energy generated must be spent in the harvesting and transport of feedstock in the case of agricultural residues.

Conclusions

Preliminary investigation into California biomass availability indicates possible flow of 55 million Mg of carbon per year. The distribution of this carbon is 19 million Mg carbon a⁻¹ from agricultural and forestry residues using only the lower limit of forestry residue availability, 3 million Mg carbon a⁻¹ from livestock manures and 33 million Mg carbon a⁻¹ from MSW. Use of CE-CERT conversion technology could amount to generation of 144 million bbl of Fischer-Tropsch products annually.

California consumed 657 million bbl of petroleum-derived products in 2001, 97.3 million of those barrels being distillate fuels¹³. The use of CE-CERT technology to convert available biomass could yield 148% of the distillate market. This amounts to 22% of total C.A. petroleum usage. The above estimates are preliminary and subject to errors but they provide a starting point and good reason to consider non-fossil biomass resources. Refinement of these estimates should incorporate secondary food processing and other industrial, even hazardous wastes.

¹² Energy density of F-T products is assumed to be 144.5 MJ/gal.

¹³ Energy Information Administration (EIA) petroleum flow report, 2003.