Title

Work Authorization to develop a white paper on the potential application of using the steam hydrogasification process to convert biomass materials prevalent in Southern California into synthetic fuels

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Final Report for

Work Authorization to develop a white paper on the potential application of using the steam hydrogasification process to convert biomass materials prevalent in Southern California into synthetic fuels

Contract Number: 500-99-013

Prepared for:

The CALIFORNIA ENERGY COMMISSION

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Executive Summary

This study is performed by the College of Engineering – Center for Environmental Research and Technology (CE-CERT) at the University of California, Riverside at the request of the California Energy Commission. The objectives are to evaluate the availability of biomass feedstocks in the Southern California region that can be used for synthetic sustainable fuel production using the thermochemical conversion technology developed by CE-CERT. The report presents five feedstocks that have been identified as the most suitable and also the energy production and process economics assessments for potential production facilities using these feedstocks. A full life cycle analysis has also been performed.

The biomass availability assessment has been performed for the entire state of California with an emphasis on Southern California. The estimates show that every year California generates 40.8 million dry tons of biomass and Southern California generates 10 million dry tons of biomass that can be effectively used for fuel production. The biomass available in the state of California can potentially yield 30 million barrels of Fischer-Tropsch (FT) diesel and 9.5 million barrels of naphtha per year. This sulfur free FT diesel can replace approximately 41% of the transportation diesel fuel consumed by California every year. Based on the biomass availability estimates for Southern California, wood residue/waste (pine, cedar), chaparral, paper/cardboard, biosolids and field residue (rice straw) have been selected as the target feedstocks for further study. These preferred feedstocks account for 4.7 million dry tons of biomass feedstocks every year. FT diesel (FTD) and electricity cogenerated along with FTD have been chosen as the target fuels. Two configurations of the CE-CERT process that can maximize these products have been analyzed in detail using computer simulation. Process economics have also been estimated for potential facility sizes of 400 dry Ton Per Day (TPD), 1000 TPD and 4000 TPD. The internal rates of return for small 400 TPD plants vary from 0.8 % to 12.1 % depending on economic variables. The internal rates of return varied from 10 % to as high as 41 % for the 1000 TPD and 4000 TPD plants. It appears that a 1000 TPD facility would be optimum based on feedstock density in most areas of Southern California. Additional scenarios were considered, in particular, a combination of hydrogen for use in fuel cell vehicles and FTD would be attractive in some areas. Laboratory scale gasification experiments of the target feedstocks have been performed at different temperatures using a stirred batch reactor system and high carbon conversions were observed for all of the feedstocks. A full fuel cycle analysis using a generic biomass feedstock in the CE-CERT process has been performed. The results are compared with other fuel/vehicle pathways such as petroleum based gasoline, diesel, cellulosic ethanol, hydrogen and electric vehicles. The results show that FT diesel produced using the CE-CERT technology results in the largest green house gas emission reductions per mile driven.

The study demonstrates that there is enormous potential for replacing a significant portion of petroleum base transportation fuels using renewable feedstocks, especially carbonaceous waste streams that are typically sent to land fills. This can result in significant reduction in greenhouse gas emissions, reduced fossil fuel usage and can also mitigate the various problems associated with the disposal of these waste streams. Based on the results of this report, a Process Demonstration Unit (PDU) scale gasifier using a comingled feedstock containing biosolids and biomass (green waste or wood) is proposed as the next step. The operation of this gasifier will provide the information necessary for the construction of a commercial or near commercial scale facility that produces sustainable synthetic fuels from carbonaceous waste streams.

1. Introduction

The University of California, Riverside, Bourns College of Engineering-Center for Environmental Research and Technology (CE-CERT) has been engaged for many years in the development of a thermo-chemical technology for the conversion of wet carbonaceous materials into synthetic fuels (hereafter referred to as the CE-CERT process). One of the unique features of the CE-CERT process is the innovative utilization of water content of the feedstock. This technology appears to be an attractive option for converting carbonaceous matter with high moisture, such as biomass and biosolids, into valuable products such as synthetic diesel fuel.

In the CE-CERT process, the carbonaceous feedstock is first converted to a fuel gas, containing a significant quantity of methane. The fuel gas is then reformed to generate synthesis gas (carbon monoxide and hydrogen). In the third step, the synthesis gas is converted in to a synthetic fuel over a high- efficiency catalyst. Examples of such synthetic fuels are methanol, dimethyl ether (DME) and Fischer-Tropsch (FT) diesel. The production of high energy density liquid fuels such as the FT diesel is particularly desirable from a fuel handling and distribution perspective. A detailed process flow diagram as envisioned by CE-CERT is shown in Figure 1.1.

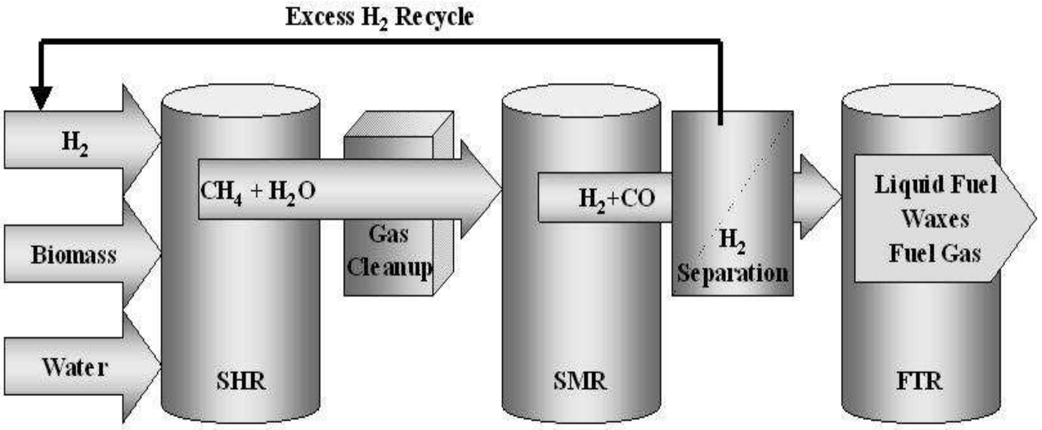


Figure 1.1 Flow diagram of the CE-CERT process

Steam hydrogasification is the first step of the CE-CERT process. The feedstock and water are fed into the Steam Hydrogasification Reactor (SHR) in slurry form along with H_2. An important aspect of this gasifier is the fact that it does not use oxygen or air as the gasifying agent. Experimental work performed in our laboratory has demonstrated that the simultaneous presence of steam and H_2 significantly enhances the rate of methane formation during gasification compared to either dry or steam pyrolysis[1]. The use of a slurry feed also avoids the feedstock drying expenses faced in conventional gasification processes. The SHR product gas contains methane, carbon monoxide, carbon dioxide, hydrogen and steam. This methane rich gas from the SHR is subjected to gas cleanup in order to remove contaminants, primarily sulfur containing species. The clean product gas is catalytically converted into a mixture of H_2 and CO, i.e., synthesis gas in the Steam Methane Reformer (SMR). In this example, the syngas is then fed into the Fischer-Tropsch Reactor (FTR), where it is converted into liquid fuel and waxes. An important aspect of the CE-CERT process is that even though the feed contains H_2, the process does not require an external source of H_2. The syngas produced by the SMR has a H_2/CO ratio of

4-5, whereas the H_2/CO ratio required for the FTR varies from 1 to 2.1. The excess H_2 is separated and fed back into the SHR along with the carbonaceous feed, making the process self sustainable in terms of the necessary H_2 supply. The use of water in the gasification step along with the recycled H_2 allows the CE-CERT process to generate syngas with a flexible H_2/CO ratio (syngas ratio). This is an important advantage since the syngas ratio is a key parameter in the production of different hydrocarbon fuels. A major disadvantage in constructing large commercial-scale biomass gasification plants, commonly known as BTL (Biomass to Liquid) plants, is the site specific restrictions in feedstock availability. Collecting feedstocks for a very large commercial plant is expensive due to the collection and transportation costs. Smaller gasification units are often considered to be economically not viable. The reason is that most of the gasification technologies currently being commercialized use oxygen or air as the gasification agent and small scale oxygen production plants are extremely expensive. The nitrogen content significantly decreases the calorific value of the product gases in air blown gasifiers. Since the CE-CERT process does not use oxygen or air, it possesses a distinct advantage. In addition, experimental work has shown that the CE-CERT process generates very low amount of tars, which are a major concern in low temperature gasification of biomass feedstocks. Hence, the CE-CERT process is an attractive option for the thermo-chemical conversion of biomass and biosolids into high calorific value fuels.

This report summarizes the results of the research activities undertaken by UCR CE-CERT and sponsored by the California Energy Commission. The main purpose of this project is to develop a white paper on the potential application of using the CE-CERT process to convert biomass materials prevalent in Southern California into synthetic sustainable fuels. There were five major tasks included in the work authorization that are summarized below and provided in Attachment A of this report:

Task 1: Provide a review of biomass materials available in Southern California and identify the major feedstocks and fuels for potential use with the CE-CERT technology.

Task 2: Select a minimum of five feedstock and fuel combination for laboratory testing and identify the properties that contribute to their suitability.

Task 3: Perform laboratory testing of the selected feedstocks to confirm their suitability with the CE-CERT technology using a laboratory batch scale reactor. Analyze these results both individually and in combination to better define their performance characteristics.

Task 4: Evaluate the range of energy products and costs produced or co-produced with the hydrogasification process using computer modeling techniques and evaluate their commercial application to Southern California.

Task 5: Perform a full fuel-cycle energy and environmental analysis for the major energy production configuration derived from the previous task and compare to major alternatives.

We will begin with an assessment of biomass availability for the entire state of California since these data were collected for our database and then provide the specifics for Southern California.

2. Target Feedstock and Product for Hydrogasification Applications (Task 1)

2.1 California Biomass Availability

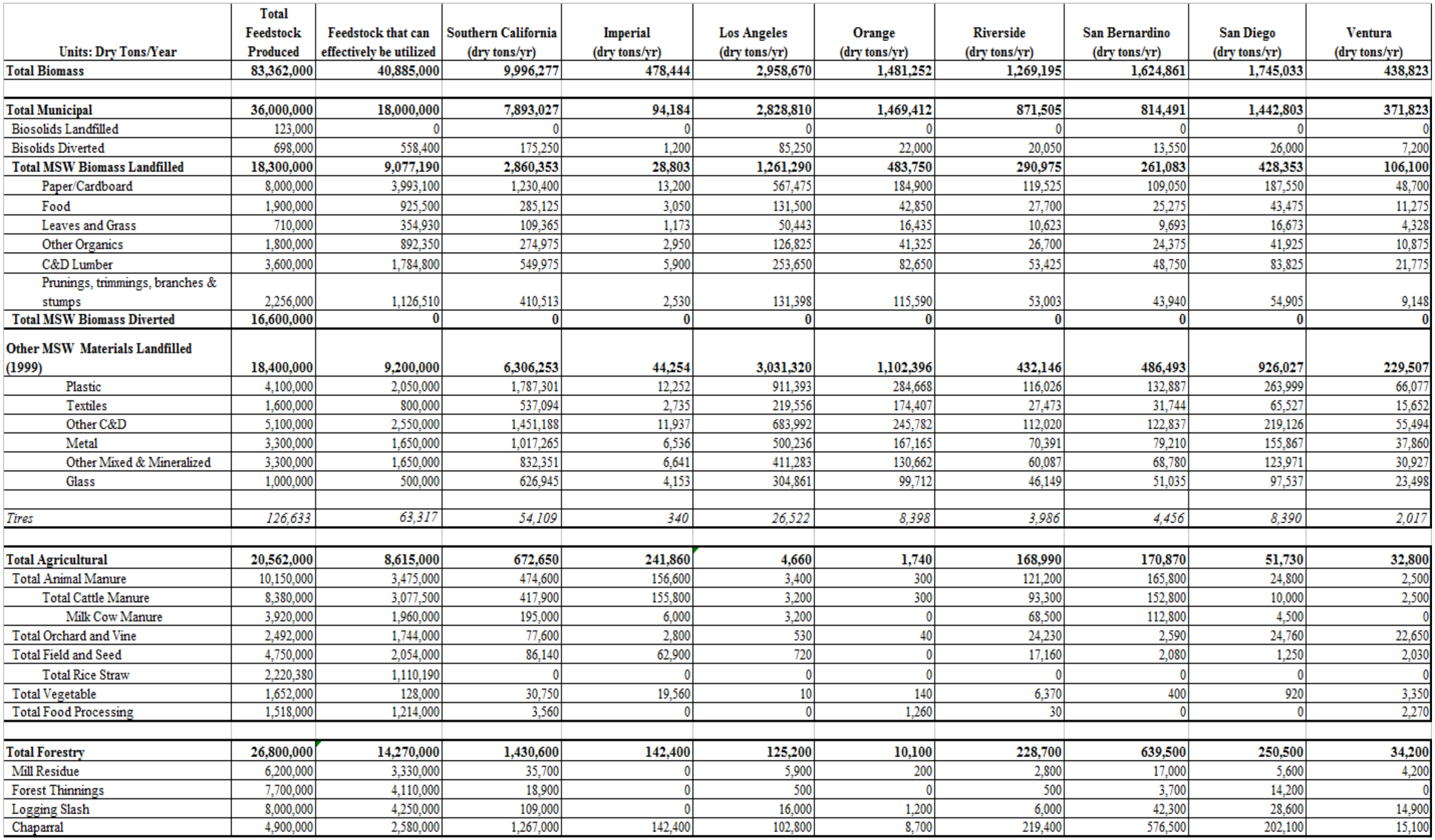
This section presents the estimates of the total biomass waste streams available for fuel production in the state of California. For completeness, municipal solid wastes (MSW) and biosolids have also been classified under biomass waste streams. Biosolids are essentially treated sewage sludge that are the residue obtained from waste water treatment facilities. A good portion of this material is landfilled and is considered a sustainable source of feedstock material. The biomass availability assessment database presented here is constructed from the biomass resource assessment report by Jenkins[2] and data from the California biomass reporting system by Williams and Gildart[3], as well as the brief on biomass as reported by Moller[4]. The municipal waste inventories are obtained from the annual report of the California Integrated Waste Management Board[5]. The biosolids data shown here was compiled mostly through personal correspondence with the public works department of each city/county office. The collected data were verified against other sources whenever possible and in some instances; the units and categories have been altered for consistency.

Table 2.1 shows the complete inventory data that covers the entire state of California with details presented for selected cities and counties in the southern California region.

The data presented in Table 2.1 shows that California generates approximately 83 million dry tons of biomass wastes per year. The 83 million dry tons of biomass produced includes the contributions of total agricultural, forestry and municipal waste. However, it must be noted that the values of other MSW materials that are landfilled are not included as part of the total value for biomass available in California. Further details will be discussed later on in this section. Considering sustainability and harvesting efficiency factors, we conclude that 40.8 million dry ton of biomass are available every year for fuel production. Effective annual production of the agricultural residues is estimated to be 8.6 million dry tons. Out of this amount, the fraction of the rice straw that can be effectively utilized annually is approximately 1.1 million dry tons[6]. Forestry residues available for effective utilization have been estimated to be 14.3 million dry tons per year.

Out of the total 36 million dry tons of municipal solid wastes (MSW) available every year, only 18 million dry tons can be utilized effectively. This estimate takes into consideration Assembly Bill 939 passed in the year 2000 requiring that 50 percent of the MSW that is collected must be diverted. The MSW that is diverted are usually recycled or composted back into the earth.

Table 2.1 Biomass and municipal waste inventory for California



Units: Dry Tons/Year	Total Feedstock Produced	Feedstock that can effectively be utilized	Southern California (dry tons/yr)	Imperial (dry tons/yr)	Los Angeles (dry tons/yr)	Orange (dry tons/yr)	Riverside (dry tons/yr)	San Bernardino (dry tons/yr)	San Diego (dry tons/yr)	Ventura (dry tons/yr)
Total Biomass	**83,362,000**	**40,885,000**	**9,996,277**	**478,444**	**2,958,670**	**1,481,252**	**1,269,195**	**1,624,861**	**1,745,033**	**438,823**
Total Municipal	**36,000,000**	**18,000,000**	**7,893,027**	**94,184**	**2,828,810**	**1,469,412**	**871,505**	**814,491**	**1,442,803**	**371,823**
Biosolids Landfilled	123,000	0	0	0	0	0	0	0	0	0
Bisolids Diverted	698,000	558,400	175,250	1,200	85,250	22,000	20,050	13,550	26,000	7,200
Total MSW Biomass Landfilled	**18,300,000**	**9,077,190**	**2,860,353**	**28,803**	**1,261,290**	**483,750**	**290,975**	**261,083**	**428,353**	**106,100**
Paper/Cardboard	8,000,000	3,993,100	1,230,400	13,200	567,475	184,900	119,525	109,050	187,550	48,700
Food	1,900,000	925,500	285,125	3,050	131,500	42,850	27,700	25,275	43,475	11,275
Leaves and Grass	710,000	354,930	109,365	1,173	50,443	16,435	10,623	9,693	16,673	4,328
Other Organics	1,800,000	892,350	274,975	2,950	126,825	41,325	26,700	24,375	41,925	10,875
C&D Lumber	3,600,000	1,784,800	549,975	5,900	253,650	82,650	53,425	48,750	83,825	21,775
Prunings, trimmings, branches & stumps	2,256,000	1,126,510	410,513	2,530	131,398	115,590	53,003	43,940	54,905	9,148
Total MSW Biomass Diverted	**16,600,000**	**0**	**0**	**0**	**0**	**0**	**0**	**0**	**0**	**0**
Other MSW Materials Landfilled (1999)	**18,400,000**	**9,200,000**	**6,306,253**	**44,254**	**3,031,320**	**1,102,396**	**432,146**	**486,493**	**926,027**	**229,507**
Plastic	4,100,000	2,050,000	1,787,301	12,252	911,393	284,668	116,026	132,887	263,999	66,077
Textiles	1,600,000	800,000	537,094	2,735	219,556	174,407	27,473	31,744	65,527	15,652
Other C&D	5,100,000	2,550,000	1,451,188	11,937	683,992	245,782	112,020	122,837	219,126	55,494
Metal	3,300,000	1,650,000	1,017,265	6,536	500,236	167,165	70,391	79,210	155,867	37,860
Other Mixed & Mineralized	3,300,000	1,650,000	832,351	6,641	411,283	130,662	60,087	68,780	123,971	30,927
Glass	1,000,000	500,000	626,945	4,153	304,861	99,712	46,149	51,035	97,537	23,498
Tires	*126,633*	*63,317*	*54,109*	*340*	*26,522*	*8,398*	*3,986*	*4,456*	*8,390*	*2,017*
Total Agricultural	**20,562,000**	**8,615,000**	**672,650**	**241,860**	**4,660**	**1,740**	**168,990**	**170,870**	**51,730**	**32,800**
Total Animal Manure	10,150,000	3,475,000	474,600	156,600	3,400	300	121,200	165,800	24,800	2,500
Total Cattle Manure	8,380,000	3,077,500	417,900	155,800	3,200	300	93,300	152,800	10,000	2,500
Milk Cow Manure	3,920,000	1,960,000	195,000	6,000	3,200	0	68,500	112,800	4,500	0
Total Orchard and Vine	2,492,000	1,744,000	77,600	2,800	530	40	24,230	2,590	24,760	22,650
Total Field and Seed	4,750,000	2,054,000	86,140	62,900	720	0	17,160	2,080	1,250	2,030
Total Rice Straw	2,220,380	1,110,190	0	0	0	0	0	0	0	0
Total Vegetable	1,652,000	128,000	30,750	19,560	10	140	6,370	400	920	3,350
Total Food Processing	1,518,000	1,214,000	3,560	0	0	1,260	30	0	0	2,270
Total Forestry	**26,800,000**	**14,270,000**	**1,430,600**	**142,400**	**125,200**	**10,100**	**228,700**	**639,500**	**250,500**	**34,200**
Mill Residue	6,200,000	3,330,000	35,700	0	5,900	200	2,800	17,000	5,600	4,200
Forest Thinnings	7,700,000	4,110,000	18,900	0	500	0	500	3,700	14,200	0
Logging Slash	8,000,000	4,250,000	109,000	0	16,000	1,200	6,000	42,300	28,600	14,900
Chaparral	4,900,000	2,580,000	1,267,000	142,400	102,800	8,700	219,400	576,500	202,100	15,100

A total of 5.6 million dry tons per year of biosolids are generated in the United States in addition to the biomass waste streams[7]. The average dry weight per capita biosolids produced after primary, secondary and even tertiary treatment is approximately 90 g per person per day[8]. A total of approximately 0.5 million tons per year of dry biosolids (2-3 million tones of wet biosolids equivalent) are available for use in the state of California alone. The waste water treatment facility located in the City of Riverside generates approximately 65 thousand tons of biosolids every year.

It must be noted that the inventory listed in Table 2.1 for the MSW also includes feedstocks that are not considered as biomass, but are also landfilled; however, we have included them in this report as potential feedstocks that may be utilized for the formation of energy products. With that being addressed, an additional 18.4 million dry tons of other MSW materials that are landfilled are produced each year and the effective amount corresponds to 9.2 million dry tons per year. This additional amount should be additionally accounted for on top of the 83 million dry tons of feedstock produced each year.

2.2 Southern California Biomass Availability

Southern California currently makes up a significant portion of the land area in California and currently houses approximately 21.6 million residents in the area. Of that value about 10.2 million residents live in Los Angeles County and the population is projected to increase to 13 million in 2020[9]. The demand for energy production is growing at a steady rate as the population of southern California continues to increase each year. As a result of the growth, the amount of biosolids will continue to escalate as well. Currently, southern California produces 0.2 million dry tons of biosolids each year and much of the biosolids generated are from Los Angeles County.

The biomass and municipal wastes generated in Southern California that are sustainably available for fuel production every year are listed in Table 2.1. Southern California generates approximately 10 million dry tons of biomass and other municipal wastes that can be used feedstocks in the CE-CERT process. As mentioned previously, biomass was separated into MSW, agricultural residues, and forestry residues. As expected with the growth of population, the amount of MSW generated increases; therefore, the amount of MSW generated in southern California exceeds that of agriculture and forestry residues. The total amount of MSW that can be effectively utilized for energy purposes in southern California is 7.9 million dry tons per year. The top contributor of the MSW landfilled is paper and cardboard, where much of it is generated from Los Angeles County. Following paper/cardboard is green waste (prunings, trimmings, branches, and stumps) and construction and demolition lumber (C&D) with an effective amount of close to 1 million dry tons per year in southern California. Both green waste and C&D lumber contribute to wood waste in MSW, where green waste consists of a mixture of woody and herbaceous materials such as wood chips, logs, stumps, tree tops, and brush[10].

The amount of agricultural residues that can be effectively utilized for energy purposes is 0.7 million dry dons per year. Most of the agricultural residues are generated in southern California are attributed by animal manure, where, approximately 0.5 million dry tons per year are produced. Most of the animal manure produced in southern California is located in Imperial, Riverside, and San Bernardino counties.

In addition, southern California currently has 1.4 million dry tons of forestry residues that can be effectively utilized. In comparison to the state of California, the southern California amount is much less because most of the forest residues are densely located in the northern Californian regions, as shown in Figure 2.1 [11]. The top constituent of forestry residues in southern California is chaparral which accounts for 1.3 million dry tons each year in southern California alone. Chaparral is a type of shrubbery (ever green plants) which is best grown in arid climates such as southern California and is considered as a type of woody biomass. More detailed information of each feedstock classification in southern California and the southern California counties are shown in Table 2.1.

Figure 2.1 Forest biomass potential in California

2.3 Selection of Target Feedstock (Task 2)

The selection of biomass as target feedstocks was chosen from the following criteria: total abundance of biomass, ease of accessibility, degree of seasonal variation, and the degree of homogeneity. The ease of accessibility was determined if the biomass was readily available for immediate use. For example, before MSW is sent to landfills, the materials must be separated in order to achieve a minimum diversion of 50%; where as other materials such as animal manure must be further processed in order to utilize the feedstock. The next criteria, degree of seasonal variation determines if the biomass feedstock can be continuously supplied year round without any changes at any point in time of the year. Lastly, the degree of homogeneity determines if the biomass feedstock has any variation in its chemical content. Therefore, under these criterions, the target feedstock is optimally chosen if the biomass is easy to assess, has little to no seasonal variation, and is homogeneous.

After a careful review of the available feedstocks, wood residue/waste (pine, cedar), chaparral, paper/cardboard, biosolids, and field residue (rice straw) were selected as the target feedstocks for this study. Table 2.2 provides the breakdown of the potential biomass feedstocks to be used in order to make energy products. From the estimates it can be seen that every year, roughly 3.6 million dry tons of biomass is available in the form of the four preferred feedstocks abundant in the Southern California region. If rice straw is also added to the estimates, 4.7 million dry tons of the five preferred feedstocks are available annually. Food and other organics was ruled out in the top 5 selection of biomass because they are not homogeneous due to the fact that there are great variations in processed and non-processed foods, for instance some will have more preservatives than others. In addition, processed foods will have variations in packaging materials. More detailed information involving the chemical composition (degree of homogeneity) of each feedstock will be discussed in later sections. Biosolids were chosen over animal manure because biosolids are easily collected in landfills and waste water treatment plants than in animal manure because it requires extensive manure management by the cattle and dairy farmers [12].

Table 2.2 Selection of biomass in southern California as feedstock

Ranking	Biomass Type	Feedstock Type by mass in Southern California (dry tons/yr)	Ease of Accessibility	Seasonal Variation	Degree of homogeneity
1	Chaparral	1,267,000	ND	L	Y
2	Paper/Cardboard	1,230,400	E	L	Y
3	Wood Waste (C&D Lumber, prunings, trimmings, branches, & stumps)	960,488	E	M	Y
4	Animal Manure	474,600	M	L	Y
5	Food	285,125	H	L	N
6	Other Organics	274,975	H	L	N
7	Bisolids Diverted	175,250	E	L	Y
8	Leaves and Grass	109,365	M	M	Y
9	Logging Slash	109,000	E	M	Y
10	Field and Seed	86,140	E	H	Y

Key

Accessibility		Seasonal Variation		Homogeneity	
E	Easy	H	High	Y	Homogeneous
M	Moderate	M	Moderate	N	Not Homogeneous
H	Hard	L	Low		
ND	Not Determined				

Since wood and field residues are abundantly distributed throughout the US (165 million dry tons per year, or 250 million wet tons per year) as well as the state of California, these can be regarded as high impact biomass feedstocks. The relatively low levels of contaminants like sulfur and chlorine provide more options for gas clean up after the SHR. As discussed previously, much of the wood residues/wastes can be collected from MSW source from green waste and C&D lumber. In 2002 alone the amount of green waste in MSW had exceeded the total volume of timber harvested from the National Forests in the United States[9]. To determine if there is any seasonal variation of the green wastes and C&D collected for the MSW, data was collected from the County of Los Angeles Department of Public Works, as shown in Figure 2.2 [13].

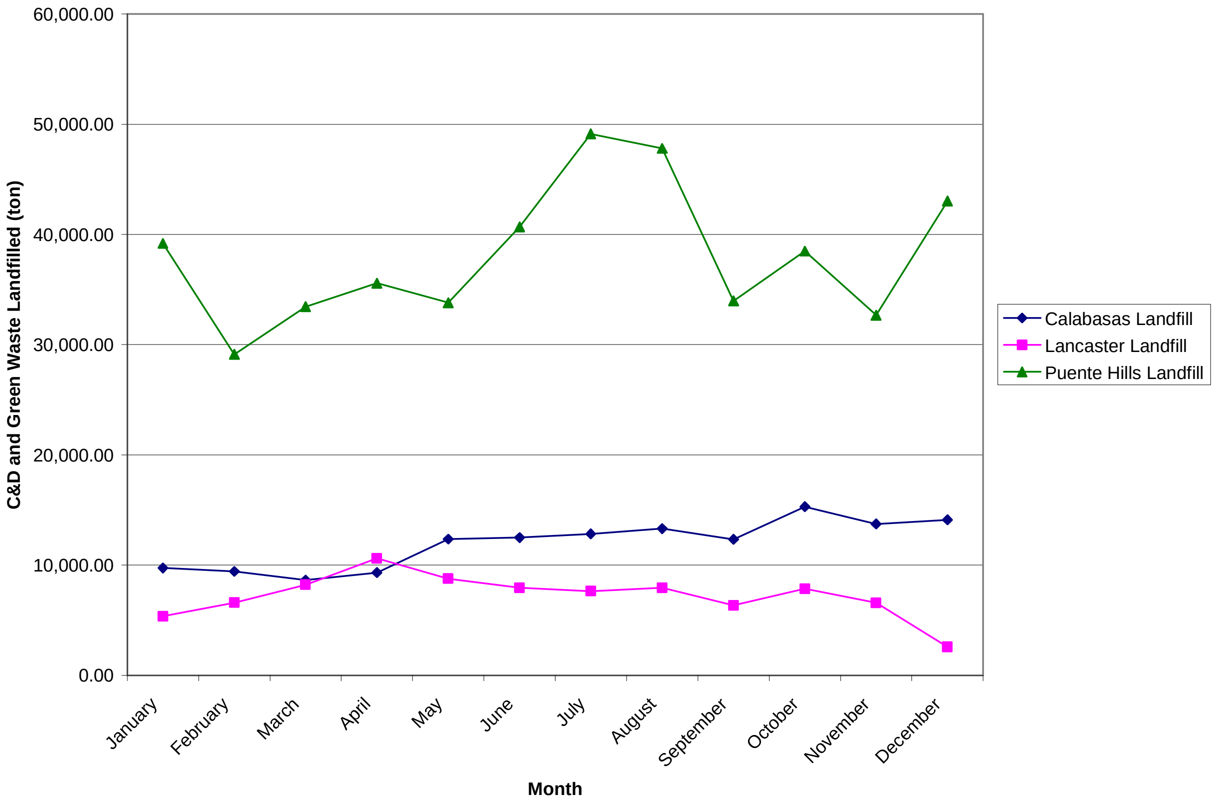


Figure 2.2 Construction and demolition and green waste sent to selected Los Angeles county landfills for 2007.

It should be noted that the rise in wood residues/waste collected from the Puente Hills Landfill during the summer months is attributed from the rapid development and construction that is taken place in the surrounding cities[14]. In addition it should be noted that the MSW landfilled generally shows no seasonal variation as reported from the Los Angeles County of Department of Public Works in Figure 2.3 and this attractive aspect is an important reason for choosing paper/cardboard as a potential feedstock.

Biosolids are very well suited for use as feedstock in the CE-CERT process since they have high moisture content, high homogeneity and low seasonal variation. Significant quantities of the biosolids are currently landfilled; hence, the usage as feedstocks for fuel production can be a step towards mitigating the problems associated with landfilling. Biosolids can be co-mingled with wood or field residues, thereby enabling the effective utilization of the high moisture content.

Even though California has a resourceful amount of chaparral available (approximately 11 million acres), there is limited information about harvesting this feedstock as a source of energy production. Every year a fraction of the chaparral in southern California is cleared as defensible space in order to reduce the number of fires that occur. In addition the removal of chaparral is due to the continuous urban development that is taking place in southern California[15]. However, it is found that erosion in hills is considerably less when harvesting chaparral than those associated with wildfire. In addition, some species of chaparral when harvested is expected to regenerate rapidly where the stocking density is still maintained. For example, the species of chaparral: Quercus dumosa, Adenostoma fasciculatum, and Ceanothus lecucodermis showed immediate growth after the first season of harvesting. In addition, the harvesting of chaparral would remove the nitrogen in the standing vegetation but it would not remove the nutrients in the soil; therefore, the severity is reduced on the nutrient balance of the system[16]. There is however, a potential to utilize chaparral for energy because the biomass contains very little sulfur, and can be converted into high-grade liquid hydrocarbon fuels[17]. Utilizing the chaparral in southern California as a feedstock for energy purposes would also aid in the reduction of fire/flood sequence that has been demonstrated in chaparral lands[18].

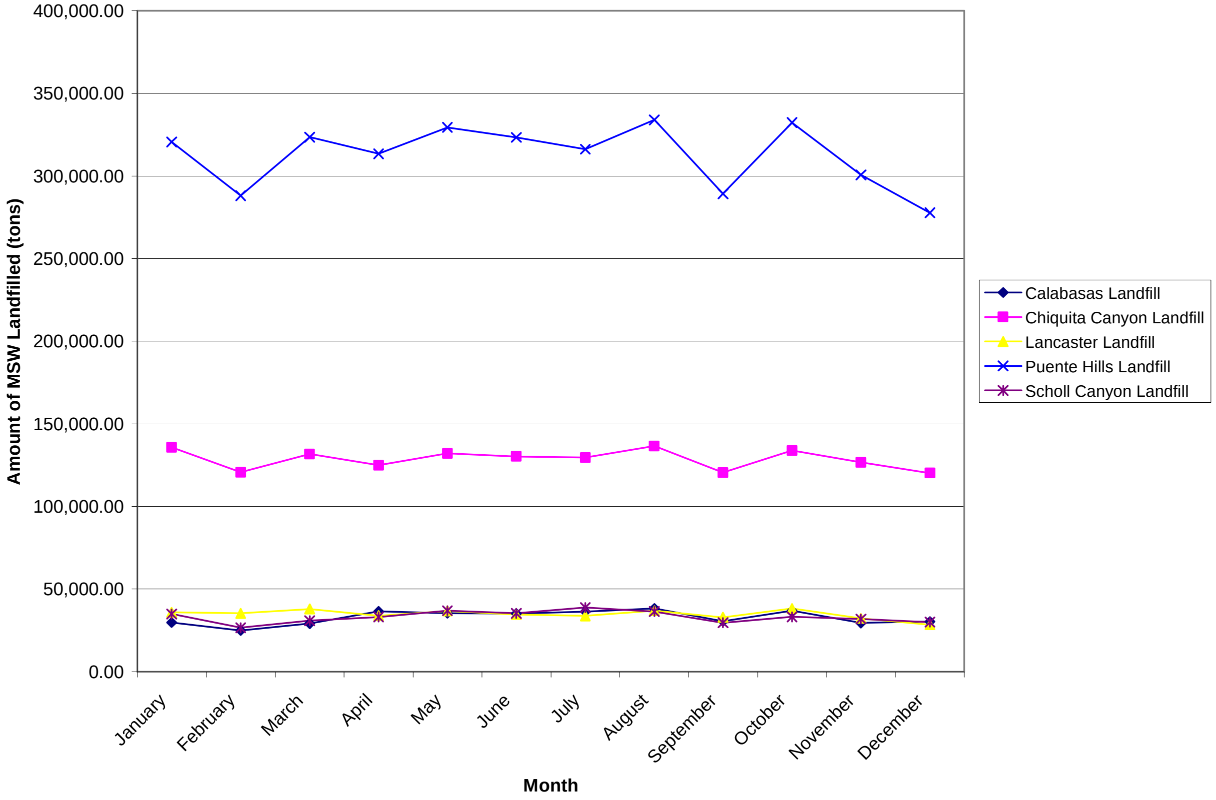


Figure 2.3 Municipal solid waste sent to selected Los Angeles county landfills for 2007.

After reviewing the available biomass feedstocks in southern California, wood residue/waste (pine, cedar), chaparral, paper/cardboard, biosolids, and field residue (rice straw) were selected as the target feedstocks for this study. It must be mentioned that even though rice straw is not highly abundant in southern California, per the request of the California Energy Commission, we have chosen rice straw as a potential feedstock for energy conversion purposes.

2.4 Selection of Target Fuel

Table 2.3 summarizes the energy content of a number of well known fuels[19]. Some of these fuels such as gasoline and diesel are in widespread use and others have generated a significant interest as fuels that can potentially contribute to reduction in fossil fuel consumption.

Table 2.3 Energy content of different fuels

Fuel / HHV	kJ/mol	MJ/kg	MJ/liter*
H_2	286	142	1.73
CH_4	890	55.5	0.04/24.0
CH_3OH	638	19.9	15.8
C_2H_5OH	1235	26.8	21.2
DME		31.7	19.2
Gasoline		46.8	34.1
Diesel		50.3	41.2
Coal, bituminous		27	21

* H_2: at 2200 psi; CH_4: at STP and as LNG

With the exception of H_2 and coal, all the fuels mentioned above can be produced from synthesis gas (syngas), a mixture of H_2 and carbon monoxide. Syngas can be converted into synthetic diesel or gasoline using the Fischer-Tropsch reaction. A life cycle analysis performed by our research group has shown that Fischer-Tropsch (FT) diesel produced from biomass feedstocks results in the highest reduction in greenhouse gas emissions per mile driven[20]. Also, FT diesel is considered a clean burning fuel due to high cetane number and the virtual absence of sulfur and possesses the highest energy content among the fuels listed here. Methanol, ethanol and dimethyl ether (DME) have generated considerable interest as potential transportation fuels. H_2 and electricity are probably the most attractive options for transportation purposes in the very long term since H_2 powered fuel cell vehicles and electric vehicles do not generate greenhouse gas emissions during vehicle operation. Hence, if the electricity or H_2 is generated through a renewable feedstock/process, such as the one presented here, the net carbon emissions into the atmosphere can be drastically reduced.

The technologies for the commercial production of the hydrocarbon fuels listed here are currently considered to be mature. The syngas ratio (H_2/CO) ratios necessary for the production of these fuels are given in Table 2.4. As mentioned earlier, the versatile nature of the CE-CERT process allows the product syngas ratio to be controlled in a relatively simple manner by varying the feed composition. This enables the production of specific desired fuels in an efficient manner irrespective of the nature of the feedstock. FT diesel, gasoline and jet fuel are the most attractive products considering the current fleet of vehicles and the market conditions. However, electricity and H_2 are also very attractive as part of a long term strategy to reduce greenhouse gas emissions. CE-CERT process generates a significant amount of fuel gases (primarily H_2) that can be combusted to generate electricity or can be used as fuel for applications such as fuel cells.

Table 2.4 Summary of processes that use synthesis gas as a feedstock[21]

Desired Product	**Chemical Process**	**Syngas Ratio Required**
Synthetic Diesel/Gasoline	FT synthesis –Co catalyst	2.05 - 2.15
Synthetic Diesel/Gasoline	FT synthesis –Fe catalyst	1.65 – 1.0
Methanol	Methanol Synthesis	2
Ethanol	Higher Alcohol Synthesis	2
DME	Methanol Dehydration	1

Simulations using the Aspen Plus simulation tool have been performed for the production of FT diesel, electricity, DME and H_2. The configuration of the process can be modified in order to maximize the yield of a specific product such FT liquids or electricity. Based on the simulation results and current transportation scenario, FT diesel and electricity have been selected as the target products. However, the amount of H_2 that can be produced along with FT diesel has also been calculated and the results are presented. Further details on the FT diesel and electricity cogeneration and potential H_2 production are presented under Task 4. The production of H_2 is attractive as the introduction of fuel cell vehicles will most probably occur in California first.

3. Feedstock Analysis and Batch Reactor Experiments (Tasks 2 and 3)

3.1 Description of the Experimental Setup

A unique batch reactor setup with a reactor volume of 220 CC was used for these experiments. The reactor was specifically designed to enable continuous stirring under high pressures. The reactor is made of Inconel® alloy and can be operated under pressures and temperatures as high as 400 psi and 800 C respectively. A schematic diagram of the reactor system along with a photograph is shown in Figure 3.1. The reactor setup is comprised of a heating system, a batch reactor, a water trap, a capillary line that allows on-line analysis of product gases, an electron ionization mass spectrometer (MS) and a data acquisition (DAQ) system monitored by using LabVIEW software. The DAQ registers reaction parameters such as temperature, pressure and heater duty into a computer.

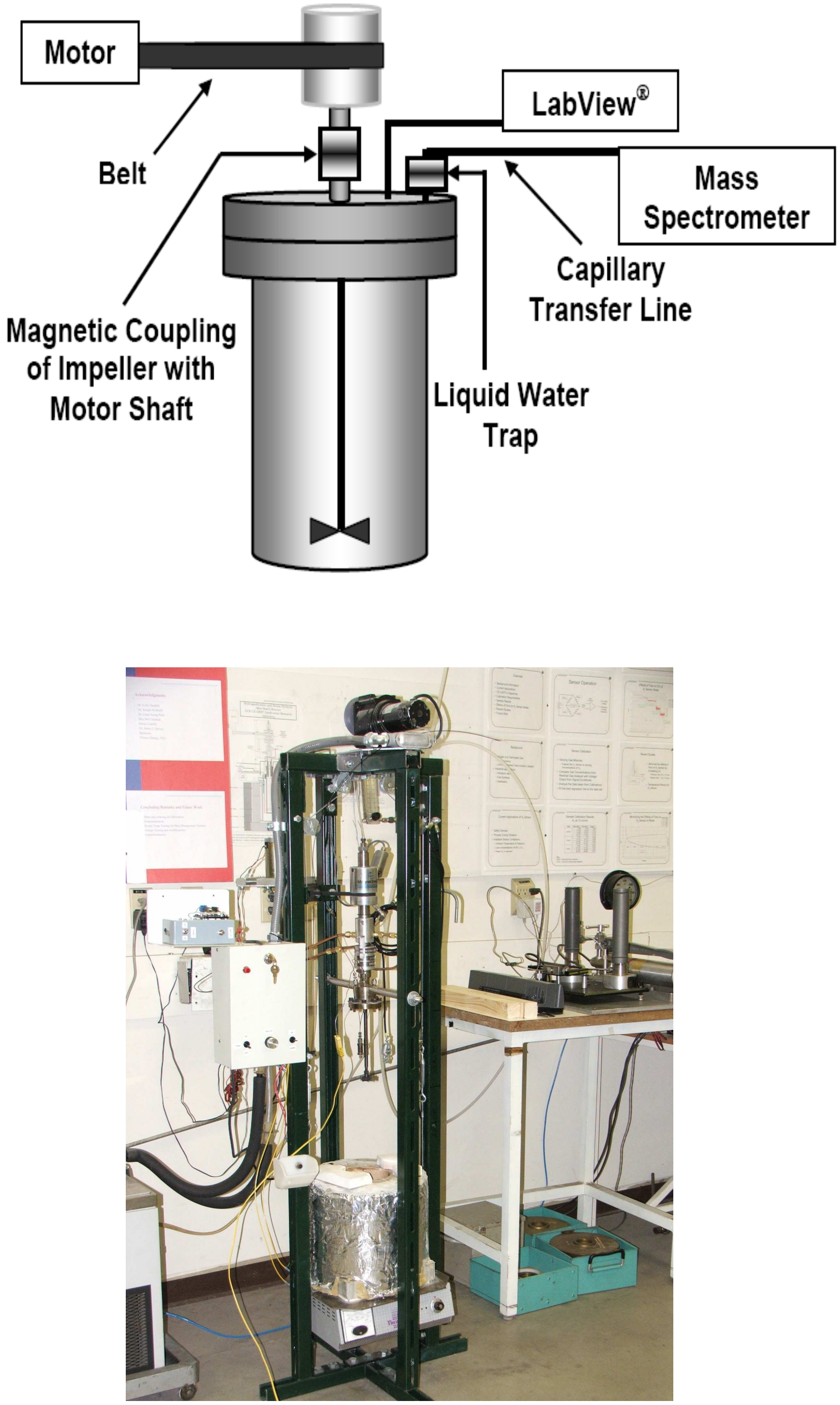


Figure 3.1 Simplified schematic diagram and photograph of the batch reactor setup

3.2 Standard Experimental Procedures

3.2.1 Feedstock Analysis

Proximate analysis, ultimate analysis and elemental component analysis were performed for all the selected feedstocks. The results of the analyses are presented in Table 3.1 [22, 23]. Selected biosolids samples weighing 4-6 g were dried over two days in a vacuum oven at a temperature of 35°C for excessive moisture removal. The samples were then sent for analysis.

3.2.2 Biomass Feedstock

3.2.2.1 Cedar Wood Feedstock

Finely ground cedar wood was used as the sample feedstock in the forestry category. The reactor was loaded with 2 g of cedar dust along with 0-2 g water. The amount of cedar wood and water for each test was decided on the basis of the desired H_2O/C ratio of the feed. The weighed feedstock and water were placed in the reaction vessel and the vessel was attached to the top flange housing consisting of the impeller shaft and magnetic drive stirrer system using bolts, nuts and locking washers. Once tightened, the reactor was opened up to a vacuum pump and was flushed three times with H_2 to remove any other gases present and then tested for leaks. The impeller and cooling systems were switched on at this time.

The reactor was brought up to the reaction temperature by immersion into an electrical heater. The reaction chamber was then monitored for the necessary time, normally from 20 to 30 minutes.

3.2.2.2 Paper and Cardboard

The same method was applied for paper and cardboard as a sample feedstock. Approximately 2g of white ledger paper or cardboard shreds was loaded into the reactor along with 0-4g of water. The amount of white ledger paper or cardboard for each test was decided on the basis o the desired H_2O/C ratio of the feed. The weighed feedstock and water were placed in the reaction vessel. The reactor was brought up to temperature and was monitored for the duration of the test.

3.2.2.3 Rice Straw

The same method was applied for rice straw. Rice straw was obtained from Earth savers in Yolo County, California. Approximately 1 to 2 g of rice straw dust was loaded into the reactor along with 0-4g of water. The amount of rice straw for each test was decided on the basis o the desired H_2O/C ratio of the feed. The weighed feedstock and water were placed in the reaction vessel. The reactor was brought up to temperature and was monitored for the duration of the test.

3.2.3 Biosolids Feedstock

Biosolids samples were taken from Riverside Regional Water Quality Treatment Plant. The Dissolved Air Flotation (DAFT) and Belt Press Cake (BPC) stages were selected as the feedstock and taken directly to the autoclave. This selection was based on the solid content of the samples from these stages, as well as the viscosity of the samples which is an important physical characteristic of the feedstock for any commercial scale reactor.

The samples were autoclaved at 121°C for 20 minutes. This step was necessary to eliminate bacteria that may be potentially harmful to laboratory personnel. The reactor was then loaded with 2g of autoclaved sample and the same experimental procedure as described for the other biomass feedstocks was followed.

3.2.4 Sampling and Analysis of the Residues and Tar

After each experiment, the left over residual material inside the reactor was collected and vacuum dried. The sample was extracted using solvent grade methylene chloride in a soxhelet reactor. After 2-3 hours of extraction, the remaining residue was retrieved, weighed and sent for analysis.

3.3 Experimental Results and Discussion

Figure 3.2 shows an example of the typical mass spectrometric data obtained during the batch reactor tests. The mass spectrometer (MS) records the ion currents of specific mass numbers in the gas sample. The gas concentrations can be calculated from this information using existing MS calibration data. The MS was calibrated at regular intervals. The ion current curve marked as mass number 44 in Figure 3.2 was used to monitor the CO_2 concentration in the reactor and the mass numbers 28 and 15 were used for CO and CH_4 respectively.

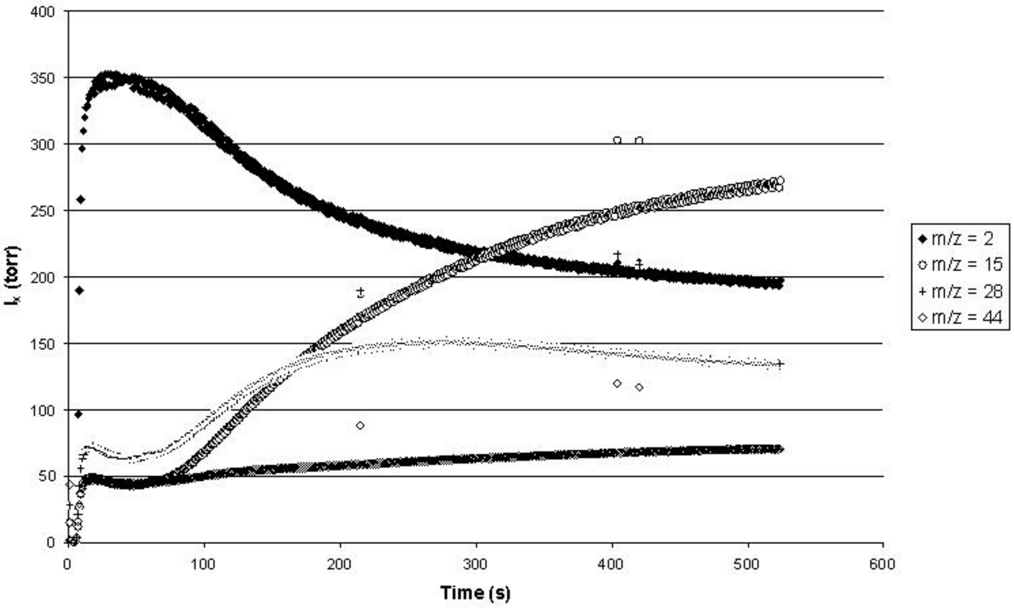


Figure 3.2 Variation of the gas concentrations with time during a batch reactor experiment m/z = 44 for CO_2, m/z = 28 for CO, m/z = 15 for CH_4, m/z = 2 for H_2.

Table 3.1 Proximate and ultimate analysis results of different feedstocks

	Analysis	**Rice Straw**	**Chaparral**	**Paper/ Cardboard**	**Cedar Wood**	**BPC Biosolids**	**DAFT Biosolids**
		Weight %					
Proximate	Moisture(M)	7.43	-	8.4	5.75	Dry Basis	Dry Basis
	Volatile Matter (VM)	67.95	75.2	85.4	72.8	-	-
	Fixed Carbon (FC)	12.98	-	-	20.83	-	-
	Ash	19.07	6.1	1	0.62	29.75	20.85
Ultimate (Dry Basis)	**C**	38.9	46.9	41.8	50.65	36.68	41.62
	H	4.74	5.08	6.05	6.07	5.39	6.03
	O	35.3	40.2	50.6	42.56	20.83	22.73
	N	1.37	0.54	0.42	0.09	5.79	7.82
	S	0.11	0.03	0.12	0.01	1.56	0.95
	Cl	0.47	0.02	-	-	-	-
	F	-	-	-	-	-	-
	Br	-	-	-	-	-	-

Table 3.2 Experiment conditions and results for the biomass and biosolids tests

Biomass Sample (g)	**Temp (C)**	**Pressure (psi)**	**H_2O/C**	**Carbon Conversion (%)**	**Biomass Type**
2	800	100	2	76.6	White Ledger
2	800	100	2	84.1	Cardboard
2	700	100	2	72.0	Rice Straw
2	700	100	2	63.4	Wood
2	800	100	2	72.7	Wood
2	800	100	0	50.0	Wood
1	700	100	6 & 11.4	98.9	BPC
1	700	100	6 & 11.4	96.2	DAFT

Table 3.2 summarizes the batch reactor test results for the different types of biomass along with BPC and DAFT biosolids. The reaction temperature was at 700 C and initial reactor pressure was set to 50 or 100 psi for these tests. As reaction proceeded, the maximum pressure inside the reactor reached up to 470 psi. Carbon conversion (CC) efficiencies were measured for each test and are presented in Table 3.2. Carbon conversion efficiency is defined as the percentage of the carbon present in the feedstock that is converted into gaseous species. It can be seen that very high carbon conversions are obtained for both BPC and DAFT samples. For the wood samples 63% of total CC was achieved at the 700 C and at 800 C the CC was increased to 72.7%. It was also observed that the CC increased significantly (50% to 72.7%) in the presence of water. The results of paper, cardboard, and rice straw experiments are also included in Table 3.2.

We believe that the higher H_2O/C ratio of the biosolids samples, combined with the very low solids content (2 g of sample including more than 80% moisture) results in the much higher carbon conversions. It is also possible that the higher metal content of the biosolids feedstock may play a catalytic role during the steam hydrogasification reaction, resulting in increased carbon conversions. The carbon conversions obtained in this batch reactor setup do not represent the limiting values. The feedstock is not placed under optimal conditions since the reactor is immersed in the heater at the start of the test and reaches the desired temperature only after 15-20 minutes. A significant amount of the water vapor may be lost through the capillary line during this initial heating. The non-ideal nature of the batch reactor tests were noted during earlier gasification experiments, the results of which are not presented here. However, in a rotary kiln type continuous reactor operating in our laboratory much higher carbon conversions were obtained. The batch reactor experiments present a consistent experimental protocol for the various candidate feedstocks but should be considered a lower bound for carbon conversion. We are conducting further studies in order to improve our database of these feedstocks in the batch and kiln reactors. Nevertheless, these experiments clearly demonstrate the versatility of this technology for various carbonaceous feedstocks.

4. Evaluate the range of energy products produced and co-produced from the hydrogasification process (Task 4)

4.1 Aspen Plus Simulation of the CE-CERT Process

A detailed process model using Aspen Plus[24] has been developed and used to predict process behavior, mass and energy balances. Aspen Plus has the ability to handle non-conventional feed stocks and process streams and has built-in process models and physical/chemical property databases. The model simulates the SHR using three separate blocks, the decomposition, pyrolysis and gasification. A non-conventional feedstock consisting of wood slurry and hydrogen is fed into the gasifier at predetermined H_2/C mole ratio and water/wood mass ratios. The feedstock used for the simulations is pine wood. The decomposition block breaks the carbonaceous feed into its elements and the pyrolysis section calculates the fixed carbon and the composition of pyrolytic gases. The products of the SHR are calculated through Gibb's free energy minimization of the species present in the gasifier.

The SMR uses a built-in equilibrium model that consists of the reactions given below.

$$CH_4 + H_2O \leftrightarrow CO + 3H_2 \quad \Delta H = 206 \text{ kJ/mol} \quad (1)$$

$$CH_4 + 2H_2O \leftrightarrow CO_2 + 4H_2 \quad \Delta H = 165 \text{ kJ/mol} \quad (2)$$

$$CH_4 + CO_2 \leftrightarrow 2CO + 2H_2 \quad \Delta H = 247 \text{ kJ/mol} \quad (3)$$

$$CO + H_2O \leftrightarrow CO_2 + H_2 \quad \Delta H = -40 \text{ kJ/mol} \quad (4)$$

The Fischer-Tropsch reactor uses an external model, which is called by the ASPEN Plus once the calculations are performed. The model was empirically developed by Hamelinck et al[25] to predict the selectivity of the Fischer-Tropsch process and has been verified to be in accordance with the results of experimental work performed on cobalt catalysts. The model can be expressed as below.

$$S_{C_{5+}} = a_1 + a_2 \cdot T + a_3 \cdot \frac{[H_2]}{[CO]} + a_4 \cdot ([H_2] + [CO]) + a_5 \cdot p_{\mathrm{Total}}$$

where Sc_{5+} is the mass fraction C_{5+} in the hydrocarbon product, a_i are parameters, $[H_2]$ and [CO] are concentrations expressed as fraction of the feed gas, T and p are temperature (K) and pressure (bar).

The Aspen Plus model calculates the details such as the material balance, the energy balance, product composition, etc based on user defined input parameters such as the feedstock composition, temperature, pressure, flow rates, etc. These results can be used to calculate the process efficiency based on both the carbon converted to useful products and also the energy content of the feedstock versus the product. Sample results for Aspen Plus simulations for biomass, biosolids and Municipal Solid Waste feedstocks are given in Figures 4.1, 4.2 and 4.3 respectively.

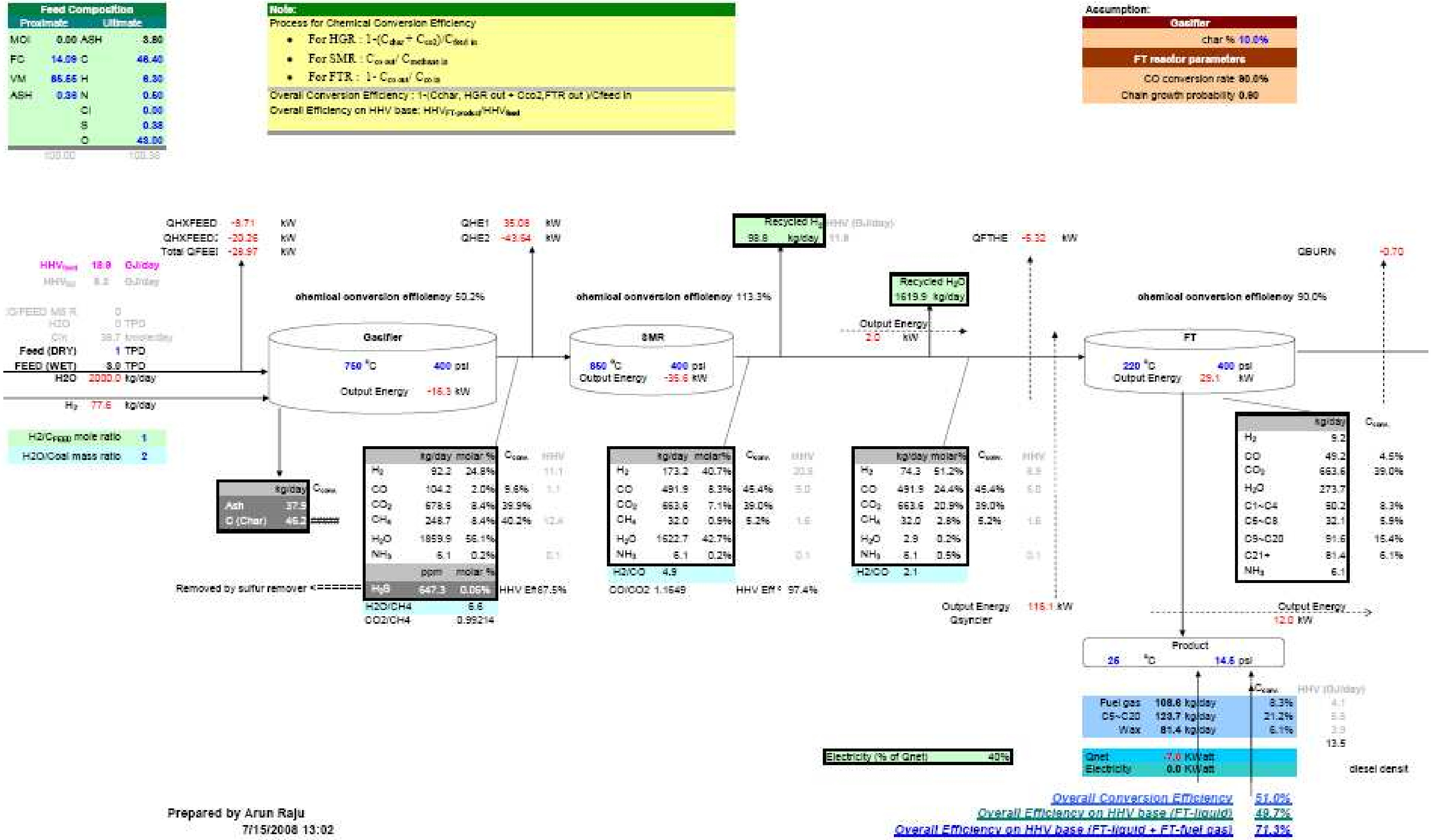
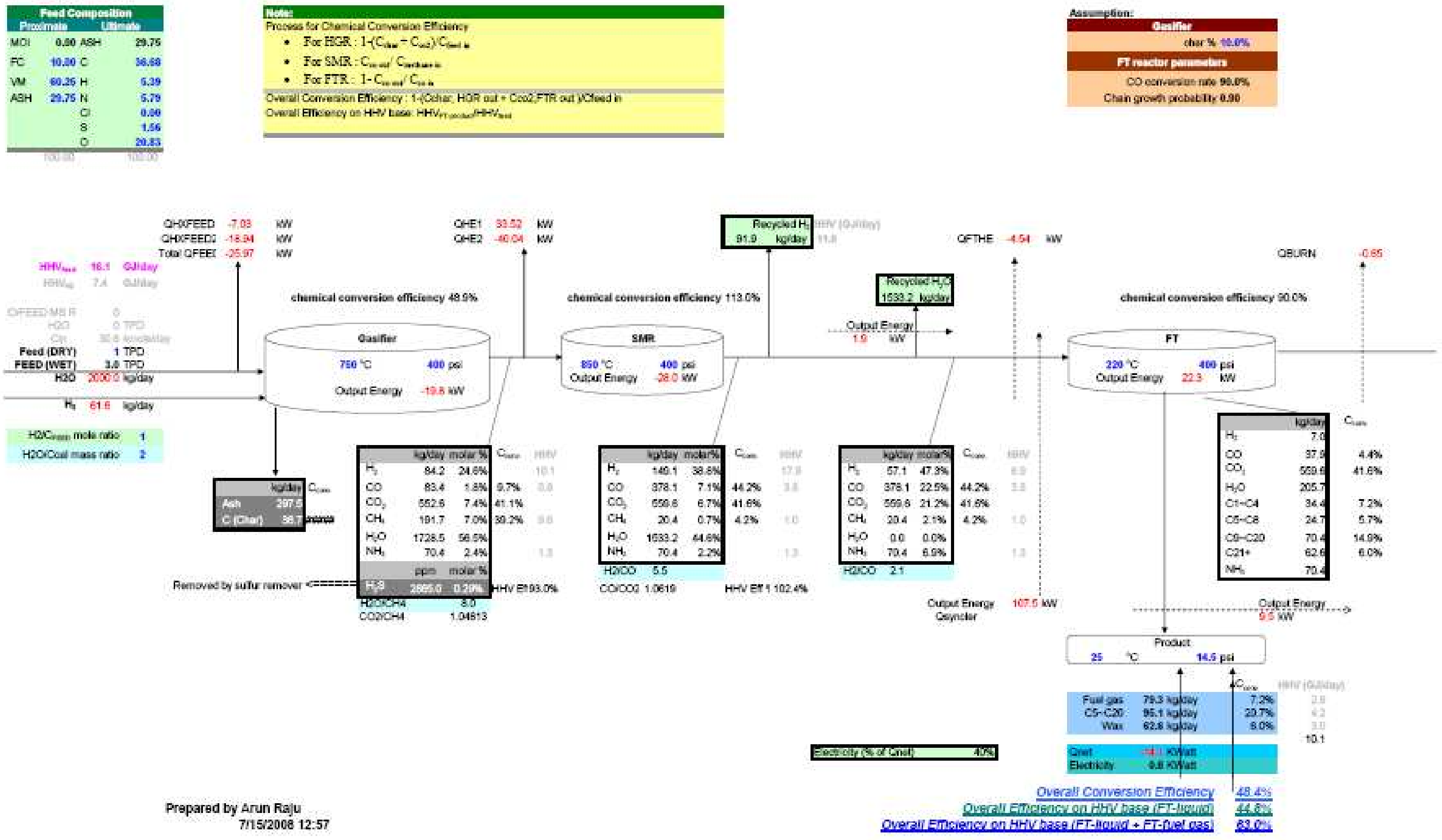


Figure 4.1 Aspen Plus simulation results with biomass feedstock



Feed Composition

Proximate		Ultimate	
MOI	0.00	ASH	29.75
FC	10.00	C	36.68
VM	60.25	H	5.39
ASH	29.75	N	5.79
		Cl	0.00
		S	1.56
		O	20.83
	100.00		100.00

Note:
Process for Chemical Conversion Efficiency
- For HGR : $1-(C_{char}-C_{co2})/C_{feed\ in}$
- For SMR : $C_{co\ out}/C_{methane\ in}$
- For FTR : $1-C_{co\ out}/C_{co\ in}$

Overall Conversion Efficiency : 1-(Cchar, HGR out + Cco2,FTR out)/Cfeed in
Overall Efficiency on HHV base: $HHV_{FT\ product}/HHV_{feed}$

Assumption:

Gasifier	
char %	10.0%
FT reactor parameters	
CO conversion rate	90.0%
Chain growth probability	0.90

	kg/day	C_{conv}
Ash	297.5	
C (Char)	38.7	

	kg/day	molar %	C_{conv}	HHV
H_2	84.2	24.6%		10.1
CO	83.4	1.8%	9.7%	0.8
CO_2	552.6	7.4%	41.1%	
CH_4	191.7	7.0%	39.2%	9.6
H_2O	1728.5	56.6%		
NH_3	70.4	2.4%		1.3
	ppm	molar %		
H_2S	2695.0	0.20%		
H2O/CH4	8.0			
CO2/CH4	1.04813			

	kg/day	molar%	C_{conv}	HHV
H_2	140.1	38.6%		17.9
CO	378.1	7.1%	44.2%	3.8
CO_2	559.6	6.7%	41.6%	
CH_4	20.4	0.7%	4.2%	1.0
H_2O	1633.2	44.6%		
NH_3	70.4	2.2%		1.3
H2/CO	5.5			
CO/CO2	1.0619			

	kg/day	molar%	C_{conv}	HHV
H_2	57.1	47.3%		6.9
CO	378.1	22.5%	44.2%	3.8
CO_2	559.6	21.2%	41.6%	
CH_4	20.4	2.1%	4.2%	1.0
H_2O	0.0	0.0%		
NH_3	70.4	6.9%		1.3
H2/CO	2.1			

	kg/day	C_{conv}
H_2	7.0	
CO	37.9	4.4%
CO_2	559.6	41.6%
H_2O	205.7	
C1~C4	34.4	7.2%
C5~C8	24.7	5.7%
C9~C20	70.4	14.9%
C21+	62.6	6.0%
NH_3	70.4	

		C_{conv}	HHV (GJ/day)
Fuel gas	79.3 kg/day	7.2%	2.8
C5-C20	95.1 kg/day	20.7%	4.2
Wax	62.8 kg/day	6.0%	3.0
			10.1

Qnet	-14.1	KWatt
Electricity	6.8	KWatt

Electricity (% of Qnet)	40%

Overall Conversion Efficiency	48.4%
Overall Efficiency on HHV base (FT-liquid)	44.8%
Overall Efficiency on HHV base (FT-liquid + FT-fuel gas)	83.0%

Prepared by Arun Raju
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Figure 4.2 Aspen Plus simulation results with biosolids feedstock

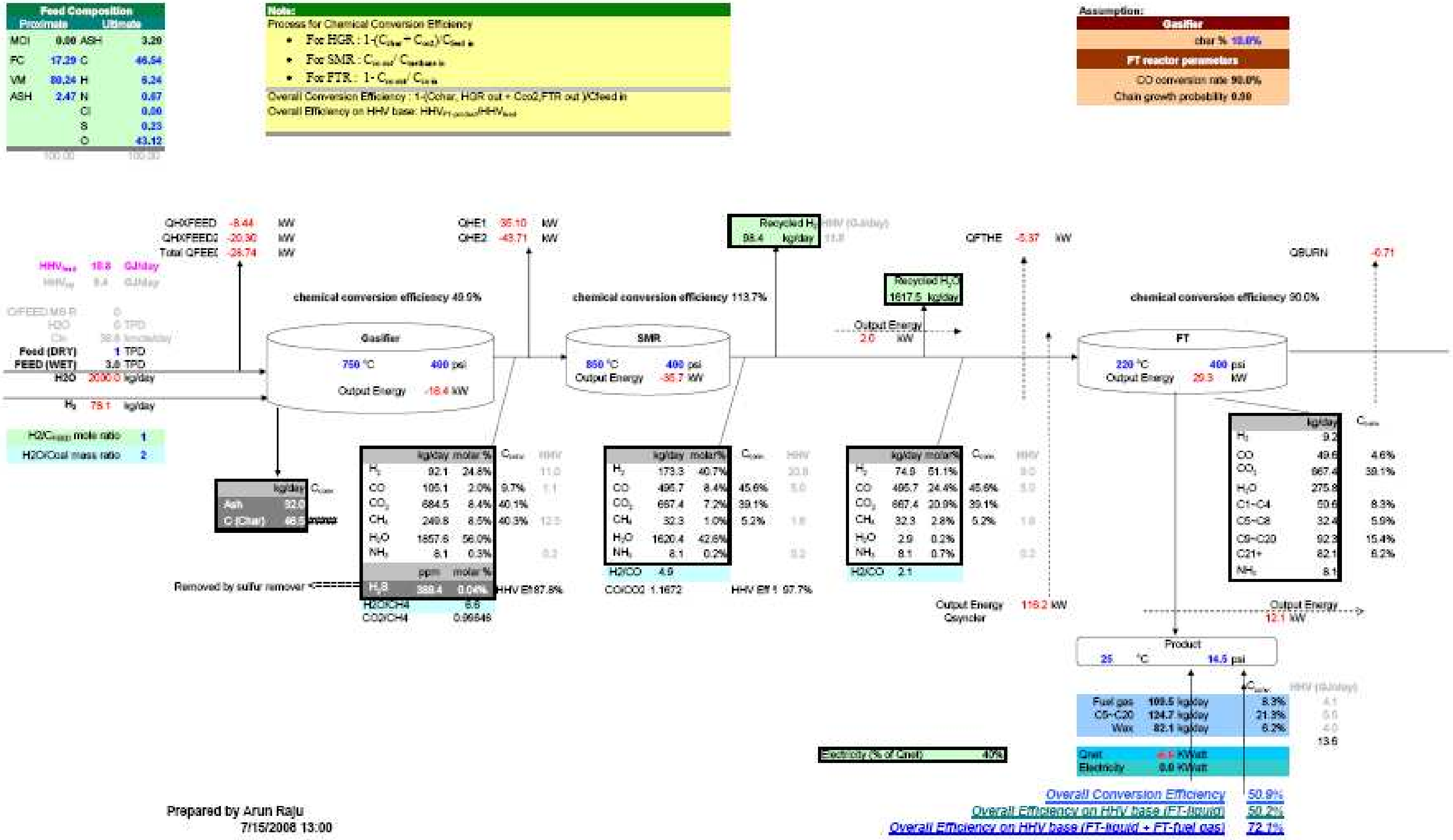

Figure 4.3 Aspen Plus simulation results with Municipal Solid Waste feedstock

The detailed simulations consider the various parameters involved in the process and by varying these parameters, we can design a number of configurations. A major modification that can be made is with respect to the fuel synthesis system. After the SMR and the hydrogen separation unit, the gas stream available is clean syngas that can be used to generate a number of different hydrocarbon fuels as mentioned earlier. These include the Fischer-Tropsch liquids that can be refined into sulfur free diesel, gasoline or jet fuel, methanol, ethanol, dimethyl ether, etc. Another option is to generate only electricity instead of fuel synthesis. It is necessary to evaluate the different configurations so as to achieve optimum performance while generating the desired products. Detailed process economic calculations including the return on investment have been performed for a number of different configurations. Based on the process efficiency, market demand for the different products and the economics, the following two configurations have been selected for further consideration.

Configuration A: The feed ratios used in this configuration are H_2O/Feed mass ratio = 2 and H_2/C mole ratio = 1. The H_2/C ratio of the synthesis gas feed to the Fischer-Tropsch reactor is 2.1. A cobalt based catalyst is assumed to be used in the FTR. This configuration is aimed at maximizing the amount of liquid fuel generated.

Configuration B: The feed ratios used in this configuration are the same as Configuration A. H_2O/Feed mass ratio = 2 and H_2/C mole ratio = 1. However, the H_2/C ratio of the synthesis gas feed to the Fischer-Tropsch reactor is 1. An iron based catalyst is assumed to be used in the FTR. Due to the low H_2/C ratio of FTR feed, there is a large amount of excess H_2 available that can be used for power generation. Hence this configuration is focused on the co-generation of electricity.

The simulations along with the process economics have been performed for these two configurations. A comparison of the key simulation results is given in Table 4.1.

Table 4.1 Comparison of simulation results

	Config A	**Config B**	Units
Process HHV efficiency	53.9	51.1	%
Syngas produced	0.8	0.8	kg syngas/ kg dry biomass
Syngas ratio produced	3.2	3.2	mole H_2/ mole CO
Syngas ratio to FTR	2.1	1.0	
Fuel produced	1.2	0.9	bbl/dry metric tonne biomass
Power generation	31.5	105	kWh/dry metric tonne biomass

As mentioned earlier, other fuels such as H_2 and DME were also considered and simulations have been performed for these cases. While the simulation results demonstrate that these fuels can be produced efficiently from biomass or similar feedstocks, further economic analysis has not been performed due to several considerations including storage and distribution networks and vehicle fleet availability.

Based on the simulations, it was estimated that a minimum of 0.07 tons of H_2 (at 370 psi and 200 C) can be generated per ton of carbon feed along with 1.6 barrels of refined FT diesel fuel. It should be noted that the overall process efficiency is improved and the capital cost decreases due to the absence of equipment and capital for the conversion of this hydrogen into electricity. Similarly, it was estimated that approximately 600 kg of DME along with excess electricity can be generated per ton of carbon feed.

The CO_2 and particulate emissions have also been estimated for these two configurations and the results were found to be comparable. The results are presented as a CERT BTL (Biomass To Liquids) pathway in the life cycle analysis presented in the next section.

4.2 Process Economy Calculations

The process economy calculations have been performed for these two configurations. Three plant sizes, 400 tonnes per day (TPD), 1000 TPD and 4000 TPD with a typical biomass feedstock were considered. The calculations are based on material and energy balance for different feedstocks calculated using the Aspen Plus simulation tool and experimental results. The key assumptions used in these calculations are given below.

Capital cost for the 400 TPD plant – 180 million USD, Capital for 1000 TPD = 312 million USD
Capital cost for the 4000 TPD plant – 716.5 million USD
Debt/Equity – 70/30 % (loan period - 10 years)
Loan interest rate – 10%, Inflation rate – 3%
Construction and startup: 3 years for 400 TPD, 4 years for 1000 TPD, 6 years for 4000 TPD
Feedstock costs: The feedstock costs are assumed to be $0/dry metric tonne. Some of the feedstocks may receive a tipping fee, as high as $59/ton for biosolids, and some of the feedstocks may cost money due to harvesting and transportation costs. In these calculations, the net feedstock cost is assumed to be $0/dry ton.
Labor costs per year – 1% of capital, Operating costs per year – 2% of capital cost
Maintenance costs per year – 2% of capital cost
The products are expected to be refined Fischer-Tropsch Diesel (FTD) and naphtha delivered at the plant gate in addition to electricity for the cogeneration case.

For a typical biomass feedstock using configuration A, the internal rate of return (IRR) is 12.1% for the 400 TPD plant and 22.7% for the 1000 TPD plant. For configuration B, the internal rate of return (IRR) is 5.4% for the 400 TPD plant and 15% for the 1000 TPD plant. The results for calculations using specific feedstocks are presented in the next section.

The feedstock availability information and experimental results indicate that a mixture of biomass and biosolids will be an attractive feed option. By comingling these feedstocks, the significant drying costs associated with biosolids can be avoided. The BPC sample at the treatment location has approximately 14.4% solids content. The H_2O/feed mass ratio in the SHR is 2. In order to obtain a 1 tonne feed equivalent to that of typical biomass along with 2 tonnes of water, 1 tonne of biomass should be mixed with 856 kg of biomass and 1.14 tonnes of water. The carbon content of the resulting feed will be 48.6%. The economics for such a comingled feedstock have also been calculated and included in the next section.

4.3 Comparison of Feedstock/Fuel Production Pathways

The comparison has been performed for different feedstock fuel combinations using three parameters. The amount of FT diesel that can be produced, the amount of electricity cogenerated and the internal rate of return have been compared for Configurations A and B using six feedstocks, wood waste, chaparral, paper/cardboard, biosolids, rice straw and a comingled biosolids and wood waste feed. The results are presented in Table 4.2.

Table 4.2 Comparison of feedstock/fuel combinations

	Feedstock		FT diesel (bbl/ton feed)	Power (kWh/ton feed)	IRR 400 TPD	IRR 1000 TPD	IRR 4000 TPD
1	Wood waste	Config A	1.4	35.5	12.1	22.7	41.8
		Config B	1.0	118.2	5.4	15.0	31.4
2	Chaparral	Config A	1.3	32.8	10.4	20.7	39.0
		Config B	0.9	109.4	3.3	12.7	28.4
3	Paper	Config A	1.1	29.3	6.7	16.5	33.4
		Config B	0.8	97.5	0.8	10.2	25.3
4	Biosolids	Config A	1.1	29.1	6.7	16.5	33.4
		Config B	0.8	97.1	0.8	10.2	25.3
5	Rice straw	Config A	1.0	27.2	4.7	14.3	30.4
		Config B	0.8	90.8	0.8	10.1	25.2
6	Biosolids+wood waste	Config A	1.3	34.0	10.4	20.7	39.1
		Config B	1.0	113.5	5.4	15.0	31.4

In order to compare the environmental benefits associated with these pathways, it is necessary to perform the full fuel cycle analysis. The results of the life cycle analysis along with the various assumptions are presented in the next section. It should be noted that due to the large number of assumptions and the various considerations during each stage of fuel generation, the results are comparable for the different feedstocks under consideration. Hence, the fuel cycle analysis is performed for a generic biomass feedstock using the CE-CERT process and the results have been compared with other alternative and conventional fuels.

4.4 Fuel Production Estimates

The available biomass and other carbonaceous waste stream estimates presented in the previous chapters can be used to estimate the potential amount of Fischer-Tropsch Diesel that can be produced using these feedstocks. These estimates are based on the detailed material and energy balance calculations performed using the Aspen Plus software and experimental work. The fuel production estimates are performed for the CE-CERT process using a single pathway instead of different configurations. The results will vary based on the specific configuration. However, these estimates demonstrate the potential of the carbonaceous waste streams as alternative fuel sources. The products considered are refined sulfur free Fischer-Tropsch diesel and naphtha. The total amount of gasoline and diesel consumption for transportation purposes in the state of California are given in Table 4.3. These estimates are based on the year 2005 consumption[26].

Table 4.3 Petroleum based transportation fuel consumption of California

	Gallons/year	**Barrels/year**	**Million bbl/year**
Gasoline	1.40E+10	3.33E+08	333.3
Diesel	3.00E+09	7.14E+07	71.4

The carbon content of various carbonaceous waste streams was assumed to be 45% on a dry basis. Although a large amount of feedstocks are available in each category, all of this feedstock can not be used for fuel production due to several issues. The primary challenges involve the collection and transportation methods and the emissions and costs associated with these steps. Whenever information was not available in the references, it was assumed that only 50% of the wastes generated are available for fuel production. Only residues resulting from harvesting or field maintenance were included in the estimates and the secondary food processing residues were not considered. The excess electricity generated during fuel production is not included in these estimates. Hence these estimates are conservative. It should also be noted that these estimates are approximate and can be used as an indicator of the potential impact of the utilization of waste streams.

The results of the fuel production estimates for California waste streams are presented in Table 4.4. From the results, it can be seen that approximately 30 million barrels of Fischer-Tropsch diesel can be produced from California’s waste streams. In addition, approximately 9.5 million barrels of naphtha can also be produced.

Table 4.4 Fuel production estimates for the state of California

	Dry tons/year	Available mass, dry metric tonnes/year	FTD production, bbl/ year	Naphtha production, bbl/year
Forest Residues	2.68E+07	1.43E+07	1.04E+07	3.32E+06
Agriculture Residues	2.06E+07	8.62E+06	6.27E+06	2.01E+06
Municipal Wastes	3.60E+07	1.80E+07	1.31E+07	4.19E+06
Total	8.34E+07	4.09E+07	2.98E+07	9.52E+06

From these results, it can be seen that the carbonaceous waste streams generated in California can be used to replace approximately 41% of the transportation diesel fuel consumed by California every year. In addition, a significant amount of naphtha is generated that can be used directly as a feedstock for gasoline production or for blending purposes with ethanol.

5. Full fuel-cycle analysis (Task 5)

Two important criteria for the selection of a suitable fuel/vehicle pathway are the total energy consumption and the net emissions of the desired pathway. It is not sufficient to simply consider the vehicle performance and emissions characteristics but the entire life cycle of the fuel must be considered. Well to wheels (WTW) analysis is considered to be the best way to accomplish such as comparison of different technologies and fuel options. This section is aimed at estimating the well to wheels emissions and energy consumption results for some of the promising fuel/vehicle pathways and also to estimate the availability of renewable feedstocks such as carbonaceous wastes. As mentioned earlier, the Green House Gas (GHG) emissions and the criteria pollutant emissions for the two configurations discussed above are very similar. Hence, the life cycle analysis is performed for CE-CERT Biomass To Liquids (CERT BTL) pathway as a single case that is applicable to both configurations.

This section presents the full Life Cycle Analysis (LCA) results for different fuels based on individual fuel production pathways and vehicle technologies. The LCA has been performed using the GREET (Greenhouse gases, Regulated Emissions, and Energy use in Transportation) model[27]. The GREET model was developed by the Argonne national laboratory and is widely acknowledged as an excellent tool for evaluating the life cycle of different fuels and pathways. This study uses GREET version 1.8b. The LCA is performed in two parts, the Well To Tank (WTT) and Tank To Wheels (TTW) estimates. The final full life cycle emissions and energy consumption information i.e., Well To Wheels (WTW) results is obtained by adding the two parts. The Well To Tank section accounts for all the fuel production steps such as resource extraction, fuel production, transport, storage, distribution and marketing. Facility fabrication and facility decommissioning during these steps are not taken into account. The Tank To Wheels part takes into account the emissions during the vehicle operation. Vehicle manufacturing and vehicle decommissioning are not taken into account during this stage.

This study considers five different fuels, nine fuel production pathways and four different vehicle technologies. The fuels investigated are diesel (conventional, ultra low sulfur diesel and Fischer-Tropsch diesel), gasoline (conventional), cellulosic ethanol (blended with 10% gasoline – E90), gaseous hydrogen and electricity. The pathways are crude oil refining, the Biomass To Liquids (BTL) pathway using the CE-CERT technology, cellulosic ethanol through fermentation, gaseous hydrogen from natural gas reforming and electricity using a mix of technologies. The vehicle technologies considered are spark ignition, compression ignition direct injection, flex fuel vehicle for E90, fuel cell vehicle and electric vehicle.

It should be noted that the H_2 and electricity production pathways considered here are based on a U.S. mix and not based on the CE-CERT process.

5.1 Methodology and Key Assumptions

GREET calculates the total energy use during the full life cycle in Btu/mile and the total greenhouse gas emissions in g/mile. The GHG emissions include CO_2, CH_4 and N_2O. The global warming potentials of each of these gases (CO_2-1, CH_4-23, N_2O-296) are used to calculate the net GHG emissions on a CO_2 equivalent basis[28]. The energy use calculated includes the total energy use and also the fossil energy use which is further split into petroleum, natural gas and coal. GREET also calculates the net emissions of criteria pollutants such as VOCs, CO, NO_x, PM_{10}, $PM_{2.5}$ and SO_x. The criteria pollutants calculated include an estimate of emissions in urban areas. The key assumptions for the different fuel pathways evaluated are given below. All calculations are performed using 2010 as the base year.

Low sulfur diesel (LSD): This pathway performs the LCA for crude oil based low sulfur diesel fuel. The vehicle technology is based on a Compression Ignition Direct Injection (CIDI) engine. The market share is assumed to be 100% for LSD as compared with conventional diesel (CD). The sulfur content of the fuel is 11 ppm. The crude recovery efficiency is 93.9% and LSD refining efficiency is 89.3%.

Gasoline: The pathway for crude oil based gasoline considers both conventional gasoline (CG) and also reformulated gasoline (RFG). The market share is assumed to be 50% for each fuel. The vehicle technology is based on a Spark Ignition (SI) engine. RFG contains 2.3% by weight corn ethanol added as oxygenate. The sulfur content is 25.5 ppm. The sulfur content is high since the usage area is assumed to be the entire United States, not just California. The crude oil recovery efficiency is 93.9% and the refining efficiency for CG is 87.7% whereas the refining efficiency for RFG is 87.2%.

CE-CERT Biomass To Liquids (CERT BTL): This pathway considers the production of Fischer-Tropsch Diesel (FTD) using the CE-CERT technology with a herbaceous biomass feedstock such as switchgrass. The BTL plant efficiency is assumed to be 50% and the engine technology is assumed to be a CIDI engine running on 100% FTD.

Ethanol: The ethanol pathway considered here uses an herbaceous biomass feedstock (switchgrass) in a fermentation process. This cellulosic ethanol is assumed to be blended with 10% gasoline and the resulting fuel is commonly represented as E90. The gasoline used for blending is 50% CG and 50% RFG. The ethanol yield is assumed to be 95 gallons/dry ton of feed and the electricity co product is -0.572 kWh/gallon of fuel produced. The herbaceous biomass farming energy use is assumed to be 217230 Btu/dry ton and the CO_2 emissions due to land use change by herbaceous biomass farming is -48500 g/dry ton. The vehicle technology used is a Flex Fuel Vehicle (FFV) with a SI engine.

Gaseous Hydrogen: The gaseous hydrogen pathway is performed for Fuel Cell Vehicles (FCV). The hydrogen production is 50% central and 50% station based. The central production is based on feedstock shares dominated by North American natural gas (60%) along with solar (10%), coal (10%) and nuclear (20%). The station produced hydrogen uses natural gas (80%) and ethanol (20%) feed. The refueling station production efficiency is 70% (NA NG feed) and 67.5% (ethanol feed) and the central plant efficiency is 71.5% (NA NG feed).

Electricity: The electricity is generated using a mix of technologies including natural gas, coal and nuclear plants. The vehicle technology is assumed to be dedicated electric cars.

Transportation and Distribution Assumptions: The conventional crude oil for use in U.S. refineries is obtained from domestic wells (Alaska – 7%, other states – 35%), offshore countries (50%) and Canada and Mexico (8%). The oil from Alaska is shipped directly to the refinery by ocean tanker (2100 miles) whereas the oil from the other sources is shipped to a bulk terminal by ocean tankers (5500 miles) and pipeline (750 miles). The transport from the bulk terminal to the refinery is accomplished using barge (1%, 500 miles) and pipeline (92%, 750 miles). The FTD produced from biomass is transported from the plant to a bulk terminal using barge (33%, 520 miles), pipeline (60%, 400 miles) and rail (7%, 800 miles). The transportation from the bulk terminal to refueling station is accomplished using Heavy Heavy-Duty Diesel Trucks (HHDDT - 30 miles). For all herbaceous biomass based fuels, the feed is transported to the plant by HHDDT (40 miles). The gaseous hydrogen is transported primarily through pipelines. The ethanol from the plant is transported to bulk terminals by barge (40%, 520 miles), rail (40%, 800 miles) and HHDDT (20%, 80 miles). HHDDT is also used for moving the ethanol from the bulk terminal to the refueling stations, assumed to be within 30 miles.

Tank To Wheels Calculations: The GHG emissions and the energy consumption during this step is primarily based on the vehicle technology used and the efficiency of the specific vehicle type. All calculations are performed for passenger cars (model year 2005). The efficiency of each different type of vehicle is converted to a gasoline equivalent miles per gallon (mpg) for simplicity. Therefore, the conventional spark ignited (SI) engine (model year 2005) using CG or RFG is the baseline vehicle with a mileage of 23.2 mpg. The diesel fuels, including both LSD and FTD are used in CIDI engines with a mileage of 27.84 mpg. The mileage of FFVs using E90 ethanol is assumed to be the same as that of the baseline value, i.e., 23.2 mpg. The FCVs using gaseous hydrogen have a mileage of 53.36 mpg where as electric vehicles have 81.2 mpg gasoline equivalent mileage.

5.2 Well To Wheels Results

The results include the total (Well To Wheels) greenhouse gas emissions per mile driven and the energy use per mile driven using the specified fuel and vehicle technology. The fossil energy use is also calculated by accounting for individual fossil fuels such as petroleum, coal and natural gas. The emission values for criteria pollutants including VOCs, CO, NOx, PM and SOx are also provided.

Figure 5.1 presents the GHG emission results for different fuel pathways. The BTL pathway provides the most attractive option in terms of the emissions followed by cellulosic ethanol. It should be noted that the values for gaseous hydrogen and electric vehicles are based on the assumed feedstock mix and these values will change as the contribution of individual feedstocks varies.

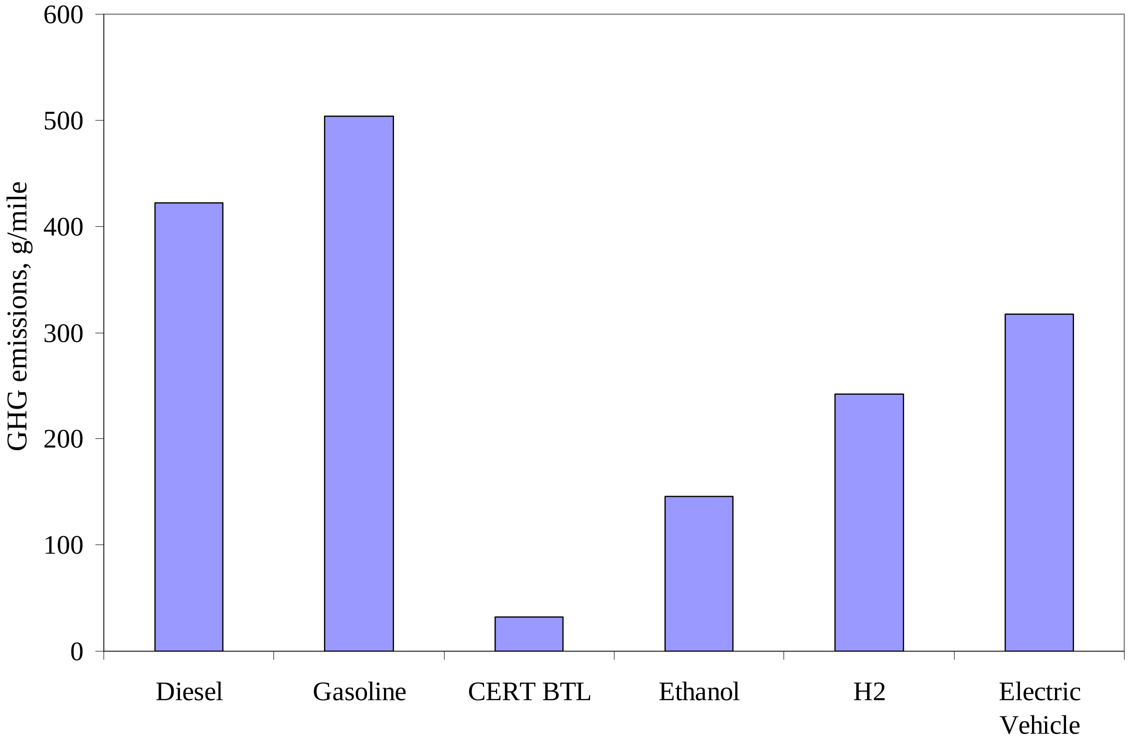

Figure 5.1. Green House Gas emissions results

The total energy consumed per mile driven for each fuel pathway is shown in Figure 5.2. The results show that the CERT BTL pathway generates 32 g of GHG emissions per mile driven and consumes energy equivalent to 8618 Btu/mile driven. As expected, the biomass based alternative fuel pathways consume more energy than crude oil based gasoline and diesel. The energy consumption of hydrogen based FCVs and electric cars are lesser, although this may vary depending on the specific fuel production technology. Overall, the energy consumption of different pathways except FCVs and EVs are not markedly different. However, the fossil energy consumption results demonstrate the inherent differences between these pathways, as shown in Figure 5.3. The fossil energy consumption of CERT BTL pathway is estimated to be 401 Btu/mile driven. Herbaceous biomass based processes such as BTL and ethanol consume minimal fossil energy when compared to other options. These technologies offer an attractive option as they primarily rely on sustainable resources and generate liquid fuels that are convenient to handle. The NOx, PM_{10} and $PM_{2.5}$ emission results are presented in Figure 5.4. These results show that the criteria pollutant emissions are comparable for different pathways.

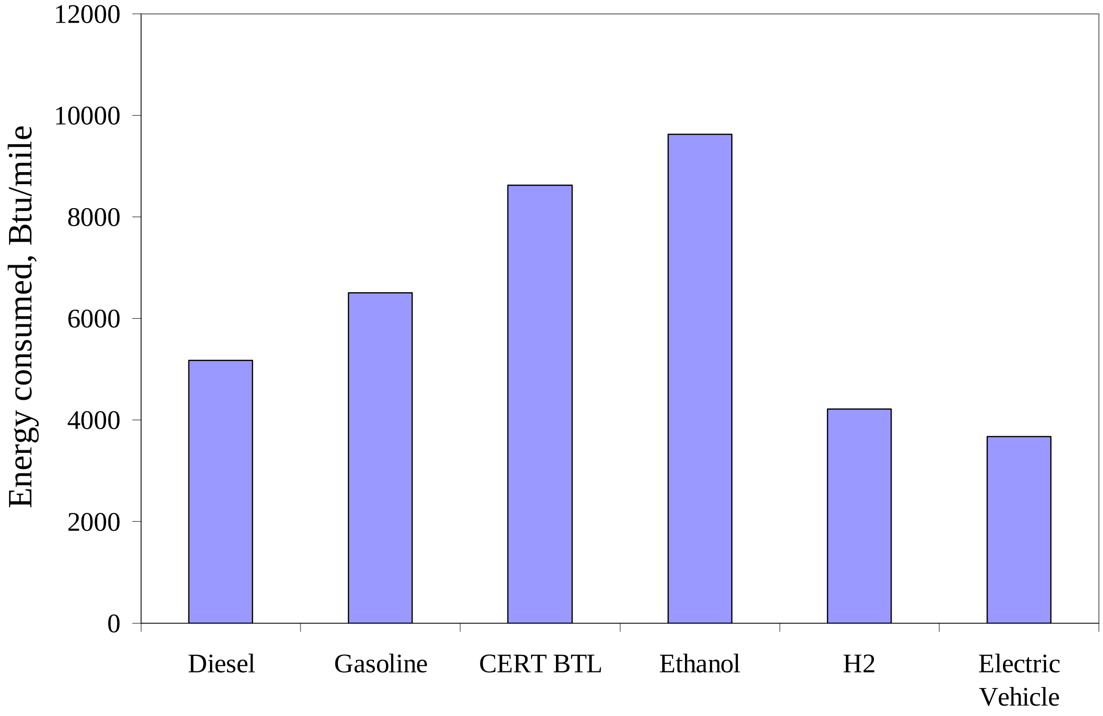

Figure 5.2. Energy consumed per mile driven for each fuel pathway

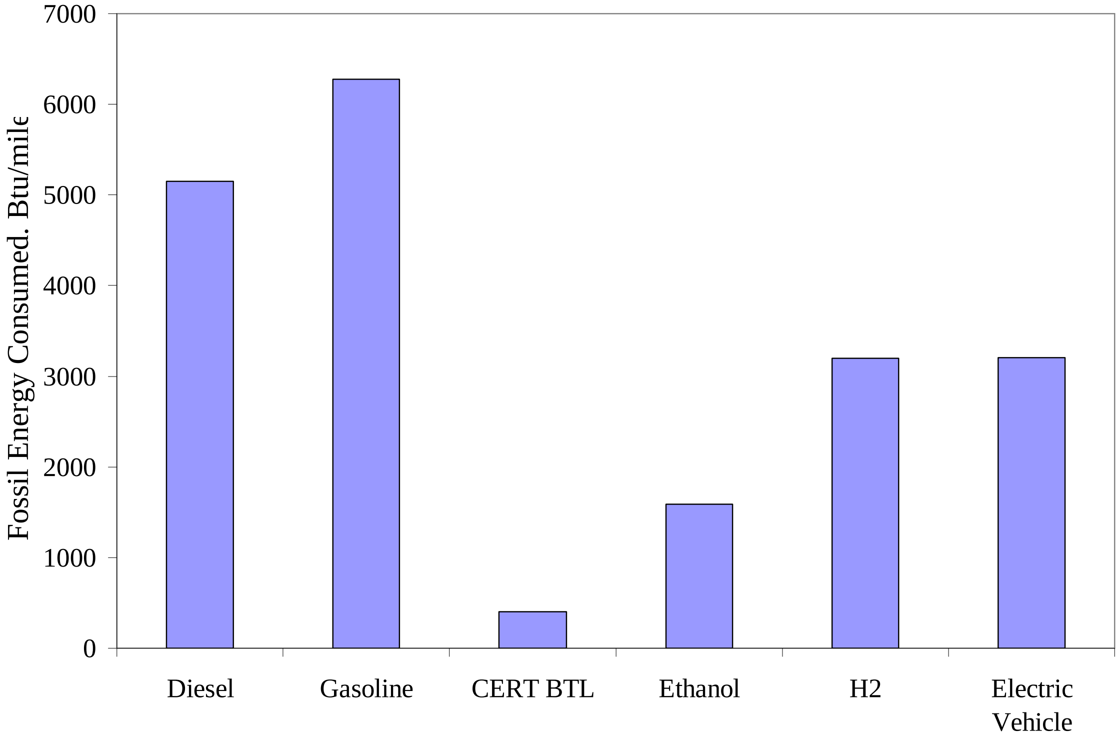

Figure 5.3. Fossil energy consumed per mile driven for each fuel pathway

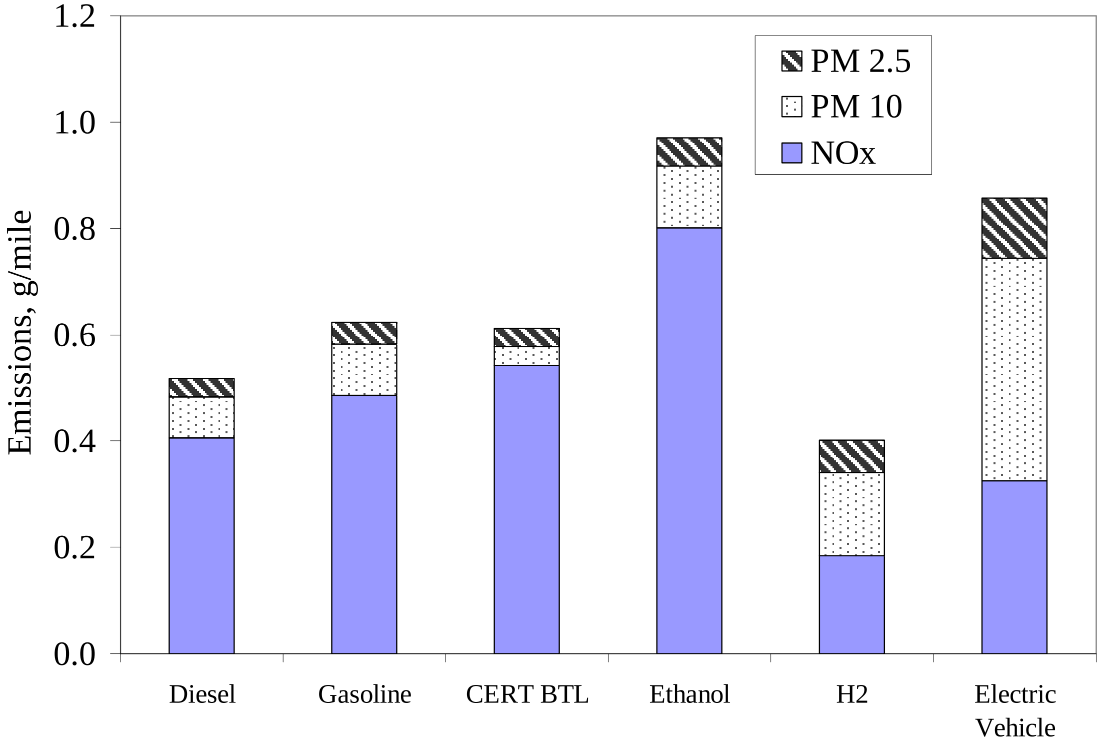

Figure 5.4. Criteria pollutant emissions results

6. Conclusions

This report summarizes the results of the research work undertaken by CE-CERT at the University of California, Riverside and sponsored by the California Energy Commission. The objective of this study is to develop a white paper on the potential application of using the CE-CERT process to convert biomass materials prevalent in Southern California into synthetic sustainable fuels. The results of the five major tasks listed in the statement of work are summarized below.

Task 1:
The biomass availability assessment has been performed for the entire state of California with an emphasis on Southern California. California generates approximately 83 million dry tons of biomass wastes per year. This estimate includes the contributions of total agricultural, forestry and municipal waste. Considering sustainability and harvesting efficiency factors, we conclude that 40.8 million dry tons of biomass are available every year for fuel production.

The Southern California region generates approximately 10 million dry tons of feedstocks every year that are effectively available for fuel production. Based on the biomass availability estimates for Southern California, wood residue/waste (pine, cedar), chaparral, paper/cardboard, biosolids and field residue (rice straw) have been selected as the target feedstocks for this study. These selections are based on the sustainability, annual mass available, seasonal variations and homogeneity of the feedstocks. Every year approximately 4.7 million dry tons of these feedstocks are generated.

Task 2:
As mentioned earlier, wood residue/waste (pine, cedar), chaparral, paper/cardboard, biosolids and field residue (rice straw) have been selected as the target feedstocks for this study. Fischer-Tropsch diesel and electricity have been selected as the target fuels. The detailed combinations of feedstock/fuel pathways along with the process economics results are presented in Table 4.2.

Task 3:
Laboratory scale batch reactor experiments have been performed for the selected feedstocks. The carbon conversions calculated from these test results range from 63 % to as high as 98 % for the selected feedstocks. The results are summarized in Table 3.2. Based on these results, a comingled biomass/biosolids feedstock is proposed for the next stage and should be evaluated in a fluidized bed reactor.

Task 4:
A number of process/fuel configurations have been evaluated using the Aspen Plus simulation tool and two configurations have been chosen for further study. Configuration A is based on a cobalt catalyzed Fischer-Tropsch reactor and is focused on the maximum production of liquid fuels. Configuration B is based on an iron catalyzed FT reactor and results in the maximum amount of electricity cogeneration. Process economy calculations have been performed for these configurations using the different feedstocks for potential facility sizes of 400 dry Ton Per Day (TPD), 1000 TPD and 4000 TPD. The internal rates of return for the 400 TPD plants vary from 0.8 % to 12.1 % depending on the parameters. For the 1000 TPD and 4000 TPD plants, the internal rates vary from 10 % to as high as 41 %. The simulation results and the process economy

calculation results are discussed in detail in Chapter 4.

The fuel production estimate results demonstrate that the biomass available in the state of California can potentially yield 30 million barrels of FT diesel and 9.5 million barrels of naphtha per year. This sulfur free clean FT diesel can replace approximately 41% of the transportation diesel fuel consumed by California every year.

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Task 5:

A full fuel cycle analysis has been performed for the CE-CERT biomass to liquids (CERT BTL) pathway using a typical biomass feedstock and process configuration using the GREET model. The fuel cycle analysis includes estimates of the Well To Wheel (WTW) greenhouse gas emissions, energy consumed per mile driven, fossil energy consumed per mile driven and criteria pollutant emissions per mile driven. The results show that the CERT BTL pathway generates 32 g of GHG emissions per mile driven and consumes energy equivalent to 8618 Btu/mile driven. The fossil energy consumption (today's fuel mix) is estimated to be 401 Btu/mile driven. The results have been compared with the fuel cycle analysis of other fuels including cellulosic ethanol, petroleum based, diesel and gasoline.

The study demonstrates that there is enormous potential for replacing a significant portion of petroleum base transportation fuels using renewable feedstocks, especially carbonaceous waste streams that are typically sent to land fills. This can result in significant reduction in greenhouse gas emissions, reduced fossil fuel usage and can also mitigate the various problems associated with the disposal of these waste streams. Based on the results of the report, a Process Demonstration Unit (PDU) scale gasifier using comingled feedstock containing biosolids and biomass would be the next step towards the commercialization of the CE-CERT technology. The operation of this gasifier will provide the information necessary for the construction of a commercial or near commercial scale facility that produces sustainable synthetic fuels from carbonaceous waste streams.

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