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Publication Date

2009-04-08

Energy Development and Technology 015

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April 2009

This paper is part of the University of California Energy Institute's (UCEI) Energy Policy and Economics Working Paper Series. UCEI is a multi-campus research unit of the University of California located on the Berkeley campus.

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The Potential of Cellulosic Ethanol Production from Municipal solid waste: A Technical and Economic Evaluation

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Abstract

Municipal solid waste (MSW) is an attractive cellulosic resource for sustainable production of transportation fuels and chemicals because of its abundance, the need to find uses for this problematic waste, and its low and perhaps negative cost. However, significant heterogeneity and possible toxic contaminants are barriers to biological conversion to ethanol and other products. In this study, we obtained six fractions of sorted MSW from a waste processing facility in Fontana, California: 1) final alternative daily cover (ADC Final), 2) ADC green, 3) woody waste, 4) grass waste, 5) cardboard, and 6) mixed paper. Application of dilute sulfuric acid pretreatment followed by enzymatic hydrolysis gave the highest sugar yields in cardboard and ADC final fractions at enzyme loadings of 100 mg enzyme protein/g sugars of raw materials. Treatment with our non-catalytic protein detoxification technology before adding enzymes improved sugar yields at low enzyme loading of 10 mg enzyme protein/g (glucan plus xylan) of raw materials. Pretreatment with 1% dilute sulfuric acid for 40 min followed by bovine serum albumin (BSA) supplemented enzymatic hydrolysis at an enzyme loading of 10 mg enzyme protein/g glucan recovered 79.1% of potential glucan and 88.2% of potential xylan in solution from ADC final, and 83.3% of potential glucan and 89.1% of potential xylan from ADC green. Experimental results were incorporated into an economic model to determine the economic feasibility of converting MSW to ethanol and identify opportunities for improving the economics. The minimum ethanol selling price for ADC final and ADC green was estimated as $0.6 per gallon and $0.91 per gallon, respectively.

Keywords: municipal solid wastes, ADC final, ADC green, acid pretreatment, ethanol, lignin blocking, bovine serum albumin, Aspen model

Introduction

Overcoming challenges of food supply, energy supply, and environment protection enables sustainable economic and social development(Lynd et al. 2008). In 2008, the world saw a stifling rise in fossil oil prices. In the United States, gasoline prices hit an all-time national average high, $4.11 per gallon, causing a surge of new research and a new consciousness in regards to the nation's dependence on imported and domestic oil. One of the primary focuses within the U.S. biofuel research community has been on developing the processes that turn various sources of cellulosic biomass into bioethanol as an alternative transportation fuels, replacing gasoline and natural gas. The first generation fuel ethanol is derived from starch and sugar crops, such as corn, sugar cane, respectively. However, the long term availability and sustainability of these crops are questionable due to competition with the world's food and animal feed supply. Thus, the second generation of bioethanol made from cellulosic feedstocks without a food use, namely cellulosic ethanol, has premise for a new industry,

A broad range of lignocellulosic biomass has been considered as cellulosic ethanol feedstocks, including agricultural residues (e.g. corn stover, wheat straw), herbaceous energy crops (e.g. switchgrass, Miscanthus), and short-rotation forest crops (e.g. hybrid poplar and willow). Although conversion of cellulosic biomass to ethanol has been studied for decades, the uncertainty of techno-economic feasibility, particularly at large scale production, prohibits commercialization of such processes. Besides the relatively high cost of some processing stages (i.e. pretreatment and enzymatic hydrolysis), the cost of feedstocks share a large portion of operating costs. The NREL 2002 report projects that for a production scale of 2000 ton of feedstock per day, at $30/ton corn stover, feedstock costs

connect to 31.3% of the overall operating costs (Aden et al. 2002). At a larger scale of 5,000 tons of corn stover per day and a higher corn stover price of $40/ton, feedstock costs were estimated to account for 71.8% of the operating costs with advanced bioconversion processes (Lynd et al. 2005). On the other hand, using seasonally harvested feedstocks, such as agricultural wastes and energy crops, also raises questions of obtaining year-long supply or feedstock storage for large scale production. Therefore, lower feedstock costs along with achieving high yields of ethanol can result in significant improvements in the economics of cellulosic ethanol.

A potentially low cost feedstocks is the municipal solid waste (MSW), but it is much less studied, specially the accurate cost-of-ethanol production data are unavailable (BR&Di 2008). Furthermore, MSW is the single largest source of cellulosic biomass in California. About 51.3% of MSW in California is cellulosic biomass, including construction and demolition wood (urban wood fuel), final alternative daily cover (ADC Final, landfill mulch), ADC green, woody and grass waste, cardboard, mixed paper and other minor biomass materials. The rich carbohydrate compositions of these cellulosic wastes, which amount to about 36.4 million tons per year, can provide a year round supply for ethanol production with zero to negative feedstock cost. Currently, a large portion of MSW is typically disposed of by incineration and/or landfill. However, environmental concerns about both options demand implementing alternative solid waste solutions. Public concerns on air pollution from incineration have halted construction projects of many new incinerators. In addition, the government, in reaction to problems associated with landfills, has mandated recycling to conserve natural resources and arrest of the flow of solid waste

into landfills (Green et al. 1990a; Laughlin et al. 1984; Li et al. 2007; Li and Khraisheh 2008). The 1989 Integrated Waste Management Act mandated local jurisdictions to divert at least 50% of waste from landfill by 2000(CaliforniaEnergyCommission 2007). In 2009, the state of California had not reached this target yet. There are urgent needs to investigate how to turn these solid wastes into beneficial products, especially energy products. MSW-based biofuels can "significantly reduce the greenhouse gas footprint and operating costs over the lifecycle of the biofuels supply chain" [DOE-EPA]. Clearly, MSW is an attractive cellulosic resource for sustainable production of transportation fuels and chemicals because it is an abundant and problematic waste that can be obtained at a low or perhaps negative cost (BR&Di 2008). The challenge is to achieve low cost conversion.

The socioeconomic and environmental benefits of using MSW-derived ethanol continue to motivate great interests in research of process development. In addition, techno-economic evaluation of large scale bioconversion of MSW to ethanol is vital to defining its potential for commercialization. In this study, we investigated several types of MSW, including final alternative daily cover (ADC Final), ADC green, woody waste, grass waste, cardboard, and mixed paper. Most of these cellulose-hemicellulose rich wastes will end up landfilled if not utilized. Pretreatment is applied to break down hemicellulose into sugars and open up the structure of the remaining solids so that enzymes known as cellulases can breakdown the cellulose fraction to glucose with high yields in a subsequent enzymatic hydrolysis operation. Dilute acid pretreatment was employed to reduce the heavy metal content of the cellulosic component of municipal solid waste that can inhibit the following biological processes for ethanol production(Barrier et al. 1991; Johnson and Eley 1992;

Porteous 1972). In a leading application of this technology, the hemicellulose fraction is broken down or hydrolyzed with about 1% sulfuric acid at moderate temperatures of about 140-190^{o}C for times of about 10 to 20 minutes to release the hemicellulose sugars into solution (Lloyd and Wyman 2005; Mosier et al. 2005). Several other pretreatment methods, including alkali (Fontaine-Delcambe et al. 1986; Klee and Rogers 1977) and wet oxidation(Lissens et al. 2004a; Lissens et al. 2004b), were reported previously using MSW as feedstock. Sugars released from cellulose and hemicellulose can be fermented into ethanol. Alternatively, such sugars could be fermented into chemicals such as lactic acid or chemically reacted into products such as levulinic acid (Lloyd and Wyman 2005; Wyman et al. 2005a; Wyman et al. 2005b). The biggest challenge is that a sustainable portion of MSW is un-convertible to ethanol by bioconversion process or toxic to enzymes and microorganisms (Chieffalo and Lightsey 1995; Chieffalo and Lightsey 1996; Grace et al. 1994; Hoge 1982; Lightsey and Chieffalo 1995). This often leads to low digestibility of pretreated solids, high enzyme loadings and/or low fermentability. Questions about suitability of the feedstock and the process can present serious impediments to commercialization of ethanol production from MSW. In addition, the lack of techno-economic information is a major drawback for technology development and applications.

In order to overcome the challenges, we assessed the technical and economic feasibility of converting the cellulosic biomass fraction in California MSW to ethanol at a low cost. Our first objective is to characterize major biomass components in representative sources of California MSW and determine the technical performance for cellulosic ethanol production via applying leading technologies for biomass pretreatment coupled with

enzymatic digestion using our established non-catalytic protein blocking techniques. Based on experimental data, our second objective is to assess the economic feasibility of using California MSW for the production of low cost fuel-grade ethanol at a commercial scale. Previously developed techno-economic models of corn stover ethanol processes were adapted to bioconversion of MSW to ethanol to project production costs and define opportunities for improvement.

Materials and Methods

Feedstock Preparation

Six types of cellulose-rich municipal solid wastes, including final alternative daily cover (ADC Final), ADC green, woody waste, grass waste, cardboard, and mixed paper, were collected from the West Valley Material Recovery Facility and Transfer Station (Fontana, CA) during summer seasons of two consecutive years (July 2007 and August 2008). The Transfer Station serves 3 out of 13 cities in Riverside and San Bernardino County. Upon receipt, MSW samples were cleaned by soaking in DI water, and the top portions were decanted off to leave apparent dirt and rocks on the bottom. The cleaned MSW portions were air dried, milled to pass through a 2 mm screen by a Model 4 Thomas Wiley Laboratory Mill (Thomas Scientific, Philadelphia, PA), mixed well, and stored sealed at -18 ºC until use.

Pretreatment

Prior to pretreatment, MSW samples were presoaked overnight in 1% w/w dilute sulfuric acid solution at room temperature. All pretreatments were conducted in a 1 L Hasteloy Parr reactor with a total reaction volume of 800 ml at 5% dry w/v solid loading.

Biomass slurries were stirred at 200 rpm with two stacked pitched blade impellers (diameter 40 mm). MSW samples were pretreated with 1% w/w H_2SO_4 at 140 °C for 40 min corresponding to a combined severity of 2.1. The combined severity factor ($\log R'_0$) is defined by the following as a function of the pretreatment temperature T (°C), pretreatment time t (min), and pH value:

$$\log R'_0 = \log(t \cdot e^{\frac{T-100}{14.75}}) - pH \qquad (1)$$

The reactor was heated to reaction temperature using two sand baths: the first set to temperature of 320 °C for rapid heat up to the target temperature, and the second set at a 2 °C higher than the target temperature to maintain the pretreated temperature. The heat up time for this system varied between 1 to 3 min and was not included in the stated reaction times or the severity calculation. The temperature was measured inside the reactor using a Type K thermocouple. After pretreatment, the reactor was submerged in a room temperature water bath until the temperature dropped to 80 °C (the cooling time is around 2 min). The slurry was filtered immediately afterwards with the temperature being always higher than 60 °C. Pretreated solids were washed with 1.5 L DI water at room temperature (Yang and Wyman 2002).

Analytical Methods

Total solids, ash, acid insoluble lignin and carbohydrate (glucan and xylan etc.) contents of untreated and pretreated MSW fractions were determined following NREL Laboratory Analytical Procedures, LAP 001, LAP 003, LAP 004 (Ehrman 1996; Ehrman 1994a; Ehrman 1994b; Templeton and Ehrman 1995). Solid recovery was calculated as a

percentage of the total solids recovered after pretreatment based on the initial sample dry weight. The liquid hydrolyzate from pretreatment was analyzed for glucose and xylose using an HPLC equipped with an Aminex HPX-H column (#125-0140, 300 x 7.8 mm) and de-ashing cartridges (#125-0119, Bio-Rad Labs, Richmond, CA, USA) after neutralization with calcium carbonate. Liquid hydrolyzate samples were post-hydrolyzed according to the NREL LAPs and then analyzed by HPLC to determine oligomeric sugar content (NREL 2004).

Enzymatic Hydrolysis

Enzymatic hydrolysis experiments were conducted in triplicates by following a modified NREL LAPs (#9, Enzymatic Saccharification of Lignocellulosic Biomass) at 1% w/w cellulose loading under NREL standard conditions (50°C, 0.05 M citrate buffer, pH 4.75) (NREL 2004). A mixture of Spezyme CP (Genencor Inc, Palo Alto, CA) and Novozyme 188 (Novozymes Inc., Davis, CA) (1: 0.08 v/v) was used for all hydrolysis experiments unless otherwise specified. The mixture had a protein content of 116.7 mg/mL, cellulase activity of 57 FBU/mL, and β-glucosidase activity of 49 CBU/mL. Hydrolysis samples were taken at 0hr, 24 hr, 72 hr, and 168 hr. Sugar concentrations were measured by HPLC as described above (NREL 2004).

Glucan-to-glucose and xylan-to-xylose hydrolysis yields were defined as shown in Eqs 2-3, where 1.111 and 1.136 are the conversion factors from glucan to glucose and xylan to xylose, respectively.

$$\%\ \text{glucan-to-glucose hydrolysis yield} = \frac{GH/1.111}{GP} \times 100 \qquad (2)$$

where: GH -- glucose released in enzymatic hydrolyzate;
GP -- glucan available in pretreated solid.

$$\% \text{ Xylan-to-xylose hydrolysis yield} = \frac{XH/1.136}{XP} \times 100 \quad (3)$$

where: XH -- xylose released in enzymatic hydrolyzate;
XP -- xylan available in pretreated solid.

Thus, the total hydrolysis yield was defined in Eq. 4.

$$\% \text{ total hydrolysis yield} = \frac{GH/1.111 + XH/1.136}{GP + XP} \times 100 \quad (4)$$

As an initial evaluation, digestibility of various pretreated MSW, including final alternative daily cover (ADC Final), ADC green, woody waste, grass waste, cardboard, and mixed paper, were investigate at very high enzyme loadings of 100 mg protein/g (total glucan and xylan in the raw biomass).The effect of enzyme loading on digestibility of ADC final and ADC green were further investigated at enzyme loadings of 5-100 mg Novozyme 188 + Spezyme CP protein/g total glucan and xylan in the raw biomass. In addition, supplementation with β-glucosidase during enzymatic hydrolysis of ADC final and ADC green was investigated at levels of 0.08-0.32 v /v (Novozyme 188 to Spezyme CP) at a fixed Spezyme CP loading of 10 mg/g total glucan and xylan in the raw biomass and at a fixed total enzyme protein loading of 10 mg/g total glucan and xylan in the raw biomass.

BSA Treatment Prior to Enzymatic Hydrolysis

In order to test the effectiveness of protein detoxification, the non-catalytic protein bovine serum albumin (BSA) was added to pretreated ADC final and ADC green at different levels (0.2-5% w/v) and incubated for 24 hr before adding enzymes. The

digestibility (glucan to glucose conversion, %) was compared with results without BSA addition at low to high enzyme loadings.

Experimental Design and Statistical Analysis

Data reported are average of duplicate or triplicate runs. A 95% confidence level was used for statistical analysis and assessing statistical differences between treatments.

Results and Discussions

Cellulosic MSW Feedstocks

Municipal solid waste (MSW), more commonly known as trash or garbage is also called urban solid waste. It includes predominantly household waste (domestic waste) with sometimes the addition of commercial wastes, generally excluding industrial hazardous wastes. MSW can be categorized into five groups: 1) biodegradable waste, such as food and kitchen waste, green waste, paper; 2) recyclable material, such as paper, glass, bottles, cans, metals, certain plastics, etc.; 3) inert waste such as construction and demolition waste, dirt, rocks, debris; 4) composite wastes such as waste clothing, Tetra Paks, and waste plastics such as toys; 5) domestic hazardous waste (also called "household hazardous waste") & toxic waste, such as medication, e-waste, paints, chemicals, light bulbs, fluorescent tubes, spray cans, fertilizer and pesticide containers, batteries, and shoe polish. As a large source of waste, MSW is currently managed through a coordinated mix of practices that include source reduction, recycling (including composting), and disposal (http://www.ciwmb.ca.gov).

The first task of our project was to search for low cost MSW rich in cellulose and/or hemicellulose that would be desirable for ethanol production. On-site investigation was conducted at the West Valley MRF and Transfer Station (Fontana, CA), which is operated by Burrtec. This transfer station serves 3 out of 13 cities in Riverside and San Bernardino County, California. MSW from different garbage bins is sorted into various fractions, which are then sent to combustors, landfills, farms or other composing facilities, or exported to other countries.

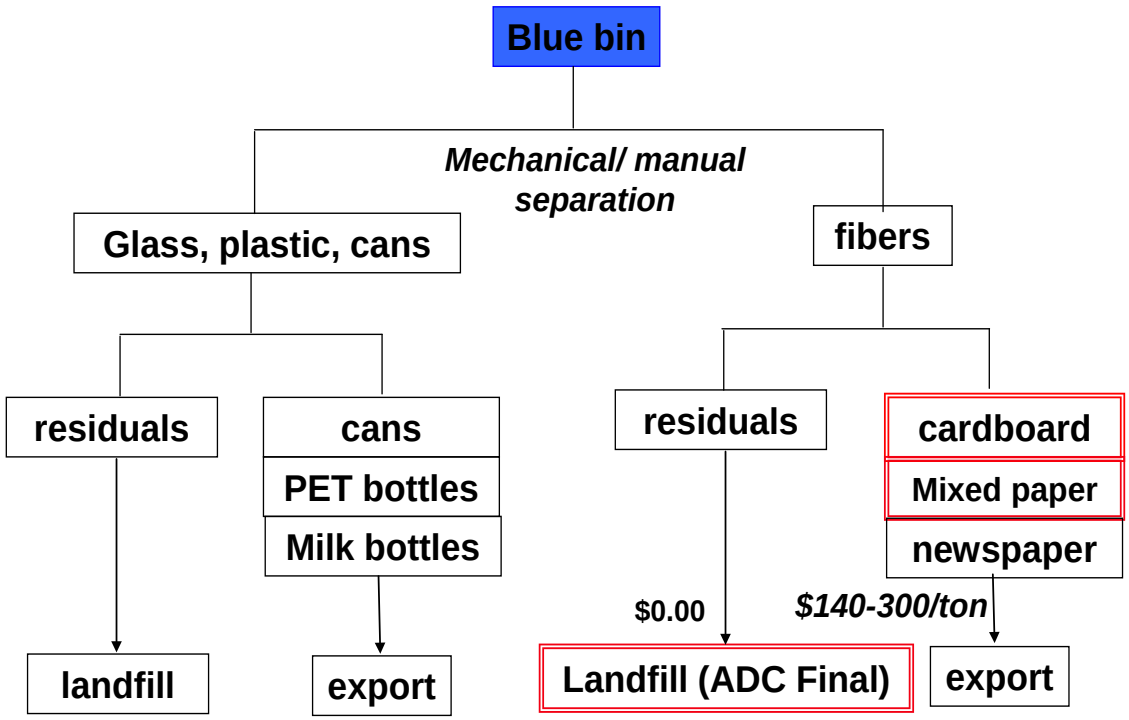

Figure 1 MSW from blue bins

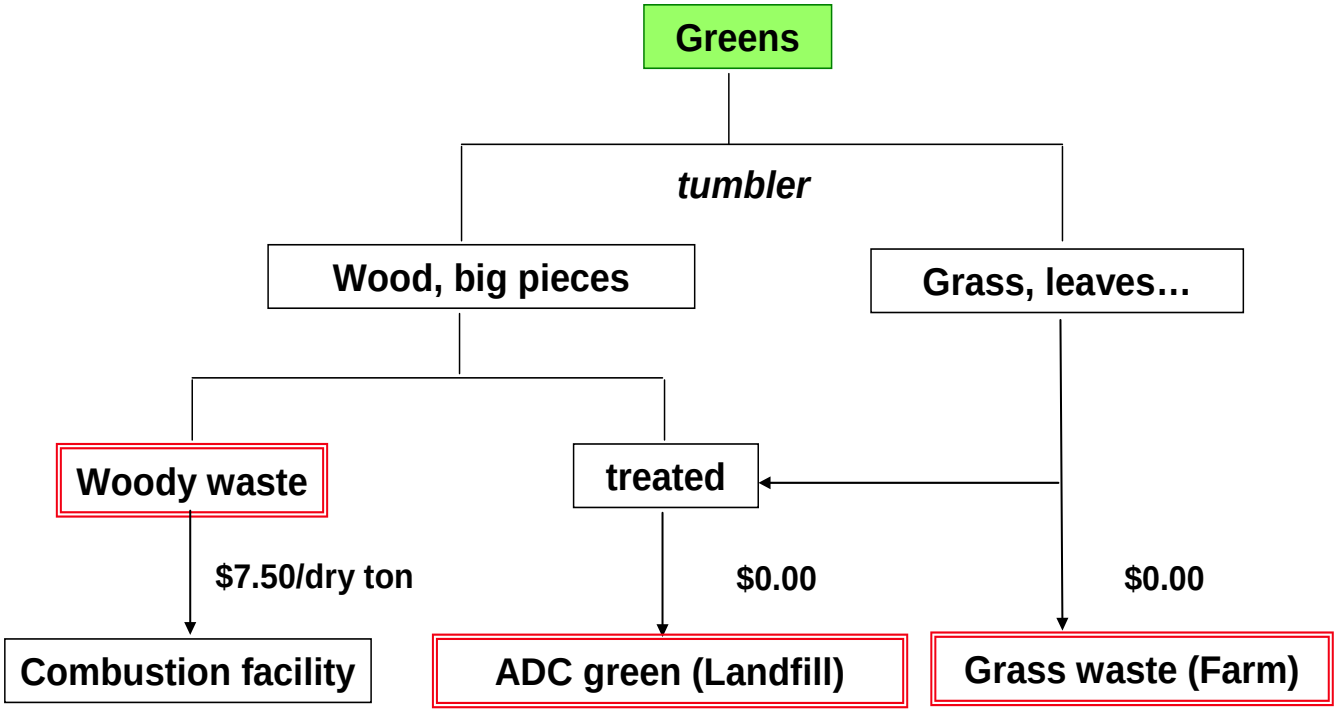

Figure 2 MSW from green bins

In the West Valley MRF and Transfer Station alone, the daily amount of MSW collected from different bins is as high as about 400 tons from blue bins, about 2000 tons from black bins, and 700 tons from green bins. MSW from blue bins contains recyclables, such as paper, cardboard, plastic, glass and cans, while that from green bins contains grass and woody wastes. Comparing with MSW from black bins, which contains un-sorted residential and commercial wastes, MSW from blue and green bins are more readily for bioconversion to fuel ethanol because it not only contains cellulose and hemicellulose rich materials but also requires less labor and operations to prepare fuel ethanol feedstocks. Certainly, with additional mechanical and manual operation, more cellulosic materials can be recovered from black bin wastes. Figures 1 and 2 show how wastes from blue and green

bins are separated, recycled, and disposed of. For this project, we considered further investigation of six MSW fractions, including mixed paper, cardboard, ADC final, woody waste, ADC green, and grass wastes. Among these fractions, ADC final and ADC green are the fractions that will be sent to landfills with the median average tipping fee of $36 if not utilized. According to California regulations, ADC final and ADC green will be prohibited from landfills in the near future. Besides ADC final and ADC green, woody wastes and grass wastes are also low cost cellulose-rich materials, with prices of $7.5/ton and zero, respectively. Although cellulose-rich materials, such as cardboard and mixed paper, can be sold at higher prices of $140-300/ton, huge amounts of such goods were returned by overseas buyers and had to be landfilled due to the global economic crisis in the last year. Thus, conversion of cardboard and mixed paper to fuel ethanol may become a promising option that can not only reduce environmental pressure on landfills but also contribute to the profit for the waste industry in difficult times.

Compositions of raw MSW fractions

In this study, we chosed various types of MSW, including mixed paper, cardboard, ADC final, woody waste, ADC green, and grass wastes, as described above. The carbohydrate portions, mainly glucan and xylan, of MSW can be potentially converted to ethanol through enzymatic saccharification and fermentation using existing technologies. Therefore, we first examined the availability of glucan and xylan in six collected raw MSW fractions through compositional analysis (Table 1). Mixed paper contained the most abundant glucan, about 64.1%, followed by cardboard, ADC final, woody waste, ADC green, where grass wastes contained the least glucan at ~20.9%. Hemicellulose, the second abundant polysaccharide in plant cell wall, usually constitutes about 20-35% of the plant materials (Wyman et al.

2005c). However, the xylan content of collected MSW fractions was only about 5-10%. The amount of other carbohydrates, such as mannan, arabinan and galactan, was negligible. Lignin, which strengthens cellulosis biomass structure by holding cellulose and hemicellulose together (Ragauskas et al. 2006) has been posed as an obstacle during enzymatic hydrolysis of cellulosic biomass. Lignin contents of most collected MSW fractions were comparable to typical agricultural and forest cellulosic biomass, mostly falling into a range of 15-30%, except that ADC final and mixed paper had much lower lignin content of 2.9 and 12.2%, respectively, probably due to lignin removal during paper pulping. The ash contents also varied from only 3% in mixed paper and to 28% in grass wastes. This study also showed that a significant portion of the waste feedstock (from 25 to 36%) was unknown impurities, such as plastics, organic matter, or other contaminants. The significant heterogeneity and possible toxic contaminants could be main barriers to biological conversion of MSW to ethanol.

Based on the compositional analysis, it was estimated that 44.9 to 128.3 gal ethanol per dry ton MSW could be potentially produced (Table 1). It indicated that there are sufficient resources from MSW to derive fuel ethanol even though the theoretical ethanol yields of five out of six MSW fractions are basically lower than that of corn stover, which is 112.7 gal ethanol per dry ton (Aden et al. 2002). The theoretical ethanol yields of ADC final, cardboard and mixed paper were close or even higher than that of corn stover. Meanwhile, unlike general biomass feedstocks, such as agricultural wastes and forestry wastes, the dominant carbohydrate in these MSWs is glucan with relatively low content of xylan. Because glucose is more readily fermented by regular yeasts with high yield and

feestock cost save low, these MSW fractions are good candidates for fuel ethanol production.

Table 1 Compositions and theorectical ethanol yield of raw MSW fractions*

Components	ADC final	Grass wastes	Woody wastes	ADC green	Card-board	Mixed paper
Glucan, %dw	48.7	20.9	33.3	24.6	48.8	64.1
Xylan, %dw	6.8	5.0	7.5	7.4	8.5	9.9
Lignin, %dw	12.2	20.1	28.2	25.2	15.3	2.9
Ash, % dw	10.0	28.0	6.5	12.5	2.6	3.0
Other, %dw	22.3	36.0	24.5	30.3	24.8	25.2
ethanol yield, gal/dry ton#	96.2	44.9	70.8	55.6	99.3	128.3

* Data shown are means of triplicate runs.
# Date based on NREL Theoretical Ethanol Yield Calculator through link: http://www1.eere.energy.gov/biomass/ethanol_yield_calculator.html.

Dilute acid pretreatment of MSW

Bioconversion of lignocellulosic biomass has been proved to be highly efficient with high yields and low by-products (Wyman 2003). Catalyzed or un-catalyzed (water-only) pretreatment of lignocellulosic biomass is a vital step to disintegrate the cell wall structure and enhance the susceptibility to cellulase enzymes (Himmel 2007; Yang and Wyman 2008). An important goal of pretreatment is to increase the surface area of lignocellulosic material, making the polysaccharides more susceptible to enzymatic hydrolysis. Along with an increase in surface area, pretreatment effectiveness and hydrolysis improvement has been correlated with removal of hemicellulose and lignin and the reduction of cellulose cyrstallinity (Yang and Wyman 2008).

In this study, we investigated one of the most promising pretreatment techniques, dilute sulfuric acid pretreatment, which has shown high yields for various lignocellulosic feedstocks (e.g. corn stover). Results shown in Table 2 summarized the effect of dilute sulfuric acid pretreatment on MSW feedstocks. Dilute acid pretreatment of MSW left most of the glucan from raw MSW. In the solids about 12 - 84% of the original xylan was released in the liquid hydrolyzate ready for fermentation to ethanol. Thus, the solids contained a much lower xylan content of 3.5 and 1.1 % for woody waste and ADC green, respectively. Xylan losses were minor for all MSW but varied with types of MSW over a range of 0-10%. The solubilization of minerals from the total ash (acid soluble ash) observed by the added acid during pretreatment can mitigate inhibition or toxicity to enzymatic hydrolysis. Furthermore, elimination of other impurities during the course of pretreatment was substantial (Ackerson et al. 1991; Green et al. 1990b). More than one third of the impurities were removed from ADC green and mixed paper. Thus, large amount of impurities in raw ADC final, grass waste, woody waste and cardboard was removed after pretreatment probably because of the solubilization of organics in pretreatment filtrate.

Table 2 Dilute acid pretreatment of MSW [@]

	ADC final	Grass wastes	Woody wastes	ADC green	Card-board	Mixed paper
Solid						
Solid Recovered, %	74.5	62.1	70.5	58.4	78.4	84.2
Glucan, %dw	56.2	22.7	47.2	36	59.2	72
Xylan, %dw	4.7	6.8	5	1.9	9.4	6.9
Lignin, %dw	18.6	24.3	40.9	28.3	25	0.7
Ash, % dw	11.5	32.9	6.2	10.8	2	3.3
Other, %dw	8.9	13.2	6.8	24.8	4.5	16.9
Overall						
Xylan removal, % *	48.5	16	50	85	12.9	41.4
Lignin removal, %*	-	24.9	-	34.5	-	79.3

Ash removal, %*	14	27.1	32.3	49.6	38.5	6.7
Others removal, %*	70.4	77.2	80.4	52.1	85.9	43.7
Xylan recovery, %#	102.9	96.0	98.7	97.3	92.9	89.9
Glucan recovery, %#	93.2	90.9	103.0	93.4	98.0	101.2

* On basis of original xylan and glucan content of raw MSW;

Recovered in pretreated solid and liquid, on basis of original xylan and glucan content of raw MSW

@ Pretreatment conditions: 1.0% w/w dilute sulfuric acid pretreatment at 140 ºC for 40 min.

Digestibility of pretreated MSW fractions

The effectiveness of pretreatment was further evaluated in terms of enzymatic digestibility of the pretreated biomass solids. Figure 1 illustrates the glucan-to-glucose conversion after enzymatic hydrolysis of pretreated MSW fractions at low and high enzyme loadings of 10 and 100 mg enzyme protein/g glucan plus xylan (G+X) in raw MSW. It was shown that desirable glucan-to-glucose yields (>80%) were achieved for cardboard, ADC final, mixed paper, and ADC green in decreasing order at a high enzyme loading of 100 mg/g (G+X in raw biomass). The digestibility of pretreated grass and woody wastes was 64.7 and 63.5%, respectively, too low for low cost ethanol production. As shown in compositional analysis, woody wastes, possibly containing softwood, had the highest lignin content of 29%, and may require much more severe pretreatment to achieve desirable enzymatic hydrolysis yields. Higher temperatures and acid concentrations or even post-treatment could be employed to ensure good enzymatic digestibility as shown by many studies elsewhere (Yang et al. 2002). The most plausible cause of low digestibility of grass waste is its high ash content (~28%), especially its over 10% acid soluble ash, which could neutralize the sulfuric acid used for pretreatment and reduce its effectiveness. Lloyd and Wyman found that mineral neutralization posed more pronounced due to bisulfate formation beyond pH drop. Mineral removal prior to pretreatment or addition acid is needed to achieve a particular pretreatment effectiveness (Lloyd Todd and Wyman Charles

2004). Unfortunately, due to limitations in time and budget for this project, we were not able to optimize pretreatment conditions for woody and grass wastes.

Cost effective enzymatic hydrolysis is the key for development of economically viable biological processes for lignocellulosic biomass to ethanol conversion. Due to the high cost of cellulases, cellulase enzymes use must be minimized. For example, typical cellulase loading of about 15 FPU/g cellulose in pretreated biomass translates into about 0.25 lbs of enzymes per gallon of ethanol made, an extremely high dosage. Thus, enzyme costs must be either reduced below about $1/lb or strategies are needed to substantially reduce loadings (Wyman 2007). To meet this requirement, pretreated MSW fractions were hydrolyzed at a low enzyme loading of 10 mg/g (G+X in raw MSW) but for longer duration of 168 hours. This enzyme loading, which is equivalent to about 7-10 FPU/g cellulose, is much lower than the previously reported low enzyme loadings (Wyman et al. 2005a). As shown in Figure 1, the overall digestibility of cardboard, ADC final and mixed paper were about 80% at the low enzyme loading. However, the digestibility of ADC green decreased dramatically from 80% at 100 mg/g (G+X in raw) enzyme loading to 36% at 10 mg/g (G+X in raw) enzyme loading. The high lignin content and other impurities in pretreated ADC green are the most plausible barriers to enzymatic digestion of cellulose at low enzyme loadings. Meanwhile, the glucan-to-glucose yields of woody and grass wastes also dropped significantly to about 38% when the enzyme loading was lowered to 10 mg/g (G+X in raw). Further investigation is needed to reach economically feasible cellulose hydrolysis yields at low enzyme loadings.

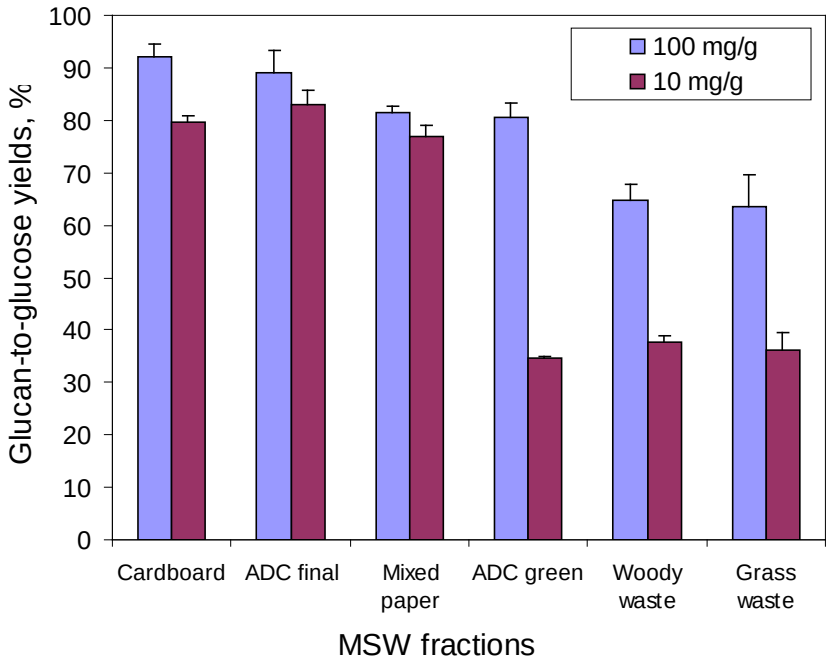

Figure 3 Enzymatic digestibility of pretreated MSW features at different enzyme loadings

Conditions: enzyme loading of 10 mg/g glucan plus xylan in raw MSW after 168 hr of hydrolysis and 100 mg/g glucan plus xylan in raw MSW after 72 hr hydrolysis.

Effects of BSA treatment and enzyme loadings on digestibility

To overcome the challenge of achieving high sugar yields from pretreated MSW at low enzyme loadings, a lignin-blocking technique (Yang and Wyman 2006), in which bovine serum albumin (BSA) and other non-catalytic proteins were used to block non-productive adsorption of cellulases during enzymatic hydrolysis, was evaluated in this study. BSA and/or other non-catalytic proteins were added prior to enzyme addition to competitively and irreversibly adsorb on lignin and other impurities, resulting in improving the effectiveness of enzymatic hydrolysis of cellulose in pretreated lignocellulosic biomass. In addition to blocking non-specific binding of cellulases, BSA or other proteins may also help stabilize enzymes during the course of hydrolysis and reduce possible inhibition by

other impurities in pretreated MSW (Yang and Wyman 2006). As shown in Table 3, pre-incubation of pretreated MSW with BSA positively augmented the performance of enzymatic hydrolysis by ~5-50% at even lower enzyme loadings of 5 mg/g (G+X in raw). These results showed that cellulose hydrolysis was improved significantly by over 20-50% for those pretreated MSW fractions that had lower glucan-to-glucose conversion at low enzyme loading before, such as ADC green and grass wastes although mild improvement of 12.2% was observed with pretreated woody wastes. For pretreated MSW that showed relatively high cellulose conversion at low enzyme loading without BSA treatment, small to mild improvements of just 5-17% were achieved with BSA treatment. It suggested that such non-catalytic protein treatment was most effective with substrates, in which enzymatic hydrolysis of cellulose was suppressed by non-productive binding on lignin and/or other impurities with chemical linkage and/or physical force (patent application in progress).

Table 3 Effect of BSA addition on cellulose conversion at low enzyme loading

MSW fractions	Digestibility increment*, %
ADC final	17.2
ADC green	52.9
Grass wastes	26.6
Woody wastes	12.2
Cardboard	5.8
Mixed paper	4.7

* Increment of glucan-to-glucose yield at 5 mg/g (G+X in raw) enzyme loading

To further investigate the relationship between the effectiveness of BSA treatment and enzyme loading, ADC green and ADC final were presoaked with 0.5% wt/v BSA and hydrolyzed at 5-100 mg/g (G+X in raw) enzyme loadings. Figure 4 showed the effect of BSA treatment (0.5% wt/v) on digestibility at low to high enzyme loadings. The most significant improvement was seen with pretreated ADC green waste. Hydrolysis yield

increased by about 50% compared to that without BSA treatment at 5-10 mg/g (G+X in raw) enzyme loadings for ADC green. By supplementing BSA, similar digestibility of 80% could be achieved with ten-fold lower enzyme loading of 10 mg/g (G+X in raw) comparing with that at high enzyme loading of 100 mg/g (G+X in raw) without BSA treatment. These results indicated that employment of lignin blocking technology improved conversion yield and lower process costs by significantly reducing enzyme usage. As for ADC final, the positive effect of BSA treatment was obvious at a very low enzyme loading of 5 mg/g (G+X in raw) while the increases of digestibility were negligible at higher enzyme loadings. The different effect of BSA treatment on enzymatic hydrolysis of pretreated ADC final and ADC green was correlated with much lower lignin and other impurities in ADC final than in ADC green (Table 2). For both pretreated substrates, BSA treatment was more effective at low enzyme loadings. Further investigation showed that BSA loading could be lowered from 0.5% wt/v to 0.2% wt/v hydrolysis solution (equivalent to ~20% wt/wt glucan in pretreated solids) resulting in the same glucose yield during enzymatic hydrolysis of ADC green. Results indicated that very high BSA loading of over 1% w/v actually decreased digestibility of pretreated ADC green and ADC final (Figure 5).

In summary, without BSA treatment, cellulose hydrolysis yields for pretreated ADC final at 10 mg/g (G+X in raw) enzyme loading could reach to 71% at 72 hr and 83% at 168 hr enzymatic hydrolysis, respectively. For ADC green with BSA treatment, the cellulose hydrolysis yield was 79% at 72 hr and 88% at 168 hr of enzymatic hydrolysis, respectively.

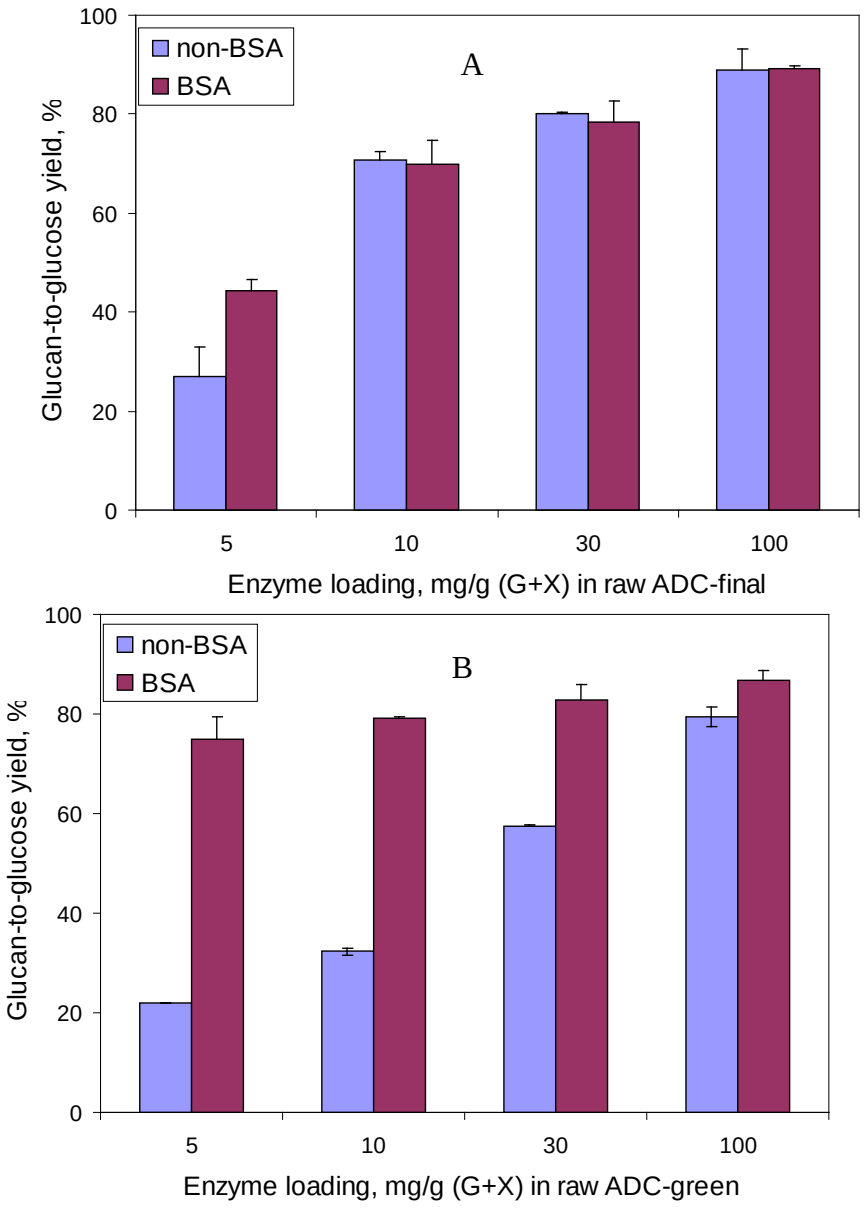

Figure 4. Effect of 0.5% wt/v BSA treatment on digestibility at 72 hr hydrolysis

5-100 mg/g (G+X in raw) enzyme loadings; ADC final (A); and ADC green (B)

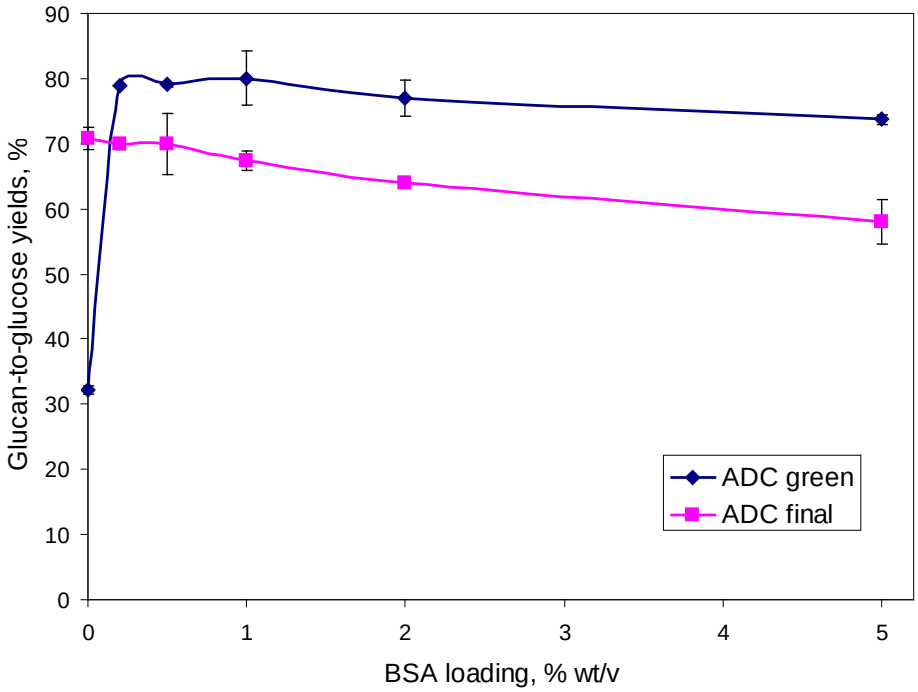

Figure 5 Effect of BSA loading on 72 hr digestibility of MSW

10 mg/g (G+X in raw) enzyme loading

Sugar release summary at optimal conditions

Sugar yields from ADC final and ADC green under optimal pretreatment and enzymatic hydrolysis conditions were illustrated in Figures 6 and Figure 7, respectively. 38.5 kg glucan and 6.0 kg xylan equivalent sugars (about 79% and 88% of the maximal available glucan and xylan, respectively) could be recovered from 100 kg of ADC final in liquid streams through pretreatment at 140°C with 1% w/w dilute sulfuric acid for 40 min followed by enzymatic hydrolysis with 0.6 kg cellulase proteins. For ADC green with BSA treatment prior to enzymatic hydrolysis, 20.5 kg glucan equivalent sugars and 6.6 kg xylan equivalent sugars (about 83% and 89% of the maximal available glucan and xylan, respectively) could be recovered from 100 kg raw materials in liquid streams through

pretreatment at 140°C with 1% w/w dilute sulfuric acid for 40 min followed by enzymatic hydrolysis with about 0.3 kg cellulase proteins and 4.2 kg BSA protein.

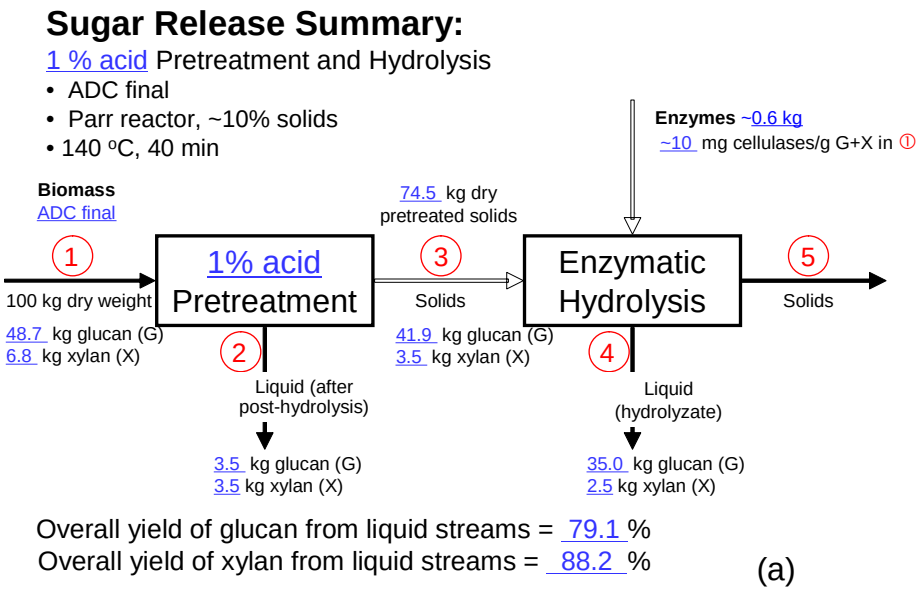

Figure 6 Sugar release summary for ADC final under optimal conditions

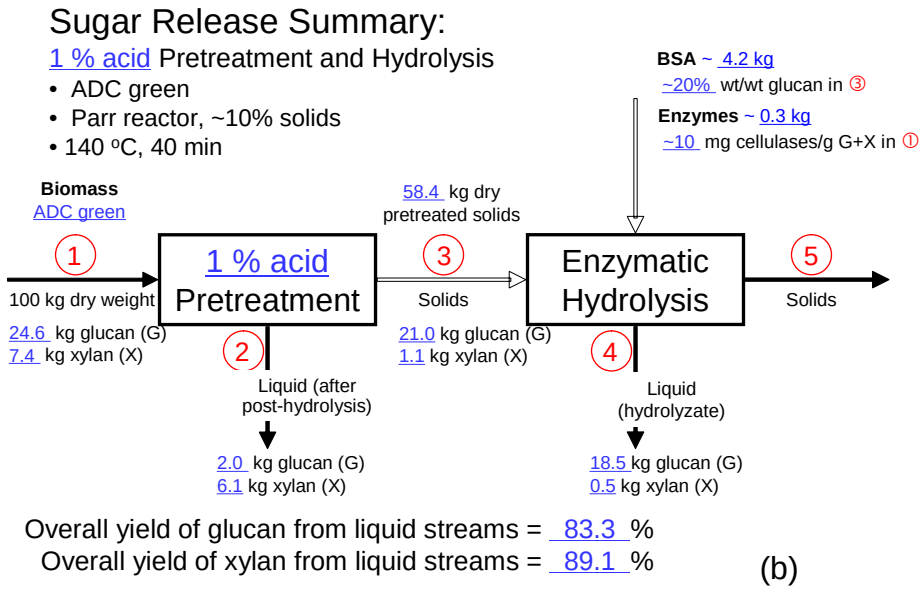

Figure 7 Sugar release summary for ADC green under optimal conditions

Economic analysis of ethanol production from MSW

The lab research results indicated that low cost ADC final and ADC green were among the best feedstocks for fuel ethanol production because of high sugar yields at low enzyme loadings. In order to evaluate the techno-economic feasibility of MSW (e.g. ADC final and ADC green) bioconversion to fuel ethanol, preliminary process design and economic analysis were conducted using Aspen Plus software based on NREL corn stover economic models (Aden et al. 2002) but using the experimental data from this study.

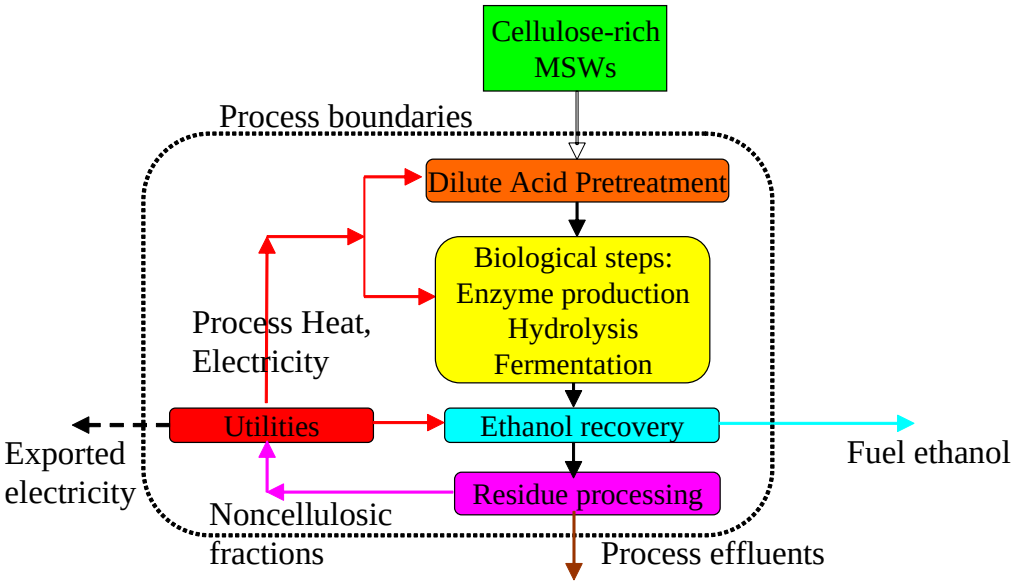

Figure 8 Bioconversion process of MSW to fuel ethanol

Based on the NREL process design, sugars (i.e. glucose and xylose) derived from cellulose-rich MSW by pretreatment and sequential enzymatic hydrolysis are co-fermented to ethanol by the recombinant *Z. mobilis* bacterium as shown in Figure 8. After ethanol recovery, the solid residue is fed to combustors to generate heat and electricity to supply energy for operation with excess electricity sold to the grid. Our process design scale with the daily feedstock loading was 1400 tons/day for 8406 operating hours per year (personal communication with Mr. Paul W. Alford from Tempico, Inc). Besides adapting of raw and

pretreated MSW compositions into the corn stover model, other major changes of process design parameters are shown in Table 3. Compared with the NREL corn stover design case, the MSW process was designed with 1% (w/w) acid concentration and similar glucan yield at the pretreatment step but lower xylan yield. At the enzymatic hydrolysis step, lower enzyme loading and lower cellulose conversion were used for MSW cases. The co-fermentation parameters were kept the same as those in the corn stover design. The overall xylan yields from pretreatment plus sequential enzymatic hydrolysis of MSW cases were slightly lower than that in the corn stover case. The heating value of MSW was estimated according to its element compositions as reported on Phyllis database (http://www.ecn.nl/phyllis/). Other design parameters of waste treatment (e.g. waste water treatment, solid waste combustion) were kept the same as those in the corn stover model.

Table 3 Comparison of process design parameters

	ADC final	ADC green	Corn stover
Pretreatment			
Acid concentration, %	1	1	1.1
Temperature, °C	140	140	190
Glucan yield, %	7.2	8.1	7
Xylan yield, %	51.5	82	90
Enzymatic hydrolysis			
Cellulase loading, FPU/g cellulose	7	7	12
Cellulose conversion, %	83	88	90
Co-Fermentation			
Glucose-ethanol yield, %	90	90	90
Xylose-ethanol yield, %	80	80	80
Overall xylan yield, %	88	89	92

After process design and simulation model using Aspen, the cost of fuel ethanol production from MSW was estimated to determine the economics of such process and compared with that of the corn stover process. Table 4 summarizes the total project investment for MSW conversion. The total project investment was based on the total

equipment cost, calculated using the ASPEN simulation. The total project investment was $172.3 MM and $166.6 MM for ADC final and ADC green, respectively, which were 13.1% and 16% lower than for the corn stover case, respectively.

Table 4 Comparison of Capital cost ($MM)

Feedstock	Corn stover	ADC final	ADC green
Feed Handling	7.5	5.9	5.9
Pretreatment	19.0	14.9	14.9
Neutralization/Conditioning	7.9	6.5	5.9
Saccharification & Fermentation	9.4	7.8	6.4
Distillation and Solids Recovery	21.9	17.3	15.3
Wastewater Treatment	3.1	1.9	2.5
Storage	2.0	1.4	1.1
Boiler/Turbogenerator	38.6	39.6	40.2
Utilities	4.6	4.3	4.2
Total Installed Equipment Cost	114.1	99.6	96.5
Added Costs (42% of TPI)	84.1	72.7	70.0
Total Project Investment	198.2	172.3	166.5

Operating costs were calculated in terms of variable and fixed operating costs. With regards to feedstock (i.e. ADC final and ADC green) costs, we considered using the median tipping fee for compacted solid waste of $36 in California (www. Ciwmb.ca.gov). The average tipping fee, which is paid for landfills of MSW, ranges from $2 to $85 in California in 2008. Unlike the corn stover case, for which the feedstock cost of corn stover was estimated at $30/dry ton, using MSW as feedstock to produce ethanol costs zero or even negatively. Table 5 and Table 6 summarized operating costs on basis of dollars/year and cents/gallon ethanol, respectively. These results show that using MSW as a feedstock resulted in credits of 50.4 cents/gal ethanol and 92.5 cents/gal ethanol for ADC final and ADC green, respectively. Feedstock credits for the MSW process could amount to $17.2 MM per year while using corn stover could cost $23.2 MM per year, which was equivalent to 33.4 cents/gal ethanol. It indicated that the MSW process could provide huge economic

benefits for large scale production in terms of feedstock costs. Cellulase costs for the MSW process, which were $4.2 and $2.1 MM per year for ADC final and ADC green, respectively, were estimated to be lower than that of corn stover process, although cellulase costs contributed more on the basis of amount of ethanol produced. Because MSW in the design case contained relatively high contents of lignin and other impurities, electricity credits, which were derived from processing residues, were estimated to be greater than for corn stover. Electricity credits significantly lowered MSW-to-ethanol operating costs. An average of 43.3 cents and 77.4 cents could be returned on investment per gallon ethanol produced using ADC final and ADC green, respectively. The average return on investment of per gallon ethanol produced was 71.3% and 203% higher for ADC final and ADC green, respectively, than using corn stover although the annual amount of average return on investment for the MSW process was lower than for corn stover due to lower annual production of ethanol.

Table 5 Comparison of operating costs ($/yr)

Feedstock	Corn stover	ADC final	ADC green
Feedstock cost	$23,200,000	-$17,200,000	-$17,200,000
Biomass to Boiler	$0	$0	$0
CSL	$1,900,000	$1,400,000	$1,400,000
Cellulase	$6,800,000	$4,200,000	$2,100,000
Other Raw Matl. Costs	$4,000,000	$2,700,000	$2,900,000
Waste Disposal	$2,500,000	$2,100,000	$2,400,000
Electricity	-$6,100,000	-$10,000,000	-$11,000,000
Fixed Costs	$7,700,000	$7,300,000	$7,200,000
Capital Depreciation	$9,900,000	$8,600,000	$8,300,000
Average Income Tax	$7,400,000	$6,500,000	$6,400,000
Average Return on Investment	$17,700,000	$14,900,000	$14,400,000

Table 6 Comparison of operating costs (cents/gal ethanol)

Feedstock	Corn stover	ADC final	ADC green
Feedstock cost	33.4	-50.4	-92.5
Biomass to Boiler	0.0	0.0	0.0
CSL	2.8	4.0	7.6
Cellulase	9.9	12.4	11.5
Other Raw Materials	5.7	8.0	15.6
Waste Disposal	3.5	6.1	12.8
Electricity	-8.7	-29.4	-59.0
Fixed Costs	11.2	21.4	38.6
Capital Depreciation	14.3	25.3	44.7
Average Income Tax	10.6	19.1	34.2
Average Return on Investment	25.5	43.7	77.4

With the total project investment, variable operating costs and fixed operating costs, a discounted cash flow analysis was used to determine the minimal ethanol selling price when the net present value of the project was set to zero with a 10% discounted cash flow rate of return over a 20 year plant life. The discounted rate, depreciation method, income tax rates, plant life, and construction start-up duration were specified as described in the NREL report (Aden et al. 2002). These results showed that the minimum ethanol selling price was reduced significantly to $0.6/gallon ethanol when using ADC final as feedstock while using ADC green resulted in similar minimum ethanol selling price $0.91/gallon ethanol as using corn stover, which was estimated as $1.08/gallon ethanol (Table 7). As summarized in Table 7, the annual ethanol production was 34 and 18.6 MM gallon for ADC final and ADC green, which was lower than that of 69.3 MM gallon for corn stover due to smaller operation scale and lower yields of MSW.

Table 7 Summary of overall process

Feedstock	Corn stover	ADC final	ADC green
Minimum Ethanol Selling Price, $/gal	1.08	0.60	0.91
Ethanol Production (MM Gal. / Year)	69.3	34.0	18.6
Ethanol Yield (Gal / Dry US Ton Feedstock)	89.8	69.4	37.9
Feedstock Cost $/Dry US Ton	30	-36	-36
Maximum Yields (100% of Theoretical)			
Ethanol Production (MM Gal/yr)	87.0	46.9	27.1
Theoretical Yield (Gal/ton)	112.7	95.7	55.3
Current Yield (Actual/Theoretical)	0.80	0.73	0.68

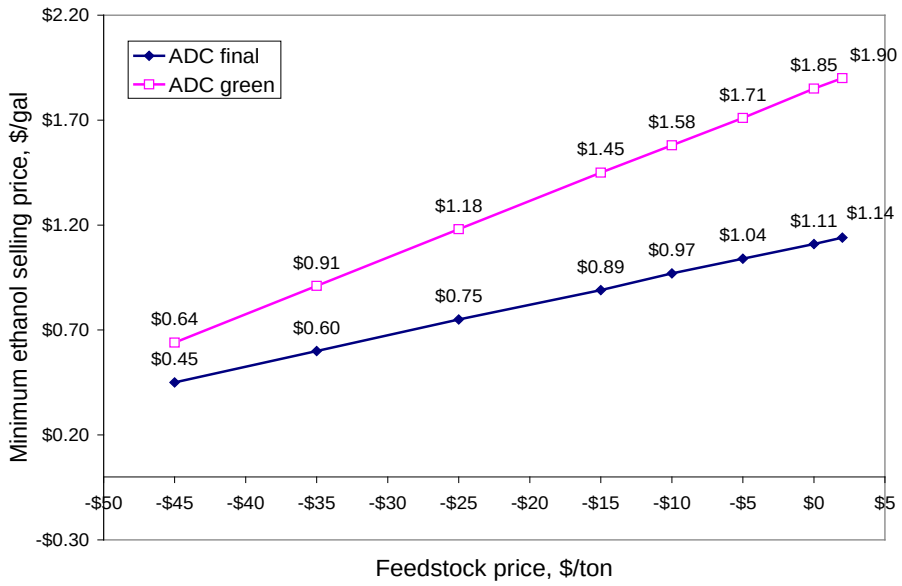

Figure 9. The sensitivity analysis by feedstock cost impact on minimum ethanol selling price

Although the techno-economic assessment of MSW-to-ethanol bioconversion provided promising results, with the limited time and budget for this project, we did not have the chance to determine the real value of important MSW feedstock costs or credits by taking into account of other factors besides tipping fee, such as collecting and transportation costs. Therefore, we conducted a sensitivity analysis of feedstock cost impact on minimum ethanol selling price over a range of feedstock costs from $-45 to $2 per ton. The results showed that feedstock costs had more impact on minimum ethanol selling price when using ADC green as a feedstock than using ADC final (Figure 9). The minimum ethanol selling price was $0.45-$1.14/gal ethanol and $0.64-$1.90 per gallon ethanol for

ADC final and ADC green, respectively. To reach lower than the minimum ethanol selling price of $1.08/gallon for corn stover, the minimum feedstock credit received needed to be $2/ton ADC final or $29/ton ADC green.

Conclusions

Municipal solid waste (MSW) is one of the lowest cost feedstock sources for cellulosic ethanol production. Clearly, MSW-ethanol can help address waste disposal challenges, augment the diversity of the domestic energy resource base, and help mitigate the impact of potential fuel supply disruptions, reduce greenhouse gas emissions, and improve energy security. In this study, through on-site investigation at the West Valley Material Recovery Facility and Transfer Station (Fontana, CA), we chosed six types of cellulose-rich MSW collected from blue and green garbage bins as potential fuel ethanol production feedstocks for further technical assessment. Among these six types of MSW, including final alternative daily cover (ADC final), ADC green, woody waste, grass waste, cardboard, and mixed paper, ADC final and ADC green are MSW fractions that extract a tipping fee for landfilling, providing zero to negative feedstock costs. Woody wastes and grass wastes are also considered low cost potential feedstocks, which are sent to combustors and farms with selling price of $7.5/ton or $0/ton, respectively. Cardboard and mixed paper, which contain high amount of cellulose, can be used as fuel ethanol feedstocks when these components of MSW end up at landfills during economic difficult times although they can be sold overseas at fairly high prices.

Upon sampling these six MSW fractions from the transfer station during the summer seasons for two consecutive years (July 2007 and August 2008), compositional analysis was conducted to determine major components of MSW and the potential ethanol

yields. Results showed that these MSW fractions contained varying amount of carbohydrates, ranging 20.9% (grass wastes) to 64.1% (mixed paper) glucan and 5% to 9.9% xylan. According to the carbohydrate content, 44.9 (grass wastes) – 128.3 (mixed paper) gallon of ethanol could be theoretically produced from each dry ton of these MSW fractions. Thus, theoretical ethanol yields of these MSW fractions could be comparable or even higher than from other conventional cellulosic biomass, such as agricultural waste corn stover (112.7 gallon ethanol/ton). Compared to other conventional cellulosic biomass, these MSW fractions contained similar or lower amount of lignin and ash, but much higher content of other impurities.

Sugar yields of these MSW fractions were determined by applying leading technologies of pretreatment and enzymatic hydrolysis. Through dilute acid pretreatment (1% w/w H_2SO_4, 140°C, 40 min), 12.9-50% xylan, 0-79.3% lignin, 6.7-49.6% ash and 43.7-85.9% other impurities were removed from MSW solids resulting in pretreated MSW solids with enhanced cellulose content and much lower amount of other impurities. 12-82.4% xylan yield in pretreatment hydrolyzate was reached by acid pretreatment. Except grass wastes, little glucan was solublized from raw MSW during pretreatment. Overall 90% of original xylan and glucan were recovered in pretreated solids and hydrolyzates with little loss. Results showed that acid pretreatment at experimental conditions was effective on these MSW fractions. For example, over 50% and 80% of the xylan was recovered in pretreatment hydrolyzate for ADC final and ADC green, respectively.

Cellulose conversion of pretreated MSW after 72 hrs of enzymatic hydrolysis at a high enzyme loading of 100 mg enzyme protein/g (G+X of raw materials) was over 80%

except cellulose conversion of pretreated woody and grass wastes was between 60-70%. At a low enzyme loading of 10 mg enzyme protein/g (G+X of raw materials), cellulose conversion of pretreated cardboard, mixed paper and ADC final, remained about 80% but cellulose conversion of pretreated ADC green dropped to as low as 36%. In order to improve the sugar yields at lower enzyme loadings, BSA addition prior to enzyme addition, was tested to block non-specific adsorption of cellulases by lignin and other impurities in pretreated MSW. Results showed that cellulose conversion during enzymatic hydrolysis of all pretreated MSW fractions improved by 5.7-52% with 0.5% wt/v BSA treatment at low enzyme loading of 5 mg enzyme protein/g (G+X of raw materials). Using ADC green and ADC final as examples, a greater improvement in cellulose conversion was achieved with adding 0.5% wt/v BSA at low enzyme loadings than that at higher enzyme loadings. With 0.2% wt/v BSA treatment, cellulose conversion of pretreated ADC green was improved from 36% to 80% at 72 hr enzymatic hydrolysis with an enzyme loading of 10 mg enzyme protein/g (G+X of raw materials). Through pretreatment followed by enzymatic hydrolysis with 10 mg enzyme protein/g (G+X of raw materials), the overall yield of xylan and glucan for ADC final reached 79.1% and 88.2%, respectively. The overall yield of xylan and glucan for ADC green was 83.3% and 89.1%, respectively, through pretreatment and enzymatic hydrolysis at 10 mg enzyme protein/g sugars of raw materials, and treated with 0.2% wt/v BSA.

Based on the technical assessment as described above, experimental data was adapted into the NREL corn stover process design model using ASPEN to estimate the techno-economic feasibility of a MSW-to-ethanol bioconversion process. ADC final and ADC green were used as feedstocks because of the high sugar yields obtained

experimentally, and these landfill MSW fractions might cost zero to negative dollars. Some important process design parameters, such as operating scale, compositions, glucan and xylan conversion etc., were changed to match with lab results and MSW operation scale. The MSW feedstock cost was estimated as the 2008 median tipping fee of $36 in California. Results showed that the total project investment was $172.3 MM and $166.6 MM for ADC final and ADC green, respectively, which were 13.1% and 16% lower than that of NREL corn stover case, respectively. Using MSW as feedstock could receive credits of 50.4 cents/gal ethanol and 92.5 cents/gal ethanol for ADC final and ADC green, respectively, based on calculated operating costs. Feedstock credits of MSW process could amount to $17.2 MM per year while using corn stover could cost $23.2 MM per year. This analysis indicated that MSW process could provide substantial economic benefits for large scale production in terms of feedstock costs. Through a discounted cash flow analysis with a 10% discounted cash flow rate of return over a 20 year plant life, the minimum ethanol selling price was $0.60/gallon ethanol and $0.91/gallon ethanol for ADC final and ADC green processes, respectively. Overall, results suggested that using ADC final as a feedstock could significantly decrease the minimum ethanol selling price by 44.4% comparing with using corn stover, which was estimated as $1.08/gallon ethanol. The techno-economic feasibility assessment indicated that using MSW as feedstock, such as ADC final and ADC green could provide positive effects on the process economics.

Acknowledgements

The authors would like to acknowledge University of California Energy Institute for funding this project. Sincere thanks to Dr. Michael Studer, Dr.Simone Brethauer, Vu Nguyen (funded by RAP program), and Brian Forsberg for their assistance in some experiments. We are also grateful to Drs. Hua-jiang Huang and Shri Ramaswamy from the University of Minnesota for their help in some Aspen modeling, and the assistance of Mr. Bill Welch from CE-CERT at UCR and Mr. Richard Crockett II from Burrtec Waste Industries for consulting on some of the MSW sampling work. We also gratefully acknowledge the Center for Environmental Research and Technology at The University of California Riverside for making this important research possible.

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