Biological Hydrogen Carriers: Harnessing Fossil Fuels in a Carbon-Constrained World[1]

Bio-combustibles que llevan hidrógeno: Restringiendo combustibles fósiles en un mundo limitado en carbono

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ABSTRACT

Due to their widespread availability, the use of lignocellulosic resources as feedstocks for fuels and chemicals is very promising. To make this a practical reality, 18 years of research at Texas A&M University have resulted in the development of a novel process known as MixAlco.™ This article compares this process with other technologies and provides some process details. At the end, a brief economic analysis is presented.

RESUMEN

Debido a una amplia disponibilidad, el uso de recursos lignocelulósicos como materia prima para producir combustibles y otros productos químicos es muy prometedor. Para hacer de esto una realidad, 18 años de investigación en la Universidad de Texas A&M han resultado en el desarrollo de un proceso novedoso denominado MixAlco.™ Este artículo compara este proceso con otras tecnologías y provee algunos detalles del proceso. Por último, se presenta un breve análisis económico.

	Theoretical (Ideal biomass)					Literature (Real biomass)	
External H_2	No			Yes		No	
Lignin converted to liquid fuel	No	Yes				No	Yes
Column number	1	2	3	4	5	6	7
Product	Ethanol	Ethanol	Alkane	Ethanol	Alkane	Alcohol	
Thermochemical Platform	—	145	95.8	289	194	—	80.1[1]
Sugar Platform							
CBP	117	175	115	289	194	100[2]	—
SSCF	113	169	111	279	187	65	—
Carboxylate Platform	—	175	115	289	194	—	127[3]

1. Mixed alcohols with 73% ethanol expressed as ethanol equivalents.
2. Expected
3. Ethanol equivalents [17].

Table 1. Yields of liquid fuels from biomass (gal/ton ash-free biomass) [3].

External h_2	No			Yes	
Column	1	2	3	4	5
	Biological step	Ethanol Product	Alkane Product	Ethanol Product	Alkane Product
Thermochemical Platform	—	67.5	63.7	73.2	70.0
Sugar Platform					
CBP	96.3[1]	81.0	76.4	80.7	76.8
SSCF	92.9[1]	78.2	73.7	77.9	74.2
Carboxylate Platform	93.4[2]	81.0	76.4	80.7	76.8

Ethanol product
Acetic acid product

Table 2. Theoretical efficiency of liquid fuels from ideal biomass (%) [3].

External H_2	No		Yes	
Product	Ethanol	Alkane	Ethanol	Alkane
Thermochemical Platform	0	0	45.4	47.4
Sugar Platform				
CBP	0	0	39.9	42.3
SSCF	0	0	39.9	42.3
Carboxylate Platform	0	0	39.9	42.3

Table 3. Theoretical energy supplied from external hydrogen (%) [3].

Hydrogen price ($/kg)	Capacity (tonne/h)	Biomass delivered price ($/tonne)						
		−60	−40	−20	0	20	40	60
1	2	1.12	1.26	1.40	1.55	1.69	1.83	1.97
	10	0.58	0.72	0.86	1.01	1.15	1.29	1.43
	40	0.37	0.51	0.65	0.80	0.94	1.08	1.22
	160	0.30	0.44	0.58	0.72	0.87	1.01	1.15
	800	0.25	0.40	0.54	0.68	0.82	0.96	1.10
2	2	1.36	1.50	1.64	1.79	1.93	2.07	2.21
	10	0.82	0.96	1.10	1.25	1.39	1.53	1.67
	40	0.61	0.75	0.89	1.04	1.18	1.32	1.46
	160	0.54	0.68	0.82	0.96	1.11	1.25	1.39
	800	0.49	0.64	0.78	0.92	1.06	1.20	1.34
3	2	1.61	1.75	1.89	2.04	2.18	2.32	2.46
	10	1.07	1.21	1.35	1.50	1.64	1.78	1.92
	40	0.86	1.00	1.14	1.29	1.43	1.57	1.71
	160	0.79	0.93	1.07	1.21	1.36	1.50	1.64
	800	0.74	0.89	1.03	1.17	1.31	1.45	1.59
4	2	1.86	2.00	2.14	2.29	2.43	2.57	2.71
	10	1.32	1.46	1.60	1.75	1.89	2.03	2.17
	40	1.11	1.25	1.39	1.54	1.68	1.82	1.96
	160	1.04	1.18	1.32	1.46	1.61	1.75	1.89
	800	0.99	1.14	1.28	1.42	1.56	1.70	1.84

Table 4. Minimum alcohol selling price (MASP) including 15% return on investment ($/gal) [7].

INTRODUCTION

Ethanol produced from corn grain and diesel produced from soybean are currently the predominant transportation biofuels in the United States [1]. Globally, the United States (using corn grain) and Brazil (using sugarcane) are the two primary producers of ethanol with 8.1 billion gallons produced in 2005 accounting for about 70% of the world consumption of bio-ethanol [2]. These paths to ethanol production are often criticized because of significant arable land and water requirements, negative environmental impacts, and competition with food resources.

Intensive work has been done to identify feedstock alternative to these resources along with corresponding conversion processes. Lignocellulosic feedstocks are promising because of their potential supply is far larger than that of food crops; consequently, several different technological configurations have arisen to use these feedstocks. In this paper, three alternative processing platforms are considered: thermochemical, sugar, and carboxylate explained as follows:

THERMOCHEMICAL PLATFORM.

Involves partial oxidation to produce synthesis gas ($CO + H_2$), which can be catalytically converted to a variety of products (e.g., alcohols and hydrocarbons). Gasification of ideal biomass may be visualized as occurring according to the following steps: (1) the lignin is separated from the polysaccharide, (2) the polysaccharide is gasified, (3) the lignin is gasified and shifted to hydrogen, and (4) the resulting gases are passed over a catalyst to yield ethanol.

SUGAR PLATFORM.

Employs the enzymatic hydrolysis of cellulose and hemicellulose to sugars, which are subsequently fermented into ethanol. Using the sugar platform to completely convert ideal biomass involves the following steps: (1) carbohydrate polymers are hydrolyzed to sugars using acid or enzyme catalysts, (2) the resulting sugars are fermented to ethanol and carbon dioxide,

(3) the remaining lignin is gasified and the resulting gases are shifted to hydrogen, and (4) the hydrogen reduces carbon dioxide to form more ethanol.

CARBOXYLATE PLATFORM.

The cellulose and hemicelluloses are fermented to carboxylic acids, which are subsequently converted into fuels or chemicals. Using the carboxylate platform to completely convert ideal biomass involves the following steps: (1) carbohydrate polymers are hydrolyzed to sugars using enzyme or acid catalysts, (2) the resulting sugars are fermented to acetic acid, (3) the remaining lignin is gasified and the resulting gases are shifted to hydrogen, and (4) the hydrogen reduces the acetic acid to form ethanol.

THEORETICAL YIELDS AND MASS BALANCES

The major components of lignocellulosic biomass are cellulose and other polysaccharides (collectively represented as $C_6H_{10}O_5$), and lignin (represented as $CH_{1.12}O_{0.377}$). Using balanced chemical reactions and the *ideal biomass* feedstock, which for the purposes of the discussion here, will be defined as 31.7% lignin and 68.3% polysaccharides on an ash-free basis; and consequently a molar ratio of 3.93:1 lignin:polysaccharide (a composition typical of hardwoods, such as poplar wood), the theoretical yield and energy efficiency can be calculated for all three platforms [3]. These results allow for a comparison on the same basis. A summary of such balances is presented in Tables 1, 2 and 3 (For a detailed explanation of these tables, see [3]). The most important results are summarized as follows:

- When converting gasified biomass directly to liquid fuels, the most efficient product is methanol (84%), whereas the higher alcohols have a lower efficiency (77 to 80%). If the gasified biomass is converted to alkanes, the overall efficiency is lower (75%).

- The efficiency of converting sunlight to plant matter is fairly low (~1%). For the same chemi-

cal energy production, less land area is required if sunlight is converted to hydrogen (10 to 20% efficiency). This external source of hydrogen can be incorporated into the biofuel products and provide 39 to 48% of the energy content in the biofuel.

• The carboxylate platform has the highest achieved product yields of the three. Additionally, the carboxylate platform has the following advantages: (1) gasified lignin is utilized by conversion to hydrogen, which is efficiently accomplished through the water-gas shift reaction. In contrast, in the other platforms, gasified lignin is utilized by conversion to carbon-containing molecules (e.g., alcohols or alkanes), which has low yields in practice (see Column 7, Table 1). (2) Biomass can be converted to carboxylic acids using a mixed culture of microorganisms, which eliminates the need for aseptic processing conditions. (3) Using a mixed culture of microorganisms allows nearly all non-lignin biomass components (e.g., polysaccharides, pectins, fats, proteins) to be biologically converted, which is more energy efficient than thermochemical conversion.

All of these advantages of the carboxylate platform have been recognized Eggeman and Verser [4], Granda and Holtzapple [5], and Flatt and van Walsum [6], all of whom are pursuing active research projects in this area.

THE MixAlco PROCESS

The MixAlco process employs a mixed culture of acid-forming microorganisms to convert biomass to carboxylic acids (e.g., acetic, propionic, and butyric acids). Provided a methanogen inhibitor is added, these acids are the low-energy, thermodynamically driven products; therefore, there is no need to maintain aseptic operating conditions. To keep the pH near neutrality, buffers (e.g., calcium carbonate, ammonium bicarbonate) are added; thus, the products

of these mixed-acid fermentations are carboxylate salts (e.g., calcium acetate, ammonium acetate). These are concentrated via vapor-compression evaporation and subsequently chemically converted to other chemical and fuel products.

The advantages of the mixed-acid fermentation may be exploited to manufacture chemical and fuel products through the carboxylate platform (Figure 1). Using well-established catalysts and chemistry, the products can be made starting either from the carboxylate salt or the carboxylic acid. Transforming ketones or carboxylic acids into alcohols requires energy input from hydrogen. This can be supplied from many sources, including the gasification of undigested residues exiting the fermentor; thus, all biomass components (including lignin) may be transformed into high-value products.
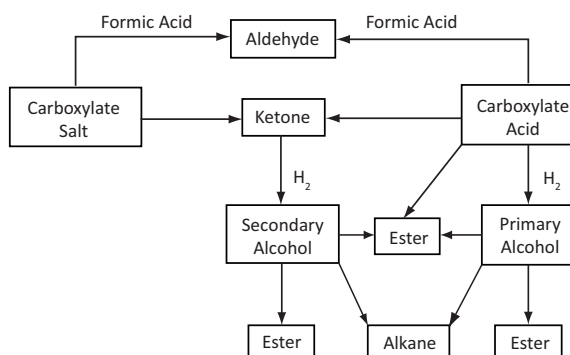

Figure 1. Overview of routes to chemical and fuel products via the carboxylate platform [7].

The process can use a wide variety of feedstocks (e.g., municipal solid waste, sewage sludge, manure, industrial biosludge, food scraps, agricultural residues, energy crops). Other important features of this process are[7]:

• Aseptic operating conditions are not required.

• Low-cost fermentors can be employed.

• No external enzymes are required.

• Microorganisms are naturally occurring, so when purged from the fermentors, they can be safely

disposed in the environment, or sold as animal feed.

• Plant operation is robust with no failures due to contaminants.

• The mixed culture of microorganisms will adapt to changes in feedstock.

• All enzymes are made under anaerobic conditions; therefore, efficiencies resulting from consolidated bioprocessing (CBP) are realized.

PROCESS OVERVIEW

Among the many products of the carboxylate platform are mixed alcohols, which may be used as transportation fuels. Routes to mixed alcohols are called the *MixAlco process* (Figure 2), which has the following steps (more details of each step can be found elsewhere [7]:

PRETREATMENT

Lignocellulosic biomass is contacted with lime, which removes lignin to enhance reactivity. Low-lignin (<10%) biomass does not require pretreatment. Medium-lignin (10 – 18%) biomass responds well to 1 – 2 h of contact with boiling lime water [8-10]. High-lignin (18 – 24%) biomass responds well to long-term lime plus air (~55°C, 1 month, 1 atm) [11]. Very-high-lignin (>24%) biomass requires lime plus oxygen (~150°C, 2 h, ~20 atm) [12, 13]. (Note: In this paper, it is assumed that the feedstock is high-lignin biomass that is pretreated with lime plus air.)

FERMENTATION

Inocula for the mixed-acid fermentation may be derived from soil, particularly from saline environments. The fermentation may be performed in submerged fermentations[14-16] or in piles [17]. Methanogen inhibitors prevent conversion of the carboxylic acids to methane and carbon dioxide. Although calcium carbonate may be used as a buffer, the process shown in Figure 2 uses ammonium bicarbonate. Laboratory experience indicates that high ammonium ion concentrations naturally inhibit methanogens; for safety, iodoform will be added also. Undigested residues from the fermentor may be sent to a gasifier where hydrogen is made. Insoluble calcium carbonate –formed from the reaction of pretreatment calcium and fermentation carbon dioxide– exits with the undigested residues. The ash from the gasifier contains alkaline salts, including calcium oxide (lime), which is used to pretreat the incoming biomass. The fermentor gas contains a mixture of hydrogen (~50 mol%) and carbon dioxide (~50 mol%), which can be easily separated.
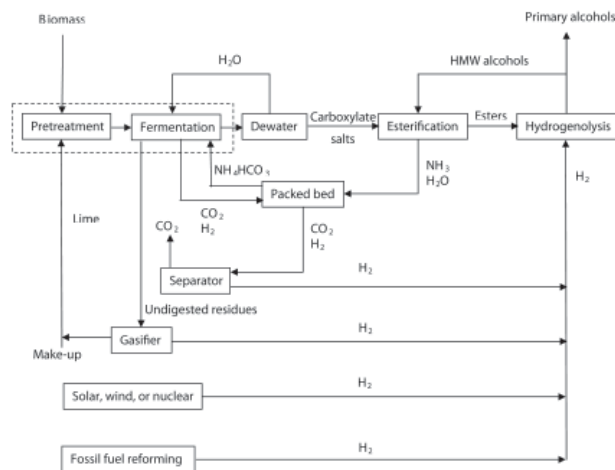

Figure 2. Overview of the MixAlco process [7].

DEWATERING

The fermentation broth is concentrated using vapor compression. Operating at elevated temperature and pressure reduces the compressor size.

ESTERIFICATION

In a distillation column, the concentrated ammonium carboxylate salts in the fermentation broth are contacted with a high-molecular-weight (HMW) alcohol and a solid-acid catalyst (e.g., USY-zeolite,). Water and ammonia exit the top of the distillation column allowing esters to form. The ammonia and water are sent to a scrubber where they react with carbon dioxide to form ammonium bicarbonate.

HYDROGENOLYSIS

The esters react with hydrogen using a catalyst (e.g., copper chromite) to form primary alcohols, which are separated in a distillation column. The low-molecular-weight (LMW) alcohols exit the top of the column and are sold as product and the HMW alcohols are recycled to the esterification reactor.

ECONOMICS

When alcohols are produced by the carboxylate platform, hydrogen is required. It can be supplied from a number of processes, including gasifying biomass, separation from fermentor gases, methane reforming, or electrolysis. Additionally, it can be obtained from renewable sources (solar, wind, nuclear) or reformed fossil fuels (coal, petroleum coke, natural gas). The hydrogen in the fermentor gas is the most economical source, but it supplies only 18% of the needs. To supply the remaining hydrogen needs, the most economical hydrogen production methods operate at large scale (steam reforming of methane, biomass gasification). Unless major breakthroughs occur, electrolysis is the least economical hydrogen source. On the basis of the biomass fed, three scenarios can be considered [7]:

SCENARIO A

Municipal solid waste. The average US tipping fee for disposing of municipal solid waste (MSW) is about $45/dry tonne (assuming 15% moisture) [18]. If it is assumed that the cost of sorting the MSW is offset by the value of recyclables (e.g., aluminum), then the organic fraction of MSW has a net tipping fee of about $45/dry tonne. A base-case plant that processes 40 tonne/h would service a city of about 800,000. If a refinery or hydrogen pipeline is available locally, then hydrogen can be obtained for about $2/kg. According to Table 4, the minimum alcohol selling price would be $0.72/gal. According to Equation 1, the corresponding gasoline selling price would be $1.14/gal. The capital cost for the alcohol plant is $36.8 million, or $0.82/annual gallon of mixed alcohol.

SCENARIO B

Small energy plantation. A base-case plant of 40 tonne/h could be supplied from 7110 ha (17,600 acre, 27.5 mi^2) assuming biomass yields of 45 tonne/(ha·yr) (20 tons/(acre·yr)), which can be achieved with high-yield sorghum being developed at Texas A&M University. If the land were 50% planted, this would require harvesting within a 7-km (4.2-mi) radius. Assume the delivered biomass cost is $60/tonne and that biomass residue and wood waste ($46/tonne) is gasified to make hydrogen. Further, assume that fermentor gases are a portion of the hydrogen source. Using these assumptions, hydrogen is $2.50/kg. According to Table 4, the minimum alcohol selling price would be $1.59/gal. According to Equation 1, the corresponding gasoline selling price would be $2.41/gal. The capital cost for the alcohol and gasification plants is $36.8 million and $66.3 million, respectively, or $2.29/annual gallon of mixed alcohol.

SCENARIO C

Large energy plantation processing 800 tonne/h could be supplied from 142,000 ha (351,000 acre, 549 mi^2) assuming the same biomass yield (45 tonne/(ha·yr)). If the land were 50% planted, this would require harvesting within a 31-km (18.6-mi) radius.

Assume the delivered cost is \$60/tonne and that biomass residue and wood waste (\$46/tonne) is gasified to make hydrogen. Further, assume that fermentor gases are a portion of the hydrogen source. Using these assumptions, hydrogen is \$1.42/kg. According to Table 4, the minimum alcohol selling price would be \$1.20/gal, and the corresponding gasoline selling price would be \$1.85/gal. The capital cost for the alcohol and gasification plants is \$496 million and \$494 million, respectively, or \$1.10/annual gallon of mixed alcohol.

To summarize, using the carboxylate platform within the MixAlco process, a base-case plant processing MSW and using hydrogen from a pipeline or refinery can sell alcohols for \$0.72/gal or gasoline for \$1.14/gal; for a small energy plantation, the minimum alcohol selling price would be \$1.59/gal, and a large energy plantation can sell alcohols for \$1.20/gal or gasoline for \$1.85/gal.

CONCLUSIONS

Colombia is extremely rich in lignocellulosic resources. Implementing a process like the MixAlco in Colombia – either in conjunction with a conventional oil refinery or on its own – would have tremendous environmental and economic impacts. The MixAlco process requires no scientific breakthroughs. It is a robust and flexible technology that is commercially ready and is economically competitive, even with oil prices near \$60/bbl.

The MixAlco process employs a mixed culture of acid-forming microorganisms to convert biomass to carboxylate salts, which are concentrated via vapor-compression evaporation and subsequently chemically converted to other chemical and fuel products. To make alcohols, hydrogen is required. One of the challenges is obtaining inexpensive hydrogen; however, it can be supplied from a number of processes, including gasifying biomass, separation from fermentor gases, methane reforming, or electrolysis. Using zeo-

lite catalysts, the alcohols can be oligomerized into hydrocarbons, such as gasoline. A 40-tonne/h plant processing municipal solid waste (\$45/tonne tipping fee) and using hydrogen from a pipeline or refinery (\$2.00/kg H_2) can sell alcohols for \$0.72/gal or gasoline for \$1.14/gal with a 15% return on investment. The capital cost is \$0.82/annual gallon of mixed alcohols. An 800-tonne/h plant processing high-yield biomass (\$60/tonne) and gasifying fermentation residues and waste biomass to hydrogen (\$1.42/kg H_2) can sell alcohols for \$1.20/gal or gasoline for \$1.85/gal with a 15% return on investment. The capital cost for the alcohol and gasification plants is \$1.10/annual gallon of mixed alcohols.

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