

## Carboxylate Platform: The MixAlco Process Part 2: Process Economics

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**Abstract** 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, which can be supplied from a number of processes, including gasifying biomass, separation from fermentor gases, methane reforming, or electrolysis. Using zeolite 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<sub>2</sub>) can sell alcohols for \$1.13/gal or gasoline for \$1.75/gal with a 15% return on investment (\$0.61/gal of alcohol or \$0.99/gal of gasoline for cash costs only). The capital cost is \$1.95/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<sub>2</sub>) can sell alcohols for \$1.33/gal or gasoline for \$2.04/gal with a 15% return on investment (\$1.08/gal of alcohol or \$1.68/gal of gasoline for cash costs only). The capital cost for the alcohol and gasification plants at 800 tonnes/h is \$1.45/annual gallon of mixed alcohols.

**Keywords** Carboxylate platform · MixAlco process · Economics · Alcohol · Hydrogen · Alkanes · Biogasoline

### Introduction

Mixed cultures of acid-forming microorganisms produce carboxylic acids (e.g., acetic, propionic, and butyric acids). Provided a methanogen inhibitor is added, these acids are the low-energy state, thermodynamically driven products; therefore, there is no need to

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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).

The advantages of employing mixed cultures of acid-forming microorganisms follow:

- Aseptic operating conditions are not required.
- Low-cost fermentors can be employed.
- 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).
- All non-lignin biomass components (e.g., free sugars, starch, cellulose, hemicellulose, pectin, fats, proteins) can be digested.
- 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 are realized.

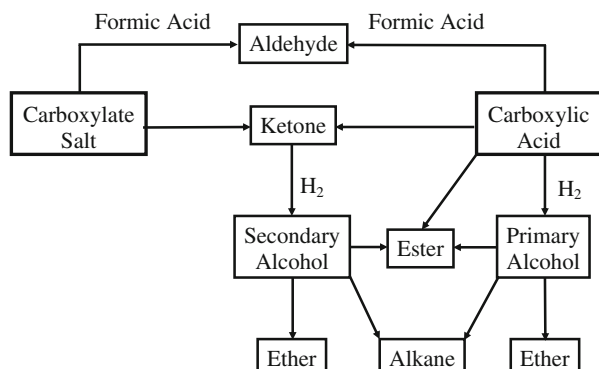
The advantages of the mixed-acid fermentation may be exploited to manufacture chemical and fuel products through the carboxylate platform (Fig. 1). Using well-established catalysts and chemistry, the products can be made starting either from the carboxylate salt or the carboxylic acid. Transforming ketones 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.

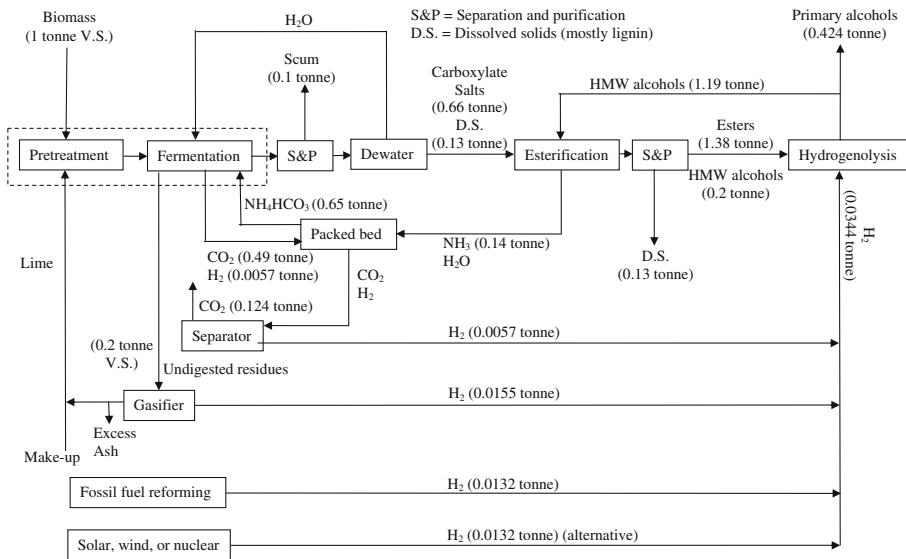
## Process Overview

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* (Fig. 2), which has the following steps:

- Pretreatment—Lignocellulosic biomass is contacted with lime, which removes lignin to enhance reactivity. Low-lignin (<10%) biomass does not require pretreatment.

**Fig. 1** Overview of routes to chemical and fuel products via the carboxylate platform





**Fig. 2** Overview of the MixAlco process and a high-level general material balance on a per tonne of biomass fed basis (volatile organics—ash free basis, water free basis)

Medium-lignin (10–18%) biomass responds well to 1–2 h of contact with boiling lime water [1–4]. High-lignin (18–24%) biomass responds well to long-term exposure to lime and air (~55°C, 1 month, 1 atm) [5]. Very-high-lignin (>24%) biomass requires contact with lime and oxygen (~150°C, 2 h, ~20 atm) [6, 7]. Note that in this paper, it is assumed that the feedstock is high-lignin biomass that is pretreated with lime and 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 [8–14] or in piles [15, 16]. 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 Fig. 2 uses ammonium bicarbonate. Laboratory experience indicates that high ammonium ion concentrations naturally inhibit methanogens; to ensure that no methane is produced, iodoform will be added also as an inhibitor. 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 may be 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.
- 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., H- $\beta$ -zeolite). Water and ammonia evaporate and 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 high-molecular-weight alcohols are recycled to the esterification reactor.

From biomass, hydrogen can be obtained from the fermentor gas or gasified fermentor residues. Additionally, hydrogen can be obtained from renewable sources (solar, wind, nuclear) or reformed fossil fuels (coal, petroleum coke, natural gas).

## Detailed Process Description

### Pretreatment/Fermentation

The pretreatment/fermentation piles are operated in a round-robin manner (Fig. 3). This example shows six piles, two pretreatment and four fermentation. As the lime pretreatment pile ages, the pH drops. Then the air is shut off, and the inoculum is added, so it becomes a fermentation pile. When the fermentation is complete, the residue is removed, and pretreatment starts with a new pile. Figure 4 shows the water circulation pattern while in the fermentation mode. This countercurrent pattern allows the most digested biomass to contact the freshest water and the freshest biomass to contact the most concentrated product, an arrangement that allows for both high product concentrations and high conversions.

To build the piles, the biomass (A-3) and lime (A-2) are conveyed into a slurry tank (A-1) where water is added using pump A-14 (Fig. 5). The slurry is pumped (A-13) to a boom, which delivers the biomass slurry to the pile. The water drains away (and is recirculated), whereas the biomass accumulates in the pile.

Figure 6 shows the pile in the pretreatment mode. A blower (A-5) pressures air and blows it through a lime-water slurry tank (A-6), which removes carbon dioxide from the air. The air then blows up through the pile, which contains both biomass and lime. The pile is located on a gravel bed lined with a geomembrane. Water accumulates in the gravel bed and is circulated to the top of the pile. The combination of lime, water, and air removes lignin from the biomass, rendering it digestible. During the pretreatment mode, the pile can be covered or uncovered. If covered, an exhaust blower (A-7) removes gas from the pile. A slight vacuum can be created, which keeps the cover pressed against the pile thereby keeping it from blowing in the wind. Liquid collected from the bottom of the pile is pumped (A-8) through a heat exchanger (A-9) onto the top of the pile.

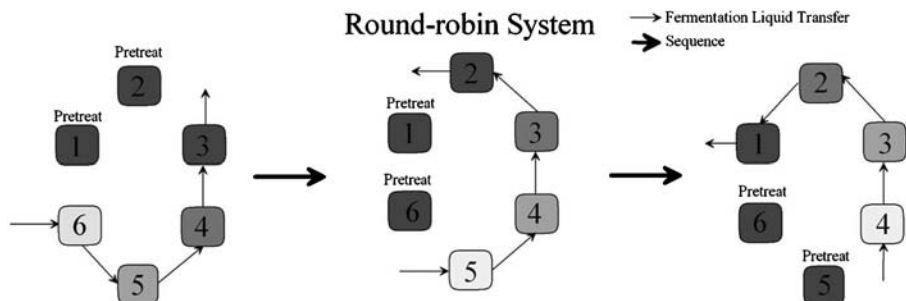
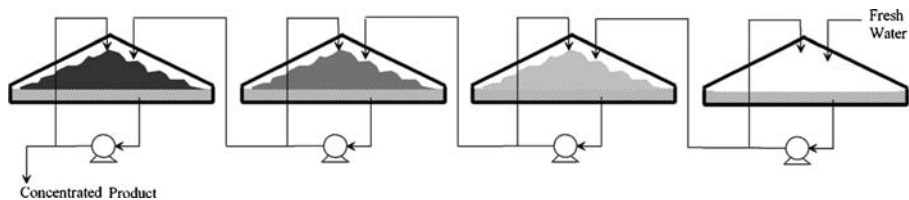


Fig. 3 Round-robin system



**Fig. 4** Water circulation through the fermentation piles

Figure 7 shows the pile in the fermentation mode. In this case, no air circulates through the pile and the exhaust gases are sent to a packed bed scrubber (A-10) where they contact ammonia and water to form ammonium bicarbonate buffer, which is stored in a holding tank (A-11) and directed to the liquid that circulates through the pile. Gases exiting the scrubber (A-10) are sent to an odor control system (A-12) if no hydrogen is present in the gas. If hydrogen is present, then the gas is sent to a hydrogen recovery unit (not shown).

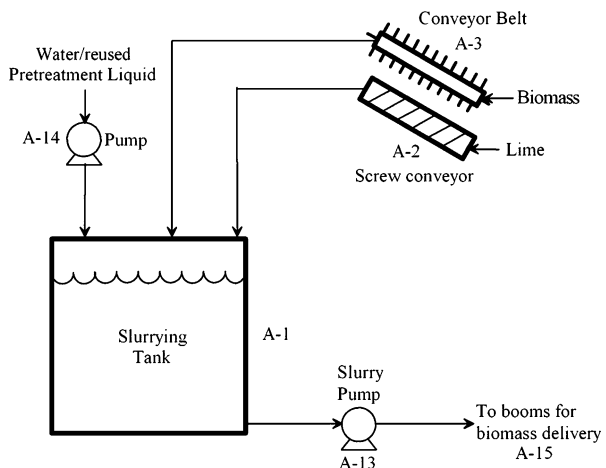
Figure 8 shows that after the fermentation is completed, the pile is dismantled by slurring the undigested residue with water (A-14) and pumping (A-13) the slurry through a filter (A-16). The undigested residue can be sent to a boiler to make process heat, a gasifier to make hydrogen, or it can be exported for other purposes (compost, electricity production).

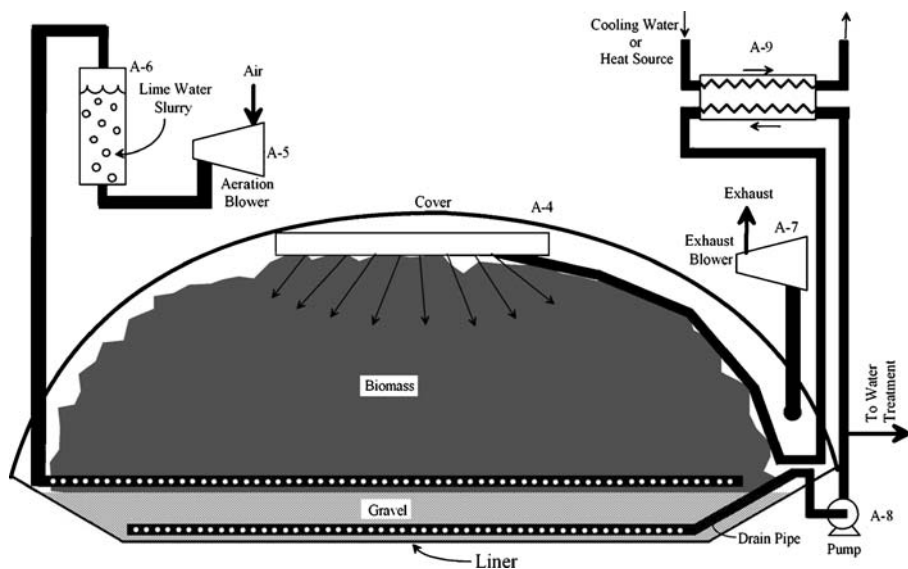
For the base-case scale (40 tonnes biomass feed/h, dry basis), a total of six fermentors are employed. Each has a cross-section of a truncated pyramid. The height is 25 m, and the base is about 100 m on a side. The pile rests on a 1-m bed of gravel, which is lined with geomembrane commonly used to line landfills. The pile is covered with the same geomembrane to exclude oxygen and contain fermentation gases. Although the above configuration is envisioned as the ultimate cost-effective design for the fermentor, a more conservative design is used in the economic evaluation provided in this paper; this conservative design includes a concrete bottom with channels to allow drainage and an airtight tensioned-fabric cover.

### Dewatering

Figure 9 shows the vapor-compression evaporator that concentrates the ammonium carboxylate salts from the fermentor. The feed enters surge tank B-17 and then is preheated

**Fig. 5** Biomass loading facilities

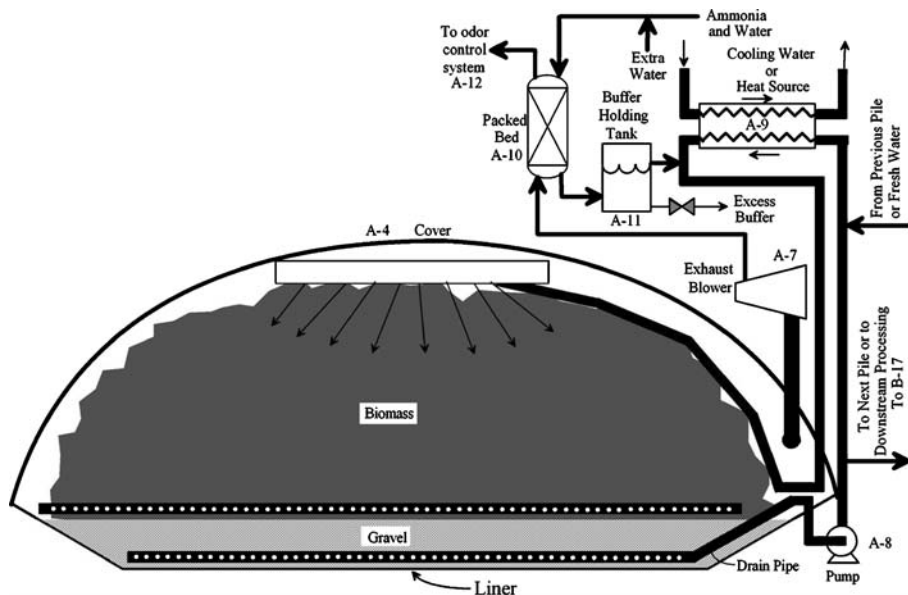




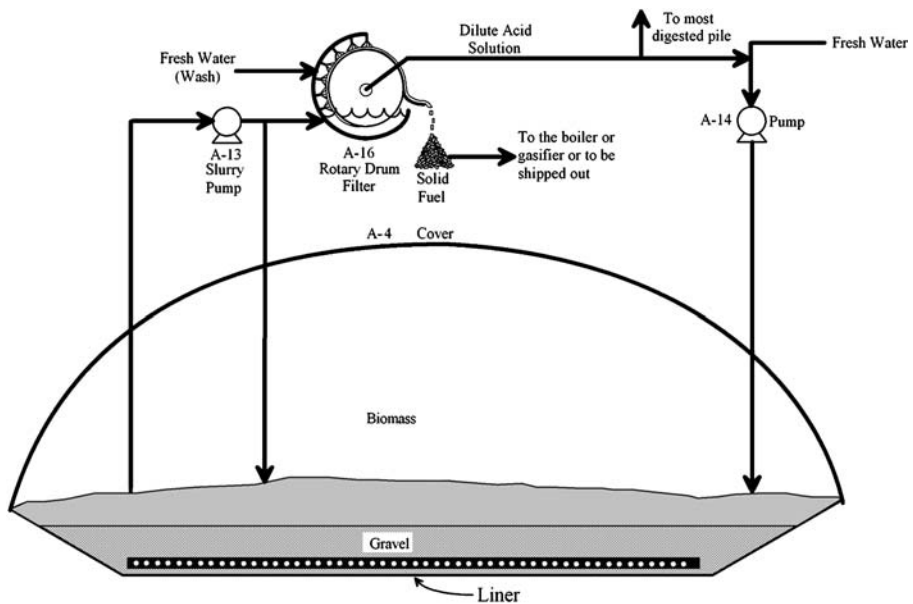
**Fig. 6** Pile in pretreatment mode

to 100°C in countercurrent sensible heat exchanger B-9. The solution is steam stripped in column B-15 to remove noncondensable gases, primarily carbon dioxide. The exiting steam is sent to the esterification column, which uses the energy again. To help remove carbon dioxide, acid may be added to the stripper.

To precipitate scum present in the fermentation broth, concentrated flocculant is added to tank B-14, which is mixed with the hot fermentation broth in tank B-12. The precipitate is

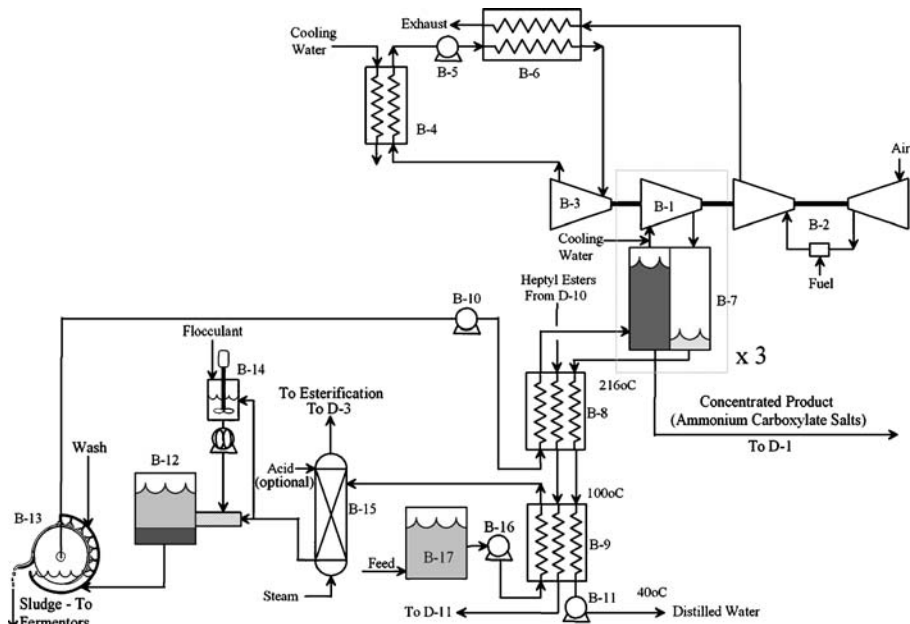


**Fig. 7** Pile in fermentation mode



**Fig. 8** Dismantling the fermentation pile

recovered in filter B-15. Pump B-10 pressurizes the feed so that it flows into countercurrent sensible heat exchanger B-8, which raises the temperature to 216°C. The hot fermentation broth enters three-stage latent heat exchanger B-7. Vapors from the salt side are compressed using compressor B-1 and enter the steam side where they condense, thus allowing more

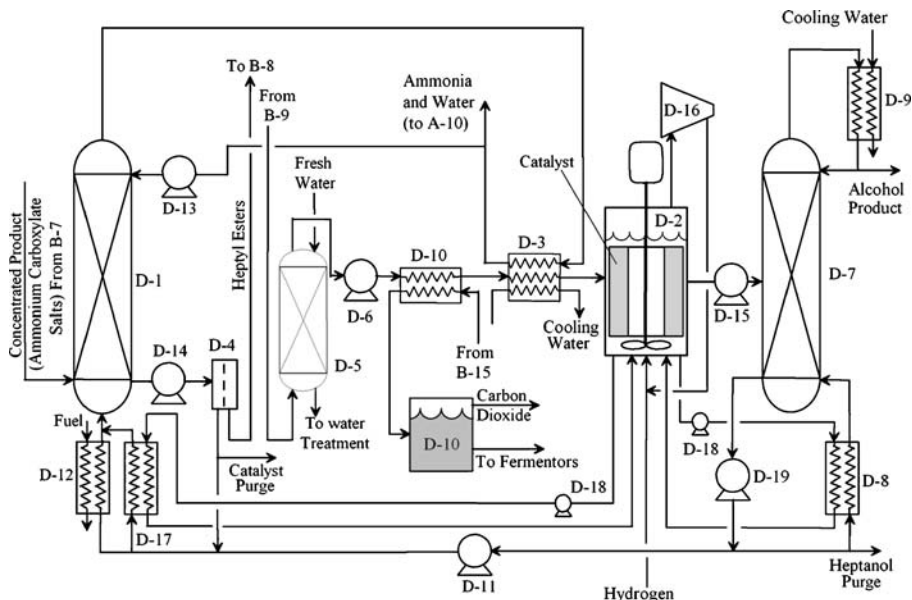


**Fig. 9** Vapor-compression evaporator

vapors to evaporate from the salt side. The compressor is driven by a combined-cycle engine consisting of natural gas turbine B-2 and Rankine cycle steam turbine B-3, which is supported by waste-heat boiler B-6 and condenser B-4. The efficiency of the combined cycle is assumed to be 50%, which is conservative.

### Esterification/Hydrogenolysis

Figure 10 shows the esterification/hydrogenolysis system. In column D-1, the concentrated mixed ammonium carboxylate salts are blended with preheated (D-12, D-17) high-molecular-weight alcohol (e.g., heptanol), which forms esters, water, and ammonia in the presence of solid acid catalyst. Water and ammonia exit the top of the column where they are condensed by heat exchanger D-3. A portion of the condensate is returned to distillation column D-1 as reflux. The esters from the bottom of column D-1 are filtered (D-4) to remove solid acid catalyst, which is returned to column D-1. The esters are sent to heat exchangers B-8 and B-9 in the dewatering system to be cooled, so they may be cleaned in column D-5 by contact with water. This removes any dissolved solids that might have been brought with the incoming broth. All the esters are very insoluble with water, but the dissolved solids will prefer the water and are extracted. The esters leaving column D-5 are clean and are sent to the hydrogenolysis reactor D-2, with preheating from heat exchangers D-10 and D-3. In reactor D-2, high-pressure hydrogen (200 psi) is added, thus forming alcohols over an appropriate catalyst (e.g., Raney nickel, reduced CuO/ZnO, or copper chromite). The hydrogen is assumed to be supplied at high pressure. Hydrogen may be recirculated, if necessary, through reactor D-2 using compressor D-16. The low-molecular-weight alcohols are separated from the HMW alcohols in distillation column D-7. Because the reaction in D-2 is exothermic, the reaction heat is used to operate reboiler D-8 for the alcohol column D-7 and provide part of the heat needed in column D-1. The LMW alcohol



**Fig. 10** Esterification/hydrogenolysis



is condensed (D-9); a portion is returned as reflux to column D-7, and the remainder is harvested as product.

## Economics

The economics that are presented in this article follow the format used by Maiorella [17]. Tables 1 and 2 show the technical assumptions and Table 3 the economic assumptions used in the economic analysis. Estimation of the fixed capital investment (FCI) required by each section of the plant for the base-case scenario (40 tonnes biomass feed/h, dry basis) was done by detailed sizing and costing of most pieces of equipment necessary. Peters, Timmerhaus, and West Plant Design and Economics for Chemical Engineers (5th edition), matche.com and PDQ\$ cost estimation software were used whenever they had equipment cost available. Otherwise, vendor quotes were used. Appropriate Lang factors (liquid-only, liquid-and-solid) are used to estimate the installed capital cost from equipment costs. The design is based on laboratory and pilot plant data, as well as some literature data for some of the downstream processing. The accuracy of the cost estimate is between an order-of-magnitude estimate and a study estimate. Some equipment might be added and others removed as the scale-up of the process continues.

Table 4 summarizes the FCI for each section of the plant for the base-case scenario (40 tonnes/h). In all cases, the pretreatment/fermentation section is the most expensive, and the esterification/hydrogenolysis section is the least expensive. This is expected; the upstream

**Table 1** Technical assumptions.

Parameters	Values
Pretreatment	
Lime loading	0.15 g CaO/g biomass <sup>a</sup>
Reaction time	39 days <sup>a</sup>
Fermentation	
Conversion	0.8 g digested/g biomass volatile solids fed <sup>b</sup>
Selectivity	0.65 g carboxylic acids/g volatile digested <sup>b</sup>
Mixed acid yield	0.52 g carboxylic acid/g biomass volatile solids fed <sup>b</sup>
Scum yield	0.1 g scum/g biomass volatile solids fed <sup>b</sup>
Carbon dioxide yield	0.124 g CO <sub>2</sub> /g biomass volatile solids fed <sup>b</sup>
Hydrogen yield	0.0057 g H <sub>2</sub> /g biomass volatile solids fed <sup>c</sup>
Concentration	50 g carboxylic acid/L (63 g carboxylate salt/L) <sup>b</sup>
Alcohol yield	533 L alcohol/tonne=141 gal/tonne <sup>d</sup>
Reaction time	92 days <sup>b, e</sup>
Esterification/hydrogenolysis	
Alcohol energy content	24.3 MJ/L (87,277 Btu/gal)
1 L equivalent ethanol	0.966 L mixed alcohols
Percentage of energy content from hydrogen	38%

<sup>a</sup> Kim and Holtzaple [5]

<sup>b</sup> Agbogbo and Holtzaple [15]; Agbogbo [16]

<sup>c</sup> Forrest and Holtzaple, unpublished data

<sup>d</sup> As per yield obtained in laboratory [15, 16]. Please refer to Part 1 of these article series on the “Carboxylate Platform” to see a comparison on theoretical yields between the thermochemical (gasification) platform, the sugar (ethanol fermentation) platform, and the carboxylate platform

<sup>e</sup> Conservative value [15, 16]

**Table 2** Technical assumptions on composition.

Component	Composition (mol %) <sup>a</sup>	
	Carboxylic acid	Alcohol
C2	88.7	88.7
C3	2.14	2.14
C4	7.19	7.19
C5	1.49	1.49
C6	0.05	0.05
C7	0.44	0.44

<sup>a</sup> [22]

section deals with bulky biomass that requires a long residence time (large equipment), whereas the downstream section deals with concentrated products with short residence times (small equipment). Table 4 shows the estimated FCI for plants both larger than and smaller than the base case. The cost of each piece of equipment was scaled using its recommended scaling exponent [18]: pump (0.33), heat exchanger (0.4 to 1.0), conveyor (0.56), tank (0.57), blower (0.59), packed bed (0.62), fermentor (0.67 smaller, 1.0 larger), filter (0.76), and compressor/turbine (0.79).

Table 5 summarizes the utilities for each section of the plant, which is assumed to be independent of scale. Table 6 summarizes the costs of each section for the base-case scenario assuming the biomass feedstock costs \$60/tonne (delivered) and hydrogen costs \$2/kg. In addition to the information presented in the economics format followed by Maiorella [17], where they only present the costs of production, we also included among the costs a 15% before-tax return on investment (ROI) for both the FCI and working capital. This ROI is typical of mature processes and is considered the minimum ROI for an economically viable process; thus, the total costs may be viewed as the minimum alcohol selling price (MASP). Figure 11 shows the MASP for a variety of biomass and hydrogen costs (Note: Negative biomass costs are for feedstocks that command a tipping fee, such as municipal solid waste or sewage sludge). Figure 12 shows the cash costs only (i.e., no depreciation or ROI) on a per gallon basis, associated with the process at different biomass and hydrogen costs. The recent ethanol market price is about \$2.2/gal, so nearly every scenario is economical in the current market, except for the smallest plant (2 tonnes/h), and with the highest prices of biomass and hydrogen for the 10-tonne/h plant.

**Table 3** Economic assumptions.

Parameters	Values
Plant operation	8,000 h/year
Local taxes	$0.03/\text{year} \times \text{FCI}$
Working capital	$0.15 \times \text{FCI}$
Return on investment	$0.15/\text{year} \times 1.15 \times \text{FCI}$
Depreciation	10-year, straight line
Insurance	$0.007/\text{year} \times \text{FCI}$
Annual maintenance <sup>a</sup>	$0.04/\text{year} \times \text{FCI}$
Dollars	May 2007

<sup>a</sup> Includes labor, materials, and supervision

**Table 4** Fixed capital investment (\$ million).

	Capacity (tonne/h)				
	2	10	40 <sup>a</sup>	160	800
Pretreatment/fermentation	7.24	19.4	46.6	114	325
Dewatering	2.84	10.1	31.3	101	408
Esterification/hydrogenolysis	1.42	3.86	9.3	23.0	66.6
Total	11.5	33.4	87.2	238	800

<sup>a</sup> Base case

## Hydrogen

The base-case plant (40 tonne/h) requires 1,380 kg/h of hydrogen, which may be obtained from the following sources: biomass gasification, separation from fermentor gas, natural gas reforming, and electrolysis.

### Biomass Gasification

Table 7 shows the technical assumptions and economics associated with converting biomass into hydrogen based upon a National Renewable Energy Laboratory (NREL) study [19]. The biomass needed for gasification is about 45% of the feed to the MixAlco process. Undigested residues from the MixAlco process are about 20% of the feed, so undigested residues can supply 45% of the biomass needed for the gasifier. In the economic scenario shown in Table 6, the undigested residues are valued at \$2.50/GJ, which equates to about \$46/tonne. Assuming that other wastes (e.g., wood waste) are available for the same price, the cost of hydrogen is about \$3.05/kg (40-tonne/h scale) to \$1.73/kg (800-tonne/h scale).

### Separation from Fermentor Gas

The fermentor gas contains about 18% of the hydrogen needs for the plant. The fermentor gas is approximately 50 mol% hydrogen, which can be easily separated from carbon dioxide using pressure swing adsorption (PSA) or other methods. The biomass gasifier system incorporates PSA separation, so fermentor gas can be introduced into this unit operation with negligible effect on capital or energy needs. The economic effect of incorporating fermentor gas into the PSA unit is to decrease the hydrogen cost by about 18% or about \$2.50/kg (40-tonne/h scale) to \$1.42/kg (800-tonne/h scale), with \$46/tonne biomass fed to the gasifier.

**Table 5** Utility summary.

	Pretreatment/ fermentation	Dewater	Esterification/ hydrogenolysis	Total
Electricity (kWh/tonne biomass)	20.8	2.9	31.2	54.8
Steam (790-kPa) (tonne steam/tonne biomass)			0.065	0.065
Natural gas (GJ/tonne biomass)		0.902	0.871	1.773
Cooling water (m <sup>3</sup> /tonne biomass)	30.4	40	12.8	83.2
Solid fuel (GJ/tonne biomass)	3.7			3.7

**Table 6** Costs for 40-tonne/h base case.

	Admin (\$/tonne)	Pretreatment/ fermentation (\$/tonne)	Dewater (\$/tonne)	Esterification/ hydrogenolysis (\$/tonne)
Feedstock				
Biomass (\$60/tonne) <sup>a</sup>		60.00		
Lime (\$100/tonne) <sup>b</sup>		15.02		
Hydrogen (\$2/kg) <sup>c</sup>				68.76
Flocculant (\$1/kg) <sup>d</sup>			1.38	
Catalysts <sup>e</sup>				1.61
Utilities				
Electricity (\$0.08/kWh) <sup>f</sup>		1.66	0.23	2.50
Steam (790-kPa) (\$22.57/tonne) <sup>f</sup>				1.47
Natural gas (\$8/GJ) <sup>f</sup>			7.22	6.97
Cooling water (\$0.06/m <sup>3</sup> ) <sup>f</sup>		1.82	2.40	0.77
Solid fuel (\$2.50/GJ) <sup>f</sup>		−9.25		
Labor				
Plant manager (\$120,000/year)	0.38			
Supervisors (\$75,000/year)	0.94			
Sales (\$65,000/year)	0.20			
Clerical (\$35,000/year)	0.33			
Workers (\$40,000/year)		2.88	1.09	1.31
Fixed charges				
Depreciation (0.10/year×FCI)		14.56	9.77	2.92
Local tax (0.03/year×FCI)		4.37	2.93	0.87
Insurance (0.007/year×FCI)		1.02	0.68	0.20
Maintenance (0.04/year×FCI)		5.82	3.91	1.17
ROI (0.15/year×1.15×FCI)		25.12	16.86	5.03
Total	1.84	123.01	46.47	93.57
Total (cash costs only)	1.84	83.34	19.84	85.63
Grand total	264.90			
Grand total (cash costs only)	190.65			

Alcohol price = \$264.90/tonne × tonne/533 L alcohol = \$0.50/L

= \$264.90/tonne × tonne/141 gal = \$1.88/gal

= \$190.65/tonne × tonne/533 L = \$0.36/L (cash costs only)

= \$190.65/tonne × tonne/141 gal = \$1.35/gal (cash costs only)

<sup>a</sup> Conservative biomass cost for sweet sorghum. Long-term estimates are around \$40/tonne (Rooney, 2008, personal communication)

<sup>b</sup> Present lime price (Chemical Lime Company, New Braunfels TX)

<sup>c</sup> From Fig. 13 for a conservative price of natural gas of about \$11.50 as of May 2007

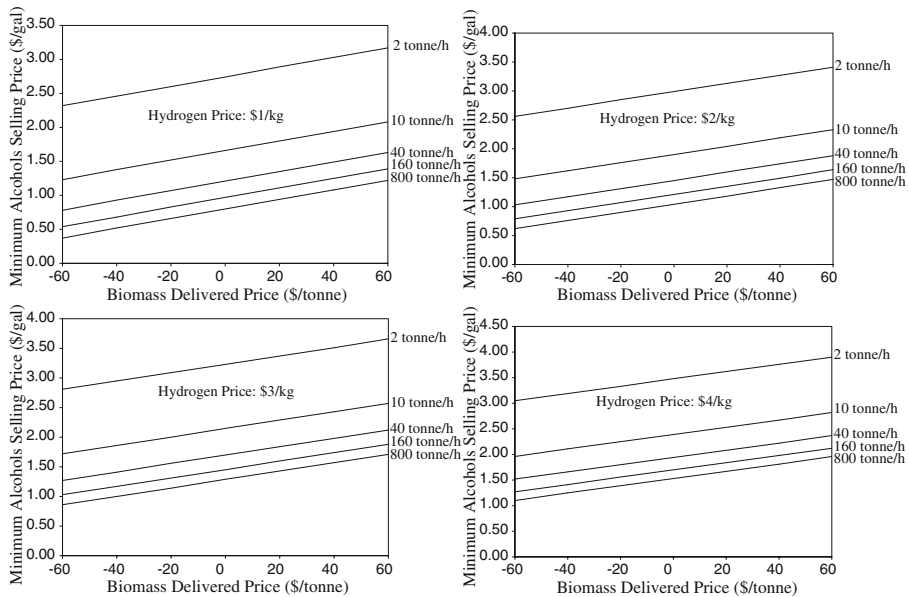
<sup>d</sup> Typical price of flocculant used in the sugar industry

<sup>e</sup> Average price for catalysts employed

<sup>f</sup> Market price as of May 2007

## Natural Gas Reforming

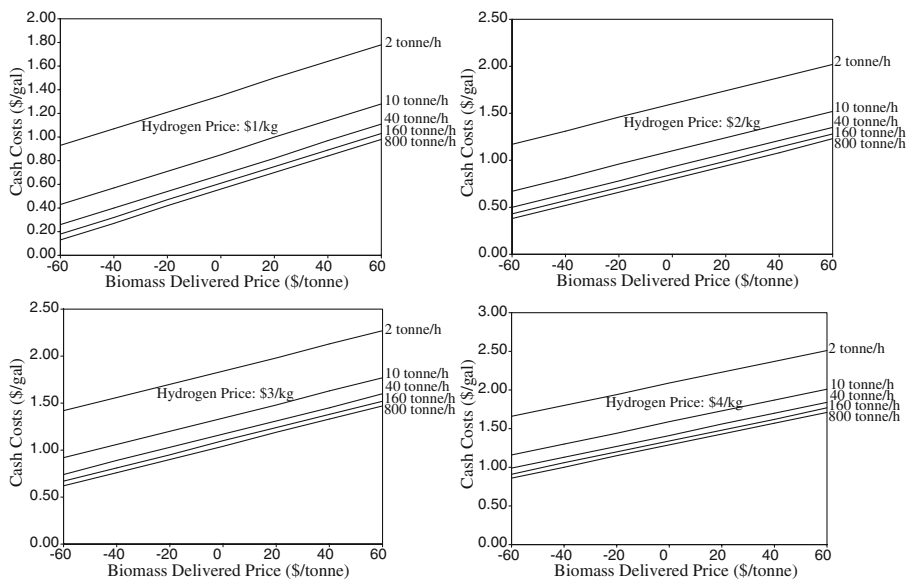
At oil refineries, natural gas is reformed into hydrogen, which is used to upgrade crude oil to refined products. In North America, there are 350 miles of hydrogen pipelines. The largest is 228 miles long and connects Laporte, TX to Lake Charles, LA. An industrial rule-



**Fig. 11** Minimum alcohol selling price including 15% return on investment and depreciation (\$/gal)

of-thumb is that the energy content of the hydrogen is worth about 1.3 times that of natural gas (Gillingham 2008, personal communication). On an energy basis, gasoline is worth about 2.3 times that of natural gas, so it is economical to incorporate methane-sourced hydrogen into the liquid fuel supply.

Figure 13 shows the cost of hydrogen (\$/kg) as a function of natural gas prices (\$/GJ). The current price of natural gas is about \$10/GJ, so the hydrogen price is about \$1.86/kg.



**Fig. 12** Total production costs (without including 15% ROI or depreciation, cash costs only) (\$/gal)

**Table 7** Cost of hydrogen from gasified biomass [19].Hydrogen yield=77.4 kg H<sub>2</sub>/tonne dry gasification feedstockPurchased electricity=1.64 kWh/kg H<sub>2</sub>

Fermentation feed rate	40 tonne/h	160 tonne/h	800 tonne/h
Hydrogen requirement	1,380 kg H <sub>2</sub> /h	5,520 kg H <sub>2</sub> /h	27,600 kg H <sub>2</sub> /h
Gasification feed rate	17.9 tonne/h	71.6 tonne/h	358 tonne/h
Fixed capital investment <sup>a</sup>	\$66.3 million	\$168 million	\$494 million
Fixed costs <sup>b</sup> (0.3495/year×FCI)	\$23.2 million/year	\$58.7 million/year	\$173 million/year
Fixed cost <sup>b</sup>	\$2.10/kg H <sub>2</sub>	\$1.33/kg H <sub>2</sub>	\$0.78/kg H <sub>2</sub>
Electricity cost (at \$0.08/kWh)	\$0.13/kg H <sub>2</sub>	\$0.13/kg H <sub>2</sub>	\$0.13/kg H <sub>2</sub>
Operating cost <sup>c</sup>	\$0.22/kg H <sub>2</sub>	\$0.22/kg H <sub>2</sub>	\$0.22/kg H <sub>2</sub>
Feedstock cost (\$/tonne)			
0	\$2.45/kg H <sub>2</sub>	\$1.68/kg H <sub>2</sub>	\$1.13/kg H <sub>2</sub>
10	\$2.58/kg H <sub>2</sub>	\$1.81/kg H <sub>2</sub>	\$1.26/kg H <sub>2</sub>
20	\$2.71/kg H <sub>2</sub>	\$1.94/kg H <sub>2</sub>	\$1.39/kg H <sub>2</sub>
30	\$2.84/kg H <sub>2</sub>	\$2.07/kg H <sub>2</sub>	\$1.52/kg H <sub>2</sub>
40	\$2.97/kg H <sub>2</sub>	\$2.20/kg H <sub>2</sub>	\$1.65/kg H <sub>2</sub>
50	\$3.10/kg H <sub>2</sub>	\$2.33/kg H <sub>2</sub>	\$1.78/kg H <sub>2</sub>
60	\$3.23/kg H <sub>2</sub>	\$2.46/kg H <sub>2</sub>	\$1.91/kg H <sub>2</sub>

<sup>a</sup> FCI =  $1.18 \times \$154 \text{ million} \left( \frac{\text{Hydrogen requirement}}{6,207 \text{ kg/h}} \right)^{0.67}$ 
<sup>b</sup> Based upon economic assumptions in Table 3

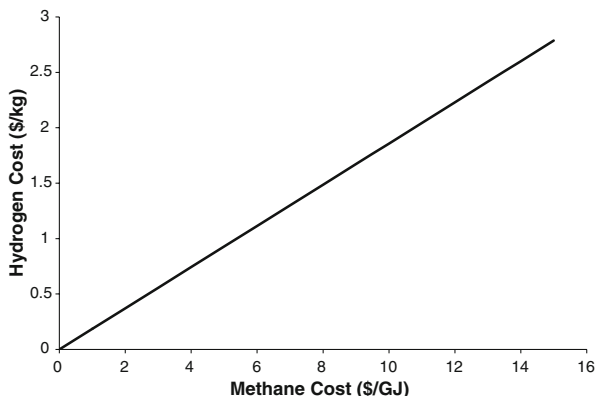
<sup>c</sup> Natural gas, catalyst, olivine, raw materials, waste disposal

The version of the MixAlco process described in this paper uses hydrogen in close proximity to the biomass source. As shown in Fig. 1, other versions of the MixAlco process convert the biomass to ketones or carboxylic acids, which can be shipped to central facilities where low-cost hydrogen is available.

### Electrolysis

Table 8 shows the costs of electrolyzing water to hydrogen as a function of electricity price. Current wholesale electricity prices are \$0.05 to \$0.10/kWh. Using current electrolyzer technology, the cost of hydrogen is about \$4.54 to \$7.21/kg. NREL projects that, as electrolyzer technology improves, the price could reduce to \$2.94 to \$5.17/kg.

**Fig. 13** Hydrogen cost from large-scale natural gas reforming (Gillingham 2008, personal communication)



**Table 8** Water electrolyzer cost [23].

	Near term	Mid term	Long term
Installed capital (\$/kW)	800	480	360
Energy (kWh/kg H <sub>2</sub> )	53.4	47.9	44.7
Required power (kW) <sup>a</sup>	73,700	66,100	61,700
Fixed capital investment <sup>a</sup>	\$59.0 mill	\$31.7 mill	\$22.2 mill
Fixed costs <sup>b</sup> (0.3495/year×FCI)	\$20.6 million/year	\$11.1 million/year	\$7.75 million/year
Capital charge (\$/kg H <sub>2</sub> ) <sup>2</sup>	1.87	1.00	0.70
Electricity cost (\$/kWh)			
0.000	\$1.87/kg H <sub>2</sub>	\$1.00/kg H <sub>2</sub>	\$0.70/kg H <sub>2</sub>
0.025	\$3.21/kg H <sub>2</sub>	\$2.20/kg H <sub>2</sub>	\$1.82/kg H <sub>2</sub>
0.050	\$4.54/kg H <sub>2</sub>	\$3.40/kg H <sub>2</sub>	\$2.94/kg H <sub>2</sub>
0.075	\$5.88/kg H <sub>2</sub>	\$4.59/kg H <sub>2</sub>	\$4.05/kg H <sub>2</sub>
0.100	\$7.21/kg H <sub>2</sub>	\$5.79/kg H <sub>2</sub>	\$5.17/kg H <sub>2</sub>
0.125	\$8.55/kg H <sub>2</sub>	\$6.99/kg H <sub>2</sub>	\$6.29/kg H <sub>2</sub>
0.150	\$9.88/kg H <sub>2</sub>	\$8.19/kg H <sub>2</sub>	\$7.41/kg H <sub>2</sub>

<sup>a</sup> Base case = 40 tonne biomass/h=1,380 kg H<sub>2</sub>/h

<sup>b</sup> Based upon economic assumptions in Table 3

Of the various hydrogen options, electrolysis is the most expensive; however, it does provide a way to incorporate other forms of renewable energy (solar, wind) or nuclear energy into the liquid fuel supply. Sometimes, renewable energy is available in remote locations. Hydrogenating biofuels offers an alternative to building expensive transmission lines.

## Hydrocarbon Production

Using a zeolite catalyst, alcohols can be dehydrated to alkenes, which are subsequently oligomerized into hydrocarbon mixtures, such as gasoline, diesel, and jet fuel. When dehydrated and oligomerized, the alcohol composition shown in Table 1 loses 36.5% of the mass as water, while retaining 63.5% of the mass as liquid hydrocarbon product. From the cost of alcohol (Alc), the cost of hydrocarbon (HC) can be estimated as follows:

$$\frac{\$}{\text{gal HC}} = \frac{\$}{\text{gal Alc}} \times \frac{\text{gal Alc}}{6.67 \text{ lb Alc}} \times \frac{\text{lb Alc}}{0.635 \text{ lb HC}} \times \frac{6.18 \text{ lb HC}}{\text{gal HC}} + \frac{\$0.10}{\text{gal HC}} \quad (1)$$

In this formula, \$0.10/gal is allowed for processing costs. For reference, crude oil is refined to gasoline for about \$0.20/gal [20].

## Scenarios

A number of scenarios are discussed below.

### 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) [21]. 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 tonnes/h would service a city of about 800,000 people. If a refinery or hydrogen pipeline is available locally, then hydrogen can be obtained for about \$2/kg. According to Fig. 11, the minimum alcohol selling price would be \$1.13/gal including 15% ROI and depreciation (\$0.61/gal of alcohol for cash costs only as per Fig. 12). According to Eq. 1, the corresponding gasoline selling price would be \$1.75/gal (\$0.99/gal of gasoline for cash cost only). The capital cost for the alcohol plant is \$87.2 million or \$1.95/annual gallon of mixed alcohol.

### Scenario B—Small Energy Plantation

A base-case plant of 40 tonnes/h could be supplied from 7,110 ha (17,600 acre, 27.5 mi<sup>2</sup>) assuming biomass yields of 45 tonnes/(ha year) (20 tons/(acre-year)), which can be achieved with high-yield sorghum being developed at Texas A&M University (Rooney, 2008, personal communication). If the land were 50% planted, this would require harvesting within a 7-km (4.2-mile) 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 Fig. 11, the minimum alcohol selling price, including 15% ROI and depreciation, would be \$2.00/gal (\$1.47/gal for cash costs only as per Fig. 12). According to Eq. 1, the corresponding gasoline selling price would be \$3.02/gal, with 15% ROI and depreciation included (\$2.25/gal of gasoline for cash costs only). The capital cost for the alcohol and gasification plants is \$87.2 million and \$66.3 million, respectively, or \$3.41/annual gallon of mixed alcohol.

### Scenario C—Large Energy Plantation

To show how economies of scale play a role, we consider a large plant processing 800 tonnes/h that could be supplied from 142,000 ha (351,000 acre, 549 mi<sup>2</sup>) assuming the same biomass yield (45 tonne/(ha-year)). If the land were 50% planted, this would require harvesting within a 31-km (18.6-mile) 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 Fig. 11, the minimum alcohol selling price, including 15% ROI and depreciation, would be \$1.33/gal (\$1.08/gal of ethanol for cash costs as per Fig. 12). According to Eq. 1, the corresponding gasoline selling price would be \$2.04/gal (\$1.68/gal of gasoline for cash costs only). The capital cost for the alcohol and gasification plants is \$800 million and \$494 million, respectively, or \$1.45/annual gallon of mixed alcohol.

## Conclusion

The carboxylate platform converts fermentable biomass to carboxylate salts. One version of the carboxylate platform is the MixAlco process, which employs a mixed culture of acid-forming microorganisms derived from saline environments. From an industrial viewpoint, a major advantage is that it does not require aseptic operating conditions. The carboxylate salts are concentrated via vapor-compression evaporation. The concentrated salts are subsequently chemically converted to other chemical and fuel products.

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. 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.

A base-case plant processing MSW and using hydrogen from a pipeline or refinery can sell alcohols for \$1.13/gal or gasoline for \$1.75/gal, including 15% ROI and depreciation (\$0.61/gal of ethanol and \$0.99/gal of gasoline for cash costs only). A large energy plantation can sell alcohols for \$1.33/gal or gasoline for \$2.04/gal, including 15% ROI and depreciation (\$1.08/gal of ethanol or \$1.68/gal of gasoline for cash costs only).

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## Collaborators

Texas A&M University (College Station TX) developed the MixAlco process and its supporting technologies. Terrabon, L.L.C., (Houston, TX) holds the world-wide exclusive license to the MixAlco process and its supporting technologies. Trimeric is a third-party, technology-neutral, and independent technical services firm.