Biomass Conversion to Mixed Alcohol Fuels Using the MixAlco Process

MARK T. HOLTZAPPLE,* RICHARD R. DAVISON, M. KYLE ROSS, SALVADOR ALDRETT-LEE, MURLIDHAR NAGWANI, CHANG-MING LEE, CHAMPION LEE, SETH ADELSON, WILLIAM KAAR, DAVID GASKIN, HIROSHI SHIRAGE, NAN-SHENG CHANG, VINCENT S. CHANG, AND MITCHELL E. LOESCHER

*Department of Chemical Engineering,
Texas A&M University, College Station, TX 77843-3122,
E-mail: MTH4500@CHENNOV1.TAMU.EDU*

Abstract

The MixAlco process is a patented technology that converts any biodegradable material (e.g., sorted municipal solid waste, sewage sludge, industrial biosludge, manure, agricultural residues, energy crops) into mixed alcohol fuels containing predominantly 2-propanol, but also higher alcohols up to 7-tridecanol. The feedstock is treated with lime to increase its digestibility. Then, it is fed to a fermentor in which a mixed culture of acid-forming microorganisms produces carboxylic acids. Calcium carbonate is added to the fermentor to neutralize the acids to their corresponding carboxylate salt. The dilute (~3%) carboxylate salts are concentrated to 19% using an amine solvent that selectively extracts water. Drying is completed using multi-effect evaporators. Finally, the dry salts are thermally converted to ketones which subsequently are hydrogenated to alcohols. All the steps in the MixAlco process have been proven at the laboratory scale. A techno-economic model of the process indicates that with the tipping fees available in New York ($126/dry tonne), mixed alcohol fuels may be sold for $0.04/L ($0.16/gal) with a 60% return on investment (ROI). With the average tipping fee in the United States rates ($63/dry tonne), mixed alcohol fuels may be sold for $0.18/L ($0.69/gal) with a 15% ROI. In the case of sugarcane bagasse, which may be obtained for about $26/dry ton, mixed alcohol fuels may be sold for $0.29/L ($1.09/gal) with a 15% ROI.

Index Entries: MixAlco process; municipal solid waste; sewage sludge; alcohol fuels; biomass.

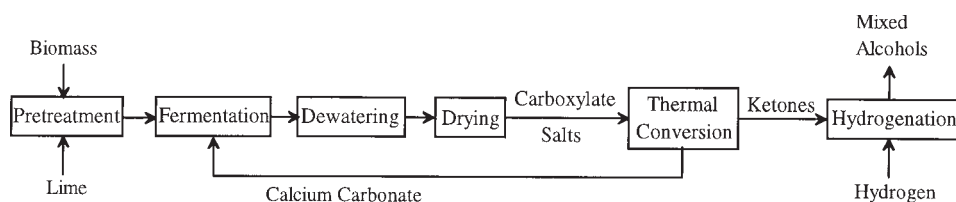*Author to whom all correspondence and reprint requests should be addressed.

Fig. 1. Overview of MixAlco process.

Introduction

Under nonsterile, anaerobic conditions, biomass is converted to acetic acid according to the following reaction.

$$C_6H_{12}O_6 + 2\ H_2O + 4\ NAD^+ \rightarrow 2\ H_3CCOOH + 2\ CO_2 + 4\ NADH + 4\ H^+ \quad (1)$$

Here, glucose represents biomass although many other components (e.g., cellulose, hemicellulose, starch, pectin, fats, proteins) also may be converted to acetic acid. The reducing power of the NADH in Eq. 1 may be released as hydrogen using endogenous hydrogen dehydrogenase.

$$NADH + H^+ \rightarrow NAD^+ + H_2 \qquad (2)$$

Methanogens are able to react the carbon dioxide produced in Eq. 1 with the hydrogen from Eq. 2 to make methane.

$$CO_2 + 4\ H_2 \rightarrow CH_4 + 2\ H_2O \qquad (3)$$

Further, acetoclastic methanogens can produce methane from acetic acid, so the potential exists to convert all the biomass to methane, a low-value product.

Methanogens prefer near-neutral pH, thus low pH may be used to inhibit their growth. Methanogens are inherently slow-growing, so if acetic acid is rapidly produced, it drops the pH leading to so-called "stuck" fermentors. In "stuck" fermentors, the reducing power that would have gone into methane production is incorporated into higher carboxylic acids, primarily propionic and butyric acids with lesser amounts of valeric, caproic, and heptanoic acids. The resulting "mixed acid" fermentation may be used to produce fuels and chemicals. Excellent review articles by Ghose (1) and Playne (2) provide more details.

The MixAlco process (Fig. 1) employs a mixed-acid fermentation to produce alcohols such as 2-propanol, 2-butanol, and higher alcohols. First, the biomass is treated with lime to increase its digestibility. Then, the lime-treated biomass is fed to a fermentor in which a mixed culture of acid-forming microorganisms produces carboxylic acids. To maintain the pH, calcium carbonate is added, which reacts with the acids to form carboxylate salts, such as calcium acetate. The carboxylate salts are dewatered and dried. Finally, the dry carboxylate salts are thermally converted to ketones, which may be hydrogenated to alcohols.

Features of the MixAlco process were employed as early as 1914 when Lefranc *(3)* patented a process to convert waste biomass into butyric acid, which was neutralized with calcium carbonate. Subsequently, the calcium butyrate was thermally converted to ketones for high-octane "Ketol" motor fuel *(4)*. Recently, Playne *(5)*, and Wise *(6)* have investigated various aspects of this technology.

Process Description

Pretreatment

In recent years, our laboratory has investigated lime treatment of biomass *(7)* including switchgrass *(8)*, corn stover *(9)*, poplar wood *(10)*, wheat straw, and bagasse *(11)*. In the case of herbaceous materials, effective lime treatment conditions are ~100°C for 1–2 h with a lime loading of 0.1 g $Ca(OH)_2$/g biomass. The pretreatment is not affected by water loading; 5–15 g H_2O/g biomass is effective provided mixing is adequate. In the case of high-lignin, woody biomass, combining lime treatment with pressurized oxygen (1.5 MPa) is effective *(10)*, although pretreatment costs increase because a pressure vessel is required.

Most of our investigations of lime pretreatment have used extracellular cellulases, as summarized by Holtzapple et al. *(12)*. In these cases, lime treatment increased digestibility by 5.6–13.3 times; the large increase resulted because untreated biomass is so nondigestible. In a few studies *(13,14)*, untreated and lime-treated biomass have been digested in a cattle rumen to simulate the fermentation conditions in the MixAlco process. In these studies, the digestibility increased by 1.06–2.03 times; the smaller increase results because rumen microorganisms are very effective at digesting even untreated biomass. Table 1 summarizes the investigations of rumen digestibility. In all cases, the digestibility of the agricultural residues nearly doubled, whereas the sorted municipal solid waste (MSW) increased by only 1.1–1.3 times. This modest increase resulted because many MSW components (e.g., copy paper) have already been extensively alkaline-treated in the paper-pulping process, and other components (e.g., newspaper, wood) are highly lignified and would need lime + oxygen treatment to become digestible. Table 2 shows the MSW composition used in this study; about 23% of the MSW components are highly lignified.

Figure 2 shows the proposed industrial implementation of the lime pretreatment process. Screw conveyors A-1 and A-2 auger biomass and lime, respectively. The pretreatment vessel A-3 is an epoxy-coated concrete tank divided into four sections, each of which is well mixed using circulation pump A-4. With four well-mixed stages, the reaction closely approximates plug flow. Live steam is injected into the pretreatment tank to maintain a temperature near 100°C. The residence time for the solids is 1 h, after which they are countercurrently washed in an epoxy-coated concrete tank A-5 divided into 10 sections. The wash water consists of fermentation broth that contains carboxylate product. Each section of the countercurrent

Table 1
Ruminant Digestibility of Untreated and Lime-Treated Agricultural Residues

Agricultural residue	Time (h)	Untreated (g digested/g fed)	Lime treated (g digested/g fed)
Sugar-cane bagasse *(14)*	48	0.308	0.627
African millet straw *(14)*	48	0.451	0.899
Sorghum straw *(14)*	48	0.541	0.829
Tobacco stalks *(14)*	48	0.344	0.679
MSW (>40 mesh) *(13)*	120	0.555	0.700
MSW (<40 mesh) *(13)*	120	0.647	0.709
Switchgrass *(13)*	120	0.439	0.792
Cardboard *(13)*	120	0.685	0.726
Newspaper *(13)*	120	0.197	0.252

Table 2
Composition of Sorted Municipal Solid Waste

Low lignin		High lignin	
Cardboard	21.6%	Newspaper	14.3%
Packaging	11.0%	Wood	6.5%
Printer paper	10.4%	Brush	2.8%
Leaves	8.0%	Total	23.6%
Misc. nonpackaging	6.5%		
Books and magazines	5.1%		
Grass	4.5%		
Food waste	4.1%		
Tissue paper	3.2%		
Greens	2.0%		
Total	76.4%		

wash tank is well mixed using impellor mixers A-7. Using pumps A-6, liquid is transferred from a downstream section and pumped through a countercurrent heat exchanger A-11 to raise its temperature so it can be put into the next upstream tank. In this manner, the wash liquid is preheated to minimize steam requirements in the pretreatment vessel A-3. The liquid exiting the pretreatment vessel is countercurrently cooled in heat exchanger A-11. Because portions of the biomass are solubilized in the pretreatment vessel, this liquid is returned to a fermentor to digest the solubilized biomass components.

To pump the biomass solids into the fermentor, a slurry pump could be employed; however, the cost of these pumps is prohibitive. An alternate method is proposed in which, by gravity, a slurry containing the solids would flow into the first of three tanks A-9. The second tank has liquid which is pumped (A-8) to the top of the slurry-containing third tank. The pumped liquid acts as a liquid piston that pushes slurry out of the third
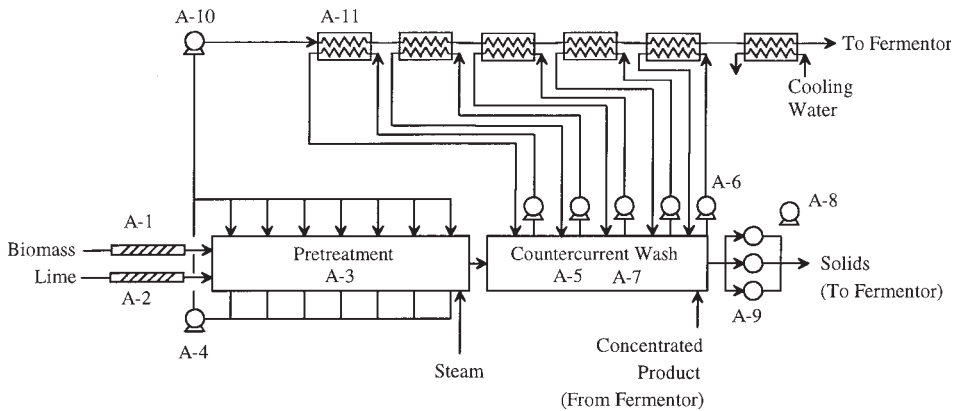
Fig. 2. Pretreatment section.

tank into the fermentor. Once the slurry in the third tank has been replaced with liquid, the functions of the tanks are rotated and the liquid in the third tank is used to push out solids from the first tank, which recently became full. The second tank, which was liquid-filled, is now empty and can receive new slurry. The functions of the three tanks are cycled indefinitely. Using this approach, the motive force is provided by a centrifugal pump, which is inexpensive relative to a slurry pump.

Fermentation

The goals of the fermentation are

1. High product concentration to minimize recovery costs;
2. High conversion to make best use of the biomass;
3. Minimal methane production to preserve product value; and
4. Affordable residence time.

The first two goals can be met using a countercurrent fermentation *(12,15)* in which solids and liquid pass in opposite directions through a series of fermentors. Fresh biomass is added to the fermentor containing the highest carboxylate concentration and fresh water is added to the fermentor with the most digested biomass. This countercurrent flow arrangement is beneficial because biomass becomes more recalcitrant as the "easy" components are digested. Also, the product carboxylate salts are *extremely* inhibitory. The fermentor with the most easily digested biomass is the most inhibited and the fermentor with the least digestible biomass is the least inhibited. In the countercurrent fermentor, both high conversions *and* high product concentrations are possible.

The third goal is met by using methanogen inhibitors. Although a number of inhibitors (e.g., 2-bromoethanesulfonic acid, monensin) have been reported in the literature *(16,17)*, we have had the greatest success with methane analogs (e.g., bromoform, iodoform), which can completely inhibit methane formation. Because bromoform and iodoform are too reac-
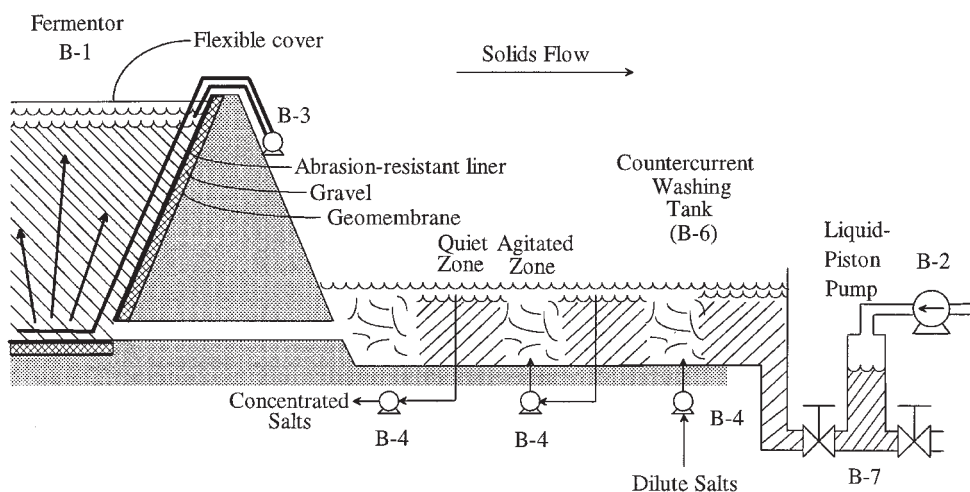
Fig. 3. Sideview of fermentation section.

tive to enter the stratosphere, they do not damage the ozone layer and hence are not regulated by the Montreal Protocol.

The fourth goal is achieved by employing inexpensive fermentors. For comparison purposes, a 40,000 m³ tank has the following costs: stainless steel, $380/m³; carbon steel, $125/m³ *(18)*; unlined concrete, $69/m³ *(19)*; in-ground plastic, $12/m³. Clearly, in-ground plastic tanks have a significant cost advantage, allowing the economical use of long residence times, which are required for the mixed-acid fermentation.

Figure 3 shows a side-view schematic of the proposed in-ground plastic tank. The walls are made of dirt dug from the fermentor interior. The slope of the dirt is 30° with respect to the horizon, which is stable without additional support. (Note: To make the figure more compact, the slope of the dirt in Fig. 3 is much steeper than will actually be employed.) The dirt is covered with a 0.5-mm geomembrane, 75 mm of gravel (or sand), and an abrasion-resistant 6.3-mm high-density polyethylene sheet. The geomembrane provides a backup in case the primary lining fails. To counterbalance the hydrostatic pressure, the gravel between the two linings would contain water of the same height as the liquid inside the fermentor. Thus, the primary liner must provide leakage resistance only; it does not need to provide structural support. The composition of the water in the gravel layer will be constantly monitored to determine if there is a leak in the primary barrier, which requires repair.

It is proposed that the fermentors (B-1) be operated with a high solids concentration, which settles to the bottom, and a relatively solids-free layer of liquid on top. To achieve mixing, the liquid will be decanted from the top, pumped (B-3), and percolated upward from distributors located on the bottom of the fermentor. To exit the fermentor, solids flow out the bottom into a countercurrent washing tank (B-6), which consists of a series of well-
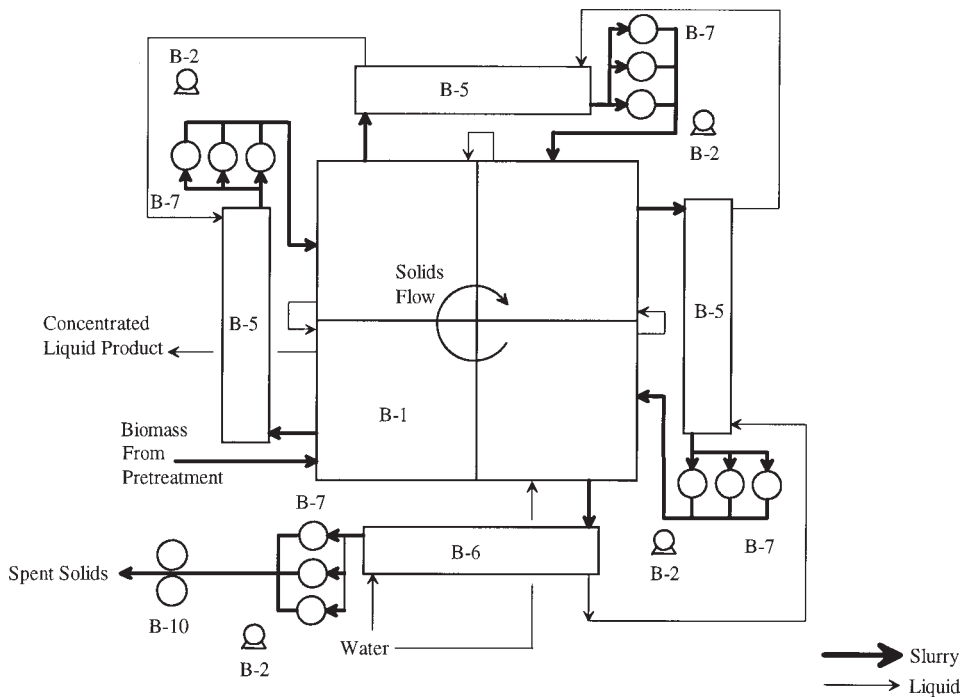
Fig. 4. Aerial view of fermentation section.

mixed zones and quiescent zones from which liquid can be decanted and pumped (B-4) countercurrently. Most of the countercurrent washing tanks employ three stages, except for the last one, which employs 10 stages to minimize loss of carboxylate product trapped within the biomass. The washed solids may be transported to the next fermentor using a liquid-piston pump, as was described earlier.

Figure 4 shows an aerial view of the proposed fermentors. There are four fermentors; solids pass in one direction and liquid passes in the other. The spent solids are sent to a screw press (B-10) that removes most of the water to prepare the solids for combustion to provide process heat. The fermentor upgrades the value of the biomass as a boiler fuel by removing less energy-rich carbohydrates while retaining energy-rich lignin. Also, the microorganisms make the fuel more dense; raw hammer-milled MSW has a density of about 50 dry kg/m^3, whereas after digestion, the residue is 400 dry kg/m^3 (1200 wet kg/m^3). For each tonne of organic MSW/sewage sludge (SS) fed to the process, 0.380 tons of undigested residue will remain. Of the undigested residue, 0.114 ton can be combusted for process heat and electricity production and the remaining 0.266 ton can be sold as fuel.

The components of MSW/SS are complex and include ash and organic materials (cellulose, hemicellulose, starch, pectin, sugars, protein, fat, lignin). The organic materials are estimated by ashing the biomass at 550°C for 2 h; the lost weight is termed "volatile solids" (VS). The composition of

MSW is 4.2% ash, 95.8% VS, and 14.1% lignin, and the composition of SS is 39.5% ash, 60.5% VS, and 0% lignin *(20)*.

Modeling the performance of the fermentor is a particular challenge because the feedstock is a mixture of biomass components, the microorganisms are a mixed culture, and the products are a mixture of carboxylates. To handle such a complex system, Loescher *(20)* developed the Continuum Particle Distribution Modeling (CPDM) method, which tracks biomass particles as they move through the fermentation train. The CPDM method requires the carboxylate concentration be measured in a series of batch cultures each operated at a different initial substrate concentration. A kinetic expression is fit to the batch data, which describe the intrinsic kinetics of the fermentation. Then, this intrinsic kinetic expression is used to model a four-stage, countercurrent fermentor.

The mixed microbial culture requires both a source of energy and nutrients. Rapier *(13)* determined that SS can provide nutrients to an MSW fermentation, optimally in an 80:20 MSW:SS ratio. From a batch study, Ross *(21)* determined that the following intrinsic kinetic expression describes the fermentation of such a mixture

$$\hat{r} = \frac{0.21(1-x)^{6.0}}{1 + 610(\phi A_e)^{4.38}} \tag{4}$$

where

$$\hat{r} = \text{reaction rate}\left(\frac{\text{g acetate equivalents produced}}{(\text{g initial VS}) \cdot \text{d}}\right)$$

$$x = \text{conversion (dimensionless)} = \frac{\left(60.05 \frac{\text{g}}{\text{mol}}\right) A_e}{S}$$

A_e = acetic acid equivalents (mol/L)

= 1.0 (acetic) + 1.75 (propionic) + 2.5 (butyric) + 3.25 (valeric)

+ 4.0 (caproic) + 4.75 (heptanoic) (Note: each acid concentration is mol/L)

S = initial substrate concentration, hydrolyzed to sugars (g/L)

$$= 1.11 \frac{\text{g glucose}}{\text{g cellulose}} \times \text{VS} \qquad \text{(Note: volatile solids assumed to be cellulose)}$$

VS = volatile solids concentration (g/L)

$$\phi = 0.58 \frac{\text{total moles of carboxylic acid}}{\text{moles of acetic acid equivalents}}$$

Using a conversion distribution function, this model was verified by predicting (within 10%) the steady-state operation of a laboratory four-stage, countercurrent fermentation with a biomass concentration in the
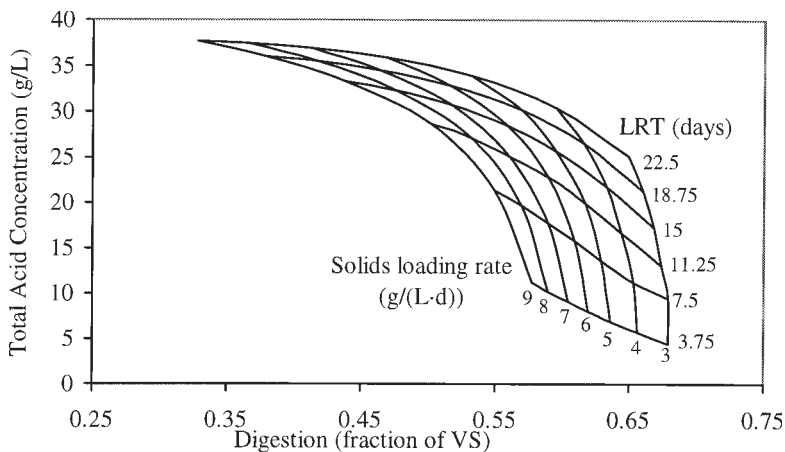
Fig. 5. CPDM model predictions for 80:20 MSW:SS. (Biomass concentration in fermentor = 300 g biomass volatile solids/L liquid. Solids loading rate is expressed/L of liquid.)

fermentors of 120 g VS/L of liquid. Figure 5 shows the predictions of an industrial-scale fermentor with a biomass concentration in the fermentors of 300 g VS/L of liquid. (Note: The laboratory reactors were operated at lower concentration because the liquid was "harvested" only once each day requiring a large liquid inventory. In contrast, the liquid in the industrial reactors would be harvested continuously, thus requiring less liquid inventory.) By selecting the desired conversion and product concentration, Fig. 5 shows the required solids loading-rate and liquid-residence time.

In the fermentation modeled in Fig. 5, calcium carbonate was the neutralizing agent that maintained the pH between 5.8 and 6.2. At this pH, the exponent on the product inhibition term is 4.38. In his studies, Loescher *(20)* employed a near-neutral pH and found the product inhibition exponent was 2.11–2.50; thus, the microorganisms are severely inhibited at lower pH. Although the reaction rate would certainly improve by operating at a near-neutral pH, this would require the neutralizing agent to be lime, rather than calcium carbonate, and would incur a significant added expense.

Dewatering

Low-molecular-weight secondary and tertiary amines (e.g., methyl diethyl amine, triethyl amine, diisopropyl amine) form a separate phase when they contact water. Typically, the amine phase contains about 30% water. Interestingly, by raising the temperature of the amine phase by about 20–25°C, most of the absorbed water drops out of solution. Further, these amines selectively remove water from salt solutions, which concentrates the salts in the water left behind. The recovered water has a small concentration of dissolved amine, which can be removed by steam stripping.

In the 1950s through the 1970s, these amines were investigated as a means to extract drinking water from brackish and sea water *(22–26)*; this

water-extraction process was demonstrated at a pilot scale *(27)*. In this water-desalination application, the technology could not compete with alternatives because

1. The amine phase less selectively rejects monovalent ions (the dominant ions in sea water) and hence they are coextracted with the water into the amine phase;
2. To meet drinking water standards, all of the amine must be stripped from the recovered water, which is difficult unless the pH is raised to volatilize the amine; and
3. Drinking water can have only a very small amount of residual salt requiring the use of reflux and additional rectifying stages.

Although the amine-dewatering technology cannot compete with alternate technologies for water desalination, it is very well suited to concentrate calcium carboxylate salts from fermentation broths. In our case, we can overcome the difficulties with water desalination because

1. The fermentor cations are divalent calcium ions, which have less tendency to be extracted into the amine phase, so the separation is more selective;
2. Lime can be added to the stripper to allow complete recovery of amine from water; and
3. Any residual salts in the recovered water are simply returned to the fermentor, thus a rectifying section is not essential.

For fermentors that operate at mesophilic temperatures (40°C), the preferred extractant is an amine solution containing 1 volume of triethyl amine and 2 volumes of methyl diethyl amine. By extracting 80–90% of the water from the fermentation broth, the amine-dewatering technology is able to concentrate the fermentation broth from 2–4% salt to about 19% salt. Further, the heat requirements are very low (140 kJ/kg water removed) compared to 770 kJ/kg water removed for triple-effect evaporators and 2310 kJ/kg for single-effect evaporators. Alternate dewatering approaches—such as reverse osmosis, electrodialysis, or vapor-compression—require too much capital to be economical.

Figure 6 shows a schematic flow diagram of the proposed dewatering technology. Lime is added to fermentation broth in mixing vessel C-1. At elevated pH, minerals and "slime" precipitate and are recovered in settling tank C-2. Then, this clarified broth is pumped (C-3) to a series of mixer/settlers C-6, which contain a mixing zone agitated by mixers C-8, a settling zone consisting of a series of closely space parallel plates, and a separation zone in which the water-rich amine floats to the top and the aqueous phase settles to the bottom. In the series of mixer/settlers, the water is pumped (C-4) from right-to-left, where it becomes increasingly concentrated in carboxylate. The amine extractant flows by gravity from left-to-right and becomes increasingly saturated with water. The water-rich amine is pumped (C-5) to a countercurrent heat exchanger C-15, where
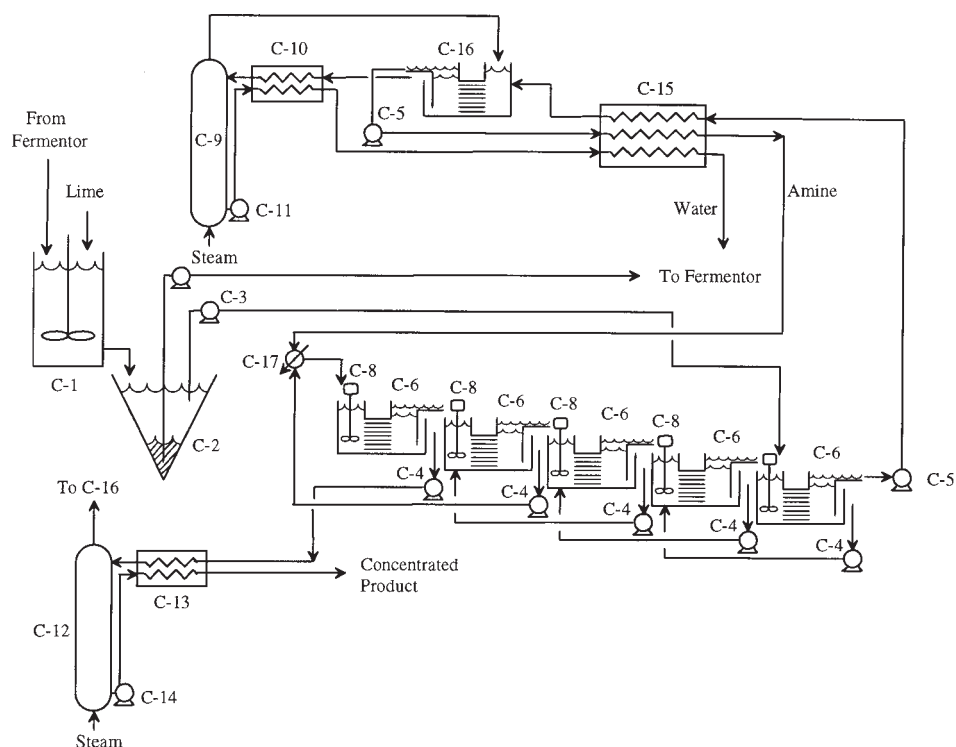
Fig. 6. Dewatering section.

it becomes prewarmed from hot water and hot water-lean amine flowing in the opposite direction. In the heat exchanger, as the temperature of the water-rich amine rises, water phases out. The latent heat required for the water to separate from the amine prevents the temperature from rising as much as it would in the absence of a phase separation. At the right of the countercurrent heat exchanger, the temperature difference between the water-rich amine and water-lean amine is small (e.g., 1.3°C), whereas at the left, the temperature difference is larger (e.g., 5.6°C). The process of warming the water-rich amine is completed in separator C-16, where hot vapors are directly introduced into the amine, raising its temperature about 20–25°C above the temperature in the mixer/settlers C-6. The water that separates from the amine is relatively salt-free, but has about 5% amine dissolved in it. This water is prewarmed in countercurrent heat exchanger C-10 and sent to stripper C-9. The vapors exiting the stripper are directed to separator C-16 to provide some of the energy requirements. (Similarly, stripper C-12 removes residual amine from the concentrated product.) The recovered water and regenerated water-lean amine are sent back through the countercurrent heat exchanger C-15. The water is returned to the fermentor and the amine is sent back to the mixer/settlers C-6 to absorb more water. When amine and water are mixed, the heat of solution is removed in heat exchanger C-17.
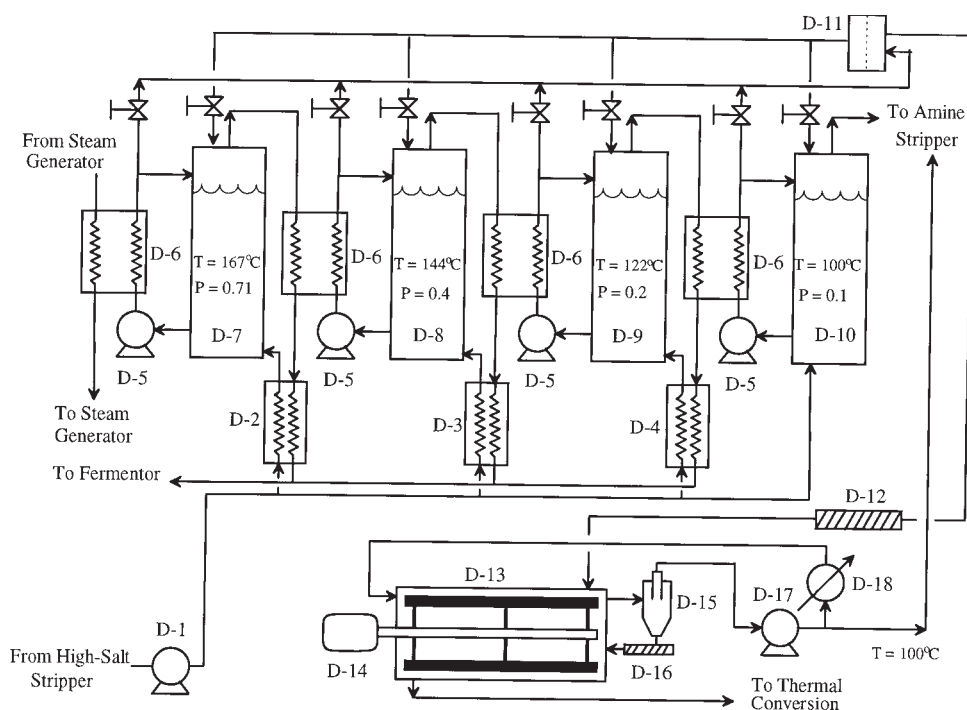
Fig. 7. Drying section. (Note: pressures are in MPa.)

Equilibrium data needed to design the water-extraction system are available for calcium acetate *(28)*, propionate, and butyrate *(29)*. The data show that as the carboxylate molecular weight increases, the amine tends to be less selective, meaning more salt is coextracted with the water. Because equilibrium data are not yet available for actual fermentation broth, the dewatering system was designed using calcium acetate data. The final cost of the system for dewatering real fermentation broth was assumed to be 20% higher because of additional costs incurred to handle the reduced selectivity of the higher carboxylates.

Drying

The concentrated carboxylate leaving the dewatering section of the plant is about 19% salt. To complete the drying process, the equipment shown in Fig. 7 is proposed. The concentrated product is preheated in countercurrent heat exchangers D-2 to D-4 and then introduced into multi-effect evaporators D-7 to D-10. Using circulation pumps D-5, the contents of tanks D-7 to D-10 are circulated through heat exchangers D-6. High-temperature steam is introduced into the left-most heat exchanger, which vaporizes water in tank D-7. As water evaporates, steam is generated at 167°C. This steam is then used to evaporate water in tank D-8, which generates steam at 144°C. This process continues until the final effect generates steam at 100°C, which is sent to the amine stripper.

As salt precipitates in the multi-effect evaporators, the salt slurry is sent to centrifuge D-11, which separates the salt and returns the liquid back to the tank. The recovered salt is still wet, so the residual water is removed in drier D-13. In the drier, superheated steam is introduced at the left; this causes water to evaporate from the wet solids. Saturated steam exits the drier through cyclone D-15, which removes any entrained salt. Most of the saturated steam is recycled using blower D-17, which passes the steam through heat exchanger D-18 where it becomes superheated. A portion of the saturated steam is bled off and directed to the amine stripper in the dewatering section of the plant.

Thermal Conversion

When calcium carboxylate salts are heated to about 430°C, the salts decompose to ketones with a reported yield as high as 99.5% of theoretical *(30)*. Adelson *(31)* determined the decomposition to be a first-order reaction. At 430°C, the half-life of the reaction is less than 1 min, so the reaction is very rapid. Reaction temperatures as high as 508°C had no effect on the ketone quality *(12)*, so possibly even higher reaction temperatures could be employed with even shorter half lives. (To provide a margin of safety, the reactor was designed with a residence time of 30 min.) It is important to remove the ketone product as rapidly as possible to prevent its destruction. One approach is to flow hot inert gas (e.g., nitrogen) through the salt to sweep out the ketone as its formed *(30)*. This approach is difficult to implement on an industrial scale because large heat exchangers are required to cool, and reheat, the circulating gas. An alternate approach is to operate the thermal convertor under vacuum conditions so the vapor density is low, and the residence time in the thermal convertor is short. For design purposes, we selected a total pressure of 20 mm Hg, but the suitability of this pressure in industrial equipment must be experimentally verified.

A schematic of the proposed thermal conversion process is shown in Fig. 8. The dry carboxylate salt enters a lock hopper on contactor E-1. Using vacuum pump E-22, interstitial air is removed from the salt. Once the air is removed, the cold salt is introduced into contactor E-1, where is contacts hot ketone vapors, thus warming the salt and cooling the ketones to prevent their decomposition. Motor E-2 agitates the contents of contactor E-1 to ensure good mixing. The prewarmed salt enters thermal convertor E-15 using screw conveyor E-14.

Steel shot is heated in heat exchanger E-19 by direct contact with hot combustion gases introduced by blower E-20. The hot shot is conveyed by screw conveyor E-21 and is introduced into a lock hopper on thermal convertor E-15. Once the shot is purged of interstitial air by vacuum pump E-22, the hot shot is introduced into thermal convertor E-15, where the hot shot and salt are mixed by motor E-17. The hot shot provides the heat of reaction for the thermal decomposition of carboxylate salts to ketones. To simulate plug flow, the thermal convertor is divided into four chambers, allowing nearly complete conversion of the calcium carboxylate to calcium
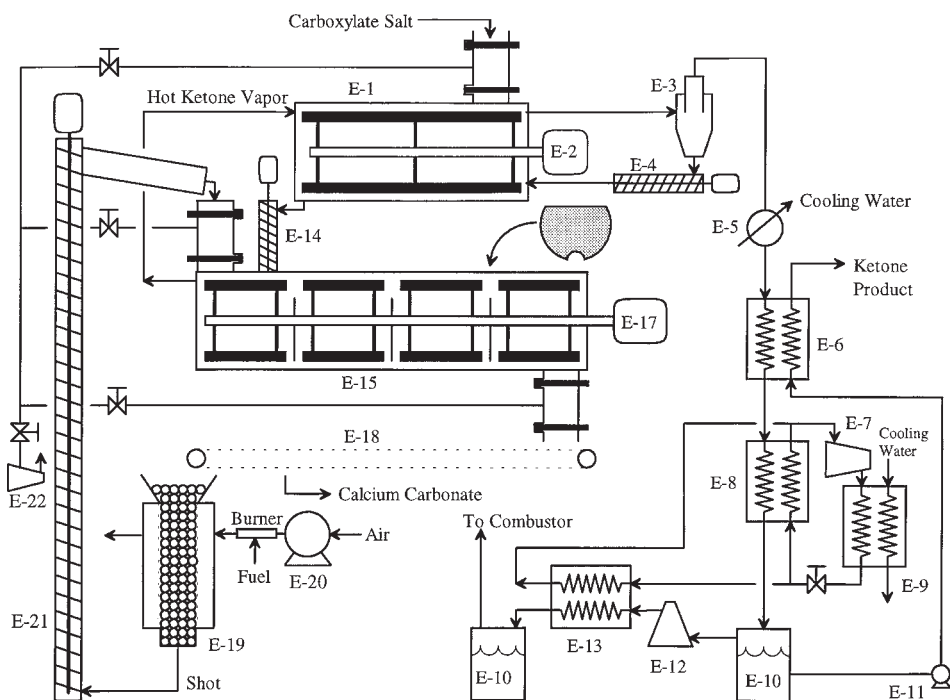
Fig. 8. Thermal conversion section.

carbonate. The hot calcium carbonate and shot exit through a lock hopper onto a vibrating conveyor E-18, which allows the fine calcium carbonate to be separated from the coarse shot. The shot is returned to heat exchanger E-19 so it can be circulated through the system.

The ketones exiting contactor E-1 are sent to cyclone E-3 to remove any entrained solids, which are returned to contactor E-1 using screw conveyor E-4. The ketones are cooled using heat exchanger E-5. The ketones flow through countercurrent heat exchanger E-6, where they are chilled. In condenser E-8, the ketone vapors liquefy at –40°C and are collected as product in tank E-10. If the product were pure acetone, the ketone vapor pressure would be 5 mm Hg. With the presence of higher ketones, the ketone vapor pressure will be much less. (Note: the other portion of the 20 mm Hg operating pressure is noncondensible gases.) The condenser is chilled using an ammonia refrigeration loop powered by compressor E-7. Any noncondensible gases in the system, which are present from leakage or from decomposition products, are removed using vacuum pump E-12. Residual ketones in the noncondensible gas stream are removed by condensation in heat exchanger E-13 and recovered in tank E-10.

Hydrogenation

Figure 9 shows a schematic of the proposed hydrogenation reactors. Optimization studies were performed using kinetics determined for a mix-
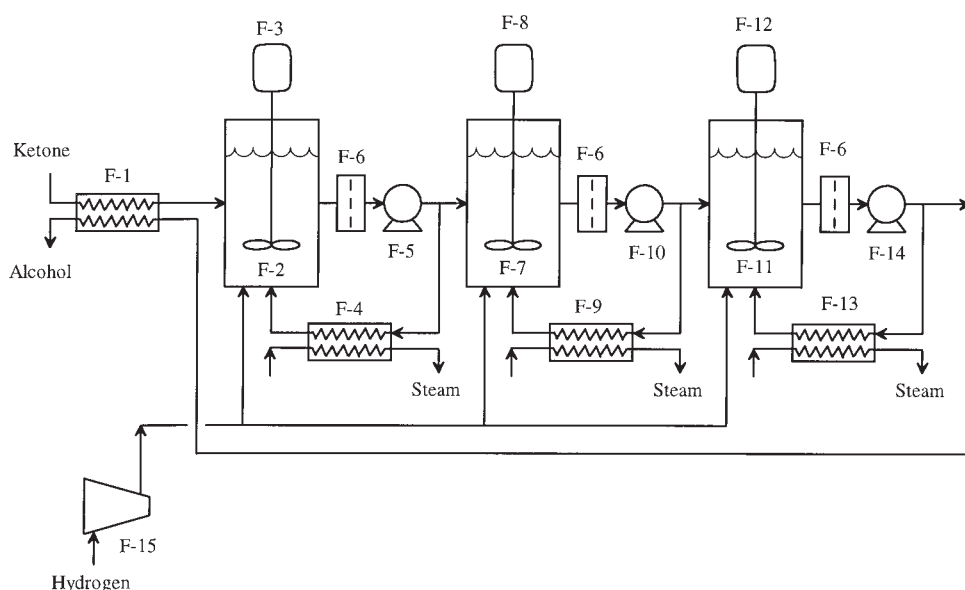
Fig. 9. Hydrogenation section.

ture of ketones similar to that which will be produced in the MixAlco process *(32)*. The optimization routine employed a simulated annealing *(33)* algorithm to minimize the hydrogenation cost/liter of alcohol while achieving a total conversion of 98%. The independent variables were temperature (130°C upperbound), hydrogen partial pressure (1.5 MPa), total pressure (2.3 MPa upperbound), Raney nickel catalyst concentration (200 g/L upperbound), number of reactors, conversion per stage, and agitation power input (6 kW/m³ upperbound). Hydrogen mass transfer was estimated using methods of Brehm and Oguz *(34)*. The optimal conditions are $T = 130°C$, $P_{hydrogen} = 1.5$ MPa, $P_{total} = 2.3$ MPa, 200 g/L Raney nickel catalyst, three stages, residence times $\theta_1 = 554$ s, $\theta_2 = 782$ s, and $\theta_3 = 750$ s, conversions $x_1 = 0.68$, $x_2 = 0.92$, $x_3 = 0.98$, and agitation powers of 6.0, 2.7, and 0.7 kW/m³ for Reactors 1, 2, and 3, respectively.

In Figure 9, the ketone is preheated in heat exchanger F-1. The ketone is introduced to Reactor 1 (F-2) where it is agitated using mixer F-3. Compressor F-15 pressurizes the hydrogen to 2.3 MPa. Catalyst is retained within the reactor using filter F-6. Pump F-5 circulates the liquid contents through heat exchanger F-4 and returns them to Reactor 1 (F-2). The heat of reaction is used to generate steam that can be employed elsewhere in the process. This process is repeated in the other two reactors. The final alcohol product is cooled in heat exchanger F-1.

Economics

A base-case design of 40 dry tonne/h was chosen. This quantity of feedstock corresponds to the SS and biodegradable MSW output from a city

Table 3
Technical Assumptions

Component	Composition (mol %)	
	Carboxylic acids	Ketones/alcohols
C2	61.5	
C3	13.5	53.4
C4	9.2	11.7
C5	4.5	10.6
C6	6.8	5.7
C7	4.6	8.0
C8		5.9
C9		2.0
C10		1.0
C11		0.9
C12		0.4
C13		0.3

Pretreatment: $t = 1$ h, $T = 100°C$, lime loading = 0.1 g $Ca(OH)_2$/g, water loading = 15 g H_2O/g

Fermentation: 0.62 g digested/g biomass VS, 0.61 g carboxylic acid/g digested, 16 µg iodoform added/L liquid added, fermentor solids concentration = 300 g VS/L of liquid

Dewatering: 1 vol triethyl amine: 2 vol methyl diethyl amine, extraction temp = 40°C, separation temp = 65°C, amine residence time = 40 s (per stage), water residence time = 5 min (per stage)

Thermal conversion: stoichiometric yield of ketones, $T = 430°C$, residence time = 30 min

of about 800,000. The technical assumptions are shown in Table 3 and the economic assumptions are shown in Table 4. The equipment was sized for the base-case capacity. The purchase price for standard items (e.g., pumps, metal tanks, shell-and-tube heat exchangers, compressors, distillation columns) was determined from standard correlations *(35)* and nonstandard equipment (e.g., fermentors, screw press, plate-and-frame heat exchangers) was determined by manufacturers' quotations. The total purchase price of the equipment was multiplied by a Lang factor to estimate the fixed capital investment (FCI). The Lang factor accounts for such costs as: installation, instrumentation, piping, electrical installation, buildings, yard improvements, service facilities, land, engineering, construction, contractor fees, and contingency. A Lang factor of 4.13 is recommended for plants that process both solids and liquids *(35)*. This method of estimating the FCI is accurate to within ± 30%. Table 5 summarizes the capital costs of each section of the plant.

Table 6 summarizes the utility requirements for each section of the plant. The process is well integrated as the amount of low-pressure steam generated in the drying section is needed in the pretreatment and dewatering sections. The electrical energy needs are only 16% of the total energy requirement, so electricity can be cogenerated. Alternatively, some of the

Table 4
Economic Assumptions[a]

Capacity exponents (35)	
	Exp
Pumps	0.33
Shell-and-tube heat exchanger	0.44
Plate-and-frame heat exchanger	1.00
Vessels	0.67
Fermentor	1.00
Blower	0.59
Compressor	0.79
Motor	0.69
Screw conveyor	0.56
Mixers	0.69
Screw press	0.67
Stripper	0.86
Centrifuge	0.49
Cyclone	0.56
Vacuum pump	0.69
Labor	0.25

[a]Plant operation = 8,000 h/yr; Working capital = 0.15 × FCI 1998 dollars. Depreciation = 10 yr, straight line; Annual maintenance = 0.04 × FCI. Annual maintenance includes labor, materials, and supervision.

Table 5
Capital Cost

	40 tonne/h	2 tonne/h	10 tonne/h	160 tonne/h	800 tonne/h
Pretreatment	2,329,142	312,899	857,790	7,100,448	29,098,798
Fermentation	14,712,398	1,418,902	4,616,745	53,754,332	235,600,470
Dewatering	4,981,554	448,339	1,534,636	17,440,418	79,171,828
Drying	2,964,126	654,121	1,464,677	6,060,011	14,087,986
Thermal conversion	3,899,216	591,438	1,601,533	9,793,068	29,716,860
Hydrogenation	1,097,911	182,836	472,818	2,598,070	7,204,010
Total	29,984,347	3,608,535	10,548,199	96,746,347	394,879,952

large power consumers (e.g., amine pump, refrigeration compressor) could be driven by steam turbines rather than electric motors.

Figure 10 shows an optimization study in which the product concentration exiting the fermentors was varied. The optimization indicates that the lowest cost of the combined fermentation/dewatering occurs at about 22 g carboxylic acids/L. At this optimal product concentration and the assumed conversion of 0.62 g digested/g biomass VS (*see* Table 3), Fig. 5 shows that the liquid residence time is about 14 d and the solids loading rate

Table 6
Utilities Summary

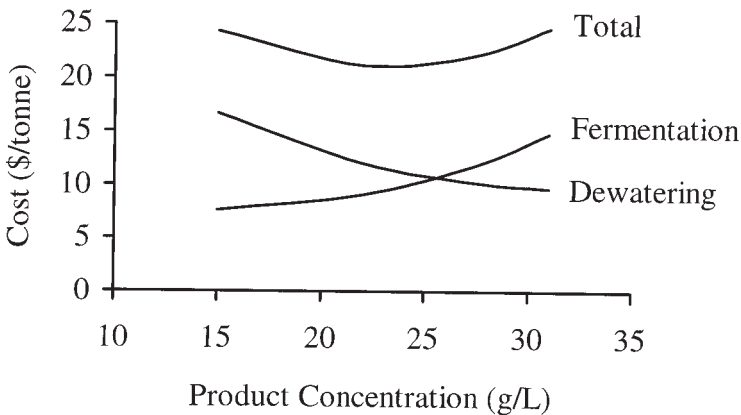| Section of plant	Electricity (kWh/tonne biomass)	High-pressure[a] steam (tonne/tonne biomass)	Low-pressure[b] steam (tonne/tonne biomass)	Fuel (GJ/tonne biomass)	Cooling water (m³/tonne biomass)
Pretreatment	10.74		0.224		16.23
Fermentation	35.41			−7.05	28.50
Dewatering	10.34		0.594		
Drying	15.00	0.666	−0.666		
Thermal conversion	17.73			0.17	6.44
Hydrogenation	5.55		−0.069		
Total	94.77	0.666	0.083	−6.88	51.17

[a]1.7 MPa.
[b]0.1 MPa.

Fig. 10. Optimization of fermentor and dewatering sections.

is 4.5 g VS/(d · L liquid in the four fermentors). The solids loading rate for an individual fermentor would be four times as large, or 18 g VS/(d · L liquid in an individual fermentor). Provided each fermentor has the same volume, the solids residence time θ_i in Fermentor *i* is calculated as follows *(21)*.

$$\theta_i = \frac{300 \ \frac{g \ VS}{L \ liquid}}{18 \frac{g \ VS}{d \cdot L \ liquid}(1 - x_i)} \tag{5}$$

The CPDM model indicates the conversion in each fermentor is $x_1 = 0.31$, $x_2 = 0.50$, $x_3 = 0.58$, and $x_4 = 0.62$. At these conversions, Eq. 5 indicates that the solids residence time in each fermentor is $\theta_1 = 24$ d, $\theta_2 = 33$ d, $\theta_3 = 39$ d, and $\theta_1 = 44$ d, giving a total solids residence time of 140 d. (Note: This 140-d

solids residence time, which is required to achieve 0.62 conversion, is longer than was reported previously *(12)*. The earlier experiments had a systematic error in which a small amount of material (~0.5 g/d) was lost through handling leading to a reported conversion that was higher than was actually achieved. For the data presented in this paper, this systematic error has been corrected.) Although such a long solids residence time would appear to be uneconomical, the fermentor volume is determined primarily by the *liquid* residence time, not the *solids* residence time. Although a 14-d liquid residence time also would appear to be inordinately long, recall that the in-ground plastic fermentors are very inexpensive compared to conventional above-ground metal fermentors.

Using the optimal carboxylic acid concentration, Table 7 shows the estimated cost for each section of the plant assuming no tipping fee, or purchase price, for the raw feedstock. Figure 11 shows the estimated selling price of alcohol fuels as a function of the net cost of the feedstock entering the pretreatment section of the plant. The following paragraph indicates how the net cost of feedstock is calculated.

In New York state, the tipping fee for MSW averages $126/dry tonne ($101/wet tonne) *(36)*. It costs about $52/dry tonne (range $26–78/dry tonne) to sort MSW *(37)*. On a dry basis, MSW contains 60% biodegradable components that can be fed to the MixAlco process, 24% recyclables (metals, glass) and 16% nonrecyclables (plastic, rubber, leather, textiles) *(38)*. Assuming no income is received for the recyclables and that nonrecyclables must be placed in a landfill (both conservative assumptions), in New York, the net tipping fee for the biodegradable components is calculated as follows:

$$\text{Net tipping fee} = \left(\frac{\$126 - \$52}{\text{dry tonne}} - \frac{0.16 \text{ tonne nonrecycl}}{\text{dry tonne}} \times \frac{\$126}{\text{tonne nonrecycl}} \right)$$

$$\frac{\text{dry tonne}}{0.6 \text{ tonne biodegrade}} = \frac{\$90}{\text{tonne biodegrade}}$$

With this net feedstock cost, Fig. 11 shows that for a 40 tonne/h plant with a 60% return on investment (ROI), mixed alcohol fuels can be sold for about $0.04/L ($0.16/gal). The average tipping fee in the U.S. is about $63/dry tonne *(37)*; sorted, the net tipping fee would be about $1.53/dry tonne of biodegradable material sent to the MixAlco process. In this scenario, Fig. 11 shows that for a 40 tonne/h plant with a 15% ROI, mixed alcohol fuels can be sold for about $0.18/L ($0.69/gal). In some regions of the U.S., sugarcane bagasse may be obtained for its heating value (~$26/tonne). In this case, a 40 tonne/h plant with a 15% ROI could sell mixed alcohol fuels for about $0.29/L ($1.09/gal).

Using the capacity exponents shown in Table 4 *(35)*, the effect of scale on the FCI is shown in Table 5. The estimates for smaller capacities are accurate; the FCI for 2 ton/h is consistent with an independent analysis of this sized plant. For very large capacities, the FCI is less accurate because

Table 7
Cost (Free Biomass) (40 tonne/h)

|	Admin ($/tonne)	Pretreat ($/tonne)	Ferment ($/tonne)	Dewater ($/tonne)	Dry ($/tonne)	Thermal conv ($/tonne)	Hydrogen ($/tonne)
Feedstock							
Lime ($43/tonne)		3.27					
Inhibitor ($3.3/kg)			0.0009				
Amine make-up ($3.3/kg)				0.03			
Hydrogen ($0.69/kg)							3.55
Utilities							
Electricity ($0.042/kWh)		0.45	1.49	0.43	0.63	0.74	0.23
Low-pressure Steam ($3.30/tonne)		0.74		1.96	-2.20		-0.23
High-pressure Steam ($7.04/tonne)					4.69		
Fuel ($1.42/GJ)			-10.03			0.25	
Cooling water ($0.0375/m^3)		0.61	1.07	1.65		0.24	
Labor							
Plant manager (1 @ $120,000/yr)	0.38						
Supervisors (4 @ $75,000/yr)	0.94						
Sales (1 @ $65,000/yr)	0.20						
Clerical (3 @ $35,000/yr)	0.33						
Workers (28 @ $40,000/yr)		1.00	0.50	0.50	0.50	0.50	0.50
Fixed charges (annual charge)							
Depreciation (0.1 × FCI)		0.73	4.60	1.56	0.93	1.22	0.34
Local Tax (0.03 × FCI)		0.22	1.38	0.47	0.28	0.37	0.10
Insurance (0.007 × FCI)		0.05	0.32	0.11	0.06	0.09	0.02
Maintenance (0.04 × FCI)		0.29	1.84	0.62	0.37	0.49	0.14
Return on investment (0.15 × 1.15 × FCI)		1.26	7.93	2.69	1.60	2.10	0.59
Total	1.84	8.62	9.10	10.02	6.86	6.00	5.24
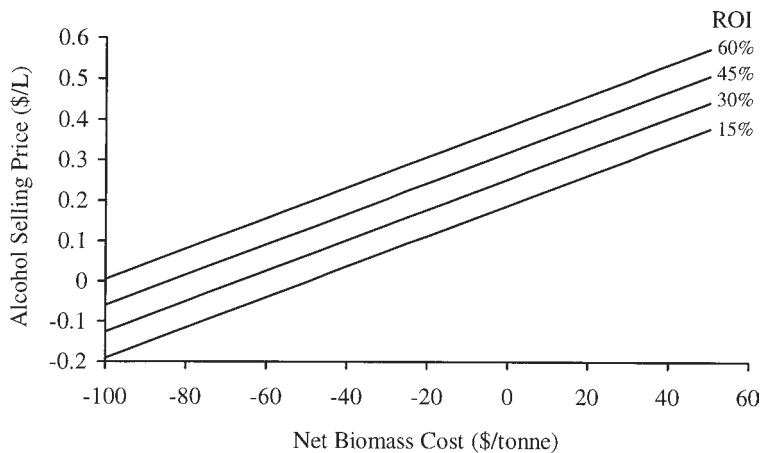
Fig. 11. Estimated selling price of mixed alcohol fuels (40 tonne/h plant capacity).

some equipment items will reach their maximum size and the appropriate capacity exponent would be 1.00, not the exponents shown in Table 4. In the U.S., the largest metropolitan area is New York City with a population of about 20 million people, so the largest realistic capacity for a plant that processes MSW and SS is about 1000 tonne/h.

Assuming free feedstock, the effect of scale on the selling price of alcohol fuels is shown in Table 8. (Note: To determine the effect of feedstock costs, for each additional $10/tonne net feedstock cost, add $0.038/L [$0.14/gal]. In the case of tipping fees, for each $10/tonne net feedstock income, subtract $0.038/L [$0.14/gal].)

The energy content of ethanol, mixed alcohols, and gasoline is 23.4, 29.0, and 34.9 MJ/L, respectively. For comparison purposes, on an energy basis, mixed alcohol fuels selling for $0.19/L ($0.71/gal) correspond to ethanol selling at $0.15/L ($0.58/gal).

Conclusion

The MixAlco process is able to produce mixed alcohol fuels at an attractive price, particularly if there are tipping fees associated with disposing of MSW and SS. In principle, the mixed alcohols could be burned as a neat fuel, but given current low oil prices, they are more likely to be blended into gasoline. The MixAlco alcohols could be blended with gasoline only, or with gasoline + ethanol, thereby acting as a cosolvent to increase the miscibility of ethanol in gasoline.

There are no scientific breakthroughs required to implement the MixAlco process; it requires only engineering and investment of capital. In the near term, it should be implemented in those regions of the country that have high tipping fees for disposing of MSW and SS. Once the technology becomes established and proven, it can be implemented in other regions where tipping fees are not as high.

Table 8
Effect of Scale on Selling Price of Ketones and Alcohols (Free Biomass)

	40 tonne/h ($/tonne)	2 tonne/h ($/tonne)	10 tonne/h ($/tonne)	160 tonne/h ($/tonne)	800 tonne/h ($/tonne)
Administration	1.84	17.49	5.20	0.65	0.19
Pretreatment	8.62	21.38	11.66	7.73	6.78
Fermentation	9.10	28.26	14.10	7.55	5.43
Dewatering[a]	12.02	22.34	14.63	11.03	10.21
Drying	6.86	22.14	10.93	5.13	3.94
Thermal conversion	6.00	18.91	9.66	4.27	2.90
ROI Hydrogenation	5.24	12.25	7.01	4.60	3.99
15% Total ($/tonne)	49.68	142.77	73.19	40.96	33.44
Alcohol selling price[b]	0.19	0.54	0.28	0.16	0.13
($/L) [$/gal]	[0.71]	[2.05]	[1.05]	[0.59]	[0.48]
Ketone selling price[c]	0.17	0.50	0.25	0.14	0.11
($/L) [$/gal]	[0.64]	[1.89]	[0.96]	[0.53]	[0.43]
30% Total ($/tonne)	66.91	181.70	95.94	54.00	44.08
Alcohol selling price[b]	0.25	0.69	0.36	0.20	0.17
($/L) [$/gal]	[0.96]	[2.60]	[1.37]	[0.77]	[0.63]
Ketone selling price[c]	0.22	0.64	0.34	0.19	0.15
($/L) [$/gal]	[0.85]	[2.43]	[1.27]	[0.71]	[0.58]
45% Total ($/tonne)	84.14	220.63	118.64	67.04	54.72
Alcohol selling price[a]	0.32	0.84	0.45	0.25	0.21
($/L) [$/gal]	[1.21]	[3.16]	[1.70]	[0.96]	[0.78]
Ketone selling price[c]	0.28	0.78	0.42	0.24	0.19
($/L) [$/gal]	[1.07]	[2.96]	[1.59]	[0.89]	[0.73]
60% Total ($/tonne)	101.37	259.56	141.34	80.08	65.36
Alcohol selling price[a]	0.39	0.99	0.54	0.30	0.25
($/L) [$/gal]	[1.47]	[3.74]	[2.04]	[1.13]	[0.95]
Ketone selling price[c]	0.34	0.92	0.50	0.29	0.23
($/L) [$/gal]	[1.29]	[3.48]	[1.89]	[1.10]	[0.87]

[a]Cost has been increased by 20% to allow for reduced selectivity of higher carboxylates.
[b]Yield = 264 L/tonne (69.8 gal alcohol/tonne).
[c]Yield = 261 L/tonne (69.0 gal ketone/tonne)

References

1. Ghose, T. K. and Bhadra, A. (1985), in Comprehensive Biotechnology, vol. 3, Moo-Young, M., Blanch, H. W., Drew, S., and Wang, D. I. C., eds., Pergamon Press, New York, NY, pp. 701–729.
2. Playne, M. J. (1985), in *Comprehensive Biotechnology*, vol. 3, Moo-Young, M., Blanch, H. W., Drew, S., and Wang, D. I. C., eds., Pergamon Press, New York, NY, pp. 731–759.
3. Lefranc, L. (1914), *British Patent* 17,776.
4. Hurd, C. D. (1929) *The Pyrolysis of Carbon Compounds*, The Chemical Catalog Company, New York, NY, p. 486.
5. Playne, M. J. (1981), in *Advances in Biotechnology*, vol. II, Moo-Young, M. and Robinson, C. W., eds., Pergamon Press, New York, NY, pp. 85–90.
6. Badawi, M. A., El-Shinnawi, M. M., Blanc, F. C., Wise, D. L., and El-Shimi, S. A. (1992), *Resources, Conservation and Recycling* **7,** 201–212.
7. Holtzapple, M. T., Davison, R. R., and Nagwani, M. (1997), U. S. Patent 5,693,296.

8. Chang, V. S., Burr, B., and Holtzapple, M. T. (1997), *Appl. Biochem. Biotechnol.* **63–65,** 3–19.
9. Kaar, W. E. and Holtzapple, M. T., *Biomass Bioenergy*, in press.
10. Chang, V. S., Holtzapple, M. T., and Davison, R. R. (1996), Final Report Part III, Subcontract No. XAW-3-11181-03, National Renewable Energy Laboratory, Golden, CO.
11. Chang, V. S., Nagwani, M., and Holtzapple, M. T., *Appl. Biochem. Biotechnol.*, in press.
12. Holtzapple, M. T., Ross, M. K., Chang, N.-S., Chang, V. S., Adelson, S. K., and Brazel, C. (1997), in *Fuels and Chemicals from Biomass*, ACS Symposium Series 666, Saha, B. C. and Woodward, J., eds., American Chemical Society, Washington, DC, pp. 130–141.
13. Rapier, C. R. (1995), Masters thesis, Texas A&M University, College Station, TX.
14. Gandi, J., Holtzapple, M. T., Ferrer, A., Byers, F. M., Turner, N. D., Nagwani, M., and Chang, S. (1997), *Animal Feed Sci. Technol.* **68,** 195–211.
15. Holtzapple, M. T., Davison, R. R., Ross, M. K., and Loescher, M., U. S. Patent (granted but not issued).
16. Slyter, L. L. (1979), *Appl. Envir. Microbiol.* **37,** 283–288.
17. Martin, S. A. and Macy, J. M. (1985), *J. Animal Sci.* **60,** 544–550.
18. Mike Piana, Exxon, Baytown, TX, personal communication.
19. Chris Hodgson, Natgun Tanks, Wakefield, MA, personal communication.
20. Loescher, M. E. (1996), PhD dissertation, Texas A&M University, College Station, TX.
21. Ross, M. K. (1998), PhD dissertation, Texas A&M University, College Station, TX.
22. Davison, R. R., Smith, W. H., and Hood, D. W. (1966), *J. Chem. Eng. Data* **11,** 304–309.
23. Davison, R. R. and Hood, D. W. (1964), *I&EC Proc. Design Dev.* **3,** 399–404.
24. Chun, K. W., Drummond, J. C., and Davison, R. R. (1974), *J. Chem. Eng. Data* **19,** 142–144.
25. Chun, K. W., Clinkscales, T. C., and Davison, R. R. (1971), *J. Chem. Eng. Data* **16,** 443–446.
26. Davison, R. R., Smith, W. H., and Hood, D. W. (1960), *J. Chem. Eng. Data* **5,** 420–423.
27. Davison, R. R., Harris, W. B., and Smith, W. H., Jr. (1967), *Desalination* **3,** 17–26.
28. Lee, C. (1993), Masters thesis, Texas A&M University, College Station, TX.
29. Gaskin, D. J. (1997), Masters thesis, Texas A&M University, College Station, TX.
30. Ardagh, E. G. R., Barbour, A. D., McClellan, G. E., and McBride, E. W. (1924), *Ind. Eng. Chem.* **16,** 1133–1139.
31. Adelson, S. K. (1994), Masters thesis, Texas A&M University, College Station, TX.
32. Chang, N.-S., Aldrett-Lee, S., Holtzapple, M. T., and Davison, R. R., *Ind. Eng. Chem. Res.*, submitted.
33. Goffe, B. E., Ferrier, A. E., and Rogers, C. L. (1994), *J. Econometr.* **60,** 65–100.
34. Brehm, A. and Oguz, H. (1988), *Proceedings of the 6th European Conference on Mixing*, Pavia, Italy, BHRA Fluid Engineering, 413–420.
35. Peters, M. S. and Timmerhaus, K. D. (1991), *Plant Design and Economics for Chemical Engineers*, 4th ed., McGraw-Hill, New York, NY.
36. Magnuson, A. (1997), *MSW Management*, 30–41.
37. Broder, J. D., Eley, M. H., and Barrier, J. W. (1993), *Municipal Solid Waste and Waste Cellulosics Conversion to Fuels and Chemicals*, vol. II, Tennessee Valley Authority, Muscle Shoals, AL.
38. Holtzapple, M. T., Lundeen, J. E., Sturgis, R., Lewis, J. E., and Dale, B. E. (1992), *Appl. Biochem. Biotechnol.* **34/35,** 5–21.