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Calcium Magnesium Acetate at Lower Production Cost: Production of CMA Deicer from Biomass

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Research and Development
Turner-Fairbank Highway Research Center
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McLean, VA 22101-2296

FOREWORD

This Report documents a study whose purpose was to investigate methods to produce low-cost calcium magnesium acetate (CMA), an alternative chemical deicer to commonly used chloride deicers. Fermentation of biomass was investigated as a means to generate acetic acid needed in CMA production; the use of other reactants needed for CMA production, viz., calcium and magnesium, was optimized. Economics for a commercial-scale facility for producing CMA were developed; integrating the economics with a market survey suggested that, based on a large-scale plant, sufficient savings could be realized to justify rapid commercialization of the technology.

The report should be of special interest to researchers and practitioners involved in the development, evaluation, and use of alternate deicing chemicals that could be used to replace and/or supplement commercially used chloride materials.

Charles J. Nemmers, P.E.
Director, Office of Engineering
Research and Developement

NOTICE

Technical Report Documentation Page

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16. Abstract

The purpose of this project was to demonstrate the technical and economic feasibility of producing Calcium Magnesium Acetate (CMA) from solid waste by gasification/fermentation. Bench-scale fermentation experiments were conducted with synthesis gases typical of those from gasification of various residues. Fast reaction rates and high yields were obtained, and phase contaminants, such as chlorides, metals, and sulfur gases in concentrations expected in syngas, were not found to affect the fermentation. The production of CMA by reacting lime and magnesium oxide with acetic acid extracted from the fermentation broth was optimized in bench-scale experiments. Procedures for using cheap grades of lime and magnesium oxide were developed. Ice melting and penetration tests, as well as analytical results, showed the laboratory CMA to be comparable (or better) quality to the industry product.

Process design and economic projections for a commercial-scale facility were developed. The cost of CMA from this plant is projected to be less than $200/ton($220/tonne). A market showed that CMA usage could be expanded to as much as 1 million lb/year (453,600 kg/yr) if prices can be significantly reduced. Earnings from a large plant at reduced CMA prices show excellent returns that would justify rapid commercialization of this technology.

Cover Photo: Scanning electron micrograph of synthetic zeolite used in acetic acid recovery.

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SI* (MODERN METRIC) CONVERSION FACTORS

APPROXIMATE CONVERSIONS TO SI UNITS

Symbol	When You Know	Multiply By	To Find	Symbol
		LENGTH		
in	inches	25.4	millimeters	mm
ft	feet	0.305	meters	m
yd	yards	0.914	meters	m
mi	miles	1.61	kilometers	km
		AREA		
in^2	square inches	645.2	square millimeters	mm^2
ft^2	square feet	0.093	square meters	m^2
yd^2	square yards	0.836	square meters	m^2
ac	acres	0.405	hectares	ha
mi^2	square miles	2.59	square kilometers	km^2
		VOLUME		
fl oz	fluid ounces	29.57	milliliters	mL
gal	gallons	3.785	liters	L
ft^3	cubic feet	0.028	cubic meters	m^3
yd^3	cubic yards	0.765	cubic meters	m^3
NOTE: Volumes greater than 1000 l shall be shown in m^3.				
		MASS		
oz	ounces	28.35	grams	g
lb	pounds	0.454	kilograms	kg
T	short tons (2000 lb)	0.907	megagrams (or "metric ton")	Mg (or "t")
		TEMPERATURE (exact)		
°F	Fahrenheit temperature	5(F-32)/9 or (F-32)/1.8	Celcius temperature	°C
		ILLUMINATION		
fc	foot-candles	10.76	lux	lx
fl	foot-Lamberts	3.426	candela/m^2	cd/m^2
		FORCE and PRESSURE or STRESS		
lbf	poundforce	4.45	newtons	N
lbf/in^2	poundforce per square inch	6.89	kilopascals	kPa

APPROXIMATE CONVERSIONS FROM SI UNITS

Symbol	When You Know	Multiply By	To Find	Symbol
		LENGTH		
mm	millimeters	0.039	inches	in
m	meters	3.28	feet	ft
m	meters	1.09	yards	yd
km	kilometers	0.621	miles	mi
		AREA		
mm^2	square millimeters	0.0016	square inches	in^2
m^2	square meters	10.764	square feet	ft^2
m^2	square meters	1.195	square yards	yd^2
ha	hectares	2.47	acres	ac
km^2	square kilometers	0.386	square miles	mi^2
		VOLUME		
mL	milliliters	0.034	fluid ounces	fl oz
L	liters	0.264	gallons	gal
m^3	cubic meters	35.71	cubic feet	ft^3
m^3	cubic meters	1.307	cubic yards	yd^3
		MASS		
g	grams	0.035	ounces	oz
kg	kilograms	2.202	pounds	lb
Mg (or "t")	megagrams (or "metric ton")	1.103	short tons (2000 lb)	T
		TEMPERATURE (exact)		
°C	Celcius temperature	1.8C + 32	Fahrenheit temperature	°F
		ILLUMINATION		
lx	lux	0.0929	foot-candles	fc
cd/m^2	candela/m^2	0.2919	foot-Lamberts	fl
		FORCE and PRESSURE or STRESS		
N	newtons	0.225	poundforce	lbf
kPa	kilopascals	0.145	poundforce per square inch	lbf/in^2

* SI is the symbol for the International System of Units. Appropriate rounding should be made to comply with Section 4 of ASTM E380.

(Revised September 1993)

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EXECUTIVE SUMMARY

A two-phase research and development program was performed in order to demonstrate the technical and economic viability of Bioengineering Resources, Inc.'s (BRI) gasification/fermentation process, and to collect valuable design and scale-up information for later process demonstration. In Phase I, the feasibility of utilizing a biological process for the conversion of Municipal Solid Waste (MSW), sewage sludge, and other waste materials to Calcium Magnesium Acetate (CMA) has been demonstrated. Gasification, a technology well developed in Europe, is used to convert the waste into a synthesis gas containing primarily CO, CO_2, and H_2. Synthesis gas is then converted to acetic acid/acetate using the BRI isolate ERI2. A 10-min GRT at atmospheric pressure is required in the Continous Stirred Tank Reactor (CSTR) with cell recycle for these oxygen-blown gasifier syngases, and the retention time decreases proportionally with increased pressure. Thus, retention times of seconds are possible at elevated pressure. The fermentation broth contains approximately 20 g/L acetic acid/acetate. The acetic acid is removed from the broth by solvent extraction. A high distribution is obtained with this solvent system, and the separation factor shows that only negligible quantities of water are extracted along with the acid. CMA production occurs by reacting dolomitic lime/MgO with the acetic acid directly in the solvent phase. A first-order rate constant of 0.258 min^{-1} is obtained. The CMA is then dried and pelletized using existing industrial technology. The BRI produced CMA was found to be essentially identical with industrial-produced CMA in physical property and ice melting, ice penetration, and eutectic-point tests.

The economics of producing CMA from wastes by gasification/fermentation are quite attractive. In Phase I the production costs from MSW and sewage sludge, without including tipping fees, were projected at \$123 and \$126/ton (\$136 and \$139/tonne), respectively. Preliminary market analyses indicate that, at this price, the potential market for CMA is 1 million tons/year (907,200 tonnes/year). Finally, an Industrial Advisory Committee has been formed to advise in developing technical and marketing strategy for the commercialization of this technology. The IAC met on March 30, 1994, in Fayetteville, AR to tour the carbon black waste gas to acetic acid pilot plant, and to review results from the Phase I research effort.

In the Phase II program, additional bench-scale research and development was carried out to yield design and scale-up data for process demonstration. Bench-scale fermentation experiments were carried out with air-blown, oxygen-blown, and steam-blown MSW syngas. The required GRTs for suitable conversions of CO and H_2 in the syngas ranged from 3 to 15 min, depending on the combined CO and H_2 content of the syngas. Typical gas phase contaminants such as chlorides, H_2S, COS, and metals were not found to be a problem in the fermentation at levels above those expected in the MSW syngases.

The CMA production process was modified to form a breakable emulsion during extraction with the solvent system, which resulted in significant increases in the rate of CMA formation from acetic acid in the solvent phase. Also, a near saturated solution of CMA is now produced in the CMA reactor, which enables inerts to be easily removed from the CMA product. This change permits the use of less expensive, lower grades of lime and MgO as feedstocks, since the inerts may simply be filtered out of the aqueous near saturated solution. Chloride and sulfate were removed from the fermentation medium in order to essentially eliminate these environmentally unfriendly compounds from the CMA. With these changes, the CMA product remained high in quality and comparable to the industrial CMA.

Carbon bed adsorption was investigated as a method of enhancing the fermentation rate by removing cellular material from the water recycle stream prior to fermentation. However, fermentation tests showed that this operation is unnecessary, as long as the free-acid concentration in the reactor is kept below inhibitory levels. Zeolites were evaluated as an alternative and less expensive method of recovering acid from the fermenter permeate. These systems look very promising, with a potential to decrease the capital costs for the gasification/fermentation process by more than 20%. The economics of producing both CMA and KAc remain promising, with returns on the investment projected at 78% in producing CMA and 109% in producing KAc from MSW.

The purpose of this project was to demonstrate the technical and economic feasibility of producing CMA from solid waste by gasification/ fermentation. Bench-scale fermentation experiments were conducted with synthesis gases typical of those from gasification of various residues. Fast reaction rates and high yields were obtained and gas phase contaminants, such as chlorides, metals, and sulfur gases, in concentrations expected in syngas, were not found to effect the fermentation. The production of CMA by reacting lime and magnesium oxide with acetic acid extracted from the fermentation broth was optimized in bench-scale experiments. Procedures for using cheap grades of lime and magnesium oxide were developed. Ice melting and penetration tests, as well as analytical results, showed the laboratory CMA to be of comparable (or better) quality to the industrial product.

Process design and economic projections for a commercial scale facility were developed. The cost of CMA from this plant is projected to be less than $200/ton ($220/tonne). A market survey showed that the CMA usage could be expanded to as much as 1 million lb/year (453,600 kg/year) if prices can be significantly reduced. Earnings from a large plant at reduced CMA prices show excellent returns that would justify rapid commercialization of this technology.

INTRODUCTION

About 17 million tons (15.4 million tonnes) of road salt are used annually in the United States for the deicing of highways and runways. Salt is an extremely effective snow and ice control agent and is very inexpensive. However, salt also causes significant damage to concrete and metals though corrosion, as well as environmental damage to vegetation and ground water. Other effective deicers, although much more expensive, include urea and glycols. These materials are toxic in high concentration to aquatic organisms and result in a high biological oxygen demand or eutrophication of surface waters.

A recent study carried out in New York State showed that 1 ton (0.9 tonnes) of road salt costs only $50 ($55/tonne), but results in more than $1400 ($1543/tonne) worth of damage to vehicles, bridges, and the environment (Hudson, 1987). Runway deicing chemicals containing glycol or urea are being phased out of use. Many regulatory authorities are requiring airports to confine deicing wastewaters for subsequent treatment. Consequently, there is an urgent need for inexpensive and environmentally compatible road and runway deicers.

Calcium magnesium acetate (CMA) and potassium acetate (KAc) have been identified as the best alternative deicer candidates (Chollar, 1984). CMA is a mixture of calcium acetate and magnesium acetate, formed by the reaction of glacial acetic acid with dolomitic lime. Similarly, KAc is formed by the reaction of acetic acid with potassium hydroxide (KOH). The deicing ability of these materials is comparable to road salt, and they are noncorrosive and harmless to vegetation, concrete, bridges, and vehicles. These deicers are biodegradable and cause no known detrimental environmental effects. CMA is the predominant alternative deicer and is used on roadways, whereas KAc is used primarily on runways.

CMA currently sells for more than $1000/ton ($1102/tonne) and competes with rock salt at $15 to $50/ton ($17 to $55/tonne). Therefore, CMA usage is limited to environmentally sensitive areas or areas where corrosion is a serious problem, such as bridges (Harrach and Wyatt, 1990). Unless prices are reduced substantially, markets will grow only gradually.

CMA and KAc contain 76% and 61% acetic acid, respectively. Glacial acetic acid costs about $400/ton ($441/tonne) and represents approximately half the cost of CMA and KAc. The key to significant price reductions is in reducing the cost of acetic acid. The current CMA usage is less than 10,000 tons/year (9072 tonnes/year), compared to a salt market that is a thousand times larger. Hence, the potential markets for CMA are huge, if prices can be reduced. A preliminary survey of the market potential for CMA at reduced prices indicated that at a price of $200/ton ($220/tonne), CMA could capture at least 10% of the salt market. Perhaps, equally important, is the substitution of cheaper KAc as an anti-icer to replace calcium and magnesium chlorides. The current combined market for these products is 600,000 tons/year (544,320 tonnes/year). Thus, the markets for both CMA and KAc could be expanded one-hundredfold if prices can be reduced.

Bioengineering Resources (BRI) has developed novel technology for the conversion of wastes into CMA by a combined thermal, chemical, and biological process. First, wastes including Municipal Solid Waste (MSW), sewage sludge, used tires, or biomass are converted into synthesis gas by thermal gasification. The resulting CO, CO_2, and H_2 are then fermented by proprietary anaerobic bacteria to produce acetic acid/acetate in dilute solution. The acetic acid is extracted into a proprietary solvent and then converted to CMA by dolomitic lime addition directly in the solvent phase. Finally, CMA is recovered, dried, and pelletized.

The process combines proven technology (gasification) with recent microbiological process innovation. The technology for pyrolysis or gasification of organic wastes has been under intensive development during the last 2 decades (Steinberg, 1988; Stasson and Stiles, 1988). Large-scale demonstration facilities have been tested (Fisher *et al.*, 1976), and commercial facilities are now in operation. Commercial biomass gasifiers are available from Texaco, Westinghouse, Lurgi (Germany), Ahlstrom (Finland), Daneco (Italy), and Terminiska (Sweden). A major advantage of gasification of organic wastes is that all of the carbon is converted into syngas, which in turn is converted to acetic acid/acetate in the fermentation process. Finally, CMA is produced from acetic acid after extraction.

PURPOSE

The purpose of this report is to present the results from a multiphase research program aimed at economically producing CMA from various raw materials by gasification/fermentation. Phase I of the study focused on the demonstration and optimization of a laboratory-scale process to produce CMA from biomass. Laboratory studies were carried out to demonstrate technical feasibility. Following this activity, cost and material balance analyses were completed for the process to determine the economics of providing a product with desirable deicing properties. A preliminary market analysis and commercialization strategy was prepared. Data necessary to estimate the commercial viability of the CMA production system were collected.

The technology was further optimized in a Department of Transportation (DOT)-industrial sponsored Phase II Commercial Development phase. Laboratory experiments involving fermentation with cell recycle, acetic acid extraction, CMA production, CMA testing, and CMA drying were carried out to demonstrate technical feasibility and to optimize the commercial process. Bench-scale fermentation experiments were performed to compare the rates and yields of acetic acid/acetate produced from air-blown, oxygen-blown, and steam-blown gasifier syngases. The effects of typical syngas impurities such as chlorides, sulfur gases, and various contaminants present in syngases produced from the gasification of various feedstocks were evaluated, and found to have little to no effect on culture performance. Less expensive raw materials for CMA and KAc (potassium acetate, a runway deicer) production were investigated. Medium optimization studies were performed to reduce the level of contaminants such as sulfate and chloride present in the CMA. Scale-up data were obtained for fermentation, extraction, and CMA production. Carbon bed adsorption was investigated as a method to enhance fermentation coupled with water recycle, and zeolites were investigated as an alternative method for acid recovery. Following this activity, cost and material balance analyses were completed for the process to determine the economics of providing a product with desirable deicing properties. Preliminary market analyses and commercialization strategies were prepared. Data necessary to estimate the commercial viability of the CMA production system were collected. Finally, economic projections and preliminary designs for the demonstration of this technology were prepared.

GASIFICATION/FERMENTATION TECHNOLOGY

CURRENT CMA PRODUCTION TECHNIQUES

In addition to the work at BRI, four other processes are currently under investigation:

- Traditional vinegar fermentation.
- Fermentation of glucose by *Clostridium thermoaceticum.*
- Modified anaerobic digestion technology.
- Conversion of lactose in cheese whey by a two-step fermentation process.

The traditional vinegar fermentation involves fermentation of sugars to ethanol by yeasts, followed by oxidation of ethanol to acetic acid/acetate by species of *Acetobacter*. The process suffers from low yields and high energy input and thus cannot compete with the natural gas-based synthetic process (Ghose and Bhadra, 1985; Marynowski *et al.*, 1982). The homoacetogenic fermentation of sugars by *C. thermoaceticum* has been studied extensively (Ljungdahl *et al.*, 1985; 1986; Schwartz and Keller, 1982a; 1982b; Wang *et al.*, 1978; Wang and Wang, 1984; Parekh and Cheryan, 1990). The process suffers mainly from the high cost of the feedstock.

Recently, anaerobic digestion has been utilized in producing CMA in a mixture of organic salts. Methane production was suppressed to allow acid and acid salts to accumulate. A variety of feedstocks were employed, including woody biomass (DeSouza and Wise, 1991; Wise and Augustein, 1988), and sewage sludge (Trantolo *et al.*, 1990; 1991). This process suffers from low acid/acid salt concentrations, slow reaction rates, and the presence of a variety of acids and acid salts produced by the mixed culture. Finally, a co-culture has been utilized in producing CMA from cheese whey (Yang *et al.*, 1992). *Streptococcus lactis* was first used to convert lactose in cheese whey to lactate, followed by conversion of lactate to acetic acid and acetate by *Clostridium formicoaceticum*. This process is only able to utilize lactose-containing feedstocks and utilizes a neutral pH, which makes acetic acid recovery difficult. Estimated CMA production costs by these alternatives range from \$300 to \$325/ton (\$331 to \$358/tonne), although product recovery costs may not be included in this analysis.

BIOLOGICAL PRODUCTION OF ACETIC ACID/ACETATE FROM BIOMASS SYNTHESIS GAS

The bioconversion of the gases H_2, CO, and CO_2 by anaerobic bacteria has been known for many years and recently demonstrated in our laboratories as having commercial potential (Barik *et al.*, 1985; 1986; 1987; Vega *et al.*, 1988; 1989a; Clausen and Gaddy, 1985; Klasson *et al.*, 1990; Gaddy and Clausen, 1987). Several bacterial species are capable of converting these gases into acetic acid/acetate, which is an intermediate in many biological pathways.

Bacterial species, such as *Acetogenium kivui* (Leigh *et al.*, 1981), *Peptostreptococcus productus* (Barik *et al.*, 1986; Lorowitz and Bryant, 1984), *Acetobacterium woodii* (Kerby *et al.*, 1983), *Clostridium thermoaceticum* (Wood *et al.*, 1982; Kerby and Zeikus, 1983), and *Eubacterium limosum* (Genthner and Bryant, 1982) produce acetic acid/acetate by the reaction:

$$4CO + 2H_2O \rightarrow CH_3COOH + 2CO_2 \qquad \Delta G = -39 \text{ kcal/reaction} \qquad (1)$$

Many anaerobic bacteria are also known to produce acetic acid and acetate from H_2 and CO_2 (Mayer *et al.*, 1977; Sleat *et al.*, 1983; Balch *et al.*, 1977). These bacterial isolates include *A. kivui, P. productus,* and *Acetobacterium sp.* (Balch *et al.*, 1977), which utilize homoacetic fermentation by anaerobically oxidizing hydrogen and reducing CO_2 according to the equation:

$$4H_2 + 2CO_2\ 6\ CH_3COOH + 2H_2O \qquad)G = -25.6\ \text{kJ/reaction} \qquad (2)$$

Acetobacterium woodii (Mayer *et al.*, 1977) and *Acetoanaerobium noterae* produce acetate/acetic acid from H_2 and CO_2 according to the above reaction, but in addition to acetate, *A. noterae* produces some propionate and butyrate. Another chemolithotrophic bacteria, *Clostridium aceticum,* also produces acetic acid/acetate from H_2 and CO_2 (Braun *et al.*, 1979). *C. acidiurici* also produces acetic acid/acetate only from CO_2 using the glycine decarboxylase pathway (Waber and Wood, 1979).

Some bacteria, such as *A. kivui, P. productus,* and *A. woodii*, produce acetic acid and acetate from either CO or H_2 and CO_2 (Vega *et al.*, 1989b, Barik *et al.*, 1986). *P. productus* gives particularly fast rates of conversion and demonstrates high tolerance to CO; however, this organism shows a preference to follow equation (1) over equation (2).

A. kivui, a gram negative, chemolithotrophic, thermophilic anaerobe, was isolated from Lake Kivu (Leigh *et al.*, 1981). The doubling time for growth on hydrogen and carbon dioxide is about 2 h. The optimum growth temperature is 66°C, and optimum pH is 6.4. Klemps *et al.*, (1987) found that in a batch fermentation at pH 6.4, the bacterium was able to produce 625 mM of acetic acid/acetate from glucose within 50 to 60 h. The value of Φmax was about 0.17 h^{-1}, and the yield was about 2.55 mole of acetic acid/mole of glucose. Yang *et al.* (1989) studied the nickel transportation by *A. kivui*. Nickel plays an essential role in the Wood pathway of acetogenesis at the level of carbon monoxide dehydrogenase (acetyl coenzyme A synthetase). The apparent Km and Vmax for nickel transport by H_2-cultivated cells was approximately 2.3 uM Ni and 670 pmol of Ni transported/min/mg (dry weight) of cells, respectively. In continuous fermentation, a maximum acetate/acetic acid concentration of 420 mM was reached at a 0.017 h^{-1} dilution rate. Yang and Drake (1990) discovered that carbon monoxide stimulated H_2-dependent growth of *A. kivui*, but inhibited glucose-dependent growth. *A. kivui* also could not be revived or maintained in a sodium-deficient medium (0.2 mM sodium) under H_2-dependent conditions, and neither lithium nor potassium replaced the sodium requirement of H_2-cultivated cells.

Kerby and Ziekus (1983) reported the first strain of *Clostridium thermoaceticum* that was capable of growth on either H_2/CO_2 or CO. The doubling times at 55°C on CO or H_2/CO_2 were 16 and 18 h, respectively. Under these conditions, the stoichiometries approximated those of equations (1) and (2). Schwartz and Keller (1982a; 1982b) reported acetic acid/acetate production at low pH ranges with glucose as the carbon and energy source.

BRI PROCESS DESCRIPTION

A gasification/fermentation process can utilize a variety of waste streams. The carbonaceous fraction of the waste can be readily gasified to produce CO, H_2 and CO_2. Cellulosic wastes, such as MSW, used tires and plastics, agricultural residues, animal wastes, and forestry residues, total more than 1 billion tons (0.9 billion tonnes) annually. All of the components of the synthesis gas from gasification of these waste streams can be used to produce acetic acid. Lignocellulosic biomass may be gasified by the approximate stoichiometry:

$$\underset{\text{Biomass}}{8CH_2O} + 2O_2 + (8N_2)\ \ 6\ \ 6CO + 2CO_2 + 6H_2 + 2H_2O + (8N_2) \qquad (3)$$

The reactions represented by equation (3) are highly exothermic and provide the energy for gasification. The amount of CO_2 in the synthesis gas is dependent on the temperature of gasification and the resultant energy requirements. The H_2 concentration is a function of the composition of the biomass and whether steam is introduced. Nitrogen will also be present if air is used instead of oxygen. Typical CO and H_2 compositions for air-blown systems are 20% to 40%, depending on the gasifier and raw material.

The CO, CO_2, and H_2 are then fermented to a mixture of acetic acid and acetate, with the composition dependent on pH. A new bacterial strain, designated as ERI2, was isolated in the BRI laboratories that is able to carry out the reactions of equations (1) and (2) at high rates and low pH. ERI2 is a mesophilic bacterium which grows rapidly on CO, CO_2, and H_2. In batch and continuous culture comparison studies with other acetogenic bacteria, it was shown that ERI2 has faster substrate utilization rates, has a higher tolerance to the product acetate/acetic acid and, in addition, is able to operate at pH levels of 4.5 to 5.0. Acetate/acetic acid concentrations at this pH level are 15 to 20 g/L from a Continuously Stirred Tank Reactor (CSTR) (both continuous gas and liquid feed) with cell recycle. More importantly, fermentation times of only 3 min have been achieved at high gas conversion rates.

Equation (3) may be combined with equations (1) and (2) to yield:

$$8CH_2O + 2O_2 + (8N_2) \rightarrow 3CH_3COOH + 2CO_2 + 2H_2O + (8N_2) \quad (4)$$

Since nearly all of the biomass (including the lignin, but not the ash) can be converted into gas by equation (3), acetic acid/acetate yields of about 75% of the total biomass are possible. This yield compares to values of only 50% for hydrolysis/fermentation processes, and, of course, depends to some extent on the type of waste and gasifier used.

The reaction to produce CMA or KAc proceeds as shown below for lime and acetic acid (magnesium not included):

$$Ca(OH)_2 + 2CH_3COOH \rightarrow Ca(CH_3COO)_2 + 2H_2O \quad (5)$$

A yield of 1.32 kg of CMA is obtained from each kg of acetic acid. Therefore, the maximum overall yield of CMA is about 1 kg/kg of biomass residue. The maximum yield of KAc is higher: 1.23 kg/kg of residue.

A process to produce CMA from MSW, sludge, or other biomass residues by gasification/fermentation is quite simple as is shown in figure 1. Following gasification of the waste, the synthesis gas, consisting of predominantly CO, CO_2, and H_2, is cooled and fed to a bioreactor where an anaerobic culture of BRI2 at low pH is maintained. The heat available in the synthesis gases can be used to dry the CMA product. A small liquid stream is also fed to the reactor to supply nutrients in the form of salts and vitamins. Typically, a CSTR has been found to be best for these gas-liquid reactions, although other types of bioreactors can be used.

A cell separation system is used to recycle cells to the reactor in order to maintain a high cell concentration. Since growth and production are coupled, a high cell concentration translates into fast reaction rates and a high product concentration. The liquid product stream containing 15 to 20 g/L acetic acid/acetate (no byproducts) is next fed to an extraction column, where a suitable solvent extracts the acetic acid to a concentration of approximately 50 g/L.

Lime is added in a stirred tank reaction vessel to produce CMA. Following separation, the solvent is returned for recycle and the CMA/water stream is fed to a dryer/pelletizer where the water is removed and dry CMA produced. Experiments in our laboratory have confirmed this simple separation scheme and have shown a 99.9% acetic acid conversion to CMA. The solvent is essentially insoluble in the aqueous phase so that no solvent is lost.

A similar process would be used in producing potassium acetate. Since a 50% solution of potassium acetate is the desired product, the dryer is eliminated. A solution of KOH is simply contacted with the solvent where the reaction to produce potassium acetate occurs. Solvent is separated from the aqueous phase by decantation and recycled as in figure 1.

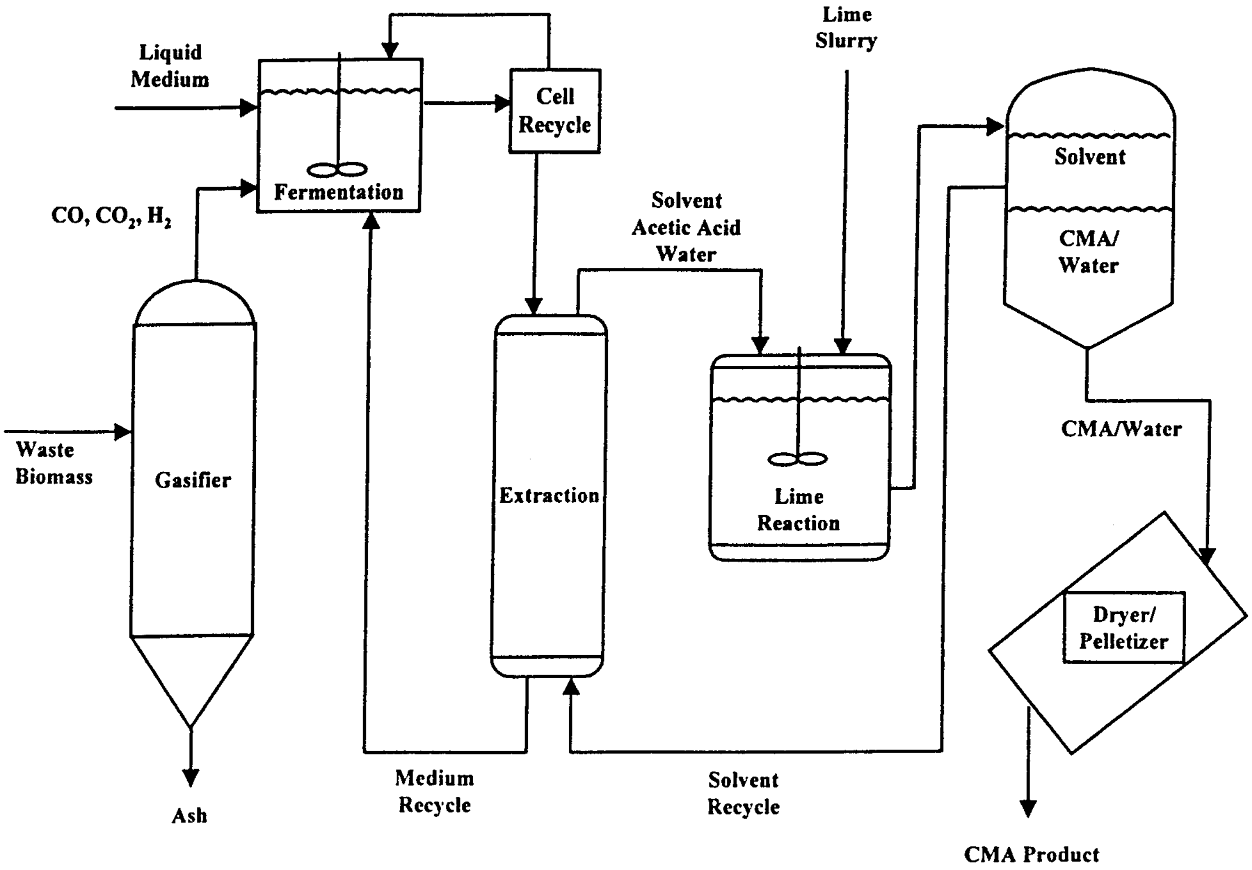


Figure 1. Process for the Production of CMA from Wastes

Small solid, liquid, and gas streams are byproducts of this process. The carbonaceous fraction of the biomass is converted into deicer. The inorganic fraction (5%) leaves the gasifier as ash, which would be landfilled, as is the current practice. A small liquid stream would be discharged from the fermenter, containing lysed cell fragments and minerals. This stream is not toxic and would be discharged to conventional wastewater treatment. The effluent gases from the bioreactor would contain primarily CO_2, with small amounts of unreacted CO and H_2. This stream would be flared. Therefore, the process is environmentally friendly in the sense that it converts solid waste streams into environmentally compatible deicers without generating or discharging any hazardous or harmful wastes.

ECONOMIC PROJECTIONS

Preliminary capital and economic projections for a facility to produce 100,000 tons (90,720 tonnes) of CMA/year are presented in tables 1 and 2. This facility would require about 320 tons (290 tonnes) of carbonaceous wastes/day. Most regions of the nation have sufficient waste to support a facility of this size. For example, this amount of MSW could be supplied from Burlington and Fort Madison, IA. In the corn belt, an area of 14.5 km square would produce the corn stover for this plant. In addition, feedlot and poultry wastes, forestry residues, or other crop residues can be used as raw materials. As shown in table 1, the capital costs for this process are projected to total $23.3 million, including the gasifier, extraction, bioreactors, CMA production, and a 20% contingency.

Table 1. Capital Costs of CMA Production Requiring 320 Tons (290 Tonnes) of MSW/Day for 100,000 Tons (90,720 Tonnes) of CMA/Year

Unit	Capital Cost (in million $)
Gasifier	$5.8
Bioreactors	6.0
Extraction	4.6
CMA Production	3.0
Contingency (20%)	3.9
Total	**$23.3**

Table 2. Economic Projection for CMA Production Requiring 320 Tons (290 Tonnes) of Agricultural Residues/Day for 100,000 Tons (90,720 Tonnes) of CMA/Year

Cost Item	Annual Amount (in million $)
Raw Materials	
Biomass - No Cost	$ 0
Lime	0.9
MgO	3.7
Utilities	
Power	1.7
Water	0.2
Labor - 4 Operators/Shift	0.6
Overhead	0.6
Supplies/Chemicals	0.7
Depreciation (10 years)	2.3
Maintenance - 5%	1.2
Insurance/Property Taxes - 2%	0.5
Total	**$12.4**
Unit Cost	**$124/ton ($137/tonne)**
Projected Revenue ($200/ton [$220/tonne])	**$20.0**
Pre-Tax Profit	7.6
Income Taxes (36%)	3.0
Net Profit	4.6
Cash Flow	6.9
Annual Return	**30%**
Payout	3.3 years

As shown in table 2, the annual operating cost totals $12.4 million, including $4.6 milion for lime and magnesium oxide. No charge or credit is included for the MSW. The total operating cost translates into a CMA cost of $124/ton ($137/tonne). Based on an expected return of 30%, a price of $200/ton ($220/tonne) is projected for the CMA. This price is only 28% of the current price and would enable a large segment of the deicer market to be captured by CMA. If the CMA price were $700/ton ($772/tonne), the return would be 70%.

PHASE I STATEMENT OF WORK

The Phase I research program focused on the optimization of a laboratory-scale process to produce CMA from biomass. Since the gasification of biomass materials is well-developed technology, the laboratory research concentrated on demonstrating each of the unit operations shown in figure 1. This technology was previously demonstrated for waste gas conversion, so that the necessary experiments could easily performed in the required time period. Synthesis gas typical of that obtained from sewage sludge and MSW was used (Zang and Khan, 1991; Davis *et al.*, 1990). Phase 1 also included cost and material balance analyses, a preliminary market analysis and commercialization strategy, and an industry outreach program. Since the primary function of BRI is to develop biotechnological processes for commercialization, considerable expertise exists in each of these areas.

TASK A. RESEARCH AND TESTING ACTIVITIES

As was mentioned previously, BRI has considerable expertise in converting CO, CO_2, and H_2 in waste gas to acetic acid/acetate by anaerobic fermentation. Also, the technology for converting biomass to syngas (CO, CO_2, H_2) is well developed. Hence, Task A concentrated on individual unit operations in converting syngas from various raw materials to acetic acid/acetate. Synthetic gas with concentrations of the major components (CO, CO_2, H_2, CH_4, N_2, sulfur gases) obtained by gasification of MSW, coal, and sewage sludge was used in the reaction experiments.

Syngas Conversion to Acetic Acid/Acetate in the Continuously Stirred Tank Reactor (CSTR). The conversion of syngas of various compositions was demonstrated in a CSTR with cell recycle. A New Brunswick Bioflo I chemostat was used in these studies. The anaerobic bacterium ERI2 was used for the conversions at pH 4.0 to 5.0. Culture transfer to reaction vessels was made from stoppered serum bottles previously incubated with the culture. Anaerobic transfer techniques were employed during culture transfer. The liquid dilution rate, agitation rate, and gas retention time were varied in order to maximize syngas (CO, CO_2/H_2) conversion and product acetic acid/acetate conversion. A gas retention of approximately 3 min at 1000 rev/min with a liquid dilution rate of 16 h^{-1} has been found optimum for waste gas conversion to acetic acid. The experiments were carried out at a constant temperature of 37°C and atmospheric pressure. Elevated pressures have been shown to be effective in significantly decreasing the effective retention time to seconds in the BRI laboratories, but equipment limitations and time limited the use of high pressure experiments. Cell recycle was used to maximize the cell concentration inside the reactor.

The cell recycle system consisted of a hollow-fiber, tangential-flow ultrafiltration device. The culture broth, after passing through a gas separator, was pumped through the 1-Φm hollow-fiber system. The concentrated cell stream was returned to the reactor, while the permeate was directed to the waste collection carboy. Various pore sizes and recycle rates were studied to arrive at the best system.

The following variables were studied in the CSTR with cell recycle:

- Retention time – gas flow rate.
- Liquid dilution rate.
- Agitation rate.
- Liquid rate through the membrane.

The inlet and outlet gas compositions were monitored to determine steady-state at a given set of reaction conditions. The variables were manipulated to achieve the maximum conversion at each gas retention time. Gas compositions were measured using gas chromatography (GC) with a hot-wire detector. Liquid compositions were measured by GC with a flame ionization detector, and cell density was monitored using a spectrophotometer. Nutrients in the form of basal salts and vitamins were supplied to the reactors as needed, to promote appropriate growth.

Solvent Extraction. Solvent extraction was used to remove the relatively dilute acetic acid from the reactor effluent stream prior to reaction with dolomitic lime to produce CMA. Several solvents are possible for this application including tributyl phosphate, tertiary amine systems, and quaternary amine systems. A solvent system with a high distribution coefficient for acetic acid that can, at the same time, extract a minimum amount of water, is desired. It was reported previously that high acetic acid-to-water ratios are necessary to permit CMA precipitation without the dissolution of a large fraction of the CMA in water. Several of the more promising solvent systems were tested in a continuous process based on the results of batch extraction experiments. Variables for study in a small extraction system included permeate flow rate from the cell recycle system and solvent to feed ratio. The objective of this set of experiments was to maximize the concentration of acetic acid in the exit stream, while minimizing the extraction of water in a continuous system.

The criteria for a suitable solvent include a high distribution coefficient for acetic acid, no toxicity to the bacteria, complete immiscibility with water, and good physical properties. The distribution of solute between solvent and aqueous phases determines the thermodynamic feasibility and the amount of solvent required to remove acetic acid, and a high coefficient is essential. The solvent comes in contact with the microorganisms and must not impair culture performance. The solubility of the solvent in water must be very low to avoid substantial solvent losses, and the components of the medium (nutrients) should not be highly soluble in the solvent. Also, the density, viscosity, vapor pressure, and freezing point of the solvent are important factors of consideration when discussing the commercialization of this concept.

Two extraction approaches were considered: extractive fermentation and traditional extraction outside the fermenter. Extraction in the fermenter (extractive fermentation) eliminates the need for separate extraction equipment. The extraction must be run at fermentation temperatures, which may not be the optimal condition for solubilities or solute transport. Also, phase toxicity to the bacteria may be more severe than molecular toxicity. Furthermore, the fermenter must be larger and the cost of agitation higher with extractive fermentation. Finally, extraction in the fermenter is equivalent to only a single equilibrium stage, and higher solvent ratios may be necessary.

With external extraction, a traditional separation of the acetic acid by solvent is achieved in a tower. This system must be coupled with cell recycle to avoid toxicity to the culture, which would interfere with the extraction. The major disadvantage of this concept is that a hollow-fiber membrane is necessary to remove the cells from the effluent stream from the fermenter to the extraction column. This system can use solvents with high distribution coefficients, since the toxicity will be less. Less solvent will be necessary, and higher acid concentrations will be sent to the distillation. Smaller fermenters can be used and the power requirements are reduced. In both systems, the solvent is regenerated, and the acid recovered by distillation.

CMA Production. The production of CMA by the reaction of acetic acid and dolomitic lime is a simple, very slightly exothermic process. The reaction is very rapid, producing a CMA slurry under the conditions proposed in this research. The major challenges as a laboratory unit operation are the feeding of the solid dolomitic lime to the reactor and the need to optimize conditions to produce a CMA slurry for easy drying. One of the major variables for study was thus the ratio of acetic acid to water in the feed to the reactor.

CMA Drying. Experiments investigating the drying of the CMA/water slurry were carried out in combination with a vendor. Variables include the water content of the slurry, the susceptibility of the

CMA to thermal damage, drying rate, etc. The purpose of these experiments was to prepare a CMA material that meets the deicing requirements set forth in *SHRP Handbook H-205*. Tests on the CMA product will be performed by BRI and an independent laboratory.

TASK B. COST AND MATERIALS BALANCE ANALYSIS

Following the technical feasibility study of Task A, a process model was developed that will calculate process economics and identify material flow (feedstock throughput, waste streams, and yield) for the preparation and recovery of acetic acid and its conversion to CMA. An ASPEN^{TM} simulation model was developed using the experimental results of Task A. The process design was based on tonnage quantities expected in a commercial-scale facility.

TASK C. PRELIMINARY MARKET ANALYSIS AND COMMERCIALIZATION STRATEGY

A preliminary market analysis and commercialization strategy was prepared using data obtained both from the literature and as a result of research undertaken in Phase One. The analysis estimated the commercial viability of the CMA production system, and included the potential market volume and application for CMA, time scale for CMA introduction into the marketplace, and viable distributors.

TASK D. INDUSTRY OUTREACH

Several potential industrial sponsors were identified who have an interest in biomass gasification, acetic acid production, or CMA manufacture. The results of the study were presented to these potential sponsors in an effort to develop a joint venture for CMA manufacture from waste biomass. BRI has significant experience in industry outreach, having identified industrial partners to design and construct a plant to produce acetic acid from the waste gases from carbon black manufacture.

TASK E. PRESENTATION AND INTERIM REPORT

After completing all activities under Tasks A through D, the contractor made a presentation to the Contracting Officer's Technical Representative (COTR) in Washington, D.C. At this time, the results of Phase One were presented and discussed. A proposed outline of this interim report was presented and reviewed.

PHASE I RESULTS AND DISCUSSION

TASK A. RESEARCH AND TESTING ACTIVITIES

TASK A1. SYNGAS CONVERSION

A CSTR with and without cell recycle was operated with various synthetic synthesis gases in order to demonstrate the feasibility of producing acetic acid/acetate from various biomass materials. As an initial step in this process, the composition of syngases produced by the gasification of various raw materials was collected from the literature. Synthetic gases were then prepared using typical or average compositions and then tested in the CSTRs.

Syngas Composition

Several syngas compositions were obtained from the literature for the gasification of MSW and sewage sludge, two raw materials of interest in CMA production. These synthesis gas compositions, shown in tables 3 and 4, vary considerably with the nature of the raw material being gasified and the gasification conditions (temperature, pressure, gasifier type, and medium, etc.). Synthesis gases produced using air as a reactant are rich in N_2. Synthesis gases produced using pure oxygen and/or steam as a reactant are richer in CO, CO_2, and H_2. Also shown in the tables are compositions of the syngases when considering CO, CO_2, and H_2 only. The combined CO and H_2 content of the gases ranges from 56% to 84%. Finally, table 5 shows the compositions of the synthetic synthesis gases used for acetic acid production. Coal syngas is a high CO, low H_2 gas; and the sewage sludge and MSW syngases are medium CO, medium H_2 gases.

Table 3. Syngas Produced From the Gasification of MSW

			(% by Vol)		
			PurOx	Bailie	PurOx
	Air	Air	Oxygen	Oxygen and Steam	Oxygen
	(Pilot)[a]	(Pilot)[b]	(Prototype)[c]	(Pilot)[c]	(Pilot)[c]
CO	22.9	15.3	49.0	20.0	40.0
CO_2	24.0	16.4	15.0	39.0	24.0
H_2	3.6	11.8	30.0	30.0	24.0
O_2	0.5				
N_2, Ar	33.1	49.4	1.0		1.0
CH_4	10.6	4.7	3.0	5.0	5.6
C_2^+	5.3	2.4	2.0	6.0	
H_2S, COS					5.4
CO-, CO_2-, H_2-Only Basis					
CO	45.3	35.2	52.1	22.5	45.4
CO_2	47.5	37.7	16.0	43.8	27.3
H_2	7.2	27.1	31.9	33.7	27.3

[a] Alden *et al.* (1991).
[b] Rensfelt and Ekstrom (1988).
[c] Groneveld and Van Swaaij (1980).

Table 4. Syngas Produced by the Gasification of Sewage Sludge

		(% by Vol)		
		Texaco	Texaco	Texaco
Component	Davis *et al.*,1990	Zimpro A, 1989	Carver-Greenfield B, 1989	Carver-Greenfield C, 1989
CO	37.0	37.09	36.40	34.96
CO_2	27.0	25.30	25.31	27.63
H_2	35.0	35.26	35.74	35.49
N_2 + Ar	0.6	1.68	1.84	1.10
H_2S, CS_2, COS	0.3	0.65	0.71	0.80
CH_4	0.1	0.02	0	0.02
CO-, CO_2-, H_2-Only Basis				
CO	37.4	38.0	37.4	35.6
CO_2	27.3	25.9	26.0	28.2
H_2	35.4	36.1	36.6	36.2

Table 5. Compositions of Synthetic Syngases Used in Acetic Acid/Acetate Production Studies With ERI2

	Composition (Vol %)			
Feedstock	CO	H_2	CO_2	CH_4
Coal[a]	65	20	11	4
Sewage Sludge[b]	35	34	26	5
MSW[c]	49	25	20	6

[a] Compilation from a variety of coal gas sources.
[b] Texaco, Carver-Greenfield (see table 4).
[c] Average composition of PurOx pilot and commercial units.

Gas Conversion Studies

Coal Synthesis Gas. Three studies were performed in the CSTR with cell recycle using Isolate ERI2 and synthetic coal-derived synthesis gas (65% CO, 20% H_2, 11% CO_2, and 4% CH_4). A schematic of the CSTR with cell recycle is shown in figure 2. These experiments were designed to measure the effects of gas retention time (GRT) [defined as the volume of the culture divided by the gas flow rate to the system], liquid dilution rate, D (defined as the liquid feed rate to the culture divided by the culture volume], and agitation rate on culture performance with a high CO- and H_2-content gas.

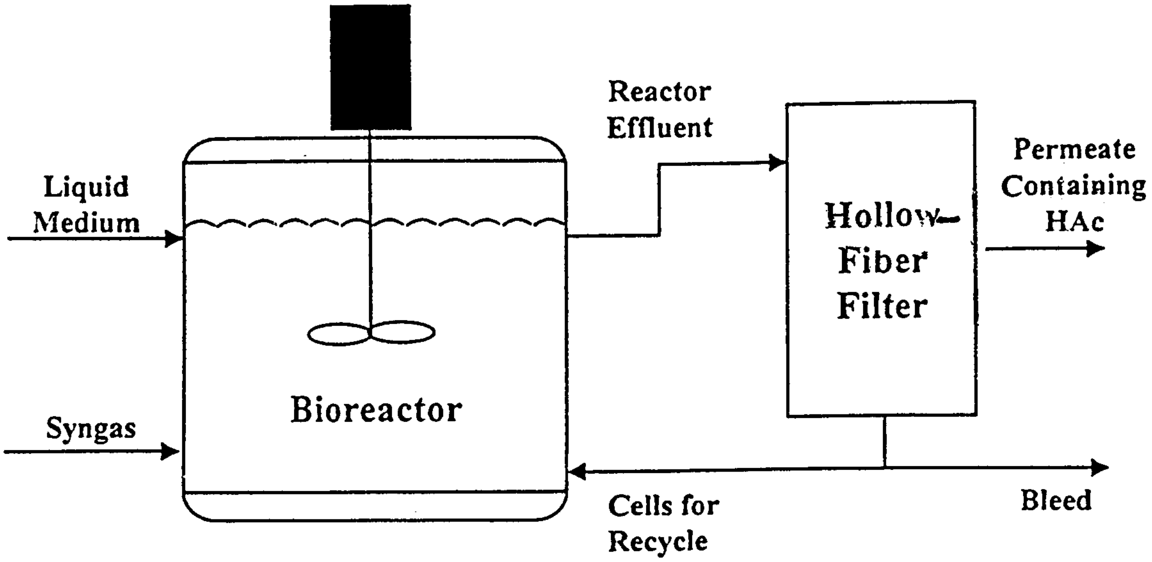


Figure 2. Schematic of CSTR With Cell Recycle

Table 6 shows the effects of GRT on ERI2 performance with coal synthesis gas. In this study, the agitation rate was held constant at 750 rev/min, and the liquid dilution rate (D) was maintained at 0.069 h^{-1}. As is shown in the table, the CO conversion was above 90% at GRTs as low as 9.7 min. The H_2

conversion was above 90% at GRTs as low as 11.4 min. Although the acetic acid/acetate concentration was not measured for all runs, it was generally in the range of 18 to 20 g/L. In converting a dilute waste gas (13% CO, 14.5% H_2, 10% CO_2, and 62.5% N_2), a 65% to 70% conversion of both CO and H_2 was obtained at a GRT of 3 min. In accounting for the differences in CO and H_2 content between the two syngases, this means that a 9.3-min GRT should be required for the same conversions with coal syngas. The data confirms that this occurred in the experimental study summarized in table 6.

Table 6. Effects of GRT on the Performance of ERI2 in the CSTR With Cell Recycle When Using Coal Syngas

GRT (min)	Agitation Rate (rev/min)	D (h^{-1})	Conversion (%)		Cell conc. (g/L)	Acetic Acid/ Acetate* (g/L)
			H_2	CO		
18.1	750	0.069	93.9	94.9	10.8	14
14.9	750	0.069	92.7	94.6	4.03	18.24
13.6	750	0.069	93.8	96.0	9.21	20.69
13.2	750	0.069	93.8	95.0	8.1	20.90
11.8	750	0.069	89.4	92.9	8.75	19.92
11.4	750	0.069	92.1	93.6	-	-
9.7	750	0.069	84.9	91.3	-	-
8.5	750	0.069	56.9	85.6	-	-
8.1	750	0.069	28.2	78.1	-	-
7.6	750	0.069	16.2	69.1	-	-

* Acetic acid/Acetate refers to total acetic acid and acetate concentration.

Table 7 presents the effects of liquid dilution rate at various GRTs on ERI2. As is noted, liquid dilution rate did not affect gas conversion appreciably, with all of the H_2 and CO conversion data in the 80% to 95% range. The acetic acid/acetate concentration varied somewhat with dilution rate, maximizing at about 20 g/L. This maximum concentration is thought to be very near the inhibitory acetic acid/acetate concentration for the bacterium. Table 8 shows the effects of agitation rate on performance at a constant GRT and liquid dilution rate. As expected, the gas conversions increased with agitation rate due to increased mass transfer. Selection of an agitation rate for bench-scale demonstration is a matter of balancing the economics of gas conversion with power requirements.

Table 7. Effects of Liquid Dilution Rate on the Performance of ERI2 in the CSTR With Cell Recycle When Using Coal Syngas

D (h^{-1})	Agitation Rate (rev/min)	GRT (min)	Conversion (%)		Cell Concentration (g/L)	Acetic Acid/ Acetate* (g/L)
			H_2	CO		
0.061	750	18.1	88.6	94.3	4.06	9.76
0.065	750	18.1	91.5	94.2	3.99	12.7
0.069	750	18.1	93.9	10.8	14	-
0.071	750	18.1	92.5	94.2	5.17	11.28
0.073	750	18.1	93.2	94.8	10.24	16.3
0.074	750	18.1	94.3	95.4	2.06	2.03
0.069	750	14.9	92.7	94.6	4.03	18.24
0.073	750	14.9	91.4	93.9	3.89	16.85
0.076	750	14.9	92.0	94.6	4.62	17.97
0.079	750	14.9	48.5	89.7	5.13	16.33
0.052	750	13.6	89.6	95.4	2.74	12.4
0.065	750	13.6	81.0	89.0	3.41	18
0.069	750	13.6	93.8	96.0	9.21	20.69
0.071	750	13.6	93.3	95.1	-	-
0.073	750	13.6	90.4	93.0	6.84	19.16
0.054	750	13.2	23.5	81.3	5.06	14.79
0.058	750	13.2	64.9	89.9	3.86	17.13
0.069	750	13.2	93.8	95.0	8.1	20.90
0.073	750	13.2	91.1	93.0	7.05	19.04
0.076	750	13.2	89.7	91.4	8.65	18.46
0.079	750	13.2	76.0	91.0	4.94	14.8
0.073	750	12.6	88.8	93.3	11.43	19.96
0.076	750	12.6	92.0	92.5	10.99	20.05
0.079	750	12.6	89.4	92.1	8.21	19.23
0.079	750	12.6	84.6	90.8	3.96	17.4
0.069	750	11.8	89.4	92.9	8.75	19.92
0.071	750	11.8	90.3	92.6	6.24	20.57
0.073	750	11.8	91.8	94.4	11.57	19.61
0.076	750	11.8	89.3	91.1	12.33	19.2
0.079	750	11.8	87.2	91.2	10.56	19.84

* Acetic Acid/Acetate refers to total acetic acid and acetate concentration.

Table 8. Effects of Agitation Rate on the Performance of ERI2 in the CSTR With Cell Recycle When Using Coal Syngas

Agitation Rate (rev/min)	D (h^{-1})	GRT (min)	Conversion (%)		Cell Concentration (g/L)	Acetic Acid/ Acetate* (g/L)
			H_2	CO		
350	0.071	13.6	51.5	52.8	-	-
500	0.069	13.6	88.3	89.9	5.98	15.33
750	0.069	13.6	93.8	96.0	9.21	20.69
850	0.069	13.6	94.3	96.1	7.44	18.86
950	0.069	13.6	96.7	97.1	-	-

* Acetic Acid/Acetate refers to total acetic acid and acetate concentration.

Sewage Sludge Gas. Studies were next performed in the Bioflo II-C CSTR with cell recycle using Isolate ERI2 and synthetic sewage sludge synthesis gas (35% CO, 34% H_2, 26% CO_2, and 5% CH_4). These experiments were designed to measure the effects of GRT, liquid dilution rate, and agitation rate on culture performance with this medium with CO- and H_2-containing gas.

Table 9 shows the effects of GRT on ERI2 performance. In this study, the agitation rate was held constant at 750 rev/min and the liquid dilution rate was maintained at 0.1 h^{-1}. The GRT was varied between 7.5 and 22 min. As is shown in the table, the CO and H_2 conversions were greater than 80% at GRTs above 9.7 min. When the GRT was greater than 12 min, no significant differences were observed in the gas conversion.

Table 9. Effects of GRT on the Performance of ERI2 in the CSTR With Cell Recycle When Using Sewage Sludge Syngas

GRT (min)	D, h^{-1}	Agitation Rate (rev/min)	H_2 Conversion (%)	CO Conversion (%)	Cell Concentration (g/L)	Acetic Acid/ Acetate* (g/L)
9.74	0.103	750	40.8	85.9	-	-
12.20	0.103	750	94.2	94.5	-	-
13.16	0.103	750	94.3	95.1	-	-
16.30	0.103	750	95.7	96.3	5.88	11.16
17.05	0.103	750	95.0	96.1	6.19	9.72
34.09	0.103	750	97.2	97.3	-	-
10.98	0.107	750	87.3	94.3	-	-
15.76	0.107	750	92.6	96.0	7.39	13.36
16.48	0.107	750	94.2	95.8	10.43	9.14
21.97	0.107	750	96.6	97.2	9.77	8.20

* Acetic Acid/Acetate refers to total acetic acid and acetate concentration.

Table 10 presents the effects of liquid dilution rate at various GRTs on ERI2. The GRT was held constant at 16.3 min and the agitation rate was 750 rev/min. As expected, liquid dilution rate did not affect gas conversion appreciably, with all of the H_2 and CO conversion data in the 90% to 100% range. Table 11 shows the effects of agitation rate on performance at a constant GRT and liquid dilution rate. As expected, the gas conversions again increased with agitation rate due to increased mass transfer.

Table 10. Effects of Liquid Dilution Rate on the Performance of ERI2 in the CSTR with Cell Recycle When Using Sewage Sludge Syngas

Agitation Rate, rev/min	D (h^{-1})	GRT (min)	H_2 Conversion (%)	CO Conversion (%)	Cell Concentration (g/L)	Acetic Acid/ Acetate* (g/L)
750	0.022	16.30	93.83	96.54	-	-
750	0.022	16.30	94.38	96.06	4.51	15.16
750	0.023	16.30	91.76	95.51	-	-
750	0.044	16.30	96.28	96.58	-	-
750	0.046	16.30	95.87	97.06	4.15	13.83
750	0.066	16.30	93.07	94.82	3.86	11.61
750	0.086	16.30	93.61	96.21	3.33	14.84
750	0.097	16.30	93.95	94.91	7.11	11.77
750	0.099	16.30	89.14	96.73	-	-
750	0.100	16.30	95.60	95.97	-	-
750	0.103	16.30	95.73	96.31	6.46	9.50
750	0.105	16.30	89.57	94.68	-	-
750	0.107	16.30	92.60	96.00	9.77	8.20
750	0.111	16.30	95.20	96.10	8.17	12.10
750	0.126	16.30	90.25	95.33	-	-
750	0.129	16.30	92.11	95.89	-	-
750	0.141	16.30	93.90	95.30	9.09	12.78
750	0.155	16.30	94.35	96.56	-	-
750	0.177	16.30	93.45	95.78	-	-
750	0.188	16.30	94.36	96.66	4.60	13.43
750	0.209	16.30	95.95	96.20	-	-
750	0.215	16.30	90.81	92.60	4.29	12.06
750	0.221	16.30	96.48	97.25	-	-
750	0.258	16.30	95.34	98.10	4.95	13.13

* Acetic Acid/Acetate refers to total acetic acid and acetate concentration.

Table 11. Effects of Agitation Rate on the Performance of ERI2 in the CSTR With Cell Recycle When Using Sewage Sludge Syngas

Agitation Rate (rev/min)	D (h^{-1})	GRT min	H_2 Conversion (%)	CO Conversion (%)	Cell Concentration (g/L)	Acetic Acid/ Acetate* (g/L)
300	0.107	12.7	39.12	45.08	6.20	6.76
400	0.107	12.7	71.84	76.51	5.22	7.04
500	0.107	12.7	83.21	87.88	7.10	12.56
600	0.107	12.7	92.09	92.92	8.77	13.76
700	0.107	12.7	93.03	95.13	4.25	8.88
750	0.107	12.7	94.21	95.82	10.43	9.14
800	0.107	12.7	94.19	95.18	-	-
850	0.107	12.7	96.31	95.90	-	-
950	0.107	12.7	96.60	96.92	-	-

* Acetic Acid/Acetate refers to total acetic acid and acetate concentration.

MSW Synthesis Gas. Tables 12 through 14 show the effects of GRT, liquid dilution rate, and agitation rate on the performance of ERI2 in the CSTR using MSW syngas (49% CO, 25% H_2, 20% CO_2, and 6% CH_4). The data showing the effects of GRT and agitation rate on gas conversion were performed in the CSTR with cell recycle. However, the data on the effects of liquid dilution rate on culture performance were performed without cell recycle. As is noted in table 12, CO and H_2 conversions of 80% to 90% were obtained at a GRT of 10.5 to 11 min. Very high gas conversions were obtained at all agitation rates above 350 rev/min.

Table 12. Effects of GRT on the Performance of ERI2 in the CSTR Without Cell Recycle When Using MSW Syngas

Agitation Rate (rev/min)	D (h^{-1})	GRT (min)	H_2 Conversion (%)	CO Conversion (%)	Cell Concentration (g/L)	Acetic Acid/ Acetate* (g/L)
750	0.103	9.49	58.88	89.09	-	-
750	0.103	10.83	90.86	92.50	-	-
750	0.103	12.61	91.72	92.58	-	-
750	0.103	13.64	90.64	94.04	8.14	15.39
750	0.103	16.49	92.35	93.23	7.30	14.61
750	0.103	17.05	93.82	96.32	5.93	14.06
750	0.103	20.00	95.37	96.20	7.58	12.07
750	0.103	21.43	96.32	96.45	10.56	11.71
750	0.103	21.43	96.74	97.99	8.35	10.71
750	0.103	23.39	100	95.32	-	-
750	0.103	26.32	100	97.26	9.612	11.30
750	0.103	27.27	100	98.54	9.779	11.26

* Acetic Acid/Acetate refers to total acetic acid and acetate concentration.

Table 13. Effects of Liquid Dilution Rate on the Performance of ERI2 in the CSTR Without Cell Recycle When Using MSW Syngas

Agitation Rate, rev/min	D (h^{-1})	GRT (min)	H_2 Conversion (%)	CO Conversion (%)	Cell Concentration (g/L)	Acetic Acid/ Acetate* (g/L)
750	0.052	22.73	3.38	56.15	4.00	11.08
750	0.053	22.73	19.39	83.52	2.89	11.73
750	0.097	22.73	94.61	97.47	2.65	10.84
750	0.103	22.73	93.20	96.63	1.51	7.86
750	0.119	22.73	93.75	97.29	1.45	7.07
750	0.160	22.73	41.54	76.14	1.24	4.68
750	0.214	22.73	4.48	72.10	1.03	4.16

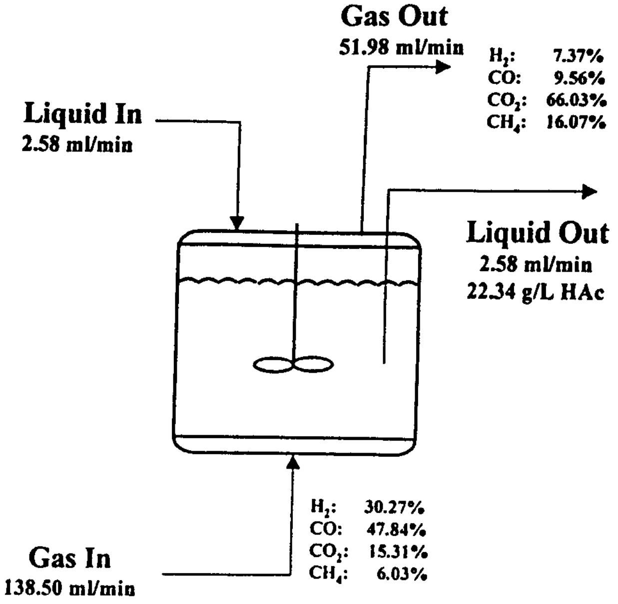
* Acetic Acid/Acetate refers to total acetic acid and acetate concentration.

Table 14. Effects of Agitation Rate on the Performance of ERI2 in the CSTR With Cell Recycle When Using MSW Syngas

Agitation Rate, rev/min	D (h^{-1})	GRT (min)	H_2 Conversion (%)	CO Conversion (%)	Cell Concentration (g/L)	Acetic Acid/ Acetate* (g/L)
350	0.103	21.43	68.45	68.67	8.07	11.05
450	0.103	21.43	86.56	89.03	7.22	10.24
650	0.103	21.43	91.88	95.44	8.45	9.74
750	0.103	21.43	93.20	96.63	8.15	11.12
850	0.103	21.43	100	98.02	8.34	9.93
950	0.103	21.43	96.74	97.99	8.35	10.71

* Acetic Acid/Acetate refers to total acetic acid and acetate concentration.

Significance. ERI2 was able to utilize CO and H_2 to produce acetic acid/acetate equally well with either the high or medium CO content gases. The bacterium was able to utilize the syngases (H_2 and CO) at a greater than 80% conversion rate when using a GRT of less than 10 min. A material balance for acetic acid/acetate production from MSW synthesis gas by ERI2 is shown in figure 3. At a 10.8-min GRT at pH 4.9, the CO and H_2 conversions are both greater than 90%. The acetic acid/acetate concentration is 22.3 g/L, which gives a yield 95% of theoretical. The acid/acetate productivity (calculated as the ratio of the concentration and the liquid retention time) is 2.3 g/L•h, and the specific acid/acetate productivity (calculated as the ratio of the productivity and the cell concentrations) is 0.24 g/g cell h. Since the reactions are mass transfer limited, the reaction rate is directly proportional to the CO partial pressure. Thus, operation at increased pressure has the potential to reduce the retention time to seconds.



	Gas In	Liquid In	Gas Out	Liquid Out
CO	161.48	0	12.11	0
H_2	92.86	0	8.49	0
CO_2	51.67	0	83.66	0
HAc	0	0	0	57.64

Culture: Isolate ERI2
Temperature: 38°C
pH: 4.9
Agitation: 750 rpm
Gas: MSW Synthesis Gas

<u>Cell Recycle System</u>
Hollow-Fiber Type: AGT CFR-2-E-4
Hollow-Fiber Flow Rate: 95 mL/min

Culture Volume: 1,500 mL
Gas Retention Time: 10.83 min
CO Conversion: 92.50%
H2 Conversion: 90.86%
Liquid Retention Time: 9.96 h
Cell Concentration: 9.81 g/L
HAc Concentration: 22.34 g/L
HAc Productivity: 2.305 g/L·h
HAc Productivity: 0.235 g/g cell·h
HAc Yield: 0.2379 mole HAc/mole gas
HAc Yield: 95.18% of Theoretical Value

Figure 3. Material Balance for Acetic Acid/Acetate Production From MSW Synthesis Gas Using ERI2

TASK A2. SOLVENT EXTRACTION

Numerous proprietary solvent mixtures have been evaluated for use in extracting acetic acid from the fermentation mixture. A partial listing of some of the more promising solvent systems and their acetic acid distribution coefficients is shown in table 15. The notation solvent i, co-solvent j has been adapted in order to protect the proprietary identity of the solvent systems. As is noted in table 14, seven of the solvent systems had acid distribution coefficients of 4.0 or above. This means that the acetic acid concentration in the solvent phase after extraction is at least 4 times greater that the corresponding acid concentration in the aqueous phase fermentation broth. A 10-g/L acetic acid concentration in the broth will then result in a 41- to 66-g/L acetic acid concentration in the solvent.

Table 15. Summary of the More Promising Co-Solvent Systems Tested for Extracting Acetic Acid From the Fermentation Broth

System	Distribution Coefficient
20% Solvent A, 80% Co-Solvent 1	5.8
20% Solvent A, 80% Co-Solvent 2	reaction*
20% Solvent A, 80% Co-Solvent 3	reaction*
20% Solvent A, 80% Co-Solvent 4	6.6
20% Solvent A, 80% Co-Solvent 5	4.9
20% Solvent A, 80% Co-Solvent 6	4.3
20% Solvent A, 80% Co-Solvent 7	4.9
20% Solvent B, 80% Co-Solvent 4	0.78
20% Solvent B, 80% Co-Solvent 8	4.1
20% Solvent B, 80% Co-Solvent 9	1.6
20% Solvent C, 80% Co-Solvent 9	1.4
20% Solvent D, 80% Co-Solvent 9	1.3
20% Solvent E, 80% Co-Solvent 9	2.7
20% Solvent A, 80% Co-Solvent 11	4.9

* Chemical reaction between acetic acid and one of the solvents during extraction.

The final selection of an optimal co-solvent system is often a matter of balancing the performance of the system with the cost of the system components. On this basis, solvent A, co-solvent 7 and solvent A, co-solvent 11 were selected for CMA production studies. Distribution coefficient and separation factor data for solvent A, co-solvent 11 as a function of composition are shown in table 16. The performance of these two systems was very similar. Solvent A, co-solvent 11 has thus been selected for bench-scale demonstration in Phase II based solely on economic considerations.

Table 16. Effects of Solvent Composition on Distribution Coefficient (Solvent A, Co-Solvent 11)

Volume %			
Solvent A	Co-Solvent 11	Acid Distribution Coefficient	Separation Factor*
0	100	0.03	-
20	80	4.9	700
40	60	10.7	700
60	40	13.3	680
80	20	15.0	590
100	0	18.0	560

* Defined as ratio of acid distribution coefficient to water distribution coefficient.

As is noted, very high distribution coefficients (3 to 15, depending on relative concentrations) are obtained, as well as very good separation factors (500 to 800). No bacterial toxicity is seen with this solvent system at solubility concentrations. The solvent system is essentially immiscible with water, both the solvent and co-solvent having ppm (parts per million) solubility levels. The density of the solvent system is 0.8 g/cm^3 and the viscosity is 1 cp (1 mPa s).

TASK A3. CMA PRODUCTION

The production of CMA may be represented by the following simplified equations:

$$2HAc + CaO\ 6\ Ca(Ac)_2 + H_2O \tag{5}$$

$$2HAc + MgO\ 6\ Mg(Ac)_2 + H_2O \tag{6}$$

Thus, 2 moles of acetic acid are reacted with either CaO or MgO to produce $Ca(Ac)_2$ or $Mg(Ac)_2$.

Batch Studies

Numerous batch experiments were performed in the BRI laboratories to demonstrate the feasibility of producing calcium acetate, magnesium acetate, and CMA from solvent extracted acetic acid directly from the solvent phase. CaO, MgO, or dolomitic lime was simply contacted with the solvent containing extracted acetic acid in a beaker. Solvent composition, agitation rate, length of mixing time, and relative compositions of lime to acetic acid were the major variables for study.

A summary of several of these batch experiments is shown in table 17. As is noted, products having Ca^{2+}/Mg^{2+} ratios of 0.02:1.22 can be produced. The pH of the solid CMA is typically 8.7 to 9.4, and the product contains 65% to 75% acetate. The yield of CMA from acetic acid and lime is 96% to 99% of theoretical.

Table 17. CMA Production in a Batch Process

Run	1	2	3	4	5	6	7
Ca^{++} (% wt)	0.46	2.05	6.61	8.18	10.10	11.53	13.35
Mg^{++} (% wt)	13.83	13.84	11.45	8.56	7.86	6.99	6.64
Ca^{++}/Mg^{++} (mole ratio)	0.02	0.09	0.35	0.58	0.78	1.00	1.22
CMA pH	8.7	8.8	8.6	9.1	9.4	9.4	9.3
Ac^{-} (% wt)	68.5	73.25	75.01	65.63	67.88	67.88	71.50
$Y_{HAc/CMA}$ (% real/theoretical)	99.19	99.62	99.12	99.94	99.41	99.23	99.87

One of the major problems encountered in producing CMA from acetic acid in the solvent phase is the time required to settle the solid CMA from the two liquid phases. This settling time was a strong function of the viscosity of the solution. Solvent A, the preferred solvent in the solvent/co-solvent system, is quite viscous. Solvent B, another potential solvent that lacks in acid extractive capability, is less viscous than solvent A. The addition of co-solvent 7, 9, or 11 helps to reduce the viscosity of the overall solvent mixture. Experiments were thus performed with various solvent/co-solvent mixtures to measure settling time as a function of solvent composition.

Table 18 shows the results from this study. A solvent mixture containing $\geq$ 30% solvent A, performed with a 1:4 solvent-to-permeate ratio, resulted in settling times of more than 24 h. The use of 20% solvent A in the mixture resulted in a settling time of 1 min, and the use of 10% solvent A resulted in a settling time of 30 s. A small sacrifice in the acid distribution coefficient thus results in a major decrease in CMA settling time.

Table 18. Effect of Solvent Composition on Settling Time During CMA Production
(Permeate contained 10 g/L acetic acid/acetate, lime + MgO mixture contained a 3:7 molar ratio of Ca^{++}/Mg^{++})

Solvent Composition	Extraction Ratio (solvent:permeate)	Acetic Acid/ Acetate in Solvent Before Reaction (g/L)	Lime and MgO Mixture Added (g)	Settling Time
10% A, 90% 11	1:4	12.0	0.2475	30 s
20% A, 80% 11	1:1	8.4	0.1738	1 min
30% A, 70% 11	1:4	27.0	0.5577	>24 h
40% A, 60% 11	1:4	31.2	0.6446	>24 h
10% B, 90% 9	1:4	5.4	0.1115	<30 s
20% B, 80% 9	1:1	4.8	0.0992	<30 s
30% B, 70% 9	1:4	7.8	0.1613	<30 s
40% B, 60% 9	1:4	8.4	0.1738	<30 s

Rate Analysis

The kinetics of acetic acid utilization during CMA formation were studied by oversupplying lime and MgO. The reactor volume was 300 mL and the agitation rate was 400 rev/min. The solvent system contained 10% solvent A and 90% co-solvent 11. Acetic acid conversions at different solvent to saturated water flow ratios were measured with time. These data were used to investigate the kinetics of acetic acid disappearance. The batch results indicated that the reaction is first-order irreversible in acetic acid:

$$-r_A = kC_A, \tag{7}$$

where C_A = concentration of acetic acid
$-r_A$ = reaction rate

Separating variables in this equation yields:

$$-\ln(1-X_A) = kt \tag{8}$$

where X_A = conversion of acetic acid to CMA, defined as $\frac{HAc_{in} - HAc_{out}}{HAc_{in}}$

Figure 4 shows a plot of $-\ln(1-X_A)$ as a function of time. The slope of the straight line is the rate constant k, equal to 0.258 min^{-1}.

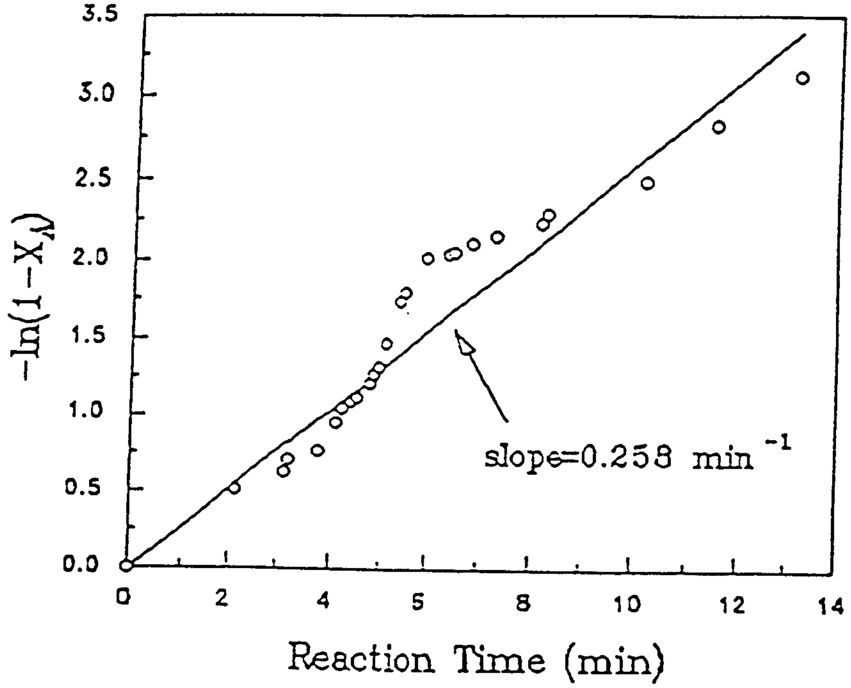


Figure 4. Reaction Rate Coefficient Determination for the Production of CMA From Acetic Acid

Continuous Studies

A small continuous CMA production unit was set-up to better study the production of CMA from acetic acid and lime directly from the solvent phase. A schematic of the unit is shown in figure 5. Dolomitic lime and MgO are reacted with solvent containing 15 g/L acetic acid in a small mixed reactor. The CMA formed is then settled and filtered to produce the CMA product for analysis. Solvent after reaction is recontacted with fermentation broth permeate containing acetic acid to replenish the acid. The water is separated from the solvent and returned to the reactor as recycle.

Data from the continuous CMA production unit are shown in table 19. As is noted, CMA yields of 99% were achieved under all conditions.

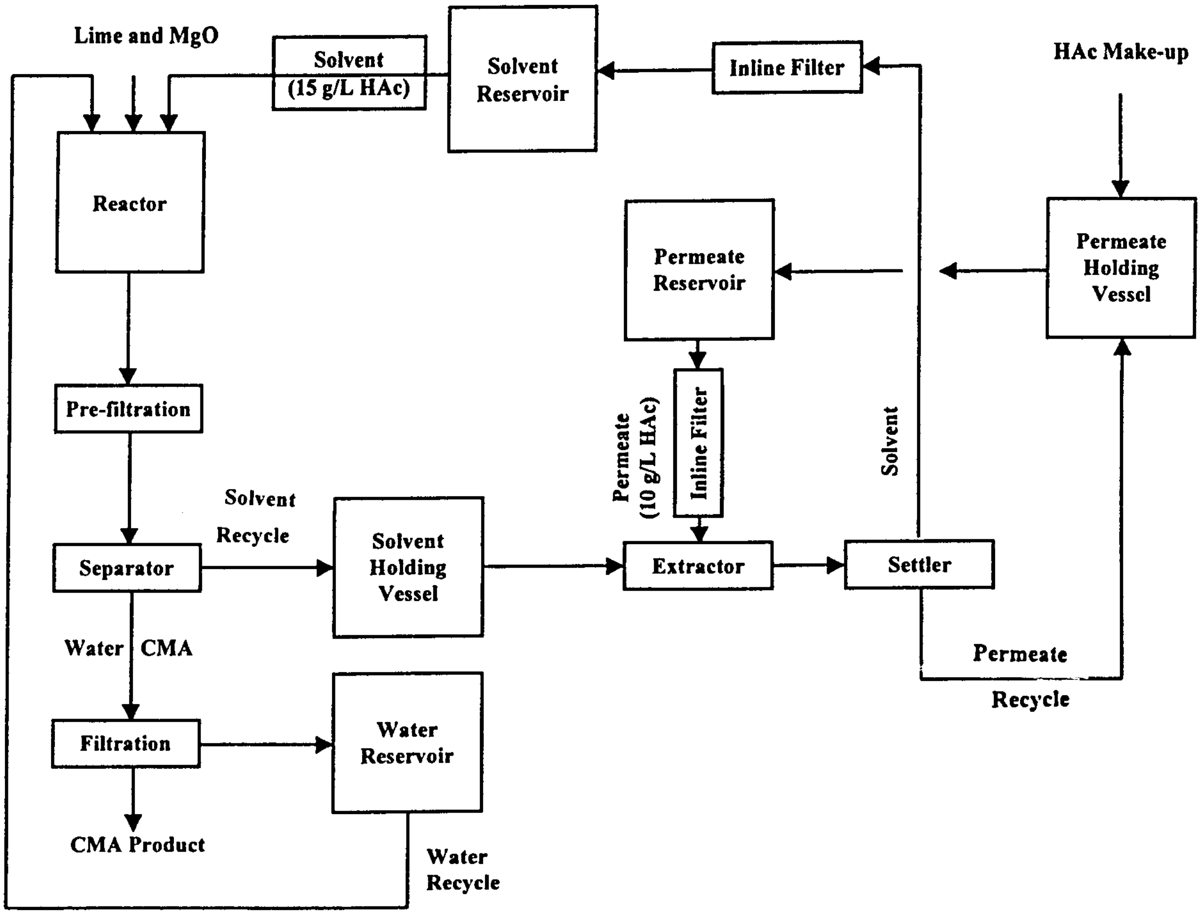


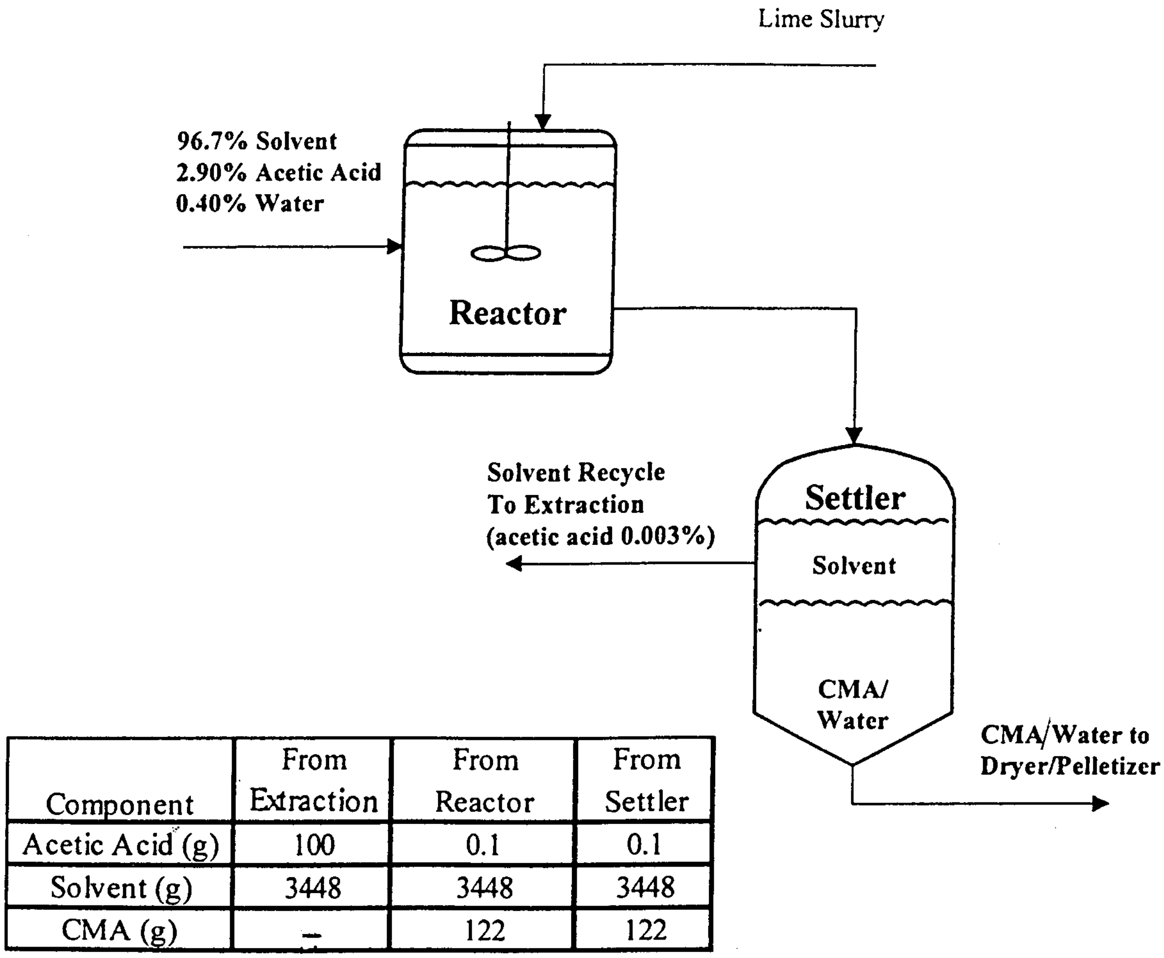
Figure 5. Schematic of Continuous Laboratory CMA Production Unit

Table 19. Continuous CMA Production
(Reactor volume: 300 mL; 10% solvent A, 90% co-solvent 11;
lime + MgO mixture containing a molar Ca^{2+}/Mg^{2+} ratio of 3:7)

Reaction Time (min)	Solvent Flow Rate:H_2O Flow Rate	HAc Conversion (%)	$Yield_{HAc/CMA}$ (% process/theoretical)
2.17	1:1	40.0	99.98
2.80	9:8	41.3	99.76
3.17	1:1	46.7	99.83
3.22	1:1	51.0	99.12
3.80	9:8	53.8	99.34
4.12	1:1	61.5	99.01
4.22	1:1	64.8	99.06
4.42	1:2	66.5	99.92
4.52	1:1	67.1	99.73
4.87	1:2	69.7	99.68
4.97	1:1	70.0	99.91
5.12	1:1	76.9	99.06
5.42	1:2	82.4	99.06
5.52	1:1	83.3	99.14
6.42	1:2	84.1	99.96
6.52	1:1	87.1	99.21
8.29	1:2	87.9	99.05
10.22	1:1	91.7	99.94
11.52	1:1	94.1	99.25
13.17	1:1	95.3	99.16

Significance

A material balance from the CMA production process is shown in figure 6. Solvent containing 96.7% solvent, 2.9% acetic acid, and 0.4% water is contacted with lime and water in the reactor. After settling, the solvent contains only 0.003% acid. The CMA product analysis, shown in table 20, indicates that the product contains no water insolubles and has in this run a Ca^{2+}/Mg^{2+} product ratio of 0.43.



Component	From Extraction	From Reactor	From Settler
Acetic Acid (g)	100	0.1	0.1
Solvent (g)	3448	3448	3448
CMA (g)	–	122	122

Figure 6. Material Balance for Continuous CMA Production Experiment

Table 20. CMA Product From a Continuous Process

Item	CMA
Ca^{++} (% wt)	7.72
Mg^{++} (% wt)	10.96
Ca^{++}/Mg^{++} (mole ratio)	0.4274
Ac^{-} (% wt)	75.94
pH	8.02
Water Insolubles (% wt)	0

Thus, the concept of producing CMA from acetic acid in the solvent phase has been confirmed. Fast reaction rates are achieved with dolomitic lime/MgO. High yields of CMA are obtained. Commercial grade CMA can be produced by this process.

TASK A4. CMA DRYING

Three drying processes have been considered for CMA production. They are natural crystallization, nonevaporative crystallization, and evaporation to dryness. As reported in Report No. FHWA/RD-87/045, *Preferred Drying Methods of Calcium Magnesium Acetate Solutions*, both natural crystallization and crystallization from/or assisted by nonaqueous solvents failed to produce a suitable solid CMA. Thus, studies at BRI will be limited to processes using evaporation to dryness. Even though the BRI process utilizes nonaqueous solvents in producing CMA from acetic acid, solvent losses, the formation of thixotropic gels, and the inability to produce granular crystals make the use of crystallization with nonaqueous solvents impossible.

The equipment used in evaporating to dryness can be classified into two categories as follows: (1) drying liquids including solutions, slurries, and pastes; and (2) drying wet solids including powders, granules, sheets, and large objects. In this application for drying CMA, equipment for the drying of liquids should be used. Table 21 lists the characteristics of seven types of dryers for the drying of liquids. Out of these seven types of dryers, continuous tray or belt dryers, spray dryers, and screw conveyer dryers are rejected because of either high equipment cost, the formation of an unsuitable final product, or a combination of both (Report No. FHWA/RD-87/045). CMA production of the remaining four suitable dryers is discussed below.

Fluidized bed drying stands out as being one of the most promising methods for producing a good granular deicing product economically and with reasonable ease. There are several advantages of this equipment:

- Dryer dries and produces a granule in a single piece of equipment.
- Layered drying produces a nonporous, less viable product.
- Fuel efficiency of the dryer is good, ranging from 1500 to 1900 Btu/lb (3.5 to 4.4 MJ/kg) of water evaporated.
- Technology is mature for commercialization.

There are 34 suppliers of fluidized bed dryers as reported in DOT Report No. FHWA/RD-87/045. Two suppliers, Niro Atomizer, Inc., and Foster-Wheeler/NSM Co. offer fluidized bed systems that are specially designed for high-volume (low-cost) production of granules. Niro Atomizer Inc., Columbia, MD, and Aeromatic, Inc., of Towaco, NJ (Report No. FHWA/RD-83/062) also provided small-scale testing for CMA drying in previous studies.

Rotary or tumble bed dryers granulate and dry solutions by successively coating layers of the liquid on a core of fine particles as they are tumbled in a rotating cylinder, drum, or pan. The advantages of tumbling bed agglomerators are similar in a few instances to those of the fluidized bed. However, being an older, less sophisticated drying/granulating technique with certain disadvantages, it has been undergoing replacement by the fluidized bed in many instances. Compared to fluidized bed, the following disadvantages are observed:

- Fuel efficiency is poor, up to 2600 Btu/lb (6.0 MJ/kg) of water evaporated, because of inefficient contact of the hot gas stream and the drying pellets.

- Drying may cause product decomposition from hot-spot formation combined with long residence times. In contrast to fluidized bed where extremely uniform temperatures are maintained throughout the well-agitated bed, particles in a tumbling bed are often overheated by the drying gas.

- Solution fed to a tumbling bed is slowly distributed by the tumbling action. Sticking to the pan or clumping of particles can occur during this slow step. There are fewer than half a dozen tumbling bed granulator manufacturers. Ferro-Tech, Inc., Wyandotte, MI, can provide small-scale drying tests.

Table 21. Equipment for the Drying of Liquids

(Adapted from Perry's *Chemical Engineering Handbook*, 5th Ed., Sect. 20, pp. 18 and 19)

1. Continuous Tray or Belt - suitable for pastes, sludges, and filter cakes. Dried products are in cake or crumb form.
2. Rotary or Tumbling Bed Dryers - solutions and slurries can be dried, if they are preblended with a stream of previously dried product. Products range from fine powders to agglomerated granules.
3. Pneumatic or Flash - hot gases vigorously mix and dry injected solutions and slurries. Fine atomization of liquid causes rapid drying. Product is a fine powder.
4. Spray - similar to 3. However, a large chamber is used in which gas velocities are low. As a result, product is a mixture of coarse porous spheres plus powder.
5. Screw Conveyor - a heated screw or an externally heated rotating cylinder gently conveys pastes or a solution/slurry wetted recycle stream of dried product. The absence of a drying gas stream eliminates dust carry out. Products are in a crumb form with some powder.
6. Fluidized Bed - a low velocity gas stream suspends and dries granules that are formed by injecting solution onto a pre-existing or recycle stream of fine particles. Hard layered granules can be made by controlling rate of liquid addition temperature and residence time.
7. Drum - solution is poured over an internally heated rotating cylinder. Dried material is scraped off. Product is granular upon process completion; however, the ultimate viability and strength of the product is dependent on the material itself.

Drum drying might form a granular CMA product if large drums are used in conjunction with thinly spread layers of CMA solution or slurry. Compared to previous two technologies, the following advantages and disadvantages have been observed:

- Fuel efficiency is very good, typically 1200 Btu/lb (2.8 MJ/kg) of water evaporated. There are no heat-removal losses by the gas stream.

- Product is not very uniform. The solution or slurry is dried as a bulk material with the heat supply coming through one side only; escape of evaporated water also occurs through one side only.

- Fluidized bed and tumble bed drying permit heat and mass evaporation at all surfaces of the drying material.
- Drying layer has to be on the order of 2 to 6 mm in order to be economical. Fluidized bed and tumble bed drying take place with incrementally thin (100 to 200 Φm) layers.
- Most apparent trouble spot with drum drying is product decomposition due to nonuniform heat transfer. There was no small-scale testing of this type of equipment in previous studies.

Flash drying has been included as a potentially appropriate method of producing CMA solids even though the fine powder produced would have to be agglomerated in a separate finishing step. Fuel-efficiency is excellent since the drying gas intimately mixes with the atomized spray of liquid. Typical fuel requirements are 1600 Btu/lb (3.7 MJ/kg) of water evaporated. The extremely short residence time of flash drying provides the advantage of avoiding product decomposition. Besides the fine powder problem, another disadvantage is potential sticking of CMA to the walls of the conduit. Agglomeration of the powder would be carried out in a tumbling bed unit of disc or drum type. However, the disc agglomerator would not be utilized for drying as previously described. Small-scale testing has been conducted using a dryer provided by Desicco Inc., Lodi, OH, followed by a disc agglomerator from Ferro-Tech, Inc., Wyandotte, MI. However, in the test conducted by Energy & Minerals Research Company (Report No. FHWA/RD-87/045), this process was not successful in the small-scale drying test due to the problem of product build-up on the dryer walls. Thus, this method will not be considered in this project.

As reported in Report No. FHWA/RD-87/045, both small-scale products from fluidized bed and tumble bed dryers were acceptable. The fluidized bed products (Niro) had higher initial ice melting rates than the tumble-bed products (Ferro-Tech) and were slightly denser. In all other respects, the small-scale products were similar. The fluidized bed and tumble drying will all be selected for further study.

Approximately 200 g of CMA produced in the small bench unit was sent to Niro, Inc. in order to perform a drying and granulation test. The test was performed on April 5, 1994. Special instructions were given to Niro to remove insolubles (unreacted lime) prior to the drying test.

The CMA was spray-granulated in the STREA-1 dryer. After a period of controlled granulation, the air-flow rate was no longer sufficient to provide fluidization of the larger particles. At this point, granulation became very fast and uncontrolled. The bed product was screened to remove particles larger than 6 mesh. The moisture of the bed product was 13.03%. The product was further dried in the glass fluid-bed dryer at an inlet temperature of 124°C for 43 min. Although granulation was somewhat uncontrolled toward the end of the test, the test demonstrated that the CMA could be granulated to the desired product specifications. A dryer unit with higher fluidizing velocities will be needed to prevent the formation of large clumps. Further tests are necessary to optimize the process. The final dried powder had a moisture of 2.80%, a mean particle size of 472 μm, and a loose bulk density of 0.417 g/cm^3.

TASK A5. CMA TESTING

The ultimate test of the biologically produced CMA product is the determination of its suitability as a CMA product in comparison to commercially available CMA. The CMA produced by BRI was thus subjected to the following physical characteristic and deicing tests:

Physical Characteristics Tests

Ca^{2+}, Mg^{2+}, acetate content

Ca^{2+}/Mg^{2+} ratio
Protein content
Moisture content
Insolubles content
pH
Ash content

Deicing Tests

Ice Penetration
Ice Melting
Eutectic Points

Some of the physical properties of CMA produced at BRI through the biological process have been studied. Test results are shown in table 22. The analytical procedures used in these samples are shown in the appendix. In addition to the BRI samples, an industrial CMA sample was also tested. The industrial pellet sample was ground before analysis. The results obtained in testing the industrial sample were very close in comparison to the specifications from industrial (90.89% vs. 91% CMA, 5.5% vs. 5% water, and 2% vs. 4% insolubles). As is shown in the table, the two products are nearly identical in physical properties.

Table 22. Physical Properties of CMA Product

	BRI CMA	Industrial CMA
Ca^{++} (% wt)	7.92	6.63
Mg^{++} (% wt)	10.22	11.66
Acetate (% wt)	72.92	72.6
CMA (% wt)	91.06	90.89
Water (% wt)	5.0	5.5
Insolubles (% wt)	3.5	2.0
Protein (% wt)	0.02	0
Ca^{++}/Mg^{++} (mol ratio)	0.47	0.34
pH	9.38	9.75
Bulk Density (g/mL)	0.84	0.84
Solubility (g/mL)	0.28	0.28
Ash (% wt)	27.3	30.2

Devices for the ice melting and ice penetration tests have been constructed according to Chappelon *et al.* (1990). A flat plexiglass dish which can provide a 23-cm-diameter and 0.3-cm-thick layer of ice will be used for the ice melting test. For the ice penetrating test, a 27.9-cm x 5.1-cm x 0.95-cm-thick plexiglass plate will be used. Fifteen 0.3-cm diameter, 3.8-cm-deep cavities were drilled in the plexiglass plate at a 1.59-cm spacing. The upper end of each cavity was enlarged with a conically shaped bit, yielding a cone 6 mm in diameter at the surface and 3.5 mm deep at the point of intersection of the cone with the 0.3-cm cavity.

Three temperatures, 10, 15, and 25°F (-12.2, -9.4, and -3.9°C), were chosen for the ice melting and ice penetration tests since published data were available at these temperatures. The experiments were conducted inside a cold room with temperature variance of ±2°F (±1.1°C). Three samples, pelletized industrial CMA, powdered industrial CMA, and powdered BRI CMA, were tested.

Tables 23 through 25 show the results from the ice melting tests for the three samples, as well as published CMA ice melting data. The CMA application rate was 3 oz/yd^2 (102 g/m^2). As is shown in the tables, BRI produced CMA melted ice faster than the industrial samples, especially at 10°F (-12.2°C). The BRI samples melted 7.6, 14.0, and 20.8 mL of ice vs. 5.0, 13.2, and 19.5 mL for the powdered industrial CMA at 10, 15, and 25°F (-12.2, -9.4, and -3.9°C), respectively. This represents an improvement of 52% at 10°F (-12.2°C), and 6% at both 15 and 25°F (-9.4 and -3.9°C). The powdered samples also melted much faster than the pelletized sample. The Chevron sample had the largest average particle size, followed by industrial pellet and the RAD samples. The two powdered samples had the lowest particle size.

Table 23. CMA Ice Melting Test Results at 10°F (-12.2°C)

Deicer Application Rate:	3 oz/yd^2 (102 g/m^2)
Temperature:	10±2°F (-12.2±1.1°C)

Time (min)	Average Brine Volume (mL)				
	RAD CMA[1]	Chevron CMA[1]	Industrial CMA Pellet	Industrial CMA Powder	BRI CMA Powder
0	0.0	Not Tested	0.0	0.0	0.0
10	0.0	"	0.0	0.0	0.0
15	0.0	"	0.0	0.2	0.2
20	0.0	"	0.0	0.7	0.8
25	0.2	"	0.0	1.3	1.6
30	0.5	"	0.2	1.8	2.6
45	1.1	"	0.5	2.5	5.1
60	2.3	"	0.9	5.0	7.6

[1] McElroy *et al.*, "Comparative Evaluation of Calcium Magnesium Acetate (CMA) and Rock Salt," presented at the Transportation Research Board Annual Meeting, Washington, D.C., January 1988.

Table 24. CMA Ice Melting Test Results at 15°F (-9.4°C)

Deicer Application Rate:	3 oz/yd^2 (102 g/m^2)
Temperature:	15±2°F (-9.4±1.1°C)

Time (min)	Average Brine Volume (mL)				
	RAD CMA[1]	Chevron CMA	Industrial CMA Pellet	Industrial CMA Powder	BRI CMA Powder
0	0.0	0.0	0.0	0.0	0.0
10	0.2	0.0	0.0	0.2	0.2
15	1.2	0.0	0.0	1.5	1.6
20	2.7	0.3	0.3	3.1	3.3
25	3.2	0.7	0.6	4.7	5.1
30	4.2	1.1	1.0	6.3	7.2
45	6.9	1.8	1.2	9.8	10.9
60	8.1	2.3	1.6	13.2	14.0

[1] McElroy *et al.*, "Comparative Evaluation of Calcium Magnesium Acetate (CMA) and Rock Salt," presented at the Transportation Research Board Annual Meeting, Washington, D.C., January 1988.

Table 25. CMA Ice Melting Test Results at 25°F (-3.9°C)

Deicer Application Rate:	3 oz/yd^2 (102 g/m^2)
Temperature:	25±2°F (-3.9±1.1°C)

Time (min)	Average Brine Volume (mL)				
	RAD CMA[1]	Chevron CMA[1]	Industrial CMA Pellet	Industrial CMA Powder	BRI CMA Powder
0	0.0	0.0	0.0	0.0	0.0
10	4.2	1.8	0.8	4.5	5.0
15	6.8	3.6	1.9	7.0	9.0
20	9.0	4.6	2.5	10.0	11.8
25	11.6	5.5	3.6	12.0	14.1
30	12.8	6.8	4.7	14.3	15.5
45	16.0	8.9	5.8	16.8	18.1
60	18.3	11.4	6.1	19.5	20.8

[1] McElroy *et al.*, "Comparative Evaluation of Calcium Magnesium Acetate (CMA) and Rock Salt," presented at the Transportation Research Board Annual Meeting, Washington, D.C., January 1988.

Tables 26 through 28 show results from the ice penetration tests. The CMA application quantity was 23 to 26 mg/cavity. None of the samples resulted in penetration at 10°F (-12.2°C). At 15 and 25°F (-9.4 and -3.9°C), the industrial CMA pellet had the fastest penetration. The penetration was affected by the particle size. The industrial pellet penetrated about 15% to 20% faster than the industrial powder sample, and the BRI powder sample had a lower penetration rate than industrial powder samples. The slower penetration rate of BRI samples could have been from the low density of the samples.

Table 26. CMA Ice Penetration Test Results at 10°F (-12.2°C)

Deicer Application Rate: 23 to 26 mg/cavity
Temperature: 10±2°F (-12.2±1.1°C)

Time (min)	**Average Brine Volume (mL)**				
	RAD CMA[1]	**Chevron CMA**[1]	**Industrial CMA Pellet**	**Industrial CMA Powder**	**BRI CMA Powder**
0	Not Tested	Not Tested	0	0	0
3	”	”	0	0	0
5	”	”	0	0	0
10	”	”	0	0	0
15	”	”	0	0	0
20	”	”	0	0	0
30	”	”	0	0	0
45	”	”	0	0	0
60	”	”	0	0	0

[1] McElroy *et al.*, “Comparative Evaluation of Calcium Magnesium Acetate (CMA) and Rock Salt,” presented at the Transportation Research Board Annual Meeting, Washington, D.C., January 1988.

Table 27. CMA Ice Penetration Test Results at 15°F (-9.4°C)

Deicer Application Rate:	23 to 26 mg/cavity
Temperature:	15±2°F (-9.4±1.1°C)

Time (min)	Average Penetration Depth (mm)				
	RAD CMA[1]	Chevron CMA[1]	Industrial CMA Pellet	Industrial CMA Powder	BRI CMA Powder
0	0.0	0.0	0.0	0.0	0.0
3	0.0	0.0	0.0	0.0	0.0
5	0.0	0.0	0.0	0.0	0.0
10	0.0	0.0	0.0	0.0	0.0
15	0.05	0.0	0.05	0.0	0.0
20	0.07	0.0	0.1	0.1	0.1
30	0.2	0.0	0.2	0.2	0.2
45	0.7	0.0	0.8	0.4	0.3
60	1.1	0.0	1.2	1.0	0.8

[1] McElroy *et al.*, "Comparative Evaluation of Calcium Magnesium Acetate (CMA) and Rock Salt," presented at the Transportation Research Board Annual Meeting, Washington, D.C., January 1988.

Table 28. CMA Ice Penetration Test Results at 25°F (-3.9°C)

Deicer Application Rate:	23 to 26 mg/cavity
Temperature:	25±2°F (-3.9±1.1°C)

Time (min)	Average Penetration Depth (mm)				
	RAD CMA[1]	Chevron CMA[1]	Industrial CMA Pellet	Industrial CMA Powder	BRI CMA Powder
0	0.0	0.0	0.0	0.0	0.0
3	0.0	0.0	0.0	0.0	0.0
5	0.0	0.0	0.5	0.5	0.4
10	0.5	0.2	0.9	1.0	0.8
15	0.9	0.6	1.9	2.0	1.5
20	1.5	1.3	2.5	2.4	2.2
30	2.1	2.1	3.8	3.4	3.0
45	3.3	3.4	4.4	4.0	3.7
60	4.1	4.7	5.4	4.7	4.3

[1] McElroy *et al.*, "Comparative Evaluation of Calcium Magnesium Acetate (CMA) and Rock Salt," presented at the Transportation Research Board Annual Meeting, Washington, D.C., January 1988.

Eutectic points for industry- and BRI-produced CMA have been measured. The experiment was conducted in a Virtis Freezemobile, Model 12EL. The samples included 5%, 10%, 15%, and 20% aqueous solutions of CMA. In the study, 0.5-mL samples were placed into 15-mL glass vials inside the Freezemobile. The starting temperature was -10°C, and the temperature was reduced by 1°C every 20 min to provide enough time to reach phase equilibrium. The temperature where a particular solution started to freeze was recorded as the eutectic point of the solution. Table 29 shows the average eutectic temperatures of duplicated samples. The values reported by Economides and Ostermann in Report No. AK-RD-83-16 to the State of Alaska DOT and Public Facilities are also included for comparison. As are shown in the table, the eutectic points obtained for the BRI samples were between the values obtained for the industrial samples and literature values.

Table 29. Eutectic Points of BRI, Industrial, and Literature CMA Samples

CMA Solution	Industrial	BRI	Report No. AK-RD-83-16
5%	-15°C	-18°C	-15°C
10%	-18°C	-20°C	-21°C
15%	-20°C	-23°C	-23°C
20%	-25°C	-28°C	-29.5°C

Significance

BRI produces a CMA product comparable in physical properties and its ability to melt ice with industrial CMA.

TASK B. COST AND MATERIAL BALANCE ANALYSIS

Material balances and cost estimations for a CMA production process to handle 500 tons (454 tonnes) of MSW or sewage sludge/day have been developed. The designs are based on the process flow sheets shown in figures 7 and 8. The process may be separated into the following four major sections: (1) gasification, (2) fermentation, (3) CMA production, and (4) CMA drying. In this process, gasification and CMA drying will utilize commercial designs since the technology is well developed. For example, drying will use standard commercial and pelletizing processes.

The major design variables of this process include the type and operating conditions of the gasifier, the fermentation pressure, and the solvent-to-feed ratio during extraction. The gasifier type and operating conditions will determine the synthesis gas composition, and amount of gas produced, and may even affect the fermentation pressure. The fermentation pressure will affect the size and number of reactors and the energy consumption in the reactor. The solvent-to-feed ratio in extraction will not only affect the size of the extraction column, but will also influence CMA production.

In the gasification section, the MSW will be ground before entering the gasifier, as is shown in figure 7. As is noted in figure 8, sewage sludge grinding is not necessary. The synthesis gas leaving the gasifier will be adjusted to the fermentation temperature and pressure.

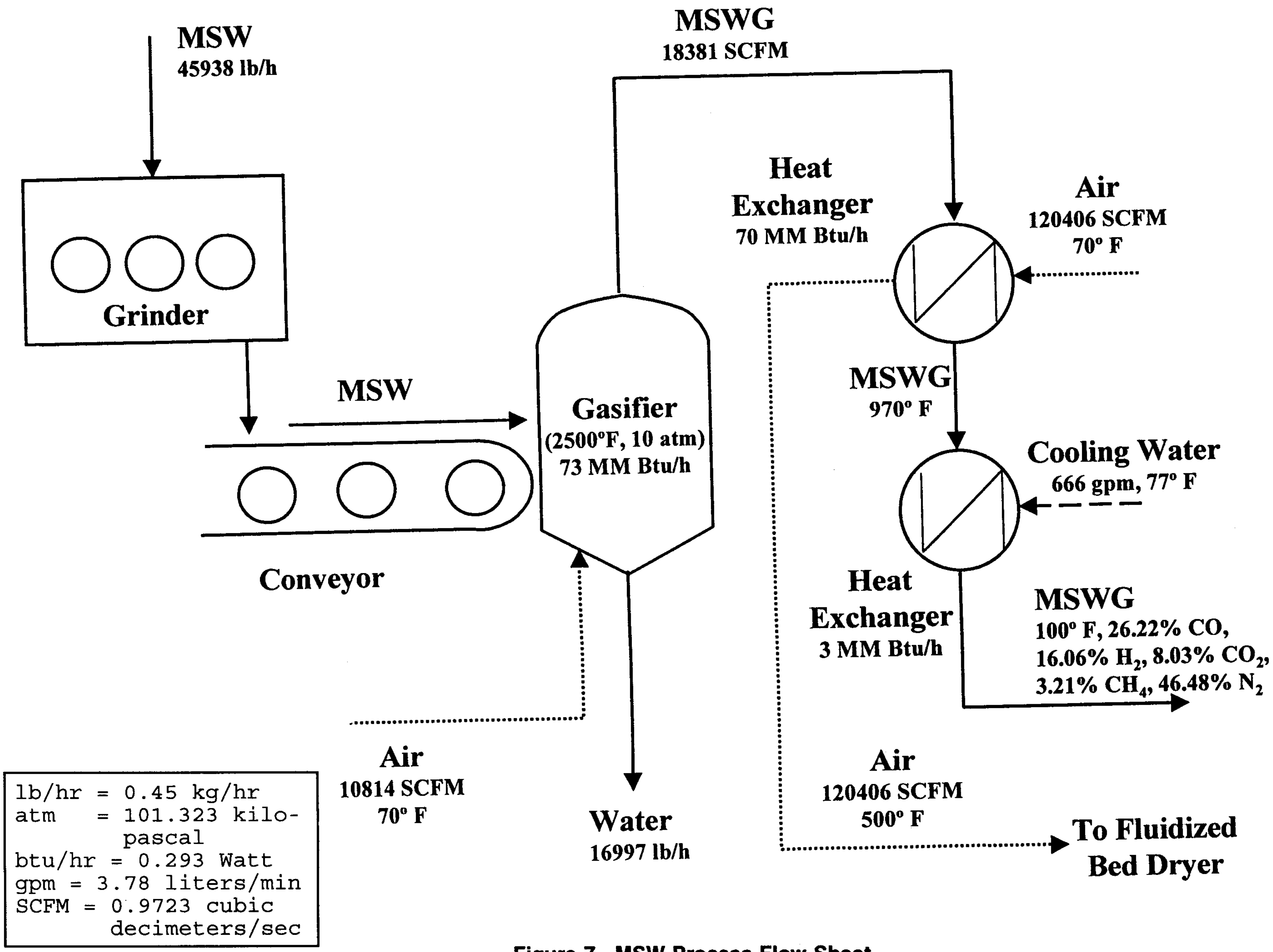


Figure 7. MSW Process Flow Sheet

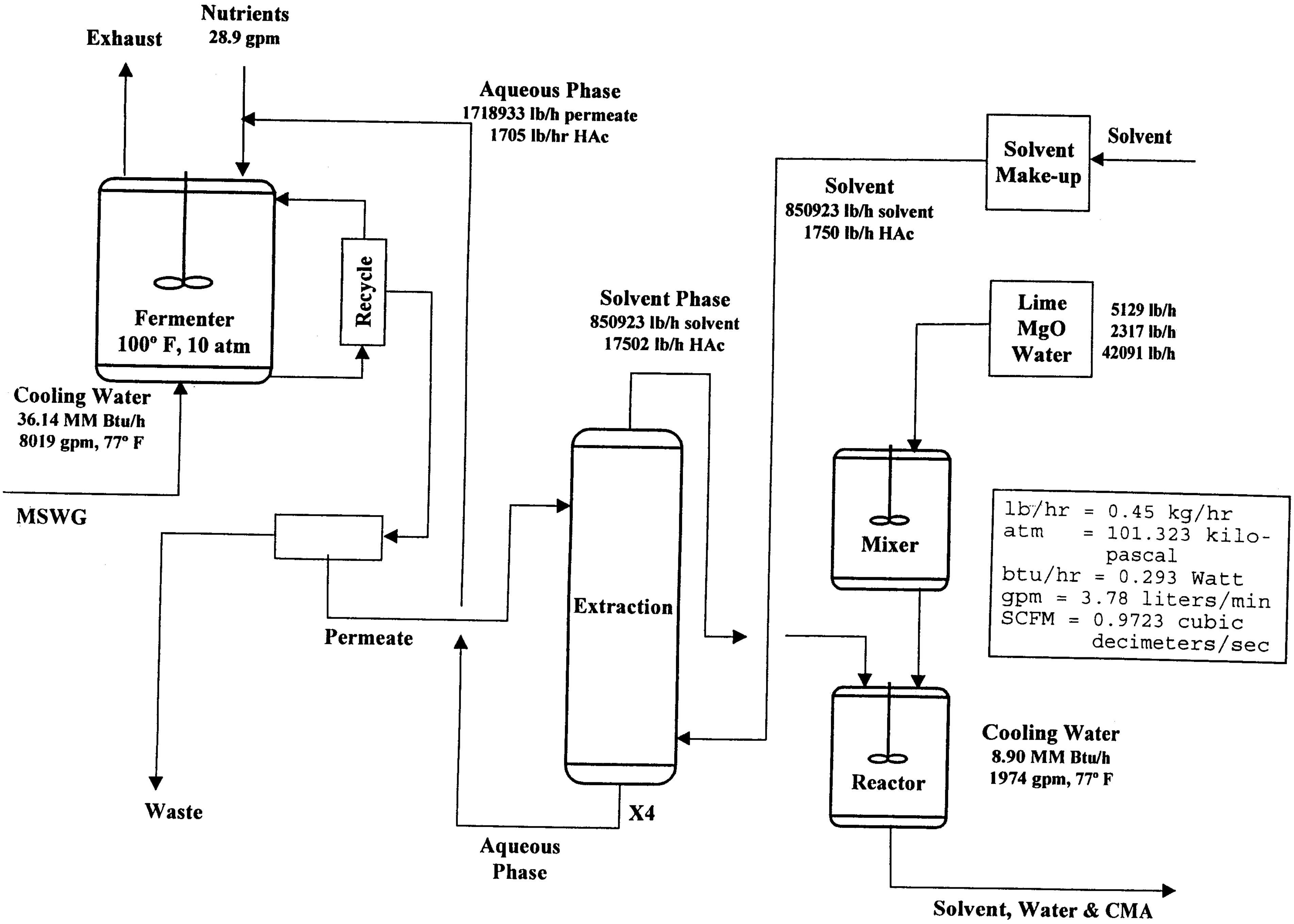


Figure 7. MSW Process Flow Sheet (continued)

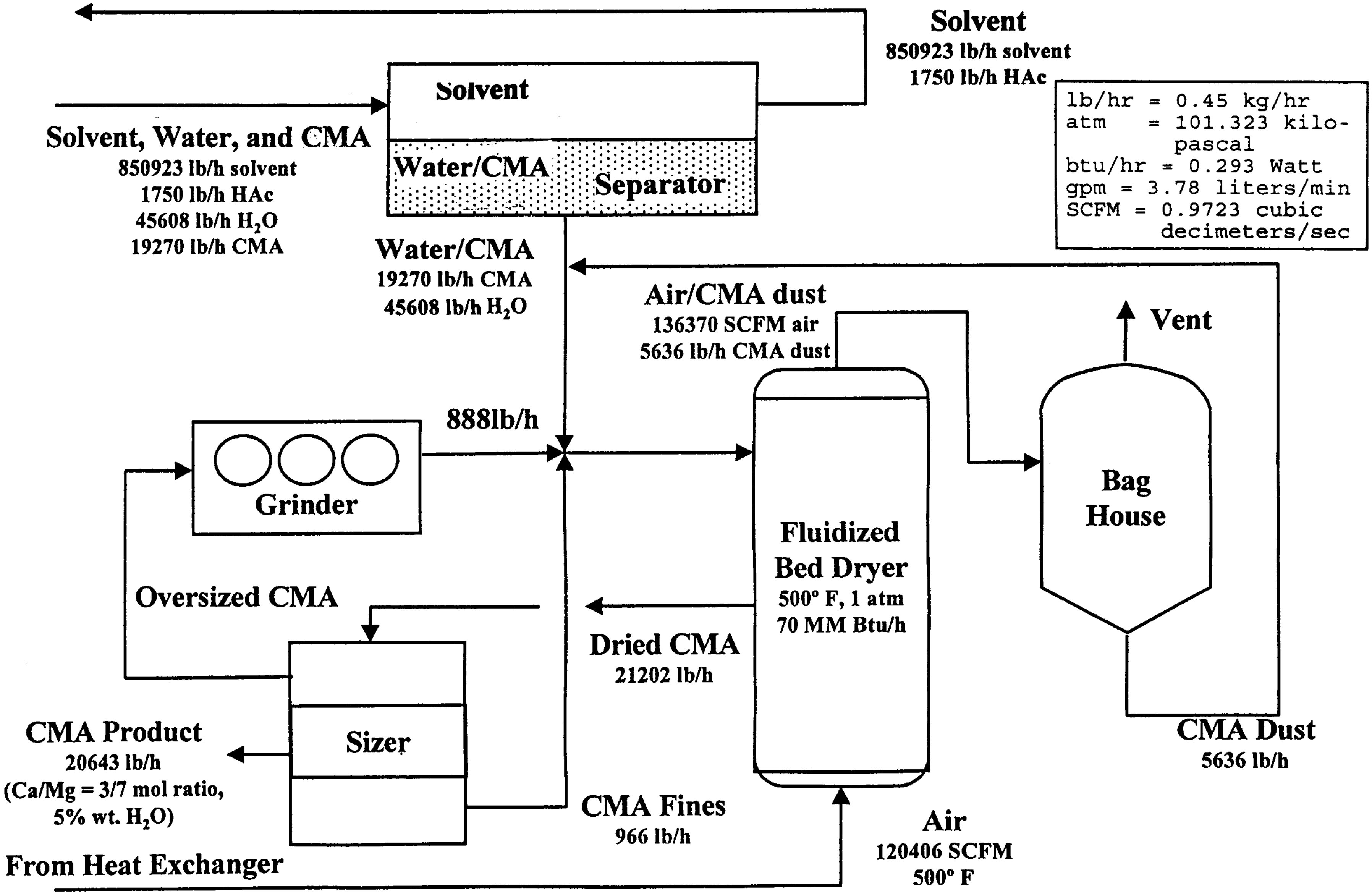
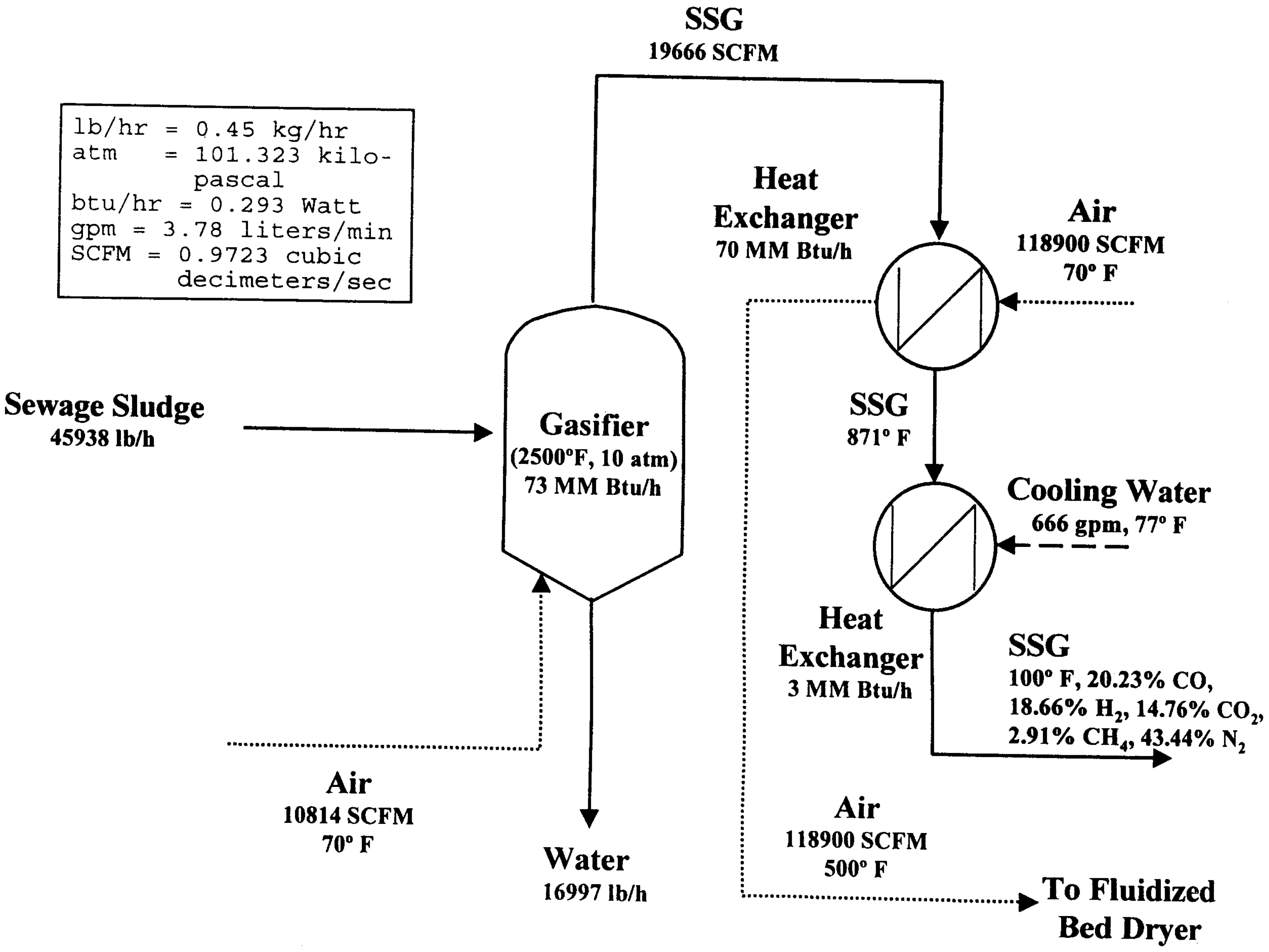
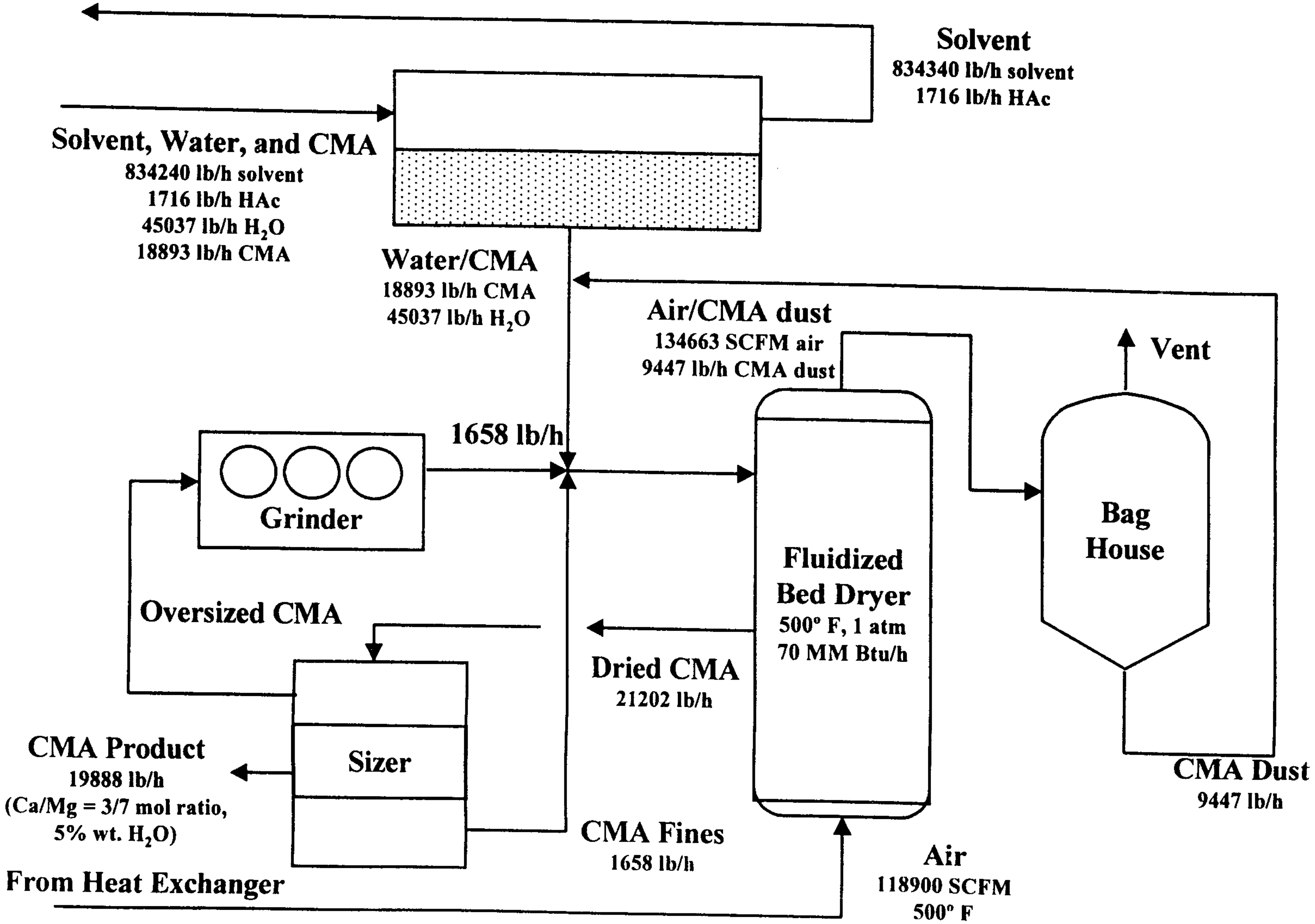


Figure 7. MSW Process Flow Sheet (continued)



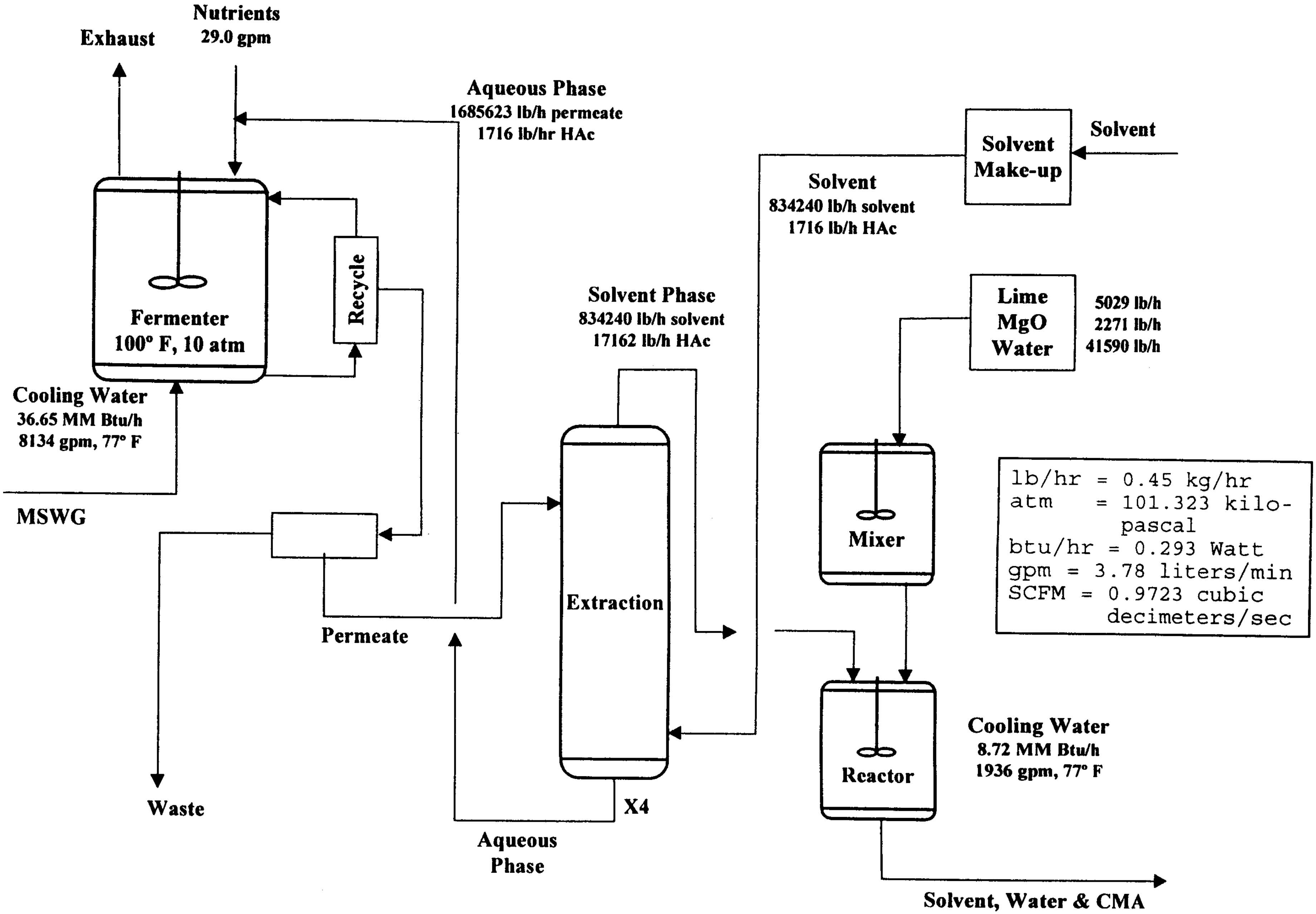
lb/hr = 0.45 kg/hr
atm = 101.323 kilo-pascal
btu/hr = 0.293 Watt
gpm = 3.78 liters/min
SCFM = 0.9723 cubic decimeters/sec

Figure 8. Sewage Sludge Process Flow Sheet



lb/hr = 0.45 kg/hr
atm = 101.323 kilo-pascal
btu/hr = 0.293 Watt
gpm = 3.78 liters/min
SCFM = 0.9723 cubic decimeters/sec

Figure 8. Sewage Sludge Process Flow Sheet (continued)



```
lb/hr = 0.45 kg/hr
atm   = 101.323 kilo-
          pascal
btu/hr = 0.293 Watt
gpm = 3.78 liters/min
SCFM = 0.9723 cubic
         decimeters/sec
```

Figure 8. Sewage Sludge Process Flow Sheet (continued)

The fermentation section is composed of a gas fermenter, a cell recycle unit, a permeate ultra-filter and may include a compressor, if necessary. The gas fermenter is a CSTR capable of high agitation rates to support the high gas transfer rate needed in acetic acid production. The cell recycle unit provides the advantages of maintaining a high cell concentration, or biocatalyst concentration, inside the reactor. In addition, the cell recycle unit also separates cells from the liquid product stream. The cell recycle unit will utilize a 0.2-µm cut-off hollow fiber. There are industrial-scale hollow-fiber modules on the market. For example, a module that can hold pressures up to 35 psi (241 kPa) and have a capacity of 10.5-gal/min (40-L/min) permeate flow rate is sold for $2500. Even though the permeate is cell-free, there will be some cellular material that can penetrate the 0.2-µm fiber. An ultra-filtration unit with a 3000 molecular weight cut-off hollow fiber will remove the majority of the lysed material.

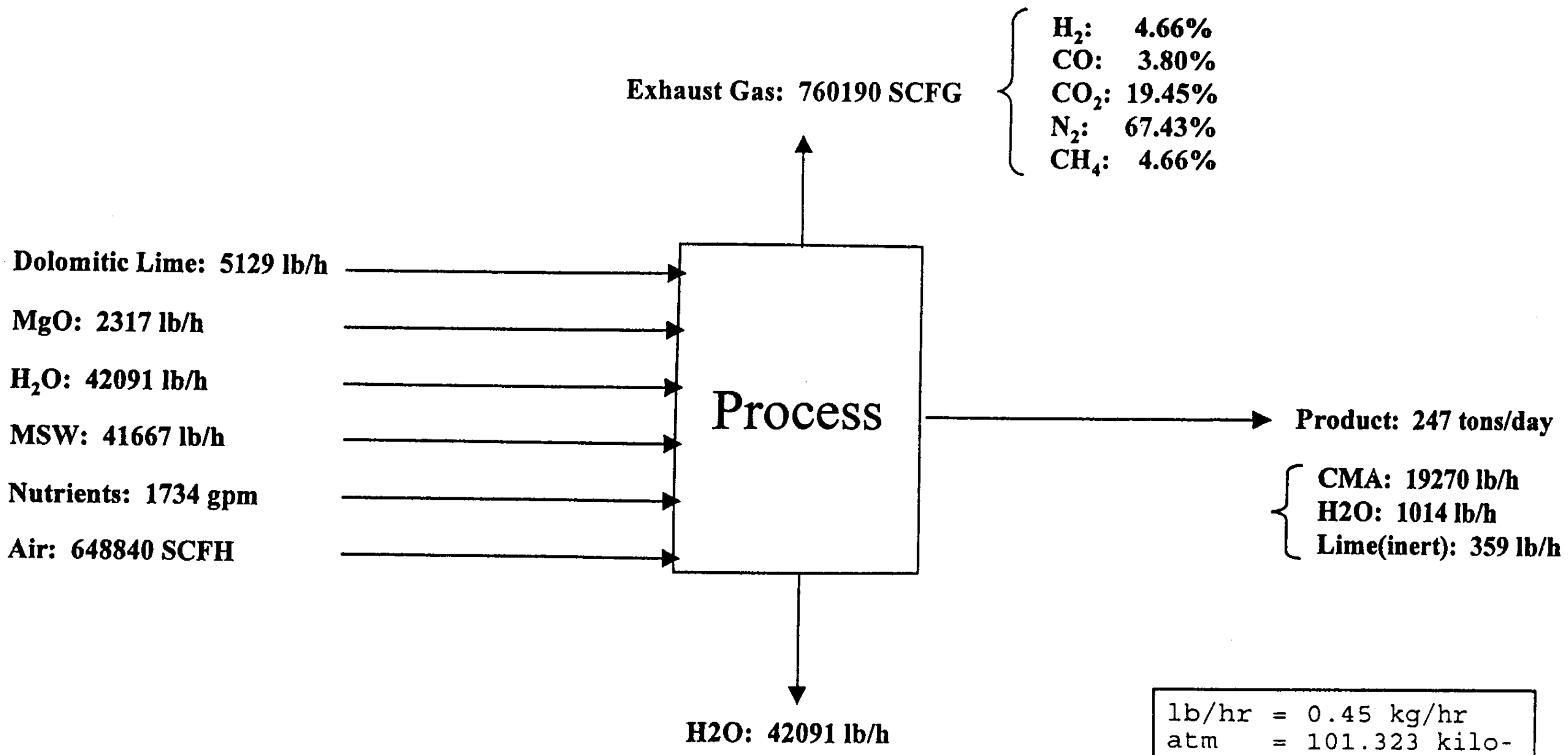
In CMA production, the acetic acid in the cell-free product stream will be extracted into a solvent phase in an extraction column. The extracted aqueous phase will be sent back to the reactor to control the pH of the reactor and to force the production of acid from acetate. The solvent is unable to extract acetate, so that the ratio of the acid to acetate in the product is totally controlled by pH. The amount of water in the solvent will be very low and solvent is inert to CMA production. The direct addition of dolomitic lime and magnesium oxide into the solvent stream will produce very highly concentrated CMA. A mixer will produce $Ca(OH)_2$ and $Mg(OH)_2$ from dolomitic lime, magnesium oxide, and water. CMA production will take place in an agitated tank by mixing solvent with $Ca(OH)_2$ and $Mg(OH)_2$ solution. The solvent and saturated CMA solution will be separated in a settler. The acid-free solvent will be recycled back to the extraction column and the CMA saturation solution will enter the drying section. One potential improvement will be producing a CMA slurry instead of a saturated solution.

As described before, CMA drying will be based on conventional processes. The CMA saturated solution, as well as CMA dust, and rejected ground CMA will be fed into a fluidized bed dryer to produce granular CMA. The fluidized bed dryer will be operated by supplying hot air. Some CMA dust will leave the dryer with air and will be collected in a bag house. The desired CMA particle size will be screened out from the dried product from the bottom of the dryer. The oversized CMA will be reground and sent back to the fluidized bed dryer with the CMA fines and dust.

The design variables are as follows:

- Fermenter pressure: 10 atm (1013 kPa).
- CO conversion: 90%.
- H_2 conversion: 80%.
- Solvent contains 10% solvent A, 90% co-solvent 11.
- Permeate flow/culture recycle: 50%.

Overall material balances for the two processes are shown in figures 9 and 10. The equipment costs and utility summary are shown in tables 30 through 33. Tables 34 and 35 show the economic summary to process 500 tons/day (454 tonnes/day) of MSW and sewage sludge, respectively. For MSW, the capital investment, including gasifier, was $20.041 million. The production cost, excluding profit, was $123/ton ($136/tonne). Table 35 shows the economic summary for the sewage sludge process. The fixed-capital investment was $20.231 million and production cost, excluding profit, was $126/ton ($139/tonne).



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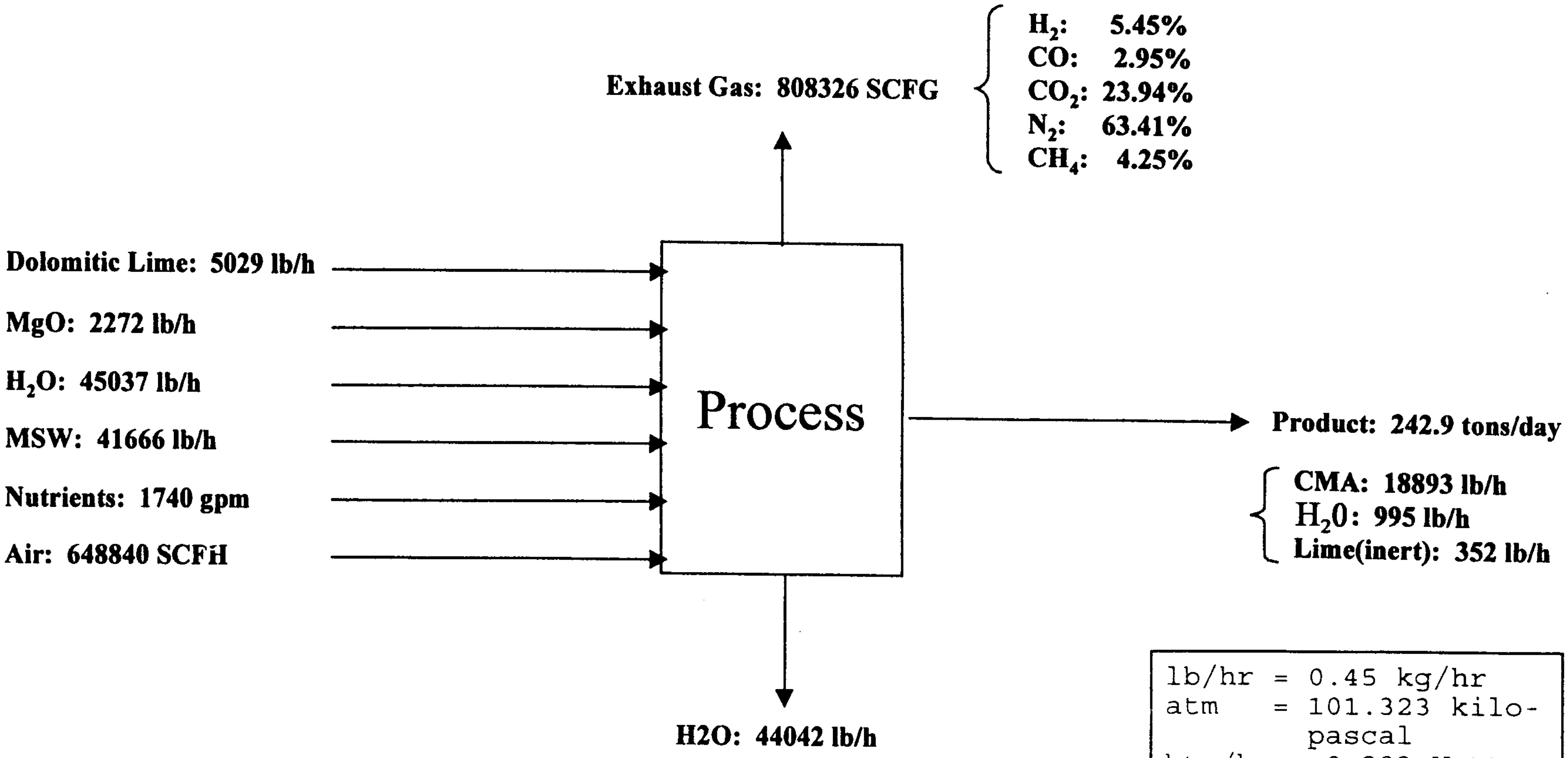
lb/hr = 0.45 kg/hr
atm   = 101.323 kilo-
          pascal
btu/hr = 0.293 Watt
gpm = 3.78 liters/min
SCFM = 0.9723 cubic
         decimeters/sec
```

Basis: 500 tons of MSW per day

$$\text{Product Yield} = \frac{15751 \text{ lb HAc/h}}{19270 \text{ lb CMA/h}} = 0.8174 \frac{\text{lb HAc}}{\text{lb CMA}}$$

Figure 9. Overall Material Balance for MSW Process



lb/hr = 0.45 kg/hr
atm = 101.323 kilo-pascal
btu/hr = 0.293 Watt
gpm = 3.78 liters/min
SCFM = 0.9723 cubic decimeters/sec

Basis: 500 tons of Sewage Sludge per day

$$\text{Product Yield} = \frac{15446 \text{ lb HAc/h}}{18893 \text{ lb CMA/h}} = 0.8176 \frac{\text{lb HAc}}{\text{lb CMA}}$$

Figure 10. Overall Material Balance for Sewage Sludge Process

Table 30. Equipment Costs for MSW, Air Gasification at 10 atm (1013 kPa), 10% Solvent A, 90% Co-Solvent 11 as Solvent System

Item	Capacity	Purchased Cost (in thousand $)
Fermenter	8.5 m x 21.3 m	$170
Fermenter Agitator	1367 hp (1020kW)	536
Fermenter Cooling	848 m^2	109
HF Recycle	(26) 50 psi (345 kPa), 0.2 µm, 262 gal/min	884
Pump for Recycle	594 hp (443 kW)	58
Pump for Permeate Out of Recycle	49 hp (37 kW)	8
Pump for Fresh Nutrient	2.5 hp (1.9 kW)	3
Extractor Column	(4) 3.7 m x 28.7 m	939
Column Tray	(4) 18 sieve	342
Pump for Permeate Into Extractor	49 hp (37 kW)	11
Pump for Permeate Out of Extractor	292 hp (218 kW)	45
Pump for Solvent Into Extractor	35 hp (26 kW)	10
Pump for Solvent Out of Extractor	35 hp (26 kW)	10
Mixer	1.2 m x 2.4 m, 2 hp (1.5 kW)	18
Pump for Lime, MgO, and H_2O Slurry	1.5 hp (1.1 kW)	2
Reactor	3.0 m x 7.6 m, 60 hp (45 kW)	161
Reactor Cooling	538 m^2	75
Pump for Solvent/CMA-H_2O Into Separator	37 hp (28 kW)	9
Separator	4.0 m x 10.7 m	60
Pump for CMA-H_2O Into Dryer	2 hp (1.5 kW)	2
Fluid-Bed Dryer	2.6 m x 7.6 m	16
Baghouse	231,829 ft^3/h (6565m^3/h)	416
Heat Exchanger for Heating Air	222 m^2	44
Fan for Air Into Dryer	875 hp (653 kW)	30
Vibrating Screen for Sizing CMA	2 decks, 1.2 m x 3.0 m, 4 hp (3.0 kW)	50
Pneumatic Conveyer for Recycling CMA	0.08 m x 24.3 m, 0.1 hp (0.07 kW)	55
TOTAL PURCHASED COST		$4,063
TOTAL FIXED-CAPITAL INVESTMENT (Chilton)		$12,041
TOTAL FIXED-CAPITAL INVESTMENT OF GASIFICATION UNIT		$8,000
TOTAL FIXED-CAPITAL INVESTMENT		$20,041

Table 31. Utility Summary for MSW, Air Gasification at 10 atm (1013 kPa), 10% Solvent A, 90% Co-Solvent 11 as Solvent System

	Electricity (hp [kW])	**Cooling Water (gal/min [L/min])**
Gasification	2039 (1521)	666 (2521)
Fermentation	2013 (1502)	8019 (30,355)
Extraction	411 (307)	-
CMA Production	101 (75)	1974 (7472)
CMA Drying	881 (657)	-
Total	**5445 (4062)**	**10,659 (40,349)**

Table 32. Equipment Costs for Sewage Sludge, Air Gasification at 10 atm (1013 kPa), 10% Solvent A, 90% Co-Solvent 11 as Solvent System

Item	Capacity	Purchased Cost (thousand $)
Fermenter	7.5 m x 21.6 m	$177
Fermenter Agitator	1531 hp (1142 kW)	580
Fermenter Cooling	860 m^2	108
HF Recycle	(27) 50 psi (345 kPa), 0.2 μm, 262 gpm	918
Pump for Recycle	583 hp (435 kW)	52
Pump for Permeate Out of Recycle	48 hp (36 kW)	10
Pump for Fresh Nutrient	2.6 hp (1.9 kW)	3
Extractor Column	(4) 3.7 m x 27.7 m	916
Column Tray	(4) 18 sieve	342
Pump for Permeate Into Extractor	49 hp (37 kW)	10
Pump for Permeate Out of Extractor	477 hp (356 kW)	44
Pump for Solvent Into Extractor	34 hp (25 kW)	9
Pump for Solvent Out of Extractor	34 hp (25 kW)	9
Mixer	1.2 m x 1.8 m, 2 hp (1.5 kW)	15
Pump for Lime, MgO, and H_2O Slurry	1.5 hp (1.1 kW)	2
Reactor	3.0 m x 8.5 m, 62 hp (46 kW)	165
Reactor Cooling	543 m^2	79
Pump for Solvent/CMA-H_2O Into Separator	26 hp (19 kW)	8
Separator	3.7 m x 11.6 m	66
Pump for CMA-H_2O Into Dryer	2 hp (1.5 kW)	2
Fluid-Bed Dryer	2.4 m x 7.0 m	15
Baghouse	231,829 ft^3/h (6565m^3/h)	410
Heat Exchanger for Heating Air	299 m^2	53
Fan for Air Into Dryer	864 hp (645 kW)	29
Vibrating Screen for Sizing CMA	2 decks, 1.2 m x 3.0 m, 4 hp (3.0 kW)	50
Pneumatic Conveyer for Recycling CMA	0.08 m x 24.3 m, 0.1 hp (0.07 kW)	55
TOTAL PURCHASED COST		$4,127
TOTAL FIXED-CAPITAL INVESTMENT (Chilton)		$12,231
TOTAL FIXED-CAPITAL INVESTMENT OF GASIFICATION UNIT		$8,000
TOTAL FIXED-CAPITAL INVESTMENT		$20,231

Table 33. Utility Summary for Sewage Sludge, Air Gasification at 10 atm (1013 kPa), 10% Solvent, 90% Co-Solvent 11 as Solvent System

	Electricity (hp [kW])	**Cooling Water (gal/min [L/min])**
Gasification	2039 (1521)	666 (2521)
Fermentation	2165 (1615)	8134 (30,790)
Extraction	594 (443)	-
CMA Production	92 (69)	1936 (7329)
CMA Drying	870 (649)	-
Total	**5760 (4297)**	**10,736 (40,640)**

Table 34. Economic Summary for CMA Production From MSW (500 Tons/Day [454 Tonnes/Day])

	Annual Cost ($)
Raw Material	
Nutrients, 28.9 gal/min (109.4 L/min), $0.039/gal ($0.010/L)	$568,000
Lime, 5129 lb/h (2327 kg/h), $40/ton ($44/tonne)	782,000
MgO, 2317 lb/h (1051 kg/h), $355/ton ($391/tonne)	3,129,000
City Water, 42,091 lb/h (19,092 kg/h), $0.20/1000 gal ($0.05/1000 L)	9,000
Solvent, 0.2105 lb/h (0.0955 kg/h), $2.00/lb ($4.41/kg)	4,000
Co-Solvent, 0.2105 lb/h (0.0955 kg/h), $1.00/lb ($2.20/kg)	2,000
Total Raw Material Costs	**$4,494,000**
Utilities	
Electricity, 5445 hp (4062 kW), $0.05/kW• h ($14/GJ)	1,705,000
Cooling Water, 10,659 gal/min (40,349 L/min), $0.04/1000 gal ($0.01/1000 L)	215,000
Total Utilities Costs	**$1,920,000**
Other Direct Costs	
Labor, 4.02 Shifts, 2 People/Shift, $40,000/year	322,000
Supervision, 30% of Labor	97,000
Maintenance, 5% of Fixed-Capital Investment (FCI)	1,002,000
Payroll Charge, 45% of Labor and Supervision	189,000
Laboratory Charge, 10% of Labor	32,000
Total Other Direct Costs	**$1,642,000**
TOTAL DIRECT COSTS	**$8,056,000**
Indirect Costs	
Depreciation	2,004,000
Plant Indirect Expenses, 2% of FCI	400,000
TOTAL INDIRECT COSTS	**$2,404,000**
TOTAL MANUFACTURING COSTS	**$10,460,000**
Product	
CMA Produced: 20,284.6 lb/h (9201.1 kg/h)	85,195 tons (77,289 tonnes)
Product Cost	**$122.78/ton ($135.34/tonne)**

Table 35. Economic Summary for CMA Production From Sewage Sludge (500 Tons/Day [454 Tonnes/Day])

	Annual Cost ($)
Raw Material	
Nutrients, 29 gal/min (110 L/min), $0.039/gal ($0.010/L)	$570,000
Lime, 5029.2 lb/h (2281.2 kg/h), $40/ton ($44/tonne)	766,000
MgO, 2271.7 lb/h (1030.4 kg/h), $355/ton ($391/tonne)	3,072,000
City Water, 45,037 lb/h (20,429 kg/h), $0.20/1000 gal ($0.05/1000 L)	9,000
Solvent, 0.2181 lb/h (0.0989 kg/h), $2.00/lb ($4.41/kg)	4,000
Co-Solvent, 0.2181 lb/h (0.0989 kg/h), $1.00/lb ($2.20/kg)	2,000
Total Raw Material Costs	**$4,423,000**
Utilities	
Electricity, 5760 hp (4297 kW), $0.05/kW• h ($14/GJ)	1,804,000
Cooling Water, 10,736 gal/min (40,640 L/min), $0.04/1000 gal ($0.01/1000 L)	216,000
Total Utilities Costs	**$2,020,000**
Other Direct Costs	
Labor, 4.02 Shifts, 2 People/Shift, $40,000/year	322,000
Supervision, 30% of Labor	97,000
Maintenance, 5% of FCI	1,012,000
Payroll Charge, 45% of Labor and Supervision	189,000
Laboratory Charge, 10% of Labor	32,000
Total Other Direct Costs	**$1,652,000**
TOTAL DIRECT COSTS	**$8,095,000**
Indirect Costs	
Depreciation	2,023,000
Plant Indirect Expenses, 2% of FCI	405,000
TOTAL INDIRECT COSTS	**$2,428,000**
TOTAL MANUFACTURING COSTS	**$10,523,000**
Product	
CMA Produced: 19,891.1 lb/h (9022.6 kg/h)	83,543 tons (75,790 tonnes)
Product Cost	**$125.96/ton ($138.84/tonne)**

TASK C. PRELIMINARY MARKET ANALYSIS AND COMMERCIALIZATION STRATEGY

Potential markets for bulk chemicals and products which may be produced from CO and H_2O are summarized in table 36. As is noted, the 10,000-ton/year (9072-tonne/year) CMA market has potential to be expanded to 10 million tons/year (9.1 million tonnes/year). Twenty State agencies responsible for highway deicing were surveyed regarding their deicing needs. A listing of the points of contact is shown in table 37, and a summary of the findings is shown in tables 38 and 39. Rock salt is the predominant deicing chemical used today primarily because of its low cost, \$40/ton (\$44/tonne) compared to \$700/ton (\$772/tonne) for CMA. Current CMA usage was about 10,000 tons (9072 tonnes) in 1993-1994, but this usage would increase to as much as 1 million tons/year (907,200 tonnes/year) if the price were reduced to \$200/ton (\$220/tonne). Replacement for anti-icers could total 600,000 tons/year (544,320 tonnes/year) with mixtures of CMA and potassium acetate. Projected costs for CMA are \$125/ton (\$138/tonne) from MSW or sewage sludge, which will result in a large market for CMA, as well as potassium acetate.

TASK D. INDUSTRY OUTREACH

An Industrial Advisory Committee (IAC) has been formed to aid in the commercialization of the technology. The IAC is made up of the following members:

- Cryotech.
- Bioneer – gasifier supplier.
- National Corn Growers.
- Black and Veatch – engineering contractor.
- Continental Edison.
- DOT/New York State Energy Research and Development Authority.

Participation by the industrial partners will be as follows:

PHASE I
    Review Data
    Process Design
    Market Analysis
    Commercialization

PHASE II
    PDU Design
    Review Data
    Commercial Design
    Case Study
    Fund (if needed)

PHASE III
    Larger Pilot Demonstration (if needed)

PHASE IV
    Commercialization

The IAC met on March 30, 1994, in Fayetteville, AR, to tour the acetic acid pilot plant and to review the results and data from the Phase I research program. Market and economic projections were presented and discussed. The committee agreed that all Phase I objectives had been met and exceeded and that the process has outstanding commercial application. A prototype demonstration is recommended in Phase II to rapidly transfer this technology to the commercial sector.

Table 36. Potential Products From Carbon Monoxide and Hydrogen

Product	Present Market	Potential Market
Ethanol	1 billion gal/year (3.8 billion L/year)	100 billion gal/year (379 billion L/year)
Acetic Acid	4 billion lb/year (1.8 billion kg/year)	4 billion lb/year (1.8 billion kg/year)
Calcium Magnesium Acetate	10,000 tons/year (9072 tonnes/year)	10 million tons/year (9.1 million tonnes/year)
Hydrogen	100 billion SCF/year (2.8 billion m^3/year)	100 billion SCF/year (2.8 billion m^3/year)
Single Cell Protein	Small	100 million tons/year (91 million tonnes/year)

Table 37. Market Analysis — States Surveyed

STATE	CONTACT
California	Gary Gallegos
Colorado	Wayne Lupton Del French
Connecticut	Thomas Daly
Idaho	Robert Ewing
Indiana	Larry Goode William Rinard
Iowa	Charles Pickett Tom Donahey Cy Queck
Kansas	David Kospa Roger Alexander
Maryland	Paul McIntyre
Massachusetts	John Wallenhaupt
Minnesota	Edward Fleege
Missouri	Tom Bargmeyer Ivan Corp Maureen Sturgeon
Nevada	Richard Nelson
New Hampshire	Gary Stephen
New York	Duane Amsler
North Dakota	John Bjorke
Ohio	Keith Swearingen
Oregon	Richard Parker
South Dakota	Dan Johnston
Washington	Phil George
Wisconsin	Thomas Martinelli

Table 38. Market Analysis — Summary Findings

- Current NaCl usage – 10 million tons/year (9.1 million tonnes/year).
  Price $15/ton ($16.50/tonne) (Kansas) -$45/ton ($49.50/tonne) (NY,Idaho)
- Current CMA usage – 10,000 tons/year (9072 tonnes/year)
  Greatest deterrent to CMA usage is cost – $900/ton ($992/tonne) some areas.
  Other complaints – not effective at low temperature.
  Some States use none, others up to 1000 tons/year (907 tonnes/year).
  Used in corrosive, environmentally sensitive areas.

- If price of CMA were reduced to $200/ton ($220/tonne), most States would use significant amounts. Estimates ranged from 5 times present usage to 10% of road salt – 50,000 to 1,000,000 tons/year (45,360 to 907,200 tonnes/year).
  Usage by industry and municipalities would become significant.

Table 39. Market Survey — New Uses

• Anti-icer usage:	$CaCl_2$ (liquid)	200,000 tons/year (181,440 tonnes/year)
	(dry)	300,000 tons/year (272,160 tonnes/year)
	$MgCl_2$ (liquid)	100,000 tons/year (90,720 tonnes/year)

Inhibited, but still corrosive.
Cost – $0.35/gal ($0.09/L) (23% solution) ($85/ton [$94/tonne]).

- Potassium acetate as 50% liquid - $3 to $5/gal ($0.79 to $1.32/L) ($750 to $1200/ton [$827 to $1323/tonne]).

- KAc reduced to $0.30/gal ($0.08/L) ($75/ton [$83/tonne]).
  CMA/KAc mixture replace $CaCl_2$, $MgCl_2$.
  Potential market – 600,000 tons/year (544,320 tonnes/year).

RECOMMENDED FURTHER DEVELOPMENT

In order to further develop the CMA from waste gas technology toward commercialization, several technical tasks are required:

- Continuous bench-scale unit required to demonstrate interactions of unit operations, especially solids handling.
- Demonstrate the technology in pilot unit, including gasification.
- Develop scale-up parameters.

A listing of the various unit operations, as well as the variables for study, areas of concentration, and design data to be collected, is summarized in table 40. In addition, industrial outreach and commercialization strategy need to be developed further and continuously updated.

Table 40. Bench-Scale Operating Criteria

UNIT OPERATION	VARIABLES FOR STUDY	AREAS OF CONCENTRATION	DESIGN DATA NEEDED
Fermentation	pH, Temperature, Medium Composition	Interaction With Solvent Extraction, Minimal Medium	Mass Transfer, Kinetic Rate Data, Scale-Up Criterion
Cell Recycle	Permeate/Recycle Rate, Fiber Size/Type Pressure Effects	Cell Lysis Rate	Scale-Up Criteria, Permeate/Recycle Rate, Fiber Size, Type
Solvent Extraction	Size and Type of Extractor, Solvent Ratio	Solvent Life, Interaction With Fermentation, Nutrient Extraction	Distribution Coefficient, Separation Factor, Equilibrium Data
CMA/KAc Production	Mixing Time, Rate, Reactor Size, Composition of Saturated Solution (CA/MA), Recycle Rate, Settling Rate, Filtration Requirements, if any	Interactions With Solvent Extraction, Solids Handling	Kinetics/Mass Transfer Rates, Recycle Rates

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PHASE II STATEMENT OF WORK

The objective of the Phase II research program was to move the BRI technology from the laboratory toward commercialization by performing experiments that yield necessary scale-up and design data for prototype demonstration. Bench-scale fermentation experiments were performed in order to help select the gasifier type (air- or oxygen-blown) and to assess the effects of syngas impurities on fermentation. Solvent extraction/CMA production studies were performed to optimize the solvent composition for maximum rates of CMA production and product recovery. A complete bench unit was operated for an extended time period to test interactions between unit operations. The CMA that is produced in the bench unit was tested for consistency and deicing properties. A detailed design was prepared for the prototype unit to be located at Ft. Madison, IA.

In addition, developmental research on the BRI MSW-to-CMA process was performed in order to better design the prototype unit for the Ft. Madison demonstration. This program concentrated on six areas:

- Assessment of the effects of potential syngas contaminants, such as heavy metals and cyanide, on fermentation performance.
- Evaluation of whether less expensive raw materials, such as potash and lower grades of lime, can be used in the production of CMA and KAc.
- Fermentation/CMA production study attempting to minimize the presence of byproducts such as sulfate and chloride in CMA.
- Evaluation of carbon bed adsorption as a method of enhancing the fermentation of CO, CO_2, and H_2 in the presence of recycled water.
- Evaluation of zeolites as an alternative method of acid recovery.
- Modification of the process design and economic analysis for both CMA and KAc production based on Phase II results.

The research studies utilized the existing BRI bench-scale unit, and addressed the complete process from fermentation to CMA production and testing.

A facility to process 4000 lb/h (1814 kg/h) of MSW has been designed for installation at Ft. Madison, IA. This facility will generate 6600 tons/year (5988 tonnes/year) of CMA and 17,400 tons/year (15,785 tonnes/year) of 50% KAc solution (or about the size of the current markets). It is projected that this facility will generate a significant rate of return, yet be small enough to serve as a demonstration unit. Once the technology has been demonstrated, larger plants will be constructed as the market dictates.

TASK 1. GASIFIER SELECTION

The gasification of carbonaceous wastes produces a mixture of predominantly CO, CO_2, H_2, and N_2. The amount of CO vs. CO_2 present in the synthesis gas is dependent on the temperature of gasification and the resultant energy requirements. The H_2 concentration is a function of the composition of the biomass and whether steam is introduced. Nitrogen will be present if air is used as the gasifying medium instead of oxygen. As examples: syngases produced with air as the gasifying medium contain N_2 as the major component, with 12% to 16% CO, 8% to 15% CO_2 and about 12% H_2. Syngases produced with oxygen as the medium are richer in CO, CO_2, and H_2, with 40% to 50% CO, 15% to 24% CO_2, and 24% to 30% H_2.

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Finally, syngases produced with oxygen and steam as the gasifying medium are perhaps a bit richer in H_2 content. As expected, the choice regarding whether to use air or oxygen as the gasifying medium depends on whether a readily available, relatively inexpensive source of oxygen can be obtained.

Continuous gas phase fermentation experiments were performed with typical air-blown, steam-blown, and oxygen-blown gasifier syngas compositions and with syngas containing various concentrations of syngas contaminants. The following variables were studied:

- Retention time – gas flow rate.
- Gas composition (typical of MSW waste gas streams, using air-blown, steam-blown, or oxygen-blown gasifiers).
- Dilution rate (liquid flow rate).

A constant agitation rate of 750 rev/min was employed, and the optimum nutrient composition found in the Phase I studies was utilized.

The objective of these experiments was to compare the performance of ERI2 in converting the N_2-rich and CO- and H_2-rich gases to acetic acid/acetate by comparing rates and yields. The results of these experiments, along with a process of economic optimization, helped to determine the feasibility of utilizing less expensive air in place of oxygen as the gasifying medium.

In gasifying wastes, low concentrations of byproduct gases are often present. Examples of these gases include sulfur gases such as H_2S, COS, and CS_2; methane; ethylene; acetylene; chlorides; and cyanide and metals. Most of these compounds may be easily scrubbed from the syngas using water. In addition, bacterial cultures are usually resistant to most of these compounds unless they are present in exceedingly high concentrations.

In evaluating the effects of gas phase contaminants on gas utilization and acetic acid/acetate production, a series of batch experiments were performed in serum-stoppered bottles to determine whether a particular contaminant is inhibitory to growth or gas uptake. The inhibitory concentration of each of the contaminants (H_2S, COS, various metals, chlorides) was first determined by employing successively higher concentrations of each of the contaminants in the bottles. The inhibitory concentration was determined by monitoring growth and CO/H_2 uptake, and determining when either of these two important variables decreased by 30% to 50% in comparison to controls without the contaminant and with bottles containing lower concentrations of the contaminant. Previous experiments with similar cultures, for example, had shown H_2S tolerances of up to 26% by volume, far exceeding the concentration of typical gasifier syngas. COS tolerances were usually a bit lower, and metal and chloride tolerances were essentially unknown, but not expected to be a problem.

Following these batch experiments, continuous culture experiments were to be carried out with the more inhibitory compounds present in the typical concentrations found in syngas, if necessary. Rate and yield comparisons with the data from Task 1A would then be made. The overall objective of these experiments was to determine whether scrubbing or other pretreatment techniques are required prior to fermentation of the syngas.

Results from the previous subtasks helped to determine whether air-blown, steam-blown, or oxygen-blown gasifiers should be selected for use in the prototype unit. Vendors were contacted to obtain performance data and cost information for various types of gasifiers. A gasifier for the prototype unit was selected based on costs, performance, and history in gasifying MSW and other biomass wastes.

TASK 2. SOLVENT EXTRACTION/CMA PRODUCTION STUDIES

A proprietary solvent mixture containing solvent A and co-solvent 11 has been found to be quite suitable in extracting acetic acid from the aqueous phase. Very high distribution coefficients for acetic acid are obtained, as well as high separation factors. The distribution coefficient increases with increasing concentration of solvent A. However, the solution viscosity and relative cost of the solvent mixture also increases with solvent A concentration. The increasing viscosity is somewhat troubling when applied to CMA production, since a viscous solution prevents rapid solid (CMA) settling during CMA production directly in the solvent phase. A solvent mixture containing ≥30% solvent A results in settling times of more than 24 h. The use of 20% solvent A in the mixture resulted in a settling time of 1 min, and the use of 10% solvent A results in a settling time of 30 s. A small sacrifice in the acid distribution coefficient thus results in a major decrease in CMA settling time.

Although these results are quite encouraging, they had not been optimized to maximize the rate and yield of CMA. High solvent A compositions maximize the amount of acetic acid extracted for a given quantity of solvent, but minimize the overall rate of CMA production through increased settling times. Low solvent A compositions result in decreased settling times, but will require a higher solvent flow rate through the CMA reactor for a given CMA production rate.

CMA production studies were thus performed to optimize the solvent mixture using the proprietary solvents from previous studies, including solvent A/co-solvent 11 and solvent B/co-solvent 9. Dolomitic lime or mixtures of dolomitic lime and MgO were used to produce CMA from acetic acid previously extracted into the solvent phase from the fermentation broth. A saturated solution of CMA in water was also used along with the lime and solvent to cause the precipitation of CMA from the two liquid phases. Filtration was used to remove the solids if necessary.

Variables for study included:

- Solvent phase/aqueous phase ratio.
- Ratio of Ca^{2+}/Mg^{2+} in the lime addition.
- Mixing time vs. conversion.
- Extraction solvent composition and concentration.

Acetic acid/acetate concentrations were monitored in both the solvent and aqueous phases. Calcium and magnesium ion concentrations and pH were followed in the aqueous phase. The variables were manipulated to maximize the CMA yield and to minimize the reaction and separation times.

TASK 3. CMA/KAc PRODUCTION

Processes to produce either solid CMA or aqueous KAc were presented previously in figure 1. In producing CMA, the solvent stream containing approximately 50 g/L acetic acid is contacted with dolomitic lime/MgO and a saturated CMA solution in a CMA reactor. The lime and MgO react with acetic acid in the solvent phase to form CMA. The solvent is returned for recycle in the extraction column, and the CMA solution is fed to a dryer/pelletizer to produce dry CMA. Experiments in the BRI laboratories have shown a 99.9% conversion to CMA, with negligible amounts of solvent present in the solid CMA.

A similar process would be used in producing potassium acetate. Since a 50% solution of potassium acetate is the desired product, the dryer is eliminated and the reaction/settling step is much simpler. A solution of KOH is simply contacted with the solvent where the reaction to produce potassium acetate occurs. Solvent is separated from the aqueous phase by decantation and recycled back to solvent extraction.

Because of the importance of these steps in the overall process, detailed experimental design and scale-up studies were performed on the CMA and KAc reactors. Overall rate analyses considering CMA or KAc production and CMA settling were performed. CMA product analyses with a particular emphasis on solvent contamination were necessary. Finally, the optimum process design for contacting lime with extracted acid in a reaction system for CMA or KAc production was necessary. Potential designs were tested in the laboratory, with appropriate data collected for process design.

TASK 4. BENCH-SCALE OPERATION

A laboratory bench-scale CMA production unit was designed and constructed utilizing the data from Tasks 1 through 3 and the Phase I feasibility studies. This unit operated continuously and served to link the unit operations of fermentation, cell recycle, solvent extraction, and CMA production. By linking unit operations in a continuous process, any problems of interaction between the units can be identified and corrected. Examples of such problems would be solvent carryover to the fermenter or nutrient extraction by the solvent.

The design of the bench-scale system included the use of a 2L New Brunswick Bioflo IIC chemostat as the continuous fermenter. The chemostat was fed synthetic gas of the desired process gas compositions. Liquid medium was fed to the culture to help maintain an active culture in the fermenter. Cell recycle used a 0.2-µm hollow-fiber membrane unit to maximize the biocatalyst concentration in the fermenter for the gas-liquid system. This unit processed up to 220 L of synthesis gas/day and was of sufficient size to define reaction kinetics and gas/liquid mass transfer coefficients.

Following fermentation, the acetic acid product was removed from the fermentation broth by solvent extraction. Because of the high distribution coefficient for acetic acid, a simple two- or three-stage mixer-settler system was suitable. Alternatively, a small countercurrent extraction column may be used. CMA production occurred by reacting dolomitic lime and MgO with acetic acid in the solvent phase in a small mixed reactor. Upon separating the phases, the CMA and water were sent to batch drying, and the organic phase, consisting of the solvent, was recycled. Thus, only a small reactor and settling tank were necessary for CMA production.

The bench-scale unit was operated for several months to obtain steady-state performance data. CMA production had not been previously demonstrated on a continuous basis, and was a focus of Task 3 and the bench unit. The mixing time and rate, the size of the CMA reactor, the concentrations of the base, and the need for filtration were variables for study. The purpose of these experiments was to define the kinetic/mass transfer rates for prototype scale-up and design. Interactions with the solvent extraction unit and solids handling were primary operating considerations.

TASK 5. CMA TESTING

Several tests were performed on the BRI-produced CMA during the Phase I laboratory studies. In addition, comparisons were made with commercially produced CMA. The results from these tests showed that the BRI-produced CMA performed as well or better than industrial CMA on each of these tests.

Another focus of the bench-scale operation was to generate sufficient quantities of CMA for testing of the deicing capabilities of the products. This continuous production and testing helped to identify any problems with the continuous technology in producing a consistent product. Two types of tests were performed: tests concerning the physical characteristics of the deicer; and deicing tests. The tests comparing the physical characteristics of CMA from the various sources were performed to ensure that the BRI-produced CMA met the standards of the commercial products.

The products were also analyzed for protein and solvent content, two potential byproducts from biological production coupled with solvent extraction. The solvent content of CMA must be negligible, not only from an environmental standpoint, but also to minimize expensive solvent losses. The protein content originates from cellular material, and must be kept low in order to meet product specifications. In addition, the product was analyzed for moisture content, insolubles content, pH, and ash content, and was compared to industrial CMA.

Deicing tests were also performed in order to compare the abilities of BRI-produced products with commercial products. Data are available from ice penetration, ice melting, and eutectic tests on CMA for comparison. These and any other deicing tests were performed in accordance with the SHRP H-205 handbook.

TASK 6. DESIGN PROTOTYPE UNIT

As was mentioned earlier, a prototype unit has been projected for installation at Ft. Madison, IA. This unit is sized to process 4000 lb/h (1814 kg/h) of MSW and produce 6600 tons (5988 tonnes) of CMA and 17,400 tons (15,785 tonnes) of 50% KAc/year. This facility size is small enough to demonstrate adequately the technology, but still large enough to show a good economic return.

The bioreactor; acid purification; solvent recirculation loop; CMA reactor with filter; and the associated exchangers, pumps, and piping will be included. Equipment sizes were computed and costs were estimated. A complete material balance was prepared and operating costs, including utilities, raw materials, nutrients, and capital charges, were determined. A complete economic analysis was prepared based on discounted cash flows.

A computer simulation model of the process was also prepared, including the fermenter, extraction, CMA production, etc. Parametric studies of the designs were performed. These studies measured the effects of key variables, such as pressure, on economics. Optimal designs were defined.

TASK 7. MANAGEMENT AND REPORTING

Weekly meetings of the research team were held to formally review the research results and progress of each task. The scope of the various elements of the task was coordinated to ensure that the schedule of accomplishments was maintained. Resources were redirected where necessary to ensure each part of the required tasks was completed on schedule.

Monthly progress reports were issued, presenting the data and results from each task. Upon completion of all tasks, a final report was prepared that detailed all experimental procedures, data, and discussion and analysis of results.

TASK 8. MSW SYNGAS CONTAMINANT STUDY

The effects of H_2S, COS, and chlorides on ERI2 performance were demonstrated earlier in Phase II. The effects of the contaminants on CMA product composition, however, were not tested.

In evaluating the effects of additional gas phase contaminants on gas utilization and acetic acid/acetate production, a series of batch experiments were first performed in serum-stoppered bottles to determine whether a particular contaminant was inhibitory to growth or gas uptake. The inhibitory concentrations of each of the contaminants (cyanide, various metals) were determined by employing successfully higher concentrations of each of the contaminants in the bottles. The inhibitory concentration is determined by monitoring growth and CO/H_2 uptake, and determining when either of these two important variables is decreased by 30% to 50% in comparison to controls without the contaminant and with bottles containing lower concentrations of the contaminant. Previous experiments with H_2S, for example, showed an H_2S tolerance of up to 7.5% by volume, far exceeding the concentration of typical gasifier syngas. Procedures for these experiments were identical to those described in Task 1.

Following these batch experiments, continuous culture experiments were to be carried out with the more inhibitory compounds present in their typical concentrations found in syngas, if necessary, using the protocol of Task 1. Once acetic acid/acetate had been produced from the syngas containing the contaminant; CMA production occurred in the bench-scale unit. The resulting CMA was analyzed for the presence of the contaminant.

TASK 9. RAW MATERIAL STUDY

An earlier economic evaluation for a plant to produce 85,000 tons/year (77,112 tonnes/year) of CMA from 500 tons/day (454 tonnes/day) of MSW shows a total manufacturing cost of $10.5 million/year or $123/ton ($136/tonne) of CMA produced. Raw materials (nutrients, lime, MgO, water, and solvent make-up) represent $4.5 million or 42% of the total manufacturing cost. Furthermore, the lime and MgO account for 70% of the raw materials cost. Similar results are shown for the production of KAc from acetic acid and potassium hydroxide.

Less expensive raw materials may be used to produce CMA and KAc from acetic acid. The dolomitic lime used by industry costs approximately $40/ton ($44/tonne) and their MgO costs about $355/ton ($391/tonne). The *Chemical Marketing Reporter* shows that potassium hydroxide costs $3000/ton ($3307/tonne). Potash, a potential substitute for potassium hydroxide, costs only $900/ton ($992/tonne).

The use of inexpensive raw materials gives an economic advantage, but also presents problems. Potash, for example, contains nearly 30% non-active ingredients. These inactive ingredients may or may not be inert to reaction, but even the inert ingredients potentially end up in the product CMA or KAc.

Less expensive raw materials were obtained and tested in the bench-scale unit for their ability to produce CMA or KAc at a suitable rate. The existing bench-scale unit was utilized. The CMA and KAc products were then analyzed for the presence of byproducts known to be present in the raw material.

TASK 10. MEDIUM OPTIMIZATION STUDY

In analyzing the product CMA from the Phase II bench studies, it was found that the BRI CMA had relatively high levels of sodium (Na), chloride (Cl^-), and sulfate (SO_4^{2-}). Industrial CMA had high levels of iron (Fe) and phosphate (PO_4^{3-}). The presence of these ions may make field application environmentally sensitive in such a manner that the ions should be removed if possible. The presence of sulfate and chloride in the BRI CMA is due to the medium used in fermentation. Several of the trace metals are present as chlorides and sulfates. In addition, the reducing agent, Na_2S, is converted to sulfate upon oxidation.

The minimization or even elimination of chloride and sulfate from the liquid phase of the reactor may be possible by medium optimization. It is likely that excess Na_2S is present in the medium for reducing power, and it is even possible that Na_2S could be completely removed from the medium since the CO and H_2 present in the syngas are, by themselves, effective reducing agents. Similarly, the metal chlorides and sulfates in the medium could easily be replaced by other less innocuous anions.

Additional fermentation studies were performed that were similar to those proposed in Task 1, but with the goal of minimizing Na_2S, sulfates, and chlorides as components of the medium. Cell recycle was then added to the fermenter once the optimization was complete. The fermentation broths were then used to produce CMA in the BRI bench-scale unit. The resulting CMA was analyzed for sulfates, chlorides, and other ions of interest.

TASK 11. DESIGN REVISIONS

Revisions to the Phase I design and economic analysis were made based on the results obtained in Tasks 8 through 10.

TASK 12. MANAGEMENT AND REPORTING

Weekly meetings of the research team were held to formally review the research results and progress of each task. The scope of the various elements of the task was coordinated to ensure that the schedule of accomplishments was maintained. Resources were redirected, where necessary, to ensure that each part of the required tasks was completed on schedule.

Monthly progress reports were issued, presenting the data and results from each task. Upon completion of all tasks, a Final Report was prepared that detailed all experimental procedures, data, and discussion and analysis of results.

TASK 13. IMPURITIES IN BRI-PRODUCED POTASSIUM ACETATE (KAc)

As was mentioned previously in Task 9, alternative grades of raw materials may potentially be used in manufacturing CMA and KAc. It is known that several grades of MgO are available, for example, in producing CMA from acetic acid, MgO, and dolomitic lime. The various grades of MgO contain different concentrations of MgO, ranging from 45% to 98%, along with inerts and potential noninert materials. Likewise, it is thought that a variety of grades of KOH or alternatives to KOH are available in producing KAc from acetic acid and KOH. As in the production of CMA, with the various grades of MgO, the alternatives to KOH (caustic potash) probably contain both inerts and undesirable constituents.

A thorough analysis of potential raw materials and their resulting contaminants was made in producing KAc from KOH and acetic acid. Vendors were contacted to supply various grades and forms of KOH and other alternative raw materials. Experiments to produce KAc were to be performed with promising grades, if feasible. The resulting KAc was then to be analyzed for the content of undesirables such as Cl^- and SO_4^{2-}.

TASK 14. CARBON BED ADSORPTION

Preliminary studies performed in both the laboratory and pilot plant showed enhancement in the fermentation if the water recycled to the fermenter after solvent extraction is first passed through a carbon bed. The materials being adsorbed were unknown, but it was expected that the adsorbed materials included cellular protein and other cell constituents, and perhaps trace quantities of solvent. Fermentation experiments were thus performed in the laboratory using recycled water from extraction both with and without carbon bed treatment. The effects of carbon treatment on fermentation were thus quantified in these steady-state experiments. Identification of the materials removed in carbon bed adsorption was to be made if possible.

TASK 15. EQUIPMENT SPECIFICATIONS/ECONOMIC PROJECTIONS

Detailed designs and economic projections were prepared for the production of both CMA and KAc using various grades of raw materials. The effects of these alterantive raw materials on the rate of return will be found for the various process alternatives.

TASK 16. ACETIC ACID RECOVERY USING ZEOLITES

Zeolites may potentially be used as an alternative to solvent extraction for acetic acid recovery. If they can be employed, a zeolite system could potentially replace both the cell recycle and acid recovery systems, while significantly altering the CMA production process. Experiments were performed in the laboratory to assess the potential for zeolites to replace acid recovery in the CMA production process. Loading curves and regeneration techniques were developed. An economic evaluation for the use of zeolites in place of acid recovery/cell recycle was prepared.

PHASE II RESULTS AND DISCUSSION

TASK 1. GASIFIER SELECTION

The objective of this task was to select the appropriate type of gasifier (air-blown, steam-blown, or oxygen-blown) for the gasification of MSW and sewage sludge to produce synthesis gas for biological CMA production. The medium for gasification (air, steam, or oxygen) affects gas composition, which will, in turn, affect the required GRT for a given conversion. The effects of typical syngas contaminants on gas conversion are also to be studied. Finally, the appropriate gasifier is to be selected considering culture performance along with cost, commercial availability, and operating history on MSW and sewage sludge.

TASK 1A. GAS COMPOSITION

Three gas mixtures have been chosen for the study, based on typical compositions found in the literature:

MIXTURE 1: 31.7% H_2, 63.2% CO, 5.1% CH_4 (representative of oxygen-blown gasifier syngas).

MIXTURE 2: 48.6% H_2, 23.2% CO, 28.2% CH_4 (representative of steam-blown gasifier syngas).

MIXTURE 3: 52.0% H_2, 23.0% CO, 19.0% CO_2, 6% CH_4 (also representative of steam-blown gasifier syngas, but with sufficient CO_2 present to convert all of the H_2 present to acetic acid).

MIXTURE 4: 13.7% H_2, 13.2% CO, 15.3% CO_2, 57.8% N_2 (representative of air-blown gasifier syngas).

As in the Phase I feasibility studies, the inlet and outlet gas compositions were monitored to determine steady-state at a given set of reaction conditions. Gas compositions were measured using gas chromatography (GC) with a hot-wire detector. Liquid compositions were measured by GC with a flame-ionization detector, and cell density was monitored using a spectrophotometer.

A liquid medium containing salts and vitamins enter the CSTR, along with the syngas of the desired composition. Inside the bioreactor, the cells grow and convert the CO, CO_2, and H_2 into acetic acid. The liquid effluent from the reactor is sent to a hollow fiber where the cells are separated from the permeate containing acetic acid. The cells are recycled back into the reactor in order to maintain a high cell density inside the reactor.

Oxygen-Blown Syngas

Results for the fermentation of the oxygen-blown syngas (Mixture 1) are shown in table 41. As is noted in the table, the GRT affects CSTR performance greatly. High agitation rates are necessary to provide adequate mass transfer of CO and H_2 into the liquid phase prior to microbial uptake. The liquid dilution rate affects the final acetic acid/acetate concentration in the liquid phase. Table 41 shows that long retention times of 15 to 20 min are necessary for high conversions of oxygen-blown syngas containing a high concentration of CO.

Table 41. Performance of ERI2 in the CSTR With Cell Recycle When Using Oxygen-Blown Syngas

GRT (min)	Agitation Rate, rev/min	D (h^{-1})	H_2 Conversion (%)	CO Conversion (%)	Acetic Acid/ Acetate* (g/L)
36.98	900	0.075	97.67	98.72	12.34
27.01	900	0.075	93.26	97.77	15.37
26.22	900	0.075	92.07	97.61	15.78
23.39	900	0.075	91.80	97.00	15.04
22.75	900	0.099	95.14	97.75	15.19
19.38	900	0.099	90.37	96.79	15.45
18.03	900	0.099	68.14	92.66	15.19
16.02	900	0.099	42.53	86.50	15.49
14.39	750	0.099	54.30	80.19	17.04
21.90	750	0.128	88.39	92.51	11.86
17.55	750	0.128	80.53	89.18	13.08
14.95	750	0.128	67.97	84.27	12.70

* Acetic Acid/Acetate refers to total acetic acid and acetate concentration.
Mixture 1 contains 31.7% H_2, 63.2% CO, and 5.1% CH_4 (representative of oxygen-blown gasifier).

Steam-Blown Syngas

Steam-blown syngas containing 48.6% H_2, 23.2% CO, and 28.2% CH_4 was next utilized in the CSTR with cell recycle with isolate ERI2. Again, these experiments were designed to measure the effects of GRT at a fixed liquid dilution rate (D) and agitation rate on culture performance.

Table 42 shows the effects of GRT on ERI2 performance. In this study, the agitation rate was held constant at 900 rev/min, and the liquid dilution rate was maintained at either 0.063 h^{-1} or 0.10 h^{-1}. The GRT varied between 22.5 and 8.2 min. For these different GRTs, the CO conversion varied between 75% and 91%, and the H_2 conversion varied between 29% and 38%. The H_2 conversion is low due to a stoichiometric excess of hydrogen present in the feed gas. Thus, CO uptake cannot liberate enough CO_2 to react with all of the H_2 present in the gas mixture. The product acetic acid/acetate concentration ranged from 10 to 13 g/L.

Table 42. Performance of ERI2 in the CSTR With Cell Recycle When Using Gas Mixture 2, Steam-Blown Gasifier Syngas

			Conversion (%)			
GRT (min)	Agitation Rate (rev/min)	D (h^{-1})	H_2	CO	Acetic Acid/ Acetate* (g/L)	Cells (g/L)
22.51	900	0.063	38.1	91.3	10.1	1.64
16.70	900	0.063	36.6	87.5	12.6	2.07
13.45	900	0.063	34.2	83.1	13.9	2.27
10.68	900	0.063	29.3	79.9	13.3	2.26
10.5	900	0.10	32.8	81.1	12.0	2.7
10.1	900	0.10	33.6	77.5	10.4	2.6
8.6	900	0.10	32.6	78.9	11.8	2.8
8.2	900	0.10	28.4	75.5	11.2	2.7

* Acetic Acid/Acetate refers to total acetic acid and acetate concentration.
Gas Mixture 2 contains 48.6% H_2, 23.2% CO, 28.2% CH_4.

Experiments were also performed in the CSTR with cell recycle using Isolate ERI2 and an alternative gas mixture containing 52% H_2, 23% CO, 19% CO_2, and 6% CH_4. This gas is a second mixture representative of steam-blown gasifier syngas. However, unlike the previously used gas, this gas mixture has sufficient CO_2 at a 61% CO conversion to completely utilize all of the H_2 present in the gas mixture.

Table 43 shows the effects of GRT on ERI2 performance. In this study, the agitation rate was held constant at 900 rev/min and the liquid dilution rate was maintained at 0.1 h^{-1}. The GRT was varied between 12.3 and 5.7 min. Experiments at each GRT were continued for at least 10 liquid retention times (1/D) to observe steady-state performance. For these four different GRTs, the CO conversion varied between 73% and 95%, and the H_2 conversion varied between 23% and 79%. The product acetic acid/acetate concentration varied between 13.2 and 16.8 g/L, which is 72% to 93% of theoretical. The cell concentration varied between 2.4 and 2.8 g/L.

In comparing the data of table 43 with the data from the previous synthetic steam gasifier syngas containing only a limited amount of CO_2, it is observed that the culture performed better without CO_2 limitation. A minimum GRT of about 8.2 min was possible with CO_2 limitation, while a minimum GRT of 5.7 min was noted in table 43 without CO_2 limitation.

Table 43. Steady-State Performance Data for Isolate ERI2 on a Second Synthetic Steam-Blown Gasifier Syngas

			Gas Conversion				
GRT (min)	Agitation Rate (rev/min)	D, h^{-1}	H_2	CO	Acetic Acid/ Acetate* (g/L)	Cells (g/L)	% of Theoretical Product Yield
12.3	900	0.1	73.9	94.8	15.04	2.77	82
9.9	900	0.1	42.7	84.1	13.26	2.42	82
8.0	900	0.1	37.0	79.7	16.88	2.64	93
5.7	900	0.1	23.2	72.7	13.99	2.65	72
12.4	900	0.1	78.5	96.1	15.3	2.56	81
9.1	900	0.1	52.9	88.4	15.1	2.88	78
8.0	900	0.1	35.8	82.5	13.3	3.13	78

* Acetic Acid/Acetate refers to total acetic acid and acetate concentration.
Gas contained 52% H_2, 23% CO, 19% CO_2, and 6% CH_4.

Air-Blown Syngas

Finally, air-blown syngas was used as a source of CO, CO_2, and H_2 for the production of acetic acid/acetate by the culture. The gas mixture contained 13.7% H_2, 13.2% CO, 15.3% CO_2, and 57.8% N_2. Steady-state results as a function of GRT, agitation rate, and liquid dilution rate (D) are shown in table 44. In these studies, the GRT was varied from 2.9 min to 9.3 min, the agitation rate was varied from 750 to 1000 rev/min, and the liquid dilution rate was varied from 0.056 to 0.137 h^{-1}. As is noted in the table, a 3-min GRT yielded a CO conversion of 74% and a H_2 conversion of 51%. Unconverted gas will be used as an energy source for drying the product. Therefore, the economic level of conversion will depend on comparing reactor size with energy requirements.

Table 44. Steady-State Performance Data for Isolate ERI2 in the CSTR With Cell Recycle When Using Air-Blown Gasifier Syngas

			Conversion (%)	
GRT (min)	Agitation Rate (rev/min)	D (h^{-1})	H_2	CO
9.30	750	0.056	74.5	80.75
9.28	750	0.068	72.0	82.1
6.40	750	0.090	49.6	74.8
6.14	750	0.075	46.5	73.6
4.05	750	0.119	58.1	65.5
3.98	900	0.120	67.9	74.3
2.89	900	0.137	33.9	66.1
3.28	900	0.123	51.3	74.6

Gas contained 13.2% CO, 13.7% H_2, 15.3% CO_2, and 57.8% N_2.

Significance

Isolate ERI2 was able to convert CO, CO_2, and H_2 in each of the syngases to acetic acid/acetate without difficulty. As expected, the required GRT increases with the combined CO and H_2 content. A GRT of about 15 min is required to obtain an 85% to 90% conversion of CO in oxygen-blown syngas, while 12 min is suitable for steam-blown syngas and 9 min is suitable for air-blown syngas. The choice of the gasifier is, thus, an economic optimization decision based on gasifier and fermenter costs. If steam-blown syngas is to be used, sufficient CO_2 must be present to react with H_2 to produce acetic acid/acetate.

TASK 1B. GAS PHASE CONTAMINANTS

The effect of the syngas contaminants H_2S, COS, and chlorides on fermenter performance was also studied. H_2S and COS are typical contaminants found in most syngases, while chlorides are present in MSW syngas if the MSW contains significant quantities of plastics such as polyvinyl chloride (PVC).

Chloride Effects

The effect of chloride on ERI2 performance was evaluated by adding increasing concentrations of NaCl to the medium. Table 45 shows the results of the chloride toxicity study. NaCl concentrations as high as 22.5 g/L were tolerated by the culture without affecting gas conversions, cell optical density (OD), or acetic acid/acetate concentrations. However, a 25.0-g/L NaCl concentration was toxic to the culture.

To test for chloride toxicity rather than sodium, KCl was substituted for NaCl in another set of experiments. The toxic concentration was 25 g/L KCl, which has the same molar concentration as 20 g/L NaCl. Since the chloride tolerance had been established, the difference in levels was judged to be within acceptable limits.

A material balance may be used to estimate the allowable HCl concentration in syngas fed to the reactor. At a 10-min GRT and a 10-h liquid retention time, the allowable HCl concentration is 16%. Thus, HCl toxicity is not judged to be a problem.

Table 45. Effect of Chloride Ion on ERI2 Performance in the CSTR

Cl^-, g/L	Salt Conc. (g/L)	Total Dissolved Solids (g/L)	H_2 Conversion (%)	CO Conversion (%)	Acetic Acid/ Acetate* (g/L)	OD (580 nm)
1.5	2.5	5.1	60	85	10.6	2.3
3.0	5.0	7.6	65	85	10.6	2.3
4.6	7.5	10.1	65	85	10.7	2.2
6.0	10.0	12.6	65	85	10.7	2.2
9.1	15.0	17.6	72	85	10.7	2.4
12.1	20.0	22.6	68	85	11.5	2.2
13.6	22.5	25.1	68	85	12.0	2.2
15.2	25.0	27.6	Toxicity Problems			

* Acetic Acid/Acetate refers to total acetic acid and acetate concentration.
GRT = 15 min; Liquid Retention Time = 26 h.

H_2S Effects

Hydrogen sulfide (H_2S) was next tested to determine its toxicity to ERI2 in terms of both growth and the ability to utilize CO and H_2. The toxicity levels were determined in 150-mL batch serum bottles incubated with ERI2 at 37°C and a 150-rev/min agitation rate. The medium consisted of basal salts and vitamins at pH 5.5. The gas phase was coal synthesis gas at 1 atm (101 kPa). Bottles were incubated in duplicate with various amounts of H_2S and COS. The cultures were monitored for growth and gas uptake with time.

Table 46 presents a summary of the results from the H_2S tests. As is noted, H_2S is not inhibitory to growth or gas uptake, even at a concentration of 7.5%. Since typical syngas contains only 1% to 2% H_2S, this sulfur compound should not be a concern in fermenting syngas.

Table 46. Batch Test of H_2S Toxicity to ERI2

Bottle	H_2 Concentration in Gas Phase (%)	Growth (Optical Density)	Gas Consumption
9	1	0.512 (24 h)	++
10	1	0.501 (24 h)	++
11	2.5	0.617 (48 h)	++
12	2.5	0.256 (48 h)	+
13	5	0.220 (48 h)	+
14	5	0.585 (48 h)	++
15	7.5	0.192 (120 h)	+
16	7.5	0.239 (120 h)	+
17	10	0.000 (120 h)	-
18	10	0.018 (120 h)	-
19	0 (control)	0.637 (120 h)	++
20	0	0.578 (120 h)	++

++ very good growth; + adequate growth; - little or no growth

The effect of H_2S on strain ERI2 was also tested in terms of growth and the ability to utilize CO and H_2 in the absence of any reducing agent (Na_2S and cysteine) as a sulfur source in the medium. Previous studies were performed in the presence of Na_2S or cysteine and could have affected culture performance.

The toxicity levels were again tested in 150-mL batch serum bottles incubated with ERI2 at 37°C, and a 150-rev/min agitation rate. The gas phase was coal synthesis gas at 1 atm (101 kPa). The bottles were incubated in duplicate with various amounts of H_2S. Two different sets of blanks were prepared, one containing 0.5 g/L cysteine and another without any cysteine. The cultures were monitored for growth and gas uptake with time.

Table 47 presents a summary of the results from the H_2S tests. As is noted, H_2S does not affect growth or gas composition up to a concentration of 7.5% H_2S, a level comparable to when reducing agents are present.

Table 47. Test of H_2S Toxicity to ERI2 Without Reducing Agents Present

Bottle	Volume % H_2S in Gas Phase	Growth (OD)	Gas Consumption
33	1	0.45 (48 h)	+
34	1	0.57 (216 h)	+
35	2.5	0.47 (48 h)	+
36	2.5	0.43 (48 h)	+
37	5	0.33 (168 h)	+
38	5	0.17 (144 h)	++
39	7.5	0.05 (216 h)	-
40	7.5	0.20 (144 h)	++
41	10	0.05 (240 h)	-
42	10	0.01 (240 h)	-
43	0	0.48 (72 h)	+
44	0	0.40 (72 h)	+
45*	0	0.57 (72 h)	+
46*	0	0.53 (72 h)	+

++ very good growth; + adequate growth; - little or no growth
* Cysteine (0.5 g/L) was added.

COS Effects

The effect of COS on culture growth and gas consumption was tested in a similar manner as H_2S. Table 48 presents a summary of the results from the COS experiments. COS is also not toxic to ERI2 up to a concentration of 7.5%. Typical COS concentrations in syngas are less than 1%. Thus, COS should not be a problem in fermenting syngas.

Significance

Neither chloride, H_2S, or COS are toxic to Isolate ERI2 at levels higher than typical levels in MSW-derived synthesis gas. Thus, these byproducts should not be a problem in the fermentation of syngas.

Table 48. Batch Test of COS Toxicity to ERI2

Bottle	COS Concentration in Gas Phase (%)	Growth (OD)	Gas Consumption
21	1	0.62 (96 h)	+
22	1	0.27 (168 h)	++
23	2.5	0.45 (168 h)	+
24	2.5	0.61 (96 h)	+
25	5	0.33 (72 h)	++
26	5	0.44 (168 h)	+
27	7.5	0.35 (168 h)	++
28	7.5	0.10 (168 h)	-
29	10	0.02 (168 h)	-
30	10	0.08 (168 h)	-
31	0 (control)	0.10 (168 h)	-
32	0	0.66 (96 h)	+

++ very good growth; + adequate growth; - little or no growth

TASK 2. SOLVENT EXTRACTION/CMA PRODUCTION STUDIES

The selection of an appropriate solvent/co-solvent mixture for acetic acid extraction and subsequent CMA production in the solvent phase is critical for smooth operation of the combined fermentation/CMA production process. The solvent mixture must have a high distribution coefficient, yet have physical properties that permit rapid separation of solid CMA produced from the solvent phase.

Distribution coefficients were measured for acetic acid between the aqueous phase and different organic phases, consisting of a solvent and a co-solvent. Two different proprietary solvents were chosen:

- Solvent A.
- Solvent B.

Five different co-solvents were studied:

- Co-Solvent 11.
- 5% Co-Solvent 12 in Co-Solvent 11.
- 10% Co-Solvent 13 in Co-Solvent 11.
- Co-Solvent 14.
- Co-Solvent 15.

Table 49 shows the results for these experiments. The solvent composition in the organic phase was chosen to be low (0 to 20%). This composition will provide a low viscosity of the organic phase and will facilitate the settling of CMA in downstream processing. A low concentration of solvent will also facilitate easier phase separation (fewer problems with emulsions). However, high distribution coefficients are desirable in order for the process to be economical.

The solvent A/co-solvent 11 mixture appears to be a good choice for acetic acid extraction, even at a low concentration of solvent A. Co-solvents 12 and 13 were added to co-solvent 11 to increase the polarity of the co-solvent, which, in turn, should provide a higher solvation effect and increased distribution coefficient. However, they did not increase the distribution coefficient significantly. Pure co-solvent 12 and co-solvent 13 were not used as co-solvents due to their high viscosity. Co-solvents 14 and 15 provided high distribution coefficients with solvent B. However, the water solubility in these two solvents is higher than that of co-solvent 11.

Table 49. Measured Acid Distribution Coefficients for Various Solvent/Co-Solvent Mixtures

Solvent	% Solvent	Co-Solvent	% Co-Solvent	Equilibrium pH	Acid Distribution Coefficient
A	0	11	100	2.98	0.15
	5		95	3.25	0.82
	10		90	3.58	2.09
	15		85	3.84	3.50
	20		80	3.98	5.00
B	0	5% Co-Solvent 12 in Co-Solvent 11	100	3.06	0.23
	5		95	3.10	0.25
	10		90	3.15	0.33
	15		85	3.19	0.34
	20		80	3.24	0.38
B	0	10% Co-Solvent 13 in Co-Solvent 11	100	3.01	0.24
	5		95	3.05	0.39
	10		90	3.12	0.49
	15		85	3.19	0.57
	20		80	3.23	0.62
B	0	14	100	3.02	0.49
	5		95	3.13	1.09
	10		90	3.22	1.84
	15		85	3.31	2.50
	20		80	3.42	3.18
B	0	15	100	3.06	0.53
	5		95	3.14	1.70
	10		90	3.36	3.86
	15		85	3.51	6.00
	20		80	3.63	7.75

Experiments were performed to better understand the mixing characteristics involved in CMA production directly from the solvent phase. Currently, dolomitic lime enriched with MgO to yield a Ca^{++}/Mg molar ratio of 0.34 is contacted with an organic phase containing extracted acetic acid from the reactor and recycled aqueous phase saturated with CMA. In mixing these multiple phases, an emulsion can form if the mixing is too vigorous or if impeller placement is varied. Experiments were thus performed to better understand the role of agitation rate, impeller placement, and other tank characteristics on the rate of CMA formation. These data are important in scaling-up the process to the pilot or commercial scale. The results indicate a preference for gentle agitation with dual impellers to prevent emulsion formation.

Significance

The solvent system solvent A/co-solvent 11 still appears to be the best choice for acetic acid extraction. A low concentration of solvent A in the mixture is preferable for rapid separation. Gentle agitation may be necessary to prevent emulsion formation. Emulsion formation will be studied extensively in Tasks 3 and 4.

TASK 3. CMA PRODUCTION

A bench-scale apparatus has been constructed to permit the production of CMA from the reactor permeate containing acetic acid. Figure 11 shows a schematic of the laboratory set-up. Permeate containing acetic acid/acetate from the bioreactor is mixed with recycled solvent in an extractor. The mixed phases are then pumped to a phase separator, where the solvent containing acetic acid is separated from the aqueous phase. The phases separate out in the separator. The aqueous phase is collected and recycled to prepare medium for the fermenter. The organic phase is sent to the CMA reactor where it is contacted with an aqueous phase containing saturated CMA. Lime (dolomitic hydrated lime enriched with MgO) and a small amount of water are added to the reactor. Agitation in the reactor is such that two distinct phases are maintained. The aqueous phase is periodically circulated to the solid CMA separator, where the solid CMA separates out and the saturated aqueous solution is circulated back to the reactor. The organic phase from the reactor is carried to the solvent separator. The recovered solvent is recycled back to the extractor.

Two experiments were performed in this set-up and mass transfer rates were measured under steady-state conditions. Both of the experiments were performed at 135 rev/min in such a manner that no emulsion is formed. Two 2-in (5-cm), six-blade turbine-type impellers were used in the first experiment, and two Lightnin A-100 axial flow impellers were used in the second experiment. The rate of reaction was calculated from the concentration difference of acetic acid between the inlet and outlet organic phase streams of the CMA reactor. The mass transfer rates were 0.001504 and 0.00094 mol/L/min, respectively. These mass transfer rates are too low with the current arrangement. The set-up will be modified to permit a higher rate of reaction and will be presented in Task 4.

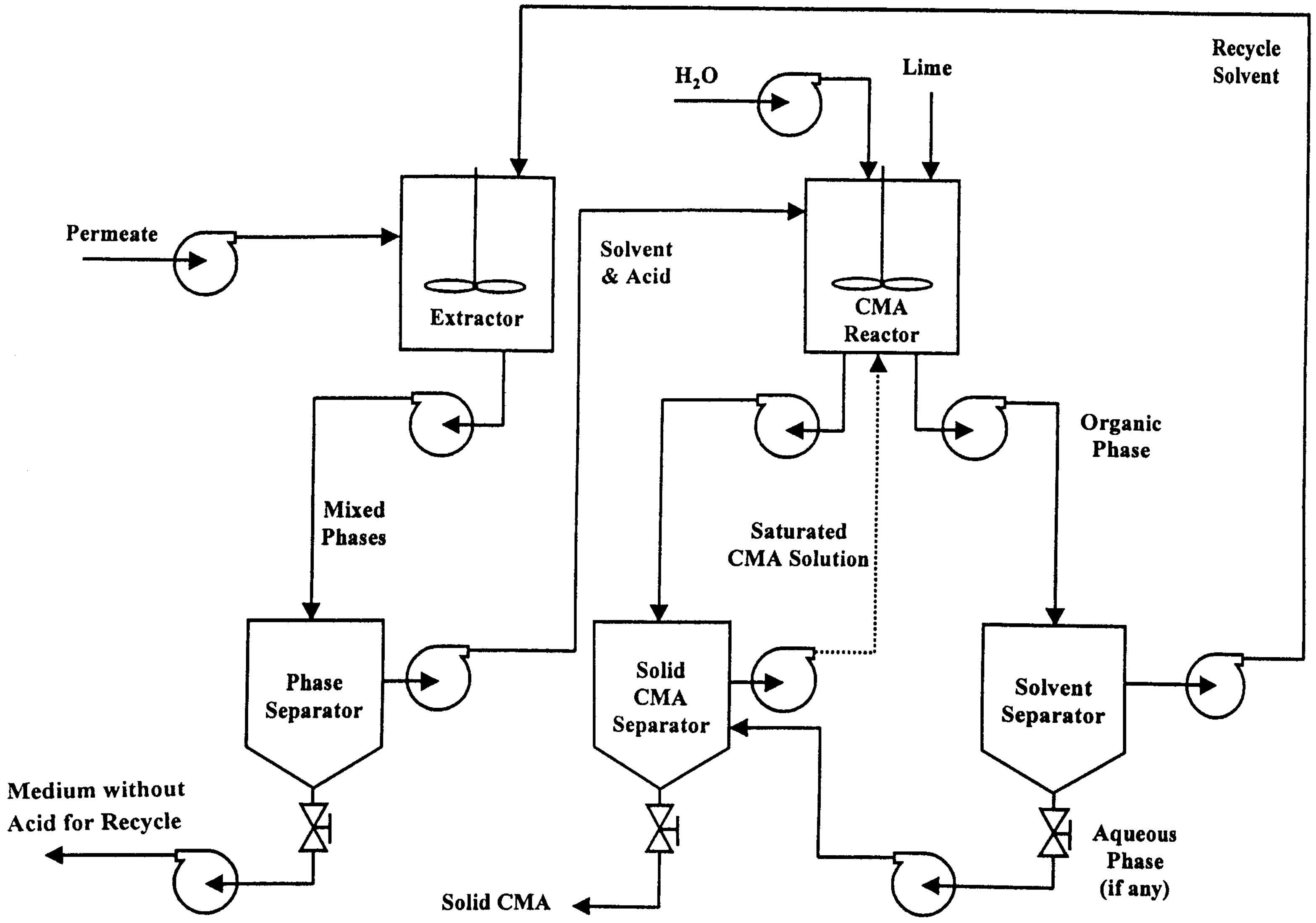

Figure 11. Schematic of Continuous Laboratory CMA Production Process

TASK 4. BENCH-SCALE OPERATION

Studies were performed with Isolate ERI2 with a less expensive medium in place of the traditional enriched medium. These studies showed that ERI2 gave identical CO and H_2 conversions, product yields, rates of substrate uptake, and rates of product formation on both media. Thus, the cheaper medium will be substituted for the traditional medium due to economic implications.

A flow diagram for a modified bench-scale unit is shown in figure 12. In this set-up, permeate from the reactor is mixed with recycled solvent in the extractor. The mixed phases are then pumped to the phase separator. The aqueous phase is pumped from the bottom of the separator and was used to prepare the medium for fermentation. The organic phase containing acetic acid is carried to the CMA reactor where it is contacted with an aqueous slurry containing dolomitic hydrated lime enriched with MgO. Agitation in the reactor is such that the two phases form an emulsion. The emulsion phase is pumped through a coalescer to break the emulsion. The liquid phases from the coalescer are returned to the solvent separator, and the recovered solvent is fed back to the extractor. The product CMA is taken from the bottom of the separator. Water recycle studies are in progress using water from the phase separator as the required water for the medium preparation for fermentation.

The continuous bench-scale CMA reactor system has been modified to enhance the reaction rate for CMA production by mixing the solvent and lime phases.

Table 50 shows data for experiments with different concentrations of lime in the slurry fed to the reactor. Two 2-in (5-cm) six-blade turbine-type impellers were used in the 300-mL reactor. The lime slurry feed rate for this set of experiments was 0.34 mL/min. The rate of reaction was calculated from the concentration difference of acetic acid between the inlet and outlet organic phase streams of the CMA reactor. The data show that liquid retention times of 15 min can be utilized in the continuous system. The reaction rate is directly proportional to lime concentration in such a manner that even lower retention times are possible with higher lime concentrations in the feed.

Table 51 shows rate data for CMA production experiments with different agitation rates and different lime feed rates. A 100-g/L lime slurry was used for these experiments, and two 2-in (5-cm) six-blade turbine-type impellers were used in a 300-mL reactor. The liquid retention time (LRT) for the organic phase in the CMA reactor was either 5 or 15 min. Dissolution of lime from the solid phase to the aqueous phase is the rate controlling step in CMA production.

Table 50. Overall Kinetic Data From the CMA Production Reactor

Lime Concentration (% W/W)	Liquid Retention Time (min)	Acetic Acid Concentration (mol/L) in Organic Phase		Acetic Acid Conversion (%)	Reaction Rate, mol/L · min
		C_{in}	C_{out}		
2	60	0.37	0.33	11	6.67 x 10^{-4}
3	60	0.36	0.30	17	10.0 x 10^{-4}
4	60	0.36	0.26	28	16.7 x 10^{-4}
5	60	0.34	0.20	41	23.3 x 10^{-4}
6	60	0.32	0.16	50	25.7 x 10^{-4}
7	60	0.23	0.05	78	31.0 x 10^{-4}
8	60	0.14	0.008	100	21.7 x 10^{-4}
9	60	0.32	0.12	63	33.3 x 10^{-4}
10	60	0.29	0.04	86	42.0 x 10^{-4}
20	60	0.47	0.03	94	73.0 x 10^{-4}
20	30	0.24	0.026	89	72.7 x 10^{-4}
20	15	0.30	0.18	40	80.7 x 10^{-4}

Table 51. CMA Production Studies in the CSTR

LRT (min)	Agitation Rate (rev/min)	Rate of Lime Addition (mol/min)	Rate of HAc Reaction (mol/min)	Reaction Rate (mol/L·min)
15	200	0.00121	0.00189	0.0063
15	200	0.001834	0.0021	0.0070
15	240	0.001834	0.0023	0.0077
15	330	0.00121	0.0020	0.0067
15	400	0.00121	0.0021	0.0070
15	555	0.00121	0.0022	0.0073
15	555	0.001834	0.0022	0.0073
5	500	0.00121	0.0023	0.023

Lime Concentration = 10% w/w.

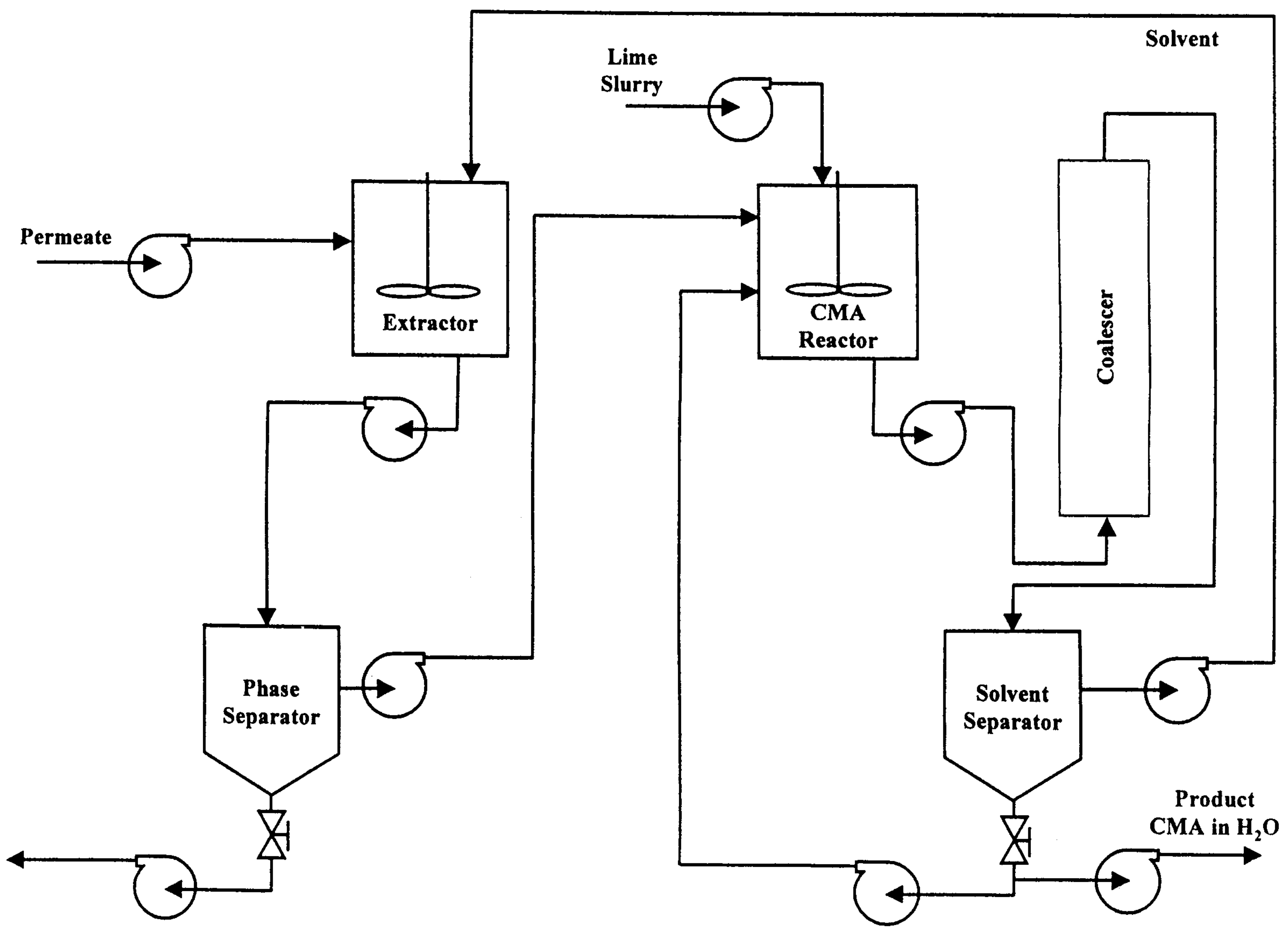

Figure 12. Bench Scale CMA Production System

The bench-scale CMA production system was operated with a second solvent system that also showed promise for economically extracting acetic acid from the fermentation broth. When a 0.00121-mol/min lime feed rate was used, the acetic acid reaction rate was 0.0023 mol/min and the specific rate was 0.023 mol/L/min. A comparison of this result with the data of previous experiments shows that the specific reaction rate is the same as that for the first solvent system. It is evident from earlier experiments that all the acetic acid from the organic phase can be extracted by lime reaction.

Significance

A better system has been constructed in the laboratory for reacting acetic acid from the permeate with lime and MgO. This system permits emulsion formation, which is later broken by a de-emulsifying column. With this system, much higher reaction rates during CMA formation are possible. The dissolution of lime from the solid phase to the aqueous phase is rate controlling. Furthermore, the system has been modified to feed near-saturated solution to the dryer/pelletizer. This change permits easy separation of undissolved inerts from the CMA liquid product.

TASK 5. CMA TESTING

A chemical analysis of the CMA produced at BRI through the biological process has been performed. Test results are shown in table 52. In addition to the BRI samples, an industrial CMA sample was also tested. The industrial pellet sample was ground before analysis. As is shown in the table, the two chemical analyses were quite close. The BRI CMA had a higher Ca^{2+}/Mg^{2+} ratio and a higher moisture content. Neither CMA had appreciable insolubles present, and the solvent content of the BRI CMA was not detectable. Both samples picked up about 5% moisture upon setting.

The amount of trace metals present in the CMA samples was also analyzed, and are as shown in table 53. Industrial CMA is rich in iron, probably because it is produced in metal reactors. BRI CMA is rich in sodium. The results of analyses for phosphate, sulfate, and chloride are shown in table 54. The BRI CMA is high in chloride and sulfate, but these levels can be readily reduced with medium optimization.

Devices for the ice melting and ice penetration tests were constructed according to Kirchner's description. A flat plexiglass dish that can provide a 22.9-cm-diameter and 0.3-cm-thick layer of ice was used for the ice melting test. For the ice penetration test, a 27.9-cm x 5.1-cm x 0.95-cm-thick plexiglass plate was used. Fifteen 0.3-cm-diameter, 3.8-cm-deep cavities were drilled in the plexiglass plate at a 1.6-cm spacing. The upper end of each cavity was enlarged with a conically shaped bit, yielding a cone 6 mm in diameter at the surface and 3.5 mm deep at the point of intersection of the cone with the 0.3-cm cavity.

Three temperatures (10, 15, and 25°F [-12.2, -9.4, and -3.9°C]) were chosen for the ice melting and ice penetration tests since published data were available at these temperatures. The experiments were conducted inside a cold chest. Two samples, powdered industrial CMA and powdered BRI CMA, were tested.

Tables 55 through 57 show the results from the ice melting tests for the two samples. The CMA application rate was 3 oz/yd^2 (102 g/m^2). As is shown in the tables, BRI-produced CMA melted ice faster than the industrial samples. These results are comparable to the results obtained in Phase I.

Table 58 shows results from the ice penetration test run at 10°F (-12.2°C). The CMA application quantity was 23 to 26 mg/cavity. Very little penetration was observed at 10°F (-12.2°C), a result that is comparable to the earlier Phase I results.

A 25% solution of CMA was prepared for both of the samples. The solutions were filtered and then frozen in tubes at -5°F (-20.6°C) for 7 days. After 7 days, the solutions were defrosted. No precipitates were observed in either sample.

Table 52. Physical Properties of CMA Products

	BRI CMA		Industrial CMA	
	As Received	Dry Basis	As Received	Dry Basis
Ca^{2+} (% wt)	5.33	6.40	7.55	8.04
Mg^{2+} (% wt)	12.15	14.59	10.94	11.65
Acetate (% wt)	65.91	79.12	75.21	80.10
Water (% wt)	16.7	-	6.1	-
Insolubles (% wt)	3.8	4.6	4.2	4.5
Ca^{2+}/Mg^{2+} (mol ratio)	0.27	0.27	0.42	0.42
Solvent Content (%)	n.d.	n.d.	-	-
Elemental Analysis				
Carbon (%)	25.1	30.1	30.2	32.2
Sulfur (%)	0.6	0.7	0.04	0.04
Moisture Pick-Up (%)	4.6	-	5.5	-

n.d. = not detectable
- = not present

Table 53. Analysis of Trace Metals (ppm)*

	BRI CMA	Industrial CMA
Fe	<5	421
Ni	<5	<5
Co	<5	<5
Cu	<2.5	<2.5
Cr	<5	<5
As	<0.3	0.9
Pb	0.4	0.4
Na	411	59

* When values are shown as <5, <2.5, or <0.3, these are the detectables limits of the instrument.

Table 54. Analysis of Anions

	BRI CMA	Industrial CMA
Phosphate, PO_4^{3-} (ppm)	90	166
Chloride, Cl^- (ppm)	1228	12
Sulfate, SO_4^{2-} (% wt)	1.76	0.14

Table 55. CMA Ice Melting Test, 10°F (-12.2°C)

Deicer Application Rate: 4.17 g/cell

Time (min)	Average Brine Volume (mL)	
	Industrial CMA Powder	BRI CMA Powder
0	0.0	0.0
10	0.0	0.0
15	0.3	0.4
20	0.8	1.5
25	2.5	3.0
30	4.2	4.6
45	5.0	6.4
60	5.4	8.4

Table 56. CMA Ice Melting Test, 15°F (-9.4°C)

Deicer Application Rate: 4.17 g/cell

Time (min)	Average Brine Volume (mL)	
	Industrial CMA Powder	BRI CMA Powder
0	0.0	0.0
10	0.3	0.4
15	3.7	3.5
20	6.6	6.8
25	8.0	9.8
30	9.8	12.0
45	12.0	15.2
60	14.4	16.5

Table 57. CMA Ice Melting Test, 25°F (-3.9°C)

Deicer Application Rate: 4.17 g/cell

Time (min)	Average Brine Volume (mL)	
	Industrial CMA Powder	BRI CMA Powder
0	0.0	0.0
10	6.0	8.2
15	3.2	11.0
20	11.4	13.0
25	13.0	15.4
30	14.6	18.0
45	17.0	22.6
60	19.7	26.0

Table 58. CMA Ice Penetration Test, 10 F (-12.2°C)

Deicer Application Rate: 23 to 26 mg/cell

Time (min)	Average Penetration Depth (mm)	
	Industrial CMA Powder (Average)	BRI CMA Powder (Average)
0	0	0
3	0	0
5	0	0
10	0	0
15	0	0
20	0	0
30	0	0.5
45	0	0.5
60	0	0.5

Table 59 shows results from the ice penetration test run at 15°F (-9.4°C), and table 60 shows results performed at 25°F (-3.9°C). The CMA application quantity was 23 to 26 mg/cavity. Moderate penetration was observed at 15°F (-9.4°C), with better penetration observed at the higher temperature.

Table 59. CMA Ice Penetration Test, 15°F (-9.4°C)

Deicer Application Rate: 23 to 26 mg/cell

	Penetration Depth (mm)	
Time (min)	BRI CMA Powder	Industrial CMA Powder
0	0	0
3	0	0
5	0	0
10	0	0
15	0	0
20	0	0
30	0.1	0.1
45	0.5	0.5
60	1.0	1.0

Table 60. CMA Ice Penetration Test, 25°F (-3.9°C)

Deicer Application Rate: 23 to 26 mg/cell

	Penetration Depth (mm)	
Time (min)	BRI CMA Powder	Industrial CMA Powder
0	0	0
3	0	0
5	0.5	0.5
10	1.0	1.0
15	2.0	2.0
20	2.5	2.5
30	3.0	3.5
45	4.0	4.5
60	4.5	5.0

Significance

The BRI and industrial CMA show nearly identical results, and these results are comparable to the earlier Phase I results.

TASK 6. DESIGN PROTOTYPE UNIT

Modified Economics

The process economic evaluations have been updated based on additional data collected in the Phase II studies. Tables 61 through 63 present the capital costs, energy requirements, and economic evaluation for CMA production from MSW. A plant size processing 500 tons/day (454 tonnes/day) of MSW, producing about 77,000 tons/year (69,854 tonnes/year) of CMA, is used as the basis. As is noted in table 61, the total fixed-capital investment is $27.5 million. Utilities usage, shown in table 62, shows that 4800 kW≅h (17.3 GJ) of electricity, 3.5 million Btu/h (1.03 million W) of steam, and 350,000 gal (1,324,890 L) of cooling water are required in the process. The economic evaluation, shown in table 63, shows revenue of $53.7 million/year, with a CMA price of $700/ton ($772/tonne). The total raw materials cost is $4.3 million/year (no cost or credit for MSW), and the total utilities cost is $1.8 million/year. The total direct costs are $9.6 million/year. The net profit after a 40% tax is $24.8 million/year, generating a cash flow of $27.6 million/year. The return on the investment is 100%, and the payout is 1 year.

Similar economics are generated for CMA production from sewage sludge. Tables 64 through 66 present the capital costs, energy requirements, and economic evaluation for CMA production from sewage sludge. A plant size processing 500 tons/day (454 tonnes/day) of sewage sludge (dry basis), producing about 75,000 tons/year (68,040 tonnes/year) of CMA, is used as the basis. As is noted in table 64, the total fixed-capital investment is $27.1 million. Utilities usage, shown in table 65, shows that 4600 kW≅h (16.6 GJ) of electricity, 3.0 million Btu/h (0.88 million W) of steam, and 340,000 gal (1,287,036 L) of cooling water are required in the process. The economic evaluation, shown in table 66, shows revenue of $52.6 million/year with CMA at $700/ton ($772/tonne). The total raw materials cost is $4.2 million/year (no cost or credit for sludge), and the total utilities cost is $1.7 million/year. The total direct costs are $9.3 million/year. The net profit after a 40% tax is $24.3 million/year, generating a cash flow of $27.1 million/year. The return on the investment is 99.8%, and the payout is 1 year.

Table 61. Fixed-Capital Investment, 500 Tons (454 Tonnes) of MSW/Day

Section	**FCI ($)**
Gasifier	$8,000,000
Fermenter	3,795,000
Cell Recycle	9,858,000
Acetic Acid Extraction	2,958,000
CMA Production	2,922,000
Total	**$27,533,000**

Table 62. Utility Summary, 500 Tons (454 Tonnes) of MSW/Day

Section	Electricity (kW≅h [GJ])	Steam (million Btu/h [million W])	Cooling Water (thousand gal/h [thousand L/h])
Gasifier	1520 (5.5)	-	40.0 (151.4)
Fermenter	1067 (3.8)	3.5 (1.0)	198.0 (749.5)
Cell Recycle	850 (3.1)	-	-
Acid Extraction	577 (2.1)	-	-
CMA Production	753 (2.7)	-	118.0 (446.7)
Total	4767 (17.2)	3.5 (1.0)	356.0 (1347.6)

- = not required

Table 63. Economic Evaluation for CMA Production, 500 Tons (454 Tonnes) of MSW/Day

Item	Annual Cost (in million $)
Revenue, 18,256.1 lb/h (8281.0 kg/h) CMA, $700/ton ($772/tonne)	**$53.673**
Raw Materials	
Medium, 1733 gal/h (6560 L/h), $0.028/gal ($0.007/L)	0.408
Lime, 4616.1 lb/h (2093.9 kg/h), $40/ton ($44/tonne)	0.776
MgO, 2085.3 lb/h (945.9 kg/h), $355/ton ($391/tonne)	3.109
Process Water, 42,091 lb/h (19,092 kg/h), $0.20/1000 gal ($0.05/1000 L)	0.009
Solvent Make-Up	0.030
Total Raw Materials Cost	**$4.332**
Utilities	
Electricity, 4767 kW• h (17.2 GJ), $0.04/kW•h ($11/GJ)	1.602
Steam, 3.5 million Btu/h (1.0 million W), $2.0/million Btu ($1.89/million KJ)	0.059
Cooling Water, 356,000 gal/h (1,347,602 L/h), $0.05/1000 gal ($0.01/1000 L)	0.150
Total Utilities Cost	**$1.811**
Labor, 6 People/Shift, $30,000/Person/year	0.756
Supervision and Overhead, 100% of Labor	0.756
Maintenance, 5% of FCI	1.377
Insurance and Taxes, 2% of FCI	0.551
Total Direct Costs	**$9.583**
Depreciation, 10% of FCI	2.753
Total Cost: $160.89/ton ($177.35/tonne) CMA	**$12.336**
Pretax Profit	41.337
Tax, 40%	16.534
Net Profit	24.803
Cash Flow	27.556
Return on Investment	**100.08%**
Payout Period	1.00 year

Table 64. Fixed-Capital Investment, 500 Tons (454 Tonnes) of Sewage Sludge/Day

Section	FCI ($)
Gasifier	$8,000,000
Fermenter	3,525,000
Cell Recycle	9,888,000
Acetic Acid Extraction	2,892,000
CMA Production	2,817,000
Total	**$27,122,000**

Table 65. Utility Summary, 500 Tons (454 Tonnes) of Sewage Sludge/Day

Section	Electricity (kW≅h [GJ])	Steam (million Btu/h [million W])	Cooling Water (thousand gal/h [thousand L/h])
Gasifier	1520 (5.5)	-	40.0 (151.4)
Fermenter	1000 (3.6)	3.0 (0.88)	184.0 (696.5)
Cell Recycle	827 (3.0)	-	-
Acid Extraction	535 (1.9)	-	-
CMA Production	744 (2.7)	-	116.0 (439.1)
Total	**4626 (16.7)**	**3.0 (0.88)**	**340.0 (1287.0)**

- = not required

Table 66. Economic Evaluation for CMA Production, 500 Tons (454 Tonnes) of Sewage Sludge/Day

Item	Annual Cost (in million $)
Revenue, 17,902.0 lb/h (8120.3 kg/h) CMA, $700/ton ($772/tonne)	**$52.631**
Raw Materials	
Medium, 1432 gal/h (5421 L/h), $0.028/gal ($0.007/L)	0.337
Lime, 4526.3 lb/h (2053.1 kg/h), $40/ton ($44/tonne)	0.760
MgO, 2044.5 lb/h (927.4 kg/h), $355/ton ($391/tonne)	3.048
Process Water, 45,037 lb/h (20,429 kg/h), $0.20/1000 gal ($0.05/1000 L)	0.009
Solvent Make-Up	0.030
Total Raw Materials Cost	**$4.184**
Utilities	
Electricity, 4626 kW• h (16.7 GJ), $0.04/kW•h ($0.14/MJ)	1.554
Steam, 3.0 million Btu/h (0.88 million W), $2.0/million Btu ($0.6/ million W)	0.050
Cooling Water, 340,000 gal/h (1,287,036 L/h), $0.05/1000 gal ($0.01/1000 L)	0.143
Total Utilities Cost	**$1.747**
Labor, 6 People/Shift, $30,000/Person/year	0.756
Supervision and Overhead, 100% of Labor	0.756
Maintenance, 5% of FCI	1.356
Insurance and Taxes, 2% of FCI	0.542
Total Direct Costs	**$9.341**
Depreciation, 10% of FCI	2.712
Total Cost: $160.89/ton ($177.35/tonne) CMA	**$12.053**
Pretax Profit	40.579
Tax, 40%	16.232
Net Profit	24.347
Cash Flow	27.059
Return on Investment	**99.77%**
Payout Period	1.00 year

Effect of Plant Size on Process Economics/Significance

Additional economic projections have been generated for CMA production from MSW as a function of plant size. Plant sizes ranging from 100 to 500 tons (91 to 454 tonnes) of MSW/day were considered. Table 67 presents a summary of the CMA production rate to each plant size and the projected fixed-capital investment. The FCI ranges from $9.12 million to process 100 tons/day (91 tonnes/day) of MSW to $27.5 million to process 500 tons/day (454 tonnes/day) of MSW. The process economics for the various plant sizes are shown in tables 68 through 72, and are summarized in figure 13. As is noted, the return on the investment ranges from 52% for a 100-ton/day (91-tonne/day) facility to 100% for a 500-ton/day (454-tonne/day) facility.

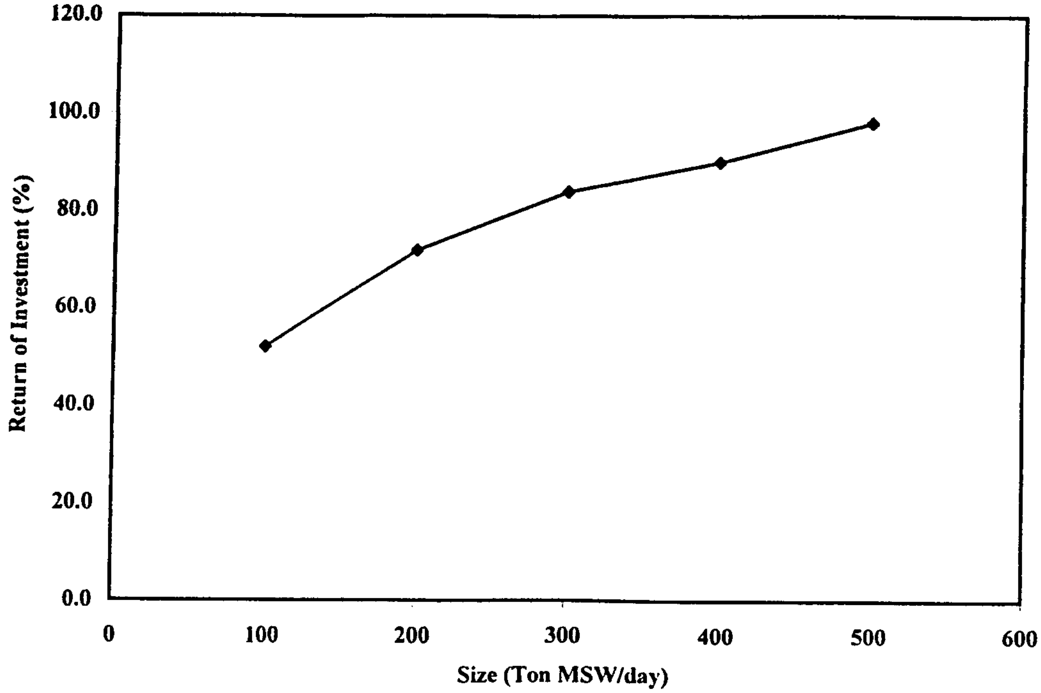

Figure 13. Return on Investment for CMA Production from MSW by Gasification/Fermentation

Table 67. Fixed-Capital Investment for CMA Production From MSW by Gasification/Fermentation

Plant Size (tons of MSW/day [tonnes of MSW/day])	CMA Production (tons/day [tonnes/day])	FCI (in million $)
100 (91)	43.8 (39.7)	$ 9.12
200 (181)	87.6 (79.5)	14.24
300 (272)	131.4 (119.2)	19.03
400 (363)	175.2 (158.9)	23.80

Table 68. Economic Evaluation for CMA Production, 100 Tons (91 Tonnes) of MSW/Day

Item	Annual Cost (in million $)
Revenue, 3651.2 lb/h (1656.2 kg/h) CMA, $700/ton ($772/tonne)	**$10.735**
Medium, 346.6 gal/h (1312.0 L/h), $0.028/gal ($0.007/L)	0.082
Lime, 923.2 lb/h (418.8 kg/h), $40/ton ($44/tonne)	0.155
MgO, 417.1 lb/h (189.2 kg/h), $355/ton ($391/tonne)	0.622
Process Water, 8418.2 lb/h (3818.5 kg/h), $0.20/1000 gal ($0.05/1000 L)	0.002
Solvent Make-Up	0.006
Total Raw Materials Cost	**$0.867**
Electricity, 1008 kW•h (3.6 GJ), $0.04/kW•h ($0.14/MJ)	0.339
Steam, 0.7 million Btu/h (0.2 million W), $2/million Btu ($0.6/ million W)	0.012
Cooling Water, 71,200 gal/h (269,520 L/h), $0.05/1000 gal ($0.01/1000 L)	0.030
Total Utilities Cost	**$0.381**
Labor, 6 People/Shift, $30,000/Person/year	0.756
Supervision and Overhead, 100% of Labor	0.756
Maintenance, 5% of FCI	0.456
Insurance and Taxes, 2% of FCI	0.182
Total Direct Costs	**$3.398**
Depreciation, 10% of FCI	0.912
Total Cost: $160.89/ton ($177.35/tonne) CMA	**$4.310**
Pretax Profit	6.425
Taxes, 40%	2.570
Net Profit	3.855
Cash Flow	4.767
Return on Investment	**52.25%**
Payout Period	1.91 years

Table 69. Economic Evaluation for CMA Production, 200 Tons (181 Tonnes) of MSW/Day

Item	**Annual Cost (in million $)**
Revenue, 7302.4 lb/h (3312.4 kg/h) CMA, $700/ton ($772/tonne)	**$21.469**
Medium, 693.2 gal/h (2624.0 L/h), $0.028/gal ($0.007/L)	0.163
Lime, 1846.4 lb/h (837.5 kg/h), $40/ton ($44/tonne)	0.310
MgO, 834.2 lb/h (378.4 kg/h), $355/ton ($391/tonne)	1.244
Process Water, 16,836.4 lb/h (7637.0 kg/h), $0.20/1000 gal ($0.05/1000 L)	0.003
Solvent Make-Up	0.012
Total Raw Materials Cost	**$1.732**
Electricity, 1957 kW•h (7 GJ), $0.04/kW•h ($0.14/MJ)	0.658
Steam, 1.4 million Btu/h (0.4 million W), $2/million Btu ($0.6/ million W)	0.024
Cooling Water, 142,400 gal/h (539,041 L/h), $0.05/1000 gal ($0.01/1000 L)	0.060
Total Utilities Cost	**$0.742**
Labor, 6 People/Shift, $30,000/Person/year	0.756
Supervision and Overhead, 100% of Labor	0.756
Maintenance, 5% of FCI	0.716
Insurance and Taxes, 2% of FCI	0.287
Total Direct Costs	**$4.989**
Depreciation, 10% of FCI	1.433
Total Cost: $160.89/ton ($177.35/tonne) CMA	**$6.422**
Pretax Profit	15.044
Taxes, 40%	6.018
Net Profit	9.026
Cash Flow	10.459
Return on Investment	**73.01%**
Payout Period	1.37 years

Table 70. Economic Evaluation for CMA Production, 300 Tons (272 Tonnes) of MSW/Day

Item	**Annual Cost (in million $)**
Revenue, 10,953.7 lb/h (4968.6 kg/h) CMA, $700/ton ($772/tonne)	**$32.204**
Medium, 1039.8 gal/h (3936.1 L/h), $0.028/gal ($0.007/L)	0.245
Lime, 2769.7 lb/h (1256.3 kg/h), $40/ton ($44/tonne)	0.465
MgO, 1251.2 lb/h (567.5 kg/h), $355/ton ($391/tonne)	1.866
Process Water, 25,254.6 lb/h (11,455.5 kg/h), $0.20/1000 gal ($0.05/1000 L)	0.005
Solvent Make-Up	0.018
Total Raw Materials Cost	**$2.599**
Electricity, 2899.4 kW•h (10.4 GJ), $0.04/kW•h ($0.14/MJ)	0.974
Steam, 2.1 million Btu/h (0.6 million W), $2/million Btu ($0.6/ million W)	0.035
Cooling Water, 213,600 gal/h (808,561 L/h), $0.05/1000 gal ($0.01/1000 L)	0.090
Total Utilities Cost	**$1.099**
Labor, 6 People/Shift, $30,000/Person/year	0.756
Supervision and Overhead, 100% of Labor	0.756
Maintenance, 5% of FCI	0.952
Insurance and Taxes, 2% of FCI	0.381
Total Direct Costs	**$6.543**
Depreciation, 10% of FCI	1.903
Total Cost: $160.89/ton ($177.35/tonne) CMA	**$8.446**
Pretax Profit	23.758
Taxes, 40%	9.503
Net Profit	14.255
Cash Flow	16.158
Return on Investment	**84.89%**
Payout Period	1.18 years

Table 71. Economic Evaluation for CMA Production, 400 Tons (363 Tonnes) of MSW/Day

Item	Annual Cost (in million $)
Revenue, 14,604.9 lb/h (6624.8 kg/h) CMA, $700/ton ($772/tonne)	**$42.938**
Medium, 1386.4 gal/h (5248.1 L/h), $0.028/gal ($0.007/L)	0.326
Lime, 3692.9 lb/h (1675.1 kg/h), $40/ton ($44/tonne)	0.620
MgO, 1668.2 lb/h (756.7 kg/h), $355/ton ($391/tonne)	2.487
Process Water, 33,672.8 lb/h (15,274.0 kg/h), $0.20/1000 gal ($0.05/1000 L)	0.007
Solvent Make-Up	0.024
Total Raw Materials Cost	**$3.464**
Electricity, 3835 kW•h (13.8 GJ), $0.04/kW•h ($0.14/MJ)	1.289
Steam, 2.8 million Btu/h (0.8 million W), $2/million Btu ($0.6/ million W)	0.047
Cooling Water, 284,800 gal/h (1,078,082 L/h), $0.05/1000 gal ($0.01/1000 L)	0.120
Total Utilities Cost	**$1.456**
Labor, 6 People/Shift, $30,000/Person/year	0.756
Supervision and Overhead, 100% of Labor	0.756
Maintenance, 5% of FCI	1.190
Insurance and Taxes, 2% of FCI	0.476
Total Direct Costs	**$8.098**
Depreciation, 10% of FCI	2.380
Total Cost: $160.89/ton ($177.35/tonne) CMA	**$10.478**
Pretax Profit	32.460
Taxes, 40%	12.984
Net Profit	19.476
Cash Flow	21.856
Return on Investment	**91.82%**
Payout Period	1.09 years

Table 72. Economic Evaluation for CMA Production, 500 Tons (454 Tonnes) of MSW/Day

Item	Annual Cost (in million $)
Revenue, 18,256.1 lb/h (8281.0 kg/h) CMA, $700/ton ($772/tonne)	**$53.673**
Medium, 1733 gal/h (6560 L/h), $0.028/gal ($0.007/L)	0.408
Lime, 4616.1 lb/h (2093.9 kg/h), $40/ton ($44/tonne)	0.776
MgO, 2085.3 lb/h (945.9 kg/h), $355/ton ($391/tonne)	3.109
Process Water, 42,091 lb/h (19,092 kg/h), $0.20/1000 gal ($0.05/1000 L)	0.009
Solvent Make-Up	0.030
Total Raw Materials Cost	**$4.332**
Electricity, 4767 kW•h (17.2 GJ), $0.04/kW•h ($0.14/MJ)	1.602
Steam, 3.5 million Btu/h (1.0 million W), $2/million Btu ($0.6/ million W)	0.059
Cooling Water, 356,000 gal/h (1,347,602 L/h), $0.05/1000 gal ($0.01/1000 L)	0.150
Total Utilities Cost	**$1.811**
Labor, 6 People/Shift, $30,000/Person/year	0.756
Supervision and Overhead, 100% of Labor	0.756
Maintenance, 5% of FCI	1.377
Insurance and Taxes, 2% of FCI	0.551
Total Direct Costs	**$9.583**
Depreciation, 10% of FCI	2.753
Total Cost: $160.89/ton ($177.35/tonne) CMA	**$12.336**
Pretax Profit	41.337
Taxes, 40%	16.534
Net Profit	24.803
Cash Flow	27.556
Return on Investment	**100.08%**
Payout Period	1.00 years

TASK 8. MSW SYNGAS CONTAMINANT STUDY

In discussing syngas composition with gasifier manufacturers, it was found that several contaminants may be present when gasifying MSW. These contaminants include heavy metals such as iron, nickel, zinc, copper, chromium, manganese, mercury, aluminum, vanadium, lead, arsenic, selenium, and cadmium, as well as sulfur compounds and chlorides. The heavy metals are typically present as aerosols in ppm or ppb (parts per billion) concentrations.

Toxicity studies with metals were performed in 150-mL serum bottles with Isolate ERI2 at 37°C and 150 rev/min. The compound was generally added as the chloride, although chromium was added as Na_2CrO_4, arsenic was added as Na_3AsO_4, and selenium was added as Na_2SeO_3. The heavy-metal compound was added to the medium in concentrations ranging from 1 µm to 100 mM. Duplicate experiments were designed for each metal ion and each concentration. Blank experiments with culture in medium without the addition of toxic metal ions were also performed. Cell growth and gas consumption were monitored for each experiment and compared with the blank experiment to determine toxicity levels. Gas consumption was monitored twice per day, and cell optical density (580 nm) was monitored once per day.

Table 73 presents a summary of the results from the 12 metal toxicity tests. As is noted, $FeCl_2$ and $NiCl_2$ are not toxic, even at the 100-mM level. $PbCl_2$ is toxic at 50 mM; Na_2CrO_4, $MnCl_2$, and $AlCl_3$ are toxic at 5 mM; $ZnCl_2$ is toxic at 1 mM; $CuCl_2$ and $HgCl_2$ are toxic at 0.5 mM; $CdCl_2$ is toxic at 50 µM; and Na_3AsO_4 and Na_2SeO_3 are toxic at 10 µM.

Table 73. Results of Batch Metal Toxicity Tests With ERI2*

Metal	Toxicity Level
Fe ($FeCl_2$)	>100 mM
Ni ($NiCl_2$)	>100 mM
Zn ($ZnCl_2$)	1 mM
Cu ($CuCl_2$)	0.5 mM
Cr (Na_2CrO_4)	5 mM
Mn ($MnCl_2$)	5 mM
Hg ($HgCl_2$)	0.5 mM
Al ($AlCl_3$)	5 mM
Cd ($CdCl_2$)	50µM
Pb ($PbCl_2$)	50 mM
As (Na_3AsO_4)	10 µM
Se (Na_2SeO_3)	10 µM

* ERI2 was incubated in batch bottles at 37°C with coal synthesis gas at 1 atm (101 kPa).

The maximum allowable metal chloride concentration at a 10-min GRT and a 10-h liquid retention is as follows for the metals. Assumptions and calculations are given in appendix A.

$FeCl_2$	5000 mg/m^3
$NiCl_2$	5000 mg/m^3
$ZnCl_2$	55 mg/m^3
$CuCl_2$	30 mg/m^3
$CrCl_3$	50 mg/m^3
$MnCl_2$	250 mg/m^3
$HgCl_2$	100 mg/m^3

$AlCl_3$	55 mg/m^3
$CdCl_2$	4 mg/m^3
$PbCl_2$	5000 mg/m^3
$AsCl_3$	0.7 mg/m^3
Se_2Cl_2	0.5 mg/m^3

As is noted, most of the metals studied are not likely to cause toxicity problems during fermentation. However, if cadmium, arsenic, or selenium are present in significant concentrations in the gas stream, they must be removed to prevent poisoning of the culture. Metal chloride removal can be accomplished by gas scrubbing.

TASK 9. RAW MATERIAL STUDY

Although the cost of CMA will be significantly reduced by using the BRI process for acetic acid production, the use of less expensive dolomitic lime, MgO, and potash with lower purities as raw materials must be investigated. The effects of purity on the CMA product must also be addressed.

Quotes were obtained from several manufacturers of dolomitic lime and magnesium oxide. The cost of hydrated dolomitic lime varies little among the manufacturers, ranging from $80 to $90/ton ($88 to $99/tonne), including freight. The lone exception to this is RCS lime dust, produced by Redland Ohio, Inc., which sells for $3.25/ton ($3.58/tonne), plus freight. However, this material is quite high in sulfur and thus would not be a satisfactory material for producing CMA. Based on this information, alternative dolomitic lime raw materials studies will not be fruitful.

Magnesium oxide is used as a supplement to dolomitic lime to boost the magnesium content of the CMA. Commercial processes use 98% magnesium oxide as the source of MgO in order to maximize reactivity and minimize chloride content. As is shown in table 74, magnesium oxide is available from the manufacturer in a variety of purities and reactivities. Magnesium oxide produced from seawater has a purity of 98%, but costs $385/ton ($424/tonne) in bulk. Magnesium oxide processed from natural sources has a lower purity (~93%), but costs only $288/ton ($317/tonne) in bulk. Mag 33, a $MgCO_3$ product, costs only $100/ton ($110/tonne). Mag 33 can be converted into MgO by calcining, which is marketed as MagOx FG at $180 to $215/ton ($198 to $237/tonne). Caustic acitivity in table 74 is a measure of solubility of MgO as determined by the rate of solubilization in 1N acetic acid.

Table 74. Magnesium Oxide Products and Their Costs

MgO Product	Product Data					Price Bag/Bulk ($/ton [$/tonne])
	MgO (%)	Size	Loss on Ignition (%)	Caustic Activity (s)	Surface Area (m^2)	
MagOx 98 HR	98	<200 mesh	3	11	65	$420/385 ($463/424)
MagOx 98 LR	98	<200 mesh	1	17	40	420/385 (463/424)
MagOx 93 HR 325	93	<325 mesh	2.7	6	35	323/288 (356/317)
MagOx 93 LR 325	93	<325 mesh	1	-	-	323/288 (356/317)
Mag 33	91 ($MgCO_3$)	<3/4 in (1.9 cm)	50	-	-	100+del (110+del)
MagneClear 95	95	<325	2	30	25	250 to 300 (276 to 331)

MagOx 98, MagOx 93, and Mag 33 are products from Premier. MagneClear is from Martin Marietta Magnesia Specialties. Mag 33 contains 91% $MgCO_3$ and 27% Mg.

Alternative grades of magnesium oxide were evaluated for their use in CMA production. Analytical experiments were performed on these raw materials to assess their MgO content, Cl^- content, and reactivity with acetic acid in aqueous solution. These data are summarized in tables 75 and 76.

To determine reactivity, 50% excess acetic acid was used to react with different sources of magnesium oxide. The reaction was conducted in aqueous solution. In preparing the MgO/lime mixtures, different sources of MgO were mixed with dolomitic lime in such a way that the molar ratio of Mg:Ca in the mixture was 3:7. Water was added into the mixtures to form slurries. Acetic acid, 50% in excess of stoichiometry, was used for the reaction to obtain CMA.

Table 75. MgO, Cl^-, and SO_4^{2-} Content of Various Raw Materials

Sample	MgO (%)	Chloride (mg/g)	Sulfate (mg/g)	Unreacted (%)
MagOx 98 LR	99.1	0.505 (1.0)*	6.78 (7.0)*	2.13
Mag 33	47.6	0.097	-	53.75
MagOx 93 LR	96.1	0.207	2.70	4.24
MagOx FG	95.9	0.209	0.76	7.72
WCD Dolomitic Lime	-	0.021	-	-
WCD MgO	99.9	0.544	-	-

* Determined by vendor.

Table 76. Reactivity of MgO/Lime Mixtures

Raw Material	Nonreacted Raw Material, (%) dry wt
MagOx 98 LR + Western Lime	3.61
MagOx 93 LR + Western Lime	5.64
MagOx FG + Western Lime	15.42
Mag 33 + Western Lime	57.35

As is noted in the tables, none of the MgO sources contained significant quantities of Cl^-. Mag 33 contains only 47.6% easily available MgO, as measured by Ethylenediaminetetraacetic Acid (EDTA) titration, because it is not calcined. All of the MgO sources except Mag 33 react well with acetic acid.

Table 77 presents the expected SO_4^{2-} and Cl^- levels of BRI-produced CMA using western lime and various grades of MagOx. Three basic assumptions were used in preparing the table:

- Western lime has a negligible SO_4^{2-} content. This is assumed based on raw material and industrial CMA SO_4^{2-} analyses.
- All SO_4^{2-} and Cl^- have been eliminated from the BRI-produced acetic acid/acetate. (This is not quite true yet.)

Table 77. Predicted SO_4^{2-}, Cl^- Content of CMA Using BRI Permeate, Western Lime, and MgO*

	Predicted Ion Content of CMA (mg/g)	
	SO_4^{2-}	Cl^-
MagOx 98 LR	0.74	0.067
MagOx 93 LR	0.31	0.035
MagOx FG	0.09	0.035

* Assumptions:

- Western lime has negligible SO_4^{2-} content.
- All SO_4^{2-} and Cl^- have been eliminated from the BRI permeate.

As is noted in table 77, the impact of using mined MgO (MagOx 93 LR or MagOx FG) in place of seawater-produced MgO (MagOx 98 LR) on SO_4^{2-} and Cl^- analyses is dramatic. The Cl^- of the CMA can be cut in half, and the SO_4^{2-} content can be reduced significantly. Thus, an additional incentive exists in addition to cost in using the lower grades of MgO.

Experiments were next completed in comparing the rates of acetic acid removal from the solvent in producing CMA using dolomitic lime and using the three grades of MgO. Estimated removal rates are shown in table 78.

Table 78. Estimated Rates of Acetic Acid Removal From the Solvent in Producing CMA Using Different Grades of MgO

MgO Grade	Estimated HAc Removal (mN/min)*
MagOx 98 LR	0.82
MagOx 93 LR	0.72
MagOx FG	0.68

* Millinormal/min - representing the concentration decrease from the solvent with time.

As is noted, the rate of removal (as a measure of the rate of transfer of acetic acid from the solvent to form CMA) is not significantly affected by the grade of MgO. This is important since the acid removal rate is proportional to the reactor size for CMA production. With similar rates of acetic acid removal, the reactor size will not be significantly impacted by MgO grade.

The CMA produced from western dolomitic lime and various grades of magnesium oxide were analyzed for pH, as well as the concentrations of calcium, magnesium, acetate, chloride, and sulfate. Samples of industrial CMA were also analyzed as a means of comparison. Results from these analyses are shown in table 79.

Table 79. Analysis of Industrial CMA and BRI CMA Produced From Western Dolomitic Lime and Various Grades of Magnesium Oxide

		BRI CMA	
	Industrial CMA*	With MagOx 98 LR	With MagOx 93 LR
pH			
0.5% solution	9.25	9.22	9.52
1.0% solution	9.35	9.35	9.53
2.0% solution	9.44	9.41	9.53
Cloudiness When Dissolved	Cloudy	Clear	Cloudy
Ca^{2+} content, % (w/w)	9.00	7.33	8.40
Mg^{2+} content, % (w/w)	11.14	11.18	12.15
Ac^- content, % (w/w)	68.26	61.83	64.98
Cl^- content, % (w/w)	<0.001	2.31	0.79
SO_4^{2-} content, % (w/w)	0.10	0.15	0.15

* Produced from western dolomitic lime and MagOx 98 LR.

As is noted in the table, the pH formed when dissolving each of the CMA products in water was 9.2 to 9.5. This relatively low pH indicates that significant quantities of undissolved lime are not present in the CMA. Industrial CMA and BRI-produced CMA using MagOx 93 LR showed some cloudiness when dissolved in water, likely due to the presence of a small amount of insolubles.

The Ca^{2+}, Mg^{2+}, and acetate concentrations in each of the samples were essentially the same. The ratio of

Mg^{2+}/Ca^{2+} can, of course, be easily manipulated by changing the proportion of MgO to lime fed to the CMA reactor. The Cl^- content of the samples ranged from 0.79% to 2.31% in the BRI samples, but was negligible in the industrial sample. Additional experiments must thus be performed to bring the Cl^- concentration to acceptable levels. The sulfate content ranged from 0.1% for the industrial sample to 0.15% for the two BRI samples.

The data in table 79 show that CMA produced with a combination of western dolomitic lime and MgO contains very little SO_4^{2-} or Cl^- as contaminants, regardless of the grade of MgO utilized. Commercial CMA, which is prepared using glacial acetic acid, western dolomitic lime, and MagOx 98 LR MgO, was shown to contain <0.001% (w/w) Cl^- and 0.10% SO_4^{2-}. Thus, any SO_4^{2-} or Cl^- found in the BRI CMA product was from the impurities present in the medium. Chloride levels of 0.8 to 2.3 (w/w) were found.

A final fermentation run was performed to essentially eliminate chloride from the fermentation medium (see Task 10 for detailed results). The chloride content of the medium was reduced from –80 ppm to 8.5 ppm. The resulting permeate showed a Cl^- concentration of 6.5 ppm. This change should result in Cl^- concentrations in the CMA of 0.1% to 0.2%, which should be satisfactory for environmental applications.

Significance

A significant cost-savings can be realized by using lower grades of MgO for CMA production. Inerts in the MgO are simply removed by filtration from the CMA/water solution after production of CMA from acetic acid in the solvent phase. Fermentation studies show that the Cl^- and SO_4^{2-} levels in the permeate can be reduced to near zero.

TASK 10. MEDIUM OPTIMIZATION STUDY

Experiments were performed in order to carry out the fermentation with lower concentrations of sulfur and chloride in the medium. It was earlier shown that the BRI-produced CMA contained high levels of sulfur and chloride, which could make it less desirable environmentally.

Sulfate Reduction

The major source of sulfur in the medium is the reducing agent cysteine-HCl. An experiment was thus performed to minimize the sulfur in the medium in such a way that the product CMA also contains a low concentration of sulfate. As a first step, the concentration of cysteine-HCl in the medium was reduced gradually to determine the lowest level of sulfur acceptable in the fermentation without sacrificing gas uptake.

A gas mixture containing 14.39% H_2, 64.69% N_2, 13.31% CO, and 7.61% CO_2 was used as the feedstock. The liquid retention time in the reactor was 9.0 h with a 5.4% cell purge. The experiment started with a medium containing 1.42 mM cysteine-HCl. The gas flow rate was gradually increased and brought to the highest level possible without excessive foam formation. The reactor remained at this level for a few days to confirm steady-state. After steady-state was established, the cysteine concentration in the medium was reduced to 1.14 mM at 147 h. Again at 287 h, the cysteine concentration was reduced to 0.85 mM. Finally, at 600 h, the cysteine concentration was reduced to 0.28 mM.

Figures 14 through 16 show changes in gas uptake, gas conversion, and cell concentration during this study. In all subsequent figures showing CO and H_2 conversion, the CO conversion is the upper line. As is shown in the figures, the gas uptake and conversions (both H_2 and CO) continued to be unaffected by the reduced concentration of cysteine. However, with 0.28 mM cysteine, the hydrogen uptake started dropping sharply. The cysteine concentration was thus increased back to 0.57 mM, and the reactor was allowed to again reach a steady-state.

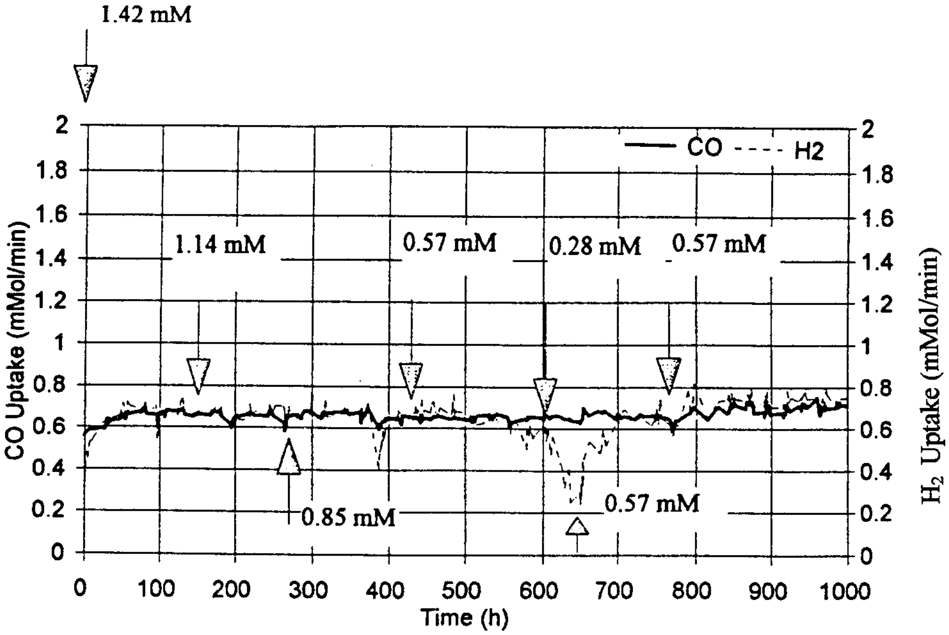

Figure 14. Gas Uptake in the CSTR

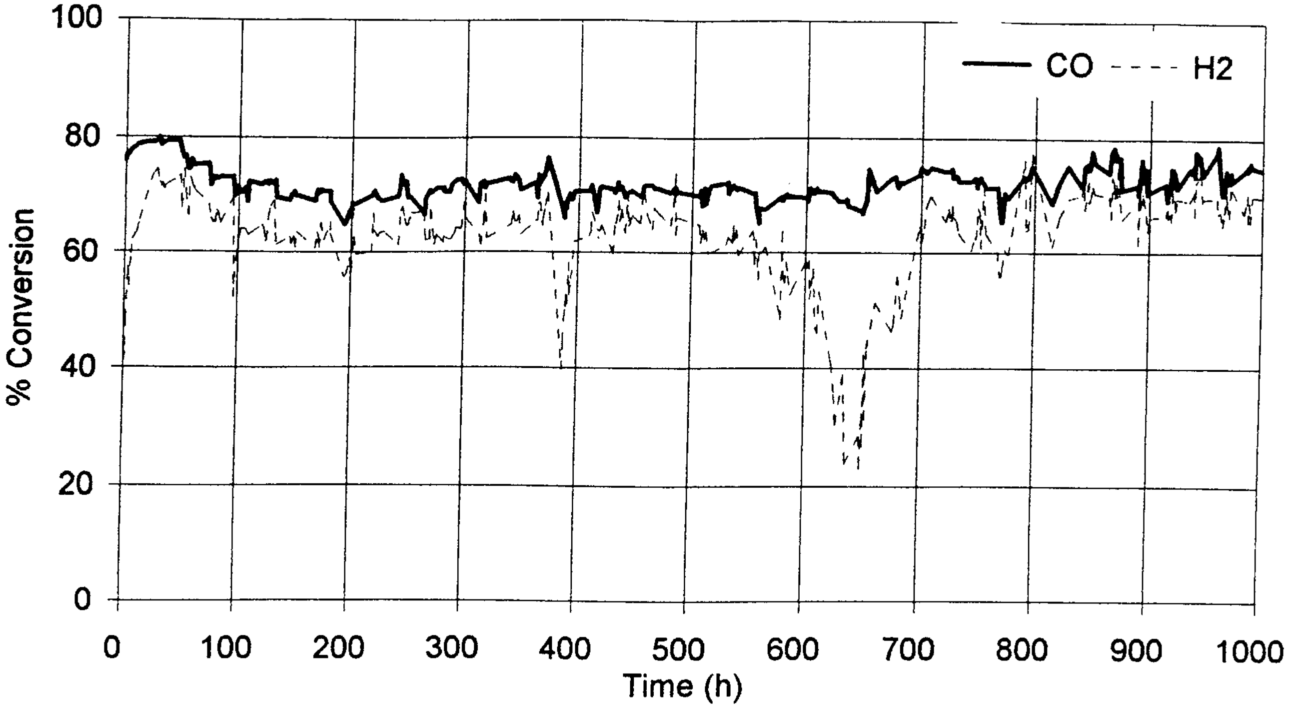

Figure 15. Gas Conversions in the CSTR

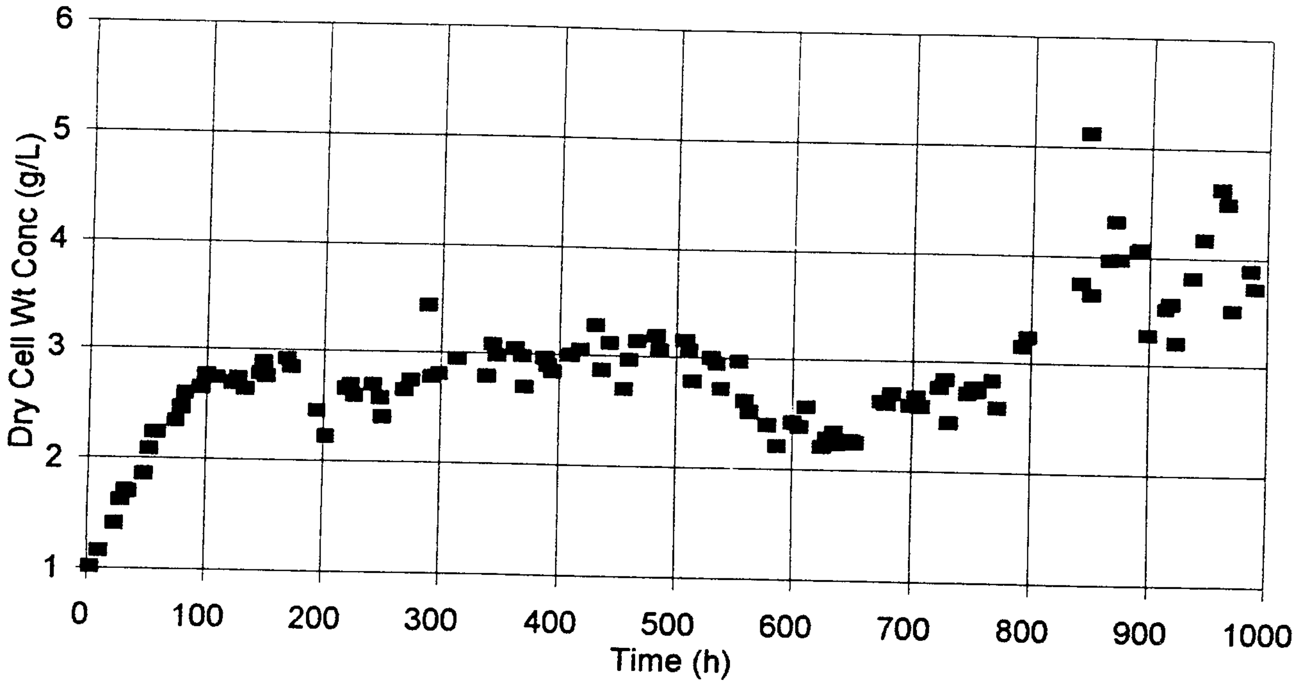

Figure 16. Dry Cell Weight Concentrations in the CSTR

At 769 h, the sulfur source in the medium was changed to sodium sulfide. The concentration of sodium sulfide in the medium was maintained at 0.57 mM. The gas uptake (both H_2 and CO) reached a marginally higher level with the sodium sulfide as the sulfur source. The cell concentration was also higher with the sodium sulfide feed. It is probable that the sulfur is more readily available to the cells from sulfide rather than from cysteine. The occasional drop in cell concentration is due to cell recycle failure and reactor washout during the night, which were taken care of promptly.

Experiments were continued with the same concentration of sulfide, with the permeate used for the production of CMA. The liquid dilution rate and gas flow rate must be adjusted so that the reactor produces at least 15 g/L combined acetate plus acetic acid. To accomplish this change, the GRT was maintained at 6.9 min, and the liquid retention time (LRT) was gradually increased with time from 9.25 h to 14.4 h.

Figures 17 through 20 show gas uptake, gas conversion, cell concentration, and product concentration inside the reactor with time. The system works quite well with Na_2S as the sulfur source. With increasing liquid retention time, the total acetic acid concentration (acetic acid plus acetate) increased from 10 to more than 15 g/L.

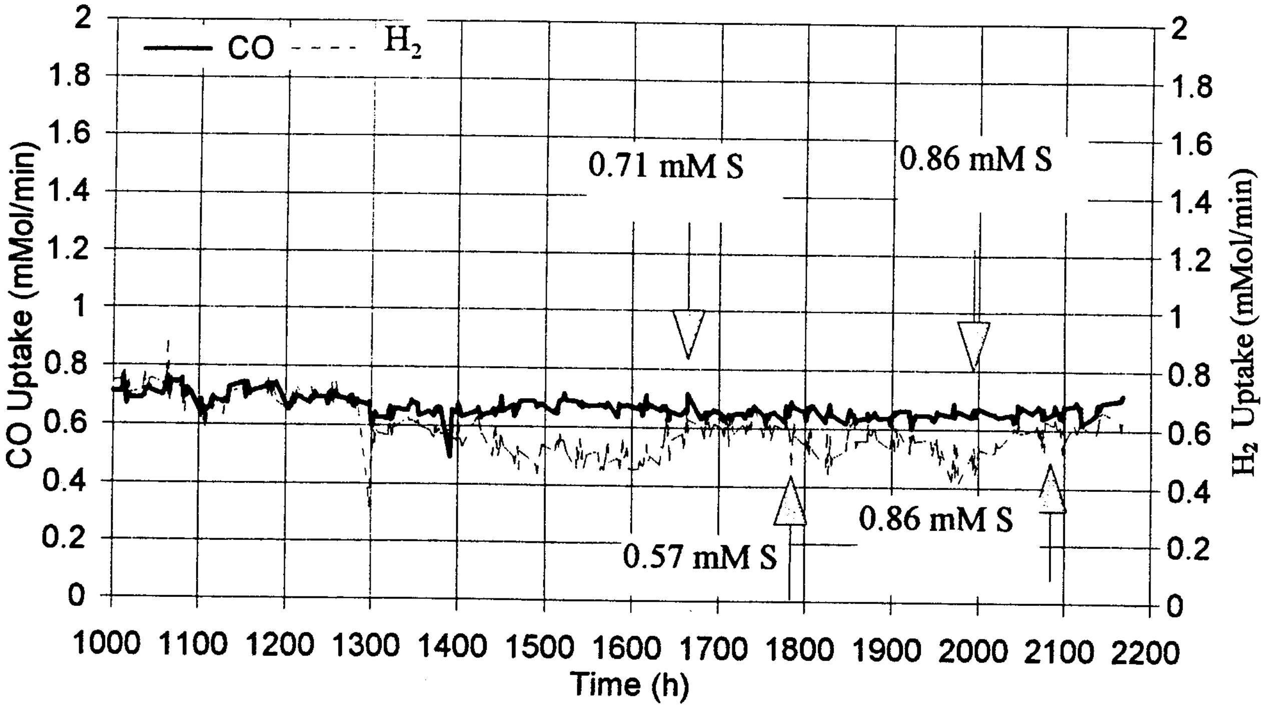

Figure 17. Gas Uptake in the CSTR When Using Na_2S as the Sulfur Source

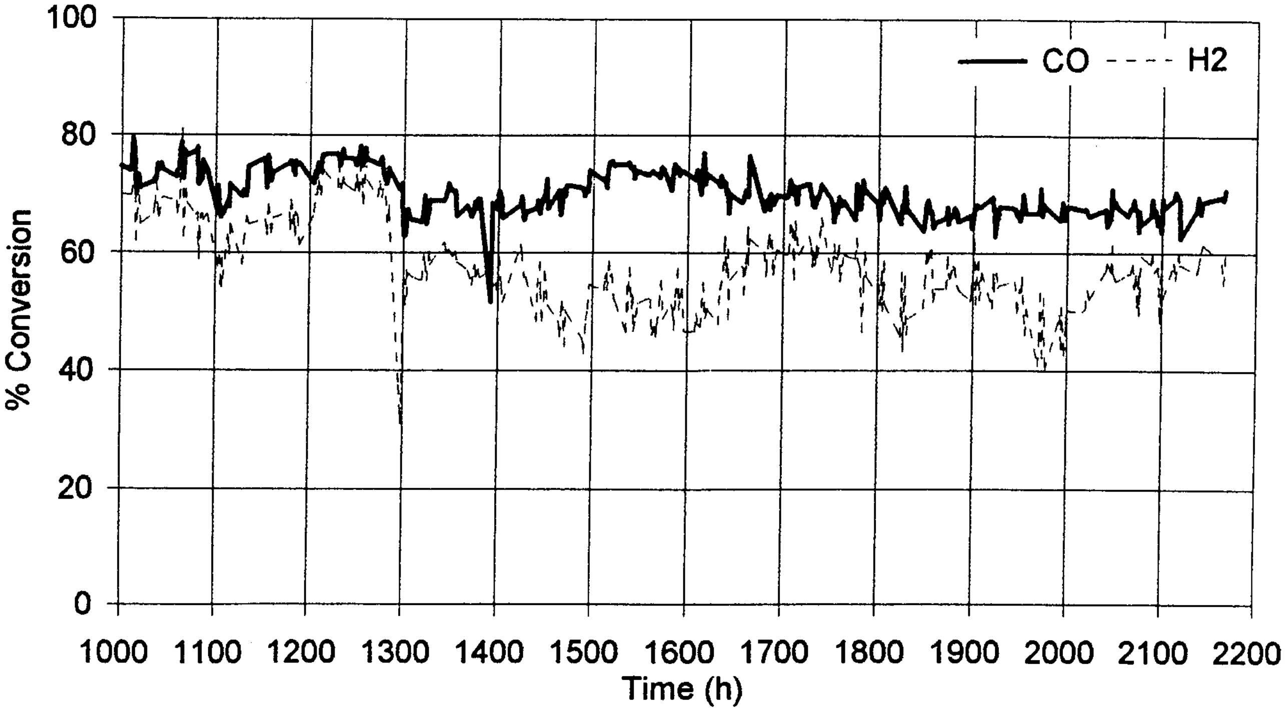

Figure 18. Gas Conversions in the CSTR When Using Na_2S as the Sulfur Source

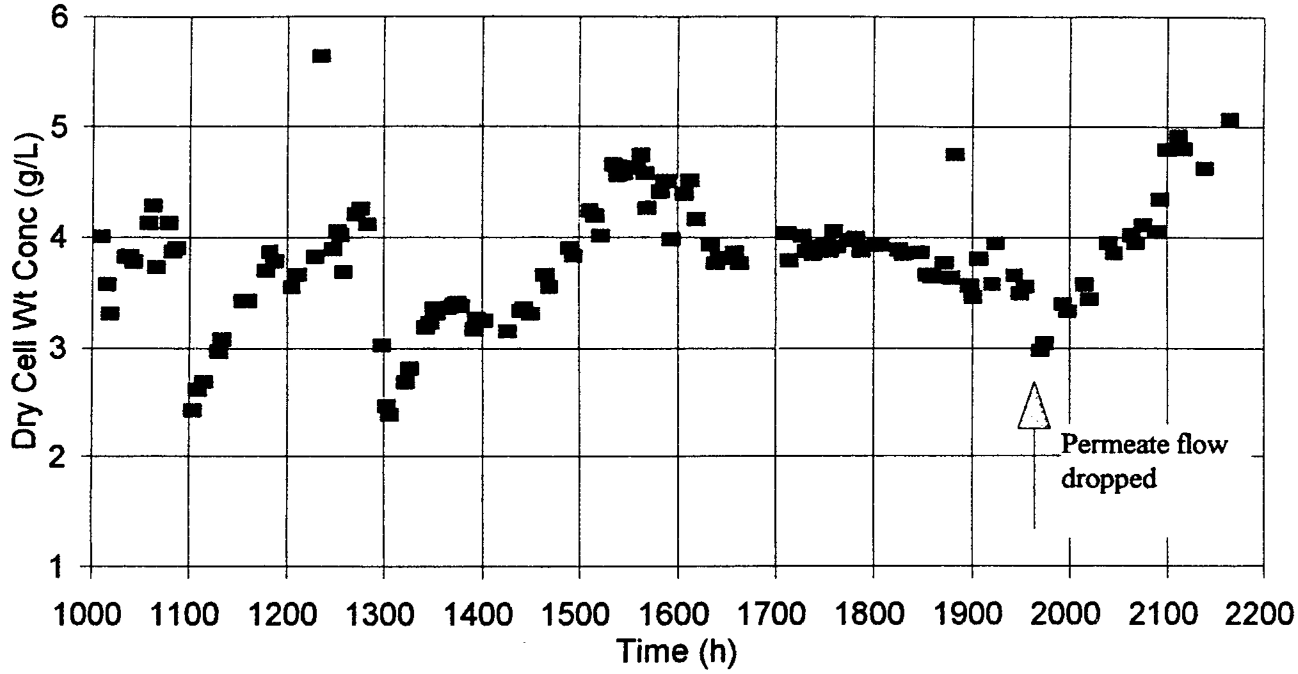

Figure 19. Dry Cell Weight Concentrations in the CSTR When Using Na_2S as the Sulfur Source

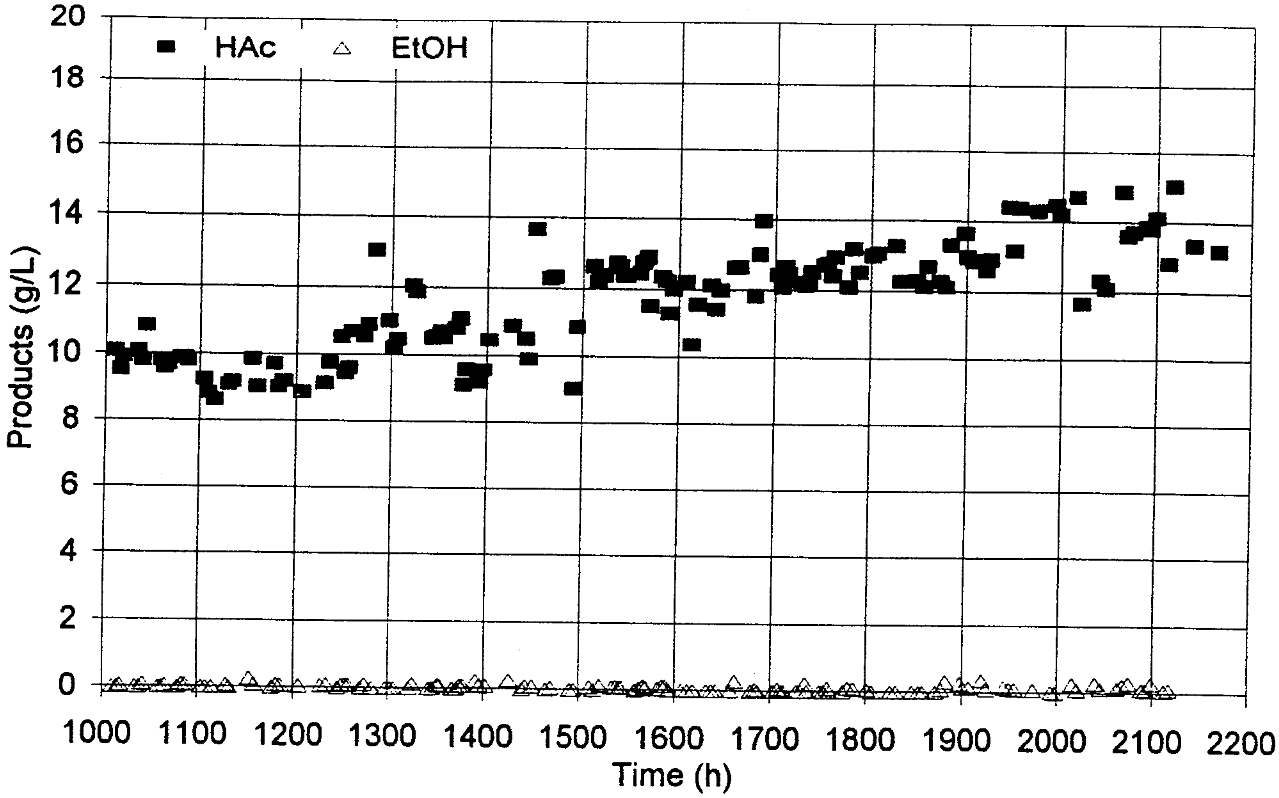

Figure 20. Product Concentrations in the CSTR When Using Na_2S as the Sulfur Source

Chloride Reduction

As was noted in Task 9, a fermentation run was performed with only 8.5 ppm Cl^- in the fermentation medium, which is a factor of 10 less than the already reduced medium. Figures 21 through 23 show cell concentrations, gas conversions, and product concentrations in the CSTR with cell recycle as a function of time. The low Cl^- was added at 2280 h and run for 18 liquid retention times. As is noted in the figures, performance in the reactor was not altered by the changes in medium. The slight decrease in H_2 conversion noted in figure 2 was because of the accompanying decrease in pH with the substitute medium. A lower Cl^- concentration in the resulting CMA is thus possible.

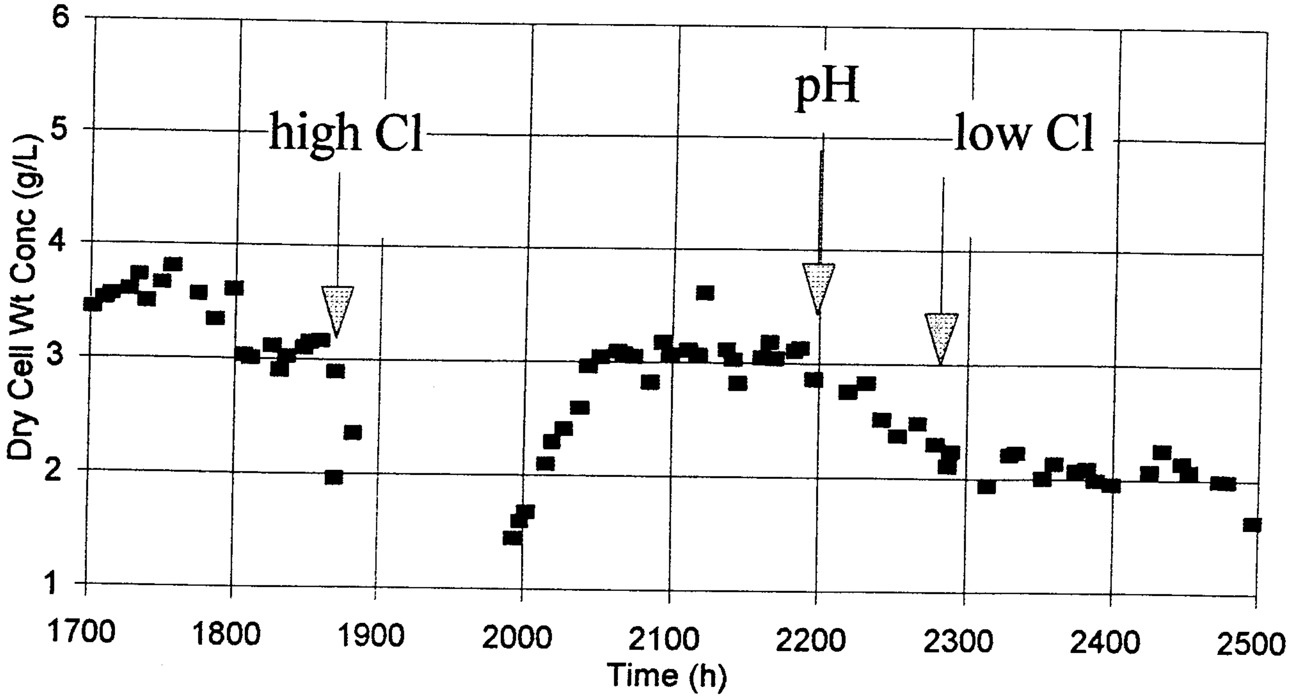

Figure 21. Cell Concentration in the CSTR With Cell Recycle Using Reduced Chloride Levels to 8.5 ppm

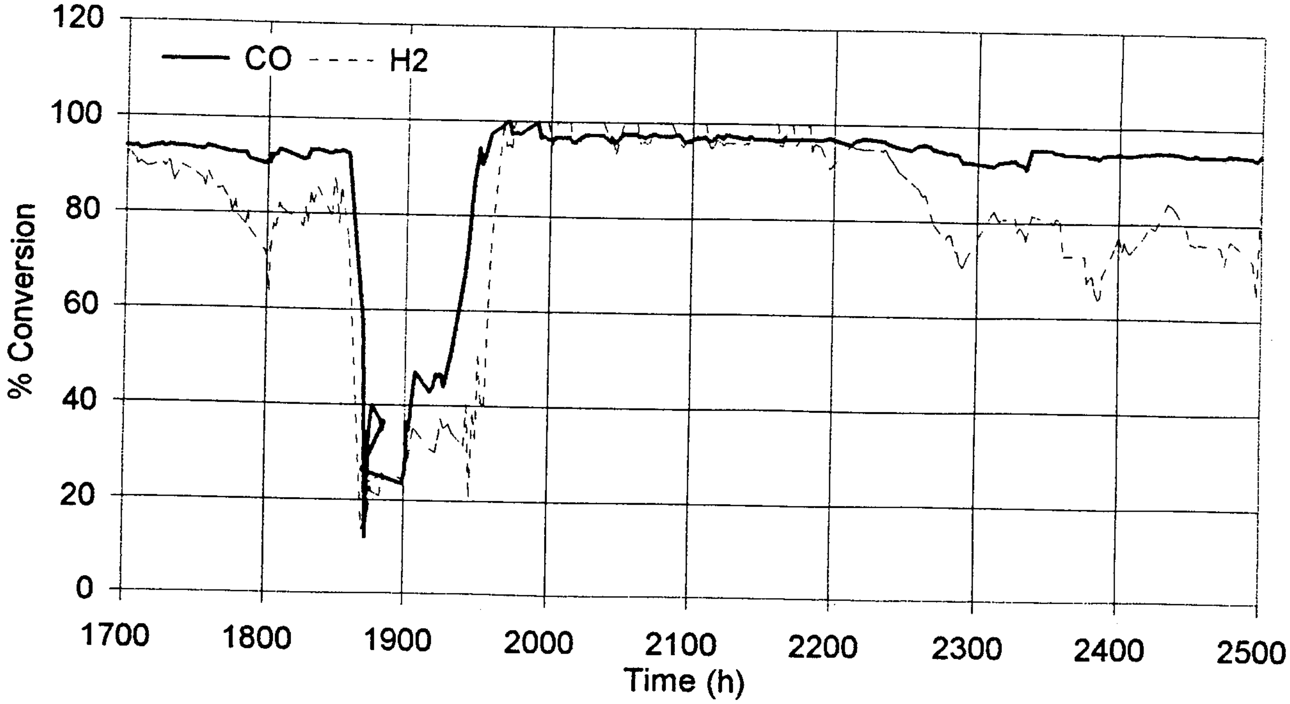

Figure 22. Gas Conversions in the CSTR With Cell Recycle Using Reduced Chloride Levels to 8.5 ppm

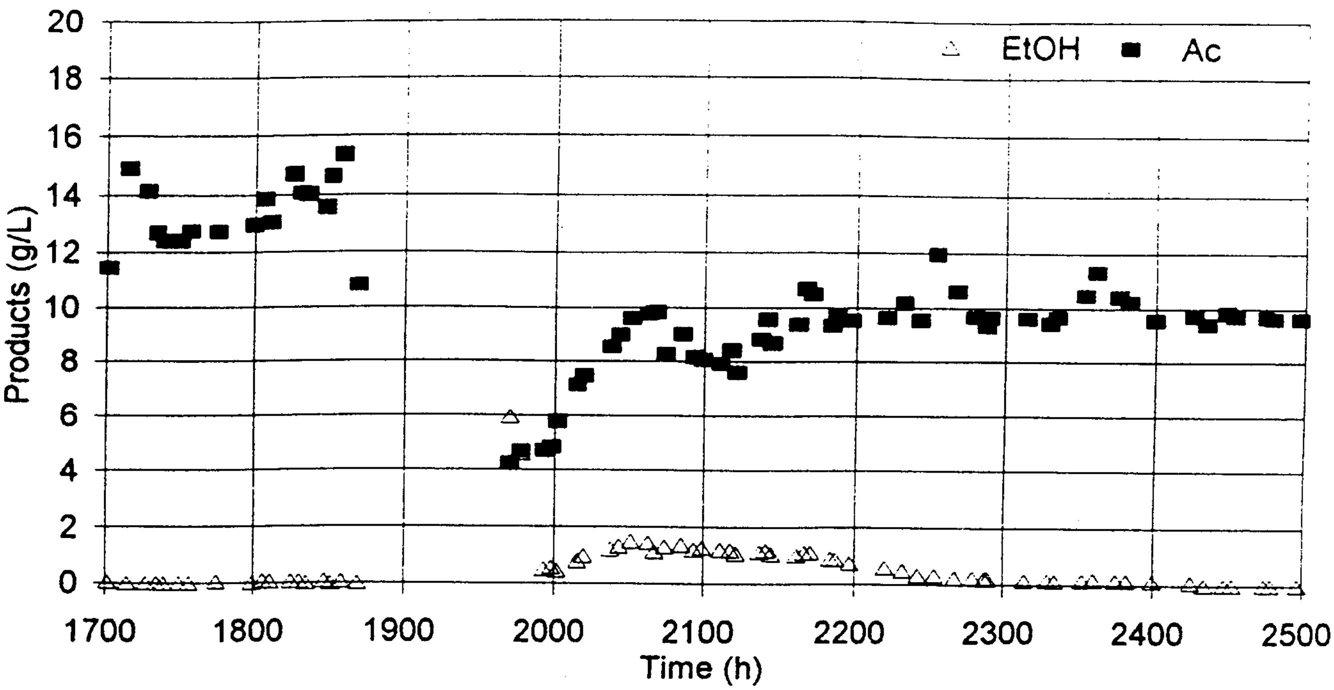

Figure 23. Product Concentrations in the CSTR With Cell Recycle Using Reduced Chloride Levels to 8.5 ppm

TASK 11. DESIGN REVISIONS

Three major design revisions were made as a result of performing Tasks 8 through 10:

- A medium containing less chloride, sulfate, and reducing agent was substituted for the more expensive nutrient medium.
- 93% MgO produced by mining was substituted for 98% MgO produced from seawater, yielding a significant reduction in raw materials cost. (A further cost-reduction may be possible by substituting feed grade MgO for 93% MgO.)
- The CMA reactor was modified to include pH control, and the CMA was produced from this reactor as a nearly saturated solution that will be sent to drying/pelletizing.

The effects of these design changes are reflected in the fixed-capital investment, utility summary, and economic evaluation presented in tables 80 through 82, respectively. The basis for this design is the production of 18,000 lb/h (8165 kg/h) of CMA from 500 tons (454 tonnes) of MSW/day. In this analysis, CMA sells for $1100/ton ($1213/tonne). Dolomitic lime costs $86/ton ($95/tonne) and MgO costs $288/ton ($317/tonne). The return on the investment is 166%, and the payout is 0.6 years. The breakeven cost for CMA is $167/ton ($184/tonne). If the CMA sells for only $700/ton ($772/tonne), the return on the investment is 99%.

Table 80. Revised Fixed-Capital Investment, 500 Tons (454 Tonnes) of MSW/Day

Section	**FCI ($)**
Gasifier	$8,000,000
Fermenter	3,795,000
Cell Recycle	9,858,000
Acetic Acid Extraction	2,958,000
CMA Production	2,922,000
Total	**$27,533,000**

Table 81. Revised Utility Summary, 500 Tons (454 Tonnes) of MSW/day

Section	**Electricity (kW≅h [GJ])**	**Steam (million Btu/h [million W])**	**Cooling Water (thousand gal/h [thousand L/h])**
Gasifier	1520 (5.5)	-	40.0 (151.4)
Fermenter	1067 (3.8)	3.5 (1.0)	198.0 (749.5)
Cell Recycle	850 (3.1)	-	-
Acid Extraction	577 (2.1)	-	-
CMA Production	753 (2.7)	-	118.0 (446.7)
Total	4767 (17.2)	3.5 (1.0)	356.0 (1347.6)

- = not required

**Table 82. Revised Economic Evaluation for CMA Production,
500 Tons (454 Tonnes) of MSW/Day**

Item	Annual Cost (in million $)
Revenue, 18,256.1 lb/h (8281.0 kg/h) CMA, $1100/ton ($1213/tonne)	**$84.343**
Raw Materials	
Medium, 1733 gal/h (6560 L/h), $0.028/gal ($0.007/L)	0.408
Lime, 4616.1 lb/h (2093.9 kg/h), $86/ton ($95/tonne)	1.667
MgO, 2197.4 lb/h (996.7 kg/h), $288/ton ($317/tonne)	2.658
Process Water, 42,091 lb/h (19,092 kg/h), $0.20/1000 gal ($0.05/1000 L)	0.009
Solvent Make-Up	0.030
Total Raw Materials Cost	**$4.772**
Utilities	
Electricity, 4767 kW•h (17.2 GJ), $0.04/kW•h ($11/GJ)	1.602
Steam, 3.5 million Btu/h (1.0 million W), $2.0/million Btu ($1.89/million KJ)	0.059
Cooling Water, 356,000 gal/h (1,347,602 L/h), $0.05/1000 gal ($0.01/1000 L)	0.150
Total Utilities Cost	**$1.811**
Labor, 6 People/Shift, $30,000/Person/year	0.756
Supervision and Overhead, 100% of Labor	0.756
Maintenance, 5% of FCI	1.377
Insurance and Taxes, 2% of FCI	0.551
Total Direct Costs	**$10.023**
Depreciation, 10% of FCI	2.753
Total Cost: $167/ton ($184/tonne) CMA	**$12.776**
Pretax Profit	71.567
Tax, 40%	28.627
Net Profit	42.940
Cash Flow	45.693
Return on Investment	**166%**
Payout Period	0.6 years

TASK 13. IMPURITIES IN BRI-PRODUCED POTASSIUM ACETATE (KAc)

In producing CMA from acetic acid and dolomitic lime supplemented with MgO, commercial manufacturers use 98% MgO in order to maximize reactivity and minimize the chloride content of the CMA. Studies at BRI showed that alternative grades of MgO are commercially available, ranging from 91% purity (Mag 33) to 98% purity (MagOx 98 LR or 98 HR). These grades contain a range of concentrations of chloride, sulfate, and other impurities/inerts, and generally vary in cost with the MgO content. CMA production studies with these various grades of MgO showed that MagOx 93 (93% MgO) could replace MagOx 98 (98% MgO) at a reduced cost without negatively affecting the final CMA product. Insoluble inerts present in the CMA reactor when using MagOx 93 could be separated from the CMA solution by simple filtration. Studies with dolomitic lime alternatives, however, showed no cost-savings potential.

The production of KAc from acetic acid and caustic potash might similarly benefit from the use of lesser grades of caustic potash, if available. Indeed, very preliminary studies indicated that a crude potash exists that might be suitable for KAc production at a reduced cost. The purpose of this task was thus to evaluate different grades of potash and their costs, and to perform laboratory studies, if necessary, to identify impurities and their concentrations in the final KAc product.

Vendors were contacted in establishing specifications and costs for potash alternatives. Each of the vendors indicated that they sold only two potash products — potash and caustic potash. Potash is KCl, which would not neutralize the acetic acid and would yield significant quantities of Cl^- in the KAc if it did react. Thus, potash is not a viable alternative for KAc production. Caustic potash, or KOH, is available in liquid form either as a 45% or 50% solution, or in solid form as flakes, crystals, or briquettes. Caustic potash grades include technical, standard, commercial, industrial, and membrane grades.

A comparison of specifications for the grades and caustic potash forms is shown in table 83. As is noted, the specifications of the various alternatives are essentially only a function of the water content of the alternative. In other words, the KOH, carbonate, chloride, chlorate, sodium, iron, and mercury content of the alternatives are essentially the same when placed on a dry basis. The exception to this is the mercury content of the alternatives, which is very low for membrane grade caustic potash and rather high for commercial and industrial grades. It is apparent that all of the alternatives are manufactured from the same sources. The best alternative for KAc production will thus involve price instead of caustic potash composition.

Table 84 shows a comparison of costs for various alternatives given by a number of vendors. It is apparent that liquid caustic potash (45% to 50% solutions) available from either Oxychem or ASHTA Chemicals is the least expensive alternative. A 45% solution of KOH is sufficiently high to yield a 50% solution of KAc.

Table 83. Commercially Available Grades of Caustic Potash

Source/Grade	(Wt % as KOH)	Carbonates (Wt % as K_2CO_3)	Chlorides (Wt % as KCl)	Chlorates (Wt % as $KClO_3$)	Sodium (ppm)	Iron (ppm)	Mercury (ppm)
Oxychem, standard flake	90 min	0.44 max	0.015 max	0.0003 max	-	2 max	0.1 max
Oxychem, standard crystal	90 min	0.44 max	0.015 max	0.0003 max	-	2 max	0.1 max
Oxychem, briquettes	90 min	0.44 max	0.015 max	0.0003 max	-	15 max	0.1 max
Vulcan, tech grade, 45% solution	45-47 min	0.10 max	0.005 max	0.0003 max	100 max	2 max	0.1 max
Oxychem, commercial grade, 45% solution	45 min	0.1 max	0.005 max	0.0003 max	-	2 max	0.25 max
Oxychem, industrial grade, 45% solution	45 min	0.1 max	0.005 max	0.0003 max	-	2 max	0.25 max
Oxychem, membrane grade, 45% solution	45 min	0.1 max	0.005 max	0.0003 max	-	2 max	<0.005 max

- = not measured or not available

Table 84. Price Quotes for Caustic Potash

Vendor	Product Name	Quote ($/ton [$/tonne])
Mallinckrodt Chemicals	Potassium Hydroxide (food grade)	$3900 ($4299)
Mallinckrodt Chemicals	Potassium Hydroxide (ACS)	4360 (4806)
Oxychem	Caustic Potash (flake, crystal, or briquette)	1040* (1146)
Oxychem	Caustic Potash (45% or 50% solution)	302* (333)
ASHTA Chemicals	Caustic Potash (flake or briquette)	1037* (1143)
ASHTA Chemicals	Caustic Potash (45% or 50% solution)	345* (380)

* Freight rates included in quote.

TASK 14. CARBON BED ADSORPTION

Water recycle from the extractor was studied to demonstrate that the solvent and other accumulated biomaterials do not hinder the fermentation process. The feed gas was synthetic MSW syngas, and contained 28.5% H_2, 33.0% N_2, 31.7% CO, and 6.8% CO_2.

Water Recycle With Carbon Bed Adsorption

The recycle water was prepared by extraction with solvent, glass wool filtration, and carbon filtration. The medium was not autoclaved. All nutrients were added in their normal concentrations to prepare the medium. Steady-state was reached before feeding the recycle water, and the gas flow rate was reduced by about 25% so that the total acetic acid plus acetate concentration did not reach inhibitory levels. Figures 24 through 27 show reactor performance data for the water recycle study. Water recycle was initiated at time (t) = 2072 h, and lasted about 100 h or approximately eight liquid retention times. At this time, performance dropped due to high levels of free acid in the reactor.

The medium was changed to a fresh-water medium at t = 2295 h. Several changes were made to the medium, and the carbon bed was changed out at t = 2505 h. The gas supply to the reactor was changed at t = 2700 h. With the change, oxygen was apparently introduced into the reactor. Approximately 1 week was required to get the reactor back to the original operating conditions. During this time, water was not recycled and water was not collected for later recycling. However, the water from the operating time before the process upset was saved for later use.

The reactor recovered by t = 2900 h. Water recycle was begun again, with the saved water used from the first recycle. Five additional water recycles were performed for a total of 13 recycles on the carbon filter. A small dip in performance was noted at t = 3050 h. This drop is due to an inefficient last acid extraction, which ultimately caused the free-acid concentration in the reactor to approach inhibitory levels.

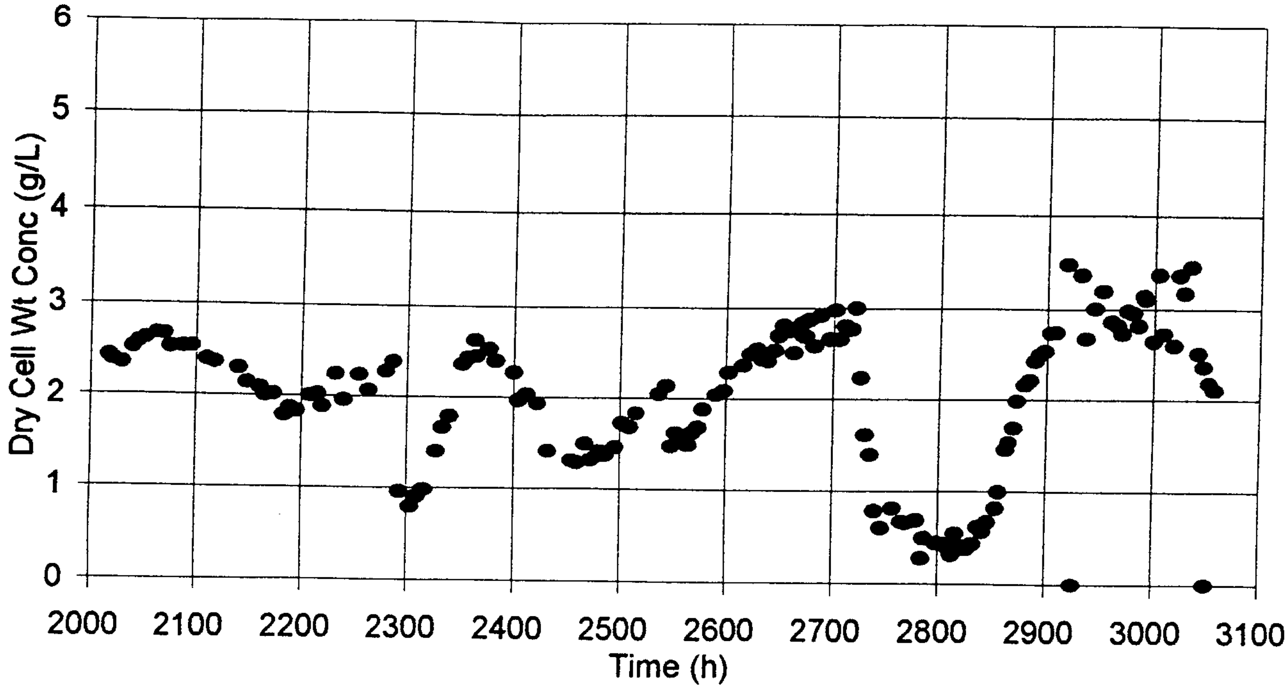

Figure 24. Dry Cell Weight Concentration in the Water Recycle Study with Carbon Bed Adsorption

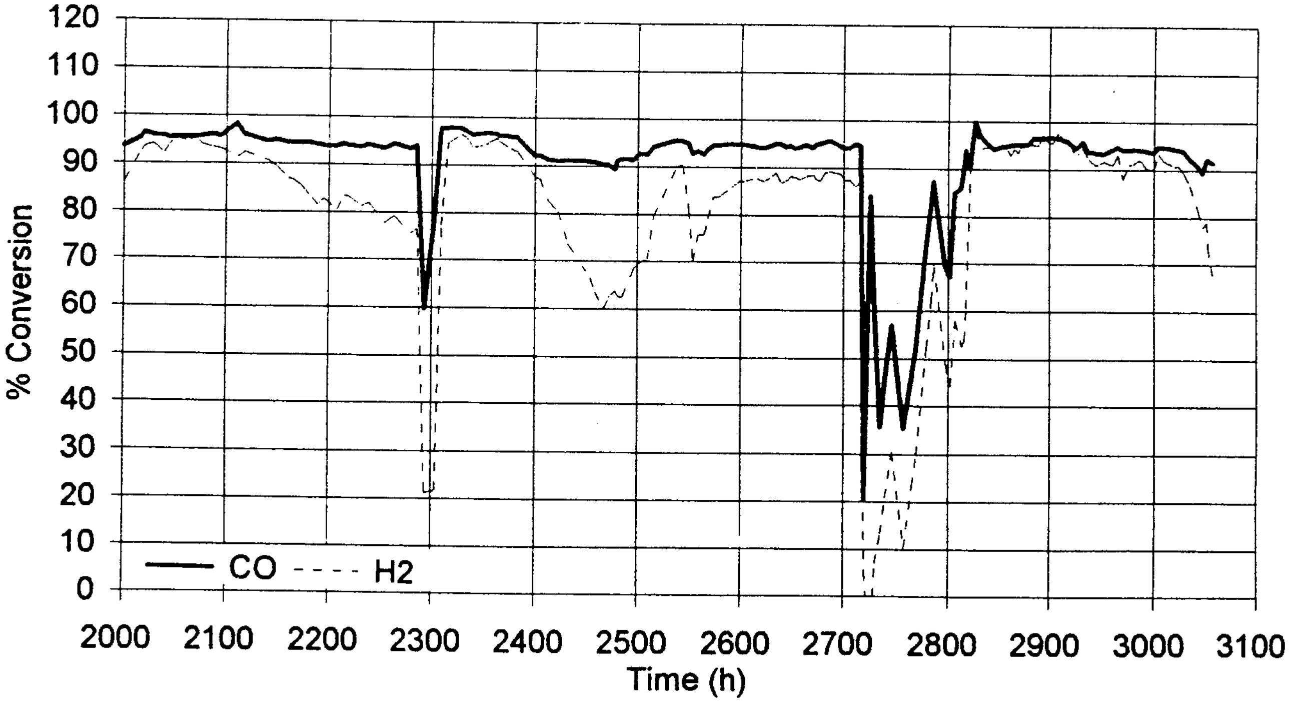

Figure 25. Gas Conversions in the Water Recycle Study with Carbon Bed Adsorption

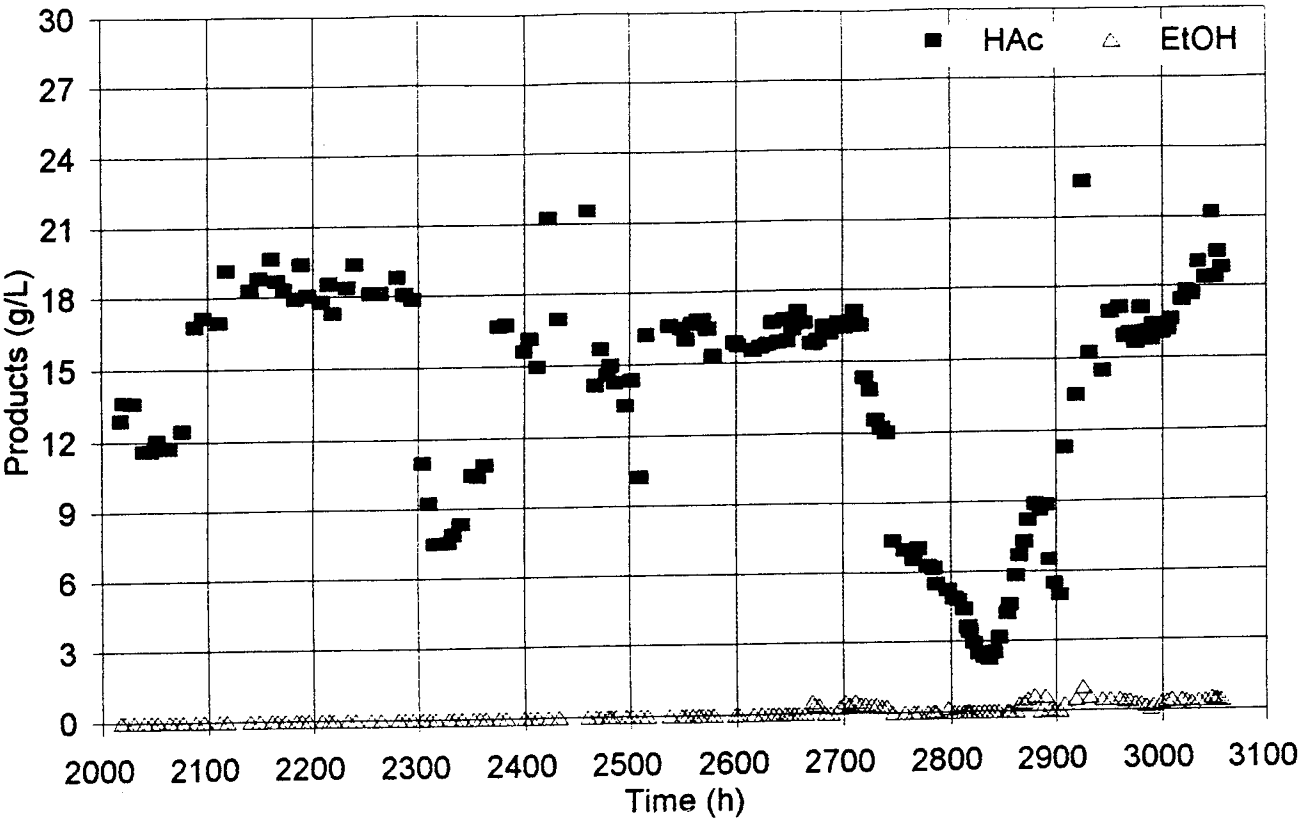

Figure 26. Product Concentrations in the Water Recycle Study With Carbon Bed Adsorption

Water Recycle Without Carbon Bed Adsorption

A series of water recycle experiments were next performed without carbon bed adsorption. In these studies, the reactor permeate was extracted with solvent, and KOH was used to remove acid in the same manner as it would be used in the production of potassium acetate. Water from the acid recovery/KAc production process was then recycled back to the reactor without further treatment.

Figures 27 through 29 show the effects of water recycle without carbon bed treatment on cell growth, gas conversions, and product formation in the CSTR with cell recycle. In these plots, t = 3000 h refers to the end of the previous reporting period in which water recycle with carbon bed adsorption was tested. After a period of time in which water was not collected or recycled, the recycle study without carbon bed filtration was started at t = 3214 h. The study continued for 170 h, during which time the recycle water was recycled 11 times. At t = 3384 h, a drop in performance (cell concentration and gas conversion) was noted, and the water recycle study was stopped. The reason for this drop in performance was a build-up of free acetic acid inside the reactor to inhibitory levels due to poor acid removal from the permeate. The recycle water was thus saved from t = 3384 h, and water recycle was stopped. Water was not collected from t = 3384 h to t = 3481 h, but instead, fresh-water medium was fed to the reactor.

Water recycle was restarted at t = 3481 h, but this time a two-stage extraction was used on the permeate to minimize the quantity of acid sent back to the reactor. Water recycle continued for about 450 h, bringing the total number of water recycles without carbon bed adsorption to 14. Water recycle without carbon bed treatment is thus quite feasible, but it is important to keep the free acetic acid concentration in the reactor below inhibitory levels.

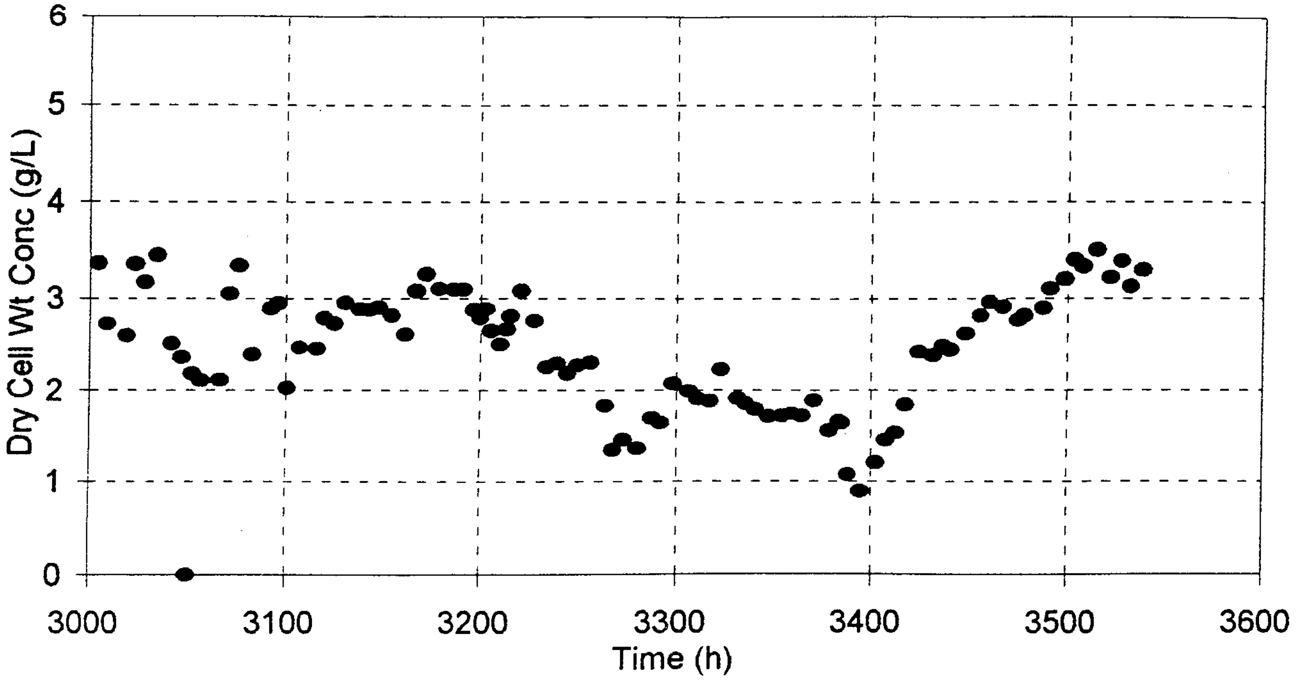

Figure 27. Dry Cell Weight Concentration in the Water Recycle Study Without Carbon Bed Adsorption

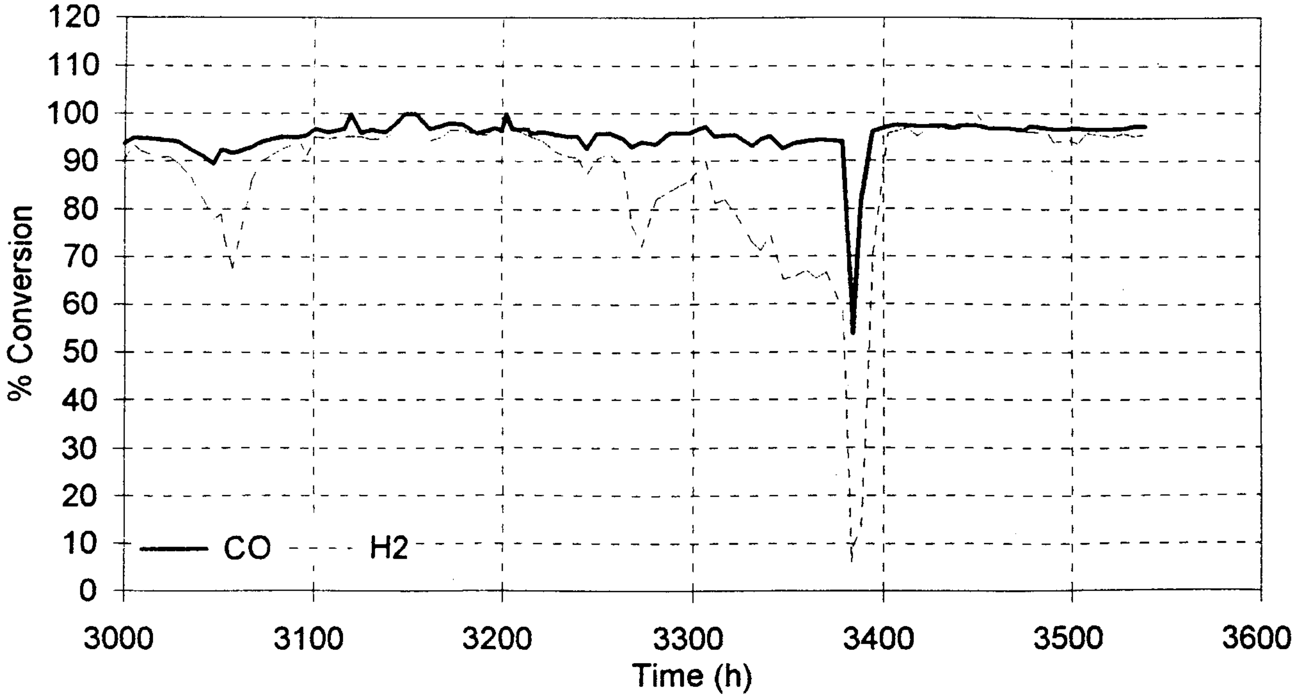

Figure 28. Gas Conversions in the Water Recycle Study Without Carbon Bed Adsorption

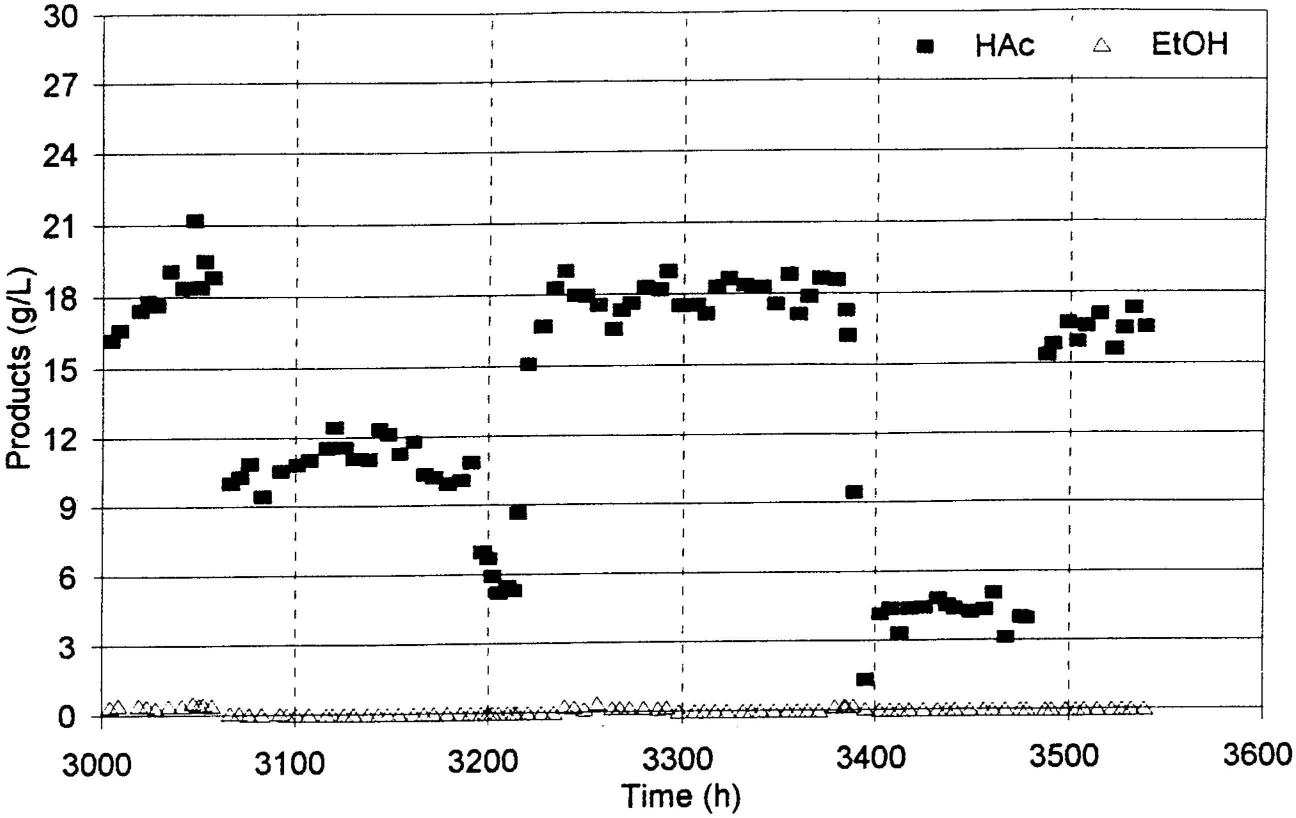

Figure 29. Product Concentrations in the Water Recycle Study Without Carbon Bed Adsorption

TASK 15. EQUIPMENT SPECIFICATIONS/ECONOMIC PROJECTIONS

CMA Production Economics

Revised economic projections have been prepared for the production of CMA and KAc from MSW and sewage sludge based on additional Phase II research results and the costs of various grades of raw material for CMA production. The equipment is essentially the same as projected earlier. Capital costs, a utility summary, and an economic evaluation for a base-case process using 500 tons/day (454 tonnes/day) of MSW and using 98% MgO as a raw material for CMA production are shown in tables 85 through 87, respectively. Changes in the process from earlier projections are a lower allowable free-acid concentration in the fermenter and revised capital costs based on first quarter 1997. As is noted in table 85, a fixed-capital investment of $35.4 million is required for the plant in processing 500 tons/day (454 tonnes/day) of MSW into 77,000 tons/year (69,854 tonnes/year) of CMA. The largest capital cost is for the cell recycle system, accounting for 44% of the fixed-capital investment. Table 86 shows that 5000 kW h (18 GJ) of electricity, 3.5 million Btu/h (1.0 million W) of steam, and 280,000 gal/h (1,059,912 L/h) of cooling water are required to run the process.

The economic evaluation is summarized in table 87. Revenue, at $700/ton ($772/tonne) of CMA, totals $53.7 million/year. The total operating costs, including raw materials, utilities, and fixed charges, total $13.8 million/year or $180/ton ($198/tonne) of CMA. The return on the investment is 77.6%. If the cost of CMA is increased to its current market value of $1100/ton ($1213/tonne), the return on the investment increases to 130%.

Table 85. Fixed-Capital Investment for Base-Case Economics in Producing CMA From 500 Tons (454 Tonnes) of MSW/Day

Section	FCI ($)
Gasifier	$8,000,000
Fermenter	3,695,000
Cell Recycle	15,556,000
Acetic Acid Extraction	4,700,000
CMA Production	3,468,000
Total	**$35,419,000**

Table 86. Utility Summary for Base-Case Economics in Producing CMA From 500 Tons (454 Tonnes) of MSW/Day

Section	Electricity (kW·h [GJ])	Steam (million Btu/h [million W])	Cooling Water (thousand gal/h [thousand L/h])
Gasifier	1520.0 (5.5)	-	40.0 (151.4)
Fermenter	357.9 (1.3)	3.5 (1.0)	125.5 (475.1)
Cell Recycle	1789.4 (6.4)	-	-
HAc Extraction	686.1 (2.5)	-	-
CMA Production	784.5 (2.8)	-	118.0 (446.7)
Total	**5137.9 (18.5)**	**3.5 (1.0)**	**283.5 (1073.2)**

- = not required

Table 87. Economic Evaluation for Base-Case Economics in Producing CMA From 500 Tons (454 Tonnes) of MSW/Day

Item	**Annual Cost (in million $)**
Revenue: 18,256.1 lb/h (8281.0 kg/h) CMA, $700/ton ($772/tonne)	**$53.673**
Medium, 1733 gal/h (6560 L/h), $0.028/gal ($0.007/L)	0.408
Lime, 4616.1 lb/h (2093.9 kg/h), $40/ton ($44/tonne)	0.776
MgO, 2085.3 lb/h (945.9 kg/h), $355/ton ($391/tonne)	3.109
Process Water, 42,091 lb/h (19,092 kg/h), $0.02/1000 gal ($0.005/1000 L)	0.009
Solvent Make-Up	0.030
Total Raw Materials Cost	**$4.332**
Electricity, 5137.9 kW•h (18.5 GJ), $0.04/kW•h ($11/GJ)	1.726
Steam, 3.5 million Btu/h (1.0 million W), $2.0/million Btu ($1.89/million KJ)	0.059
Cooling Water, 283.5 thousand gal/h (1073.2 thousand L/h), $0.05/thousand gal ($0.01/thousand L)	0.119
Total Utilities Cost	**$1.904**
Labor, 6 People/Shift, $30,000/Person/year	0.756
Supervision and Overhead, 100% of Labor	0.756
Maintenance, 5% of FCI	1.771
Insurance and Taxes, 2% of FCI	0.708
Total Direct Costs	**$10.227**
Depreciation, 10% of FCI	3.542
Total Costs	**$13.769**
Pretax Profit	39.904
Taxes, 40%	15.962
Net Profit	23.942
Cash Flow	27.484
Return on Investment	**77.60%**
Payout Period	1.29 years

A similar capital cost summary, utility summary, and economic evaluation in processing 500 tons/day (454 tonnes/day) of sewage sludge to produce CMA are shown in tables 88 through 90, respectively. The fixed-capital investment decreases slightly to \$33.5 million. Again, the equipment for cell recycle accounts for 42% of the fixed-capital investment. The requirements for running the process include 4900 kW·h (17.6 GJ) of electricity, 4.2 million Btu/h (1.2 million W) of steam, and 280,000 gal/h (1,059,912 L/h) of cooling water. The economic analysis shows that \$51.0 million/year are produced from revenue for CMA sales at \$700/ton (\$772/tonne). The total operating costs are \$13.2 million/year, and the return on the investment is 77.8%. If the cost of CMA is increased to its current market value of \$1100/ton (\$1213/tonne), the return on the investment increases to 130%.

Table 88. Fixed-Capital Investment for Base-Case Economics in Producing CMA From 500 Tons (454 Tonnes) of Sewage Sludge/Day

Section	FCI (\$)
Gasifier	\$8,000,000
Fermenter	3,936,000
Cell Recycle	14,131,000
Acetic Acid Extraction	4,011,000
CMA Production	3,372,000
Total	**\$33,450,000**

Table 89. Utility Summary for Base-Case Economics in Producing CMA From 500 Tons (454 Tonnes) of Sewage Sludge/Day

Section	Electricity (kW·h [GJ])	Steam (million Btu/h [million W])	Cooling Water (thousand gal/h [thousand L/h])
Gasifier	1520.0 (5.5)	-	40.0 (151.4)
Fermenter	392.8 (1.4)	4.2 (1.2)	130.3 (493.2)
Cell Recycle	1622.1 (5.8)	-	-
HAc Extraction	626.4 (2.3)	-	-
CMA Production	784.0 (2.8)	-	112.0 (424.0)
Total	**4909.3 (17.7)**	**4.2 (1.2)**	**282.3 (1068.6)**

- = not required

Table 90. Economic Evaluation for Base-Case Economics in Producing CMA From 500 Tons (454 Tonnes) of Sewage Sludge/Day

Item	Annual Cost (in million $)
Revenue: 17,330.5 lb/h (7861.1 kg/h) CMA, $700/ton ($772/tonne)	**$50.952**
Medium, 1645 gal/h (6227 L/h), $0.028/gal ($0.007/L)	0.387
Lime, 4382 lb/h (1988 kg/h), $40/ton ($44/tonne)	0.736
MgO, 1980 lb/h (898 kg/h), $355/ton ($391/tonne)	2.951
Process Water, 39,957 lb/h (18,124 kg/h), $0.02/1000 gal ($0.005/1000 L)	0.009
Solvent Make-Up	0.028
Total Raw Materials Cost	**$4.111**
Electricity, 4909.3 kW• h (17.7 GJ), $0.04/kW• h ($11/GJ)	1.650
Steam, 4.2 million Btu/h (1.2 million W), $2.0/million Btu ($1.89/million KJ)	0.071
Cooling Water, 282.3 thousand gal/h (1068.6 thousand L/h), $0.05/thousand gal ($0.01/thousand L)	0.119
Total Utilities Cost	**$1.840**
Labor, 6 People/Shift, $30,000/Person/year	0.756
Supervision and Overhead, 100% of Labor	0.756
Maintenance, 5% of FCI	1.673
Insurance and Taxes, 2% of FCI	0.669
Total Direct Costs	**$9.805**
Depreciation, 10% of FCI	3.345
Total Costs	**$13.150**
Pretax Profit	37.802
Taxes, 40%	15.121
Net Profit	22.681
Cash Flow	26.026
Return on Investment	**77.81%**
Payout Period	1.29 years

The effect of raw material cost on the return on the investment is shown in table 91. Only one grade of dolomitic lime was found, but MgO is available in a number of grades, including MagOx 98 LR (98% MgO), MagOx 93 LR (93% MgO), MagOx FG or MagneClear (95% MgO), and Mag 33 (48% MgO). All but Mag 33 are potential sources of MgO for the process. As is noted in table 91, the use of lesser grades of MgO improves the return on the investment by 1% to 2%. If MagneClear 95 or MagOx FG is substituted for MagOx 98, the return on the investment improves to 79.3% when using MSW as the feedstock, and to 79.6% when using sewage sludge as the feedstock.

Table 91. Effect of MgO Grade on CMA Economics

MgO Grade	% MgO	Cost ($/ton [$/tonne])	Return on Investment (%)	
			MSW*	Sewage Sludge**
MagOx 98 LR	98	$355 ($391)	77.6	77.8
MagOx 98 HR	98	355 (391)	77.6	77.8
MagOx 93 HR	93	265 (292)	78.7	78.9
MagOx 93 LR	93	265 (292)	78.7	78.9
MagneClear 95	95	230 (254)	79.3	79.6

* Based on process of tables 88 through 90 in processing 500 tons/day (454 tonnes/day) of MSW to CMA.

** Based on process of tables 85 through 87 in processing 500 tons/day (454 tonnes/day) of sewage sludge to CMA.

KAc Production Economics

Economic projections for producing KAc from MSW are shown in tables 92 through 94. In producing KAc, KOH in either liquid or pellet form is reacted with acetic acid in the liquid phase to produce a 50% solution of KAc. Only one grade of KOH is available, but it is available in solid form as pellets or flakes, or in liquid form as a 40% to 50% solution.

The fixed-capital investment for producing KAc from 500 tons/day (454 tonnes/day) MSW is shown in table 92. A total investment of $34.4 million is required, with 45% of the investment required for cell recycle. Requirements to produce this process include 4500 kW•h (16.2 GJ) of electricity, 3.5 million Btu/h (1.0 million W) of steam, and 300,000 gal/h (1,135,620 L/h) of cooling water (see table 93). The economic evaluation for KAc production from MSW is summarized in table 94. Revenue at $2.45/gal ($0.65/L) totals $113 million/year. This KAc price is one-half of the current KAc price of $4.90/gal ($1.29/L). The total operating costs total $56.4 million/year or $230/ton ($254/tonne) of 50% KAc produced. The return on the investment is 109%. If the price of KAc is increased to its current market value of $4.90/gal ($1.29/L), the return on the investment increases to 305%.

Table 92. Fixed-Capital Investment for Base-Case Economics in Producing KAc From 500 Tons (454 Tonnes) of MSW/Day

Section	FCI ($)
Gasifier	$8,000,000
Fermenter	3,695,000
Cell Recycle	15,556,000
Acetic Acid Extraction	4,700,000
KAc Production	2,493,000
Total	**$34,444,000**

Table 93. Utility Summary for Base-Case Economics in Producing KAc From 500 Tons (454 Tonnes) of MSW/Day

Section	Electricity (kW·h [GJ])	Steam (million Btu/h [million W])	Cooling Water (thousand gal/h [thousand L/h])
Gasifier	1520.0 (5.5)	-	40.0 (151.4)
Fermenter	357.9 (1.3)	3.5 (1.0)	125.5 (475.1)
Cell Recycle	1789.4 (6.4)	-	-
HAc Extraction	686.1 (2.5)	-	-
KAc Production	102.9 (0.4)	-	140.0 (530.0)
Total	**4451.3 (16.0)**	**3.5 (1.0)**	**305.5 (1156.4)**

- = not required

Table 94. Economic Evaluation for Base-Case Economics in Producing KAc From 500 Tons (454 Tonnes) of MSW/Day

Item	**Annual Cost (in million $)**
Revenue: 58,239.44 lb/h (26,417.41 kg/h) 50% KAc, $2.45/gal ($0.65/L)	**$113.008**
Medium, 1733 gal/h (6560 L/h), $0.028/gal ($0.007/L)	0.408
45% KOH, 18.489 tons/h (16.773 tonnes/h), $302/ton ($333/tonne)	46.903
Process Water, 42,091 lb/h (19,092 kg/h), $0.20/1000 gal ($0.05/1000 L)	0.009
Solvent Make-Up	0.030
Total Raw Materials Cost	**$47.350**
Electricity, 4451.3 kW•h (16.0 GJ), $0.04/kW•h ($11/GJ)	1.496
Steam, 3.5 million Btu/h (1.0 million W), $2.0/million Btu ($/million KJ)	0.059
Cooling Water, 305.5 thousand gal/h (1156.4 thousand L/h), $0.05/thousand gal ($0.01/thousand L)	0.128
Total Utilities Cost	**$1.683**
Labor, 6 People/Shift, $30,000/Person/year	0.756
Supervision and Overhead, 100% of Labor	0.756
Maintenance, 5% of FCI	1.722
Insurance and Taxes, 2% of FCI	0.689
Total Direct Costs	**$52.956**
Depreciation, 10% of FCI	3.444
Total Costs	**$56.400**
Pretax Profit	56.608
Taxes, 40%	22.643
Net Profit	33.965
Cash Flow	37.409
Return on Investment	**108.61%**
Payout Period	0.92 years

If 500 tons/day (454 tonnes/day) of sewage sludge is used as the raw material for KAc production, the fixed-capital investment is $32.5 million (see table 95). In addition, 4300 kW≅h (15.5 GJ) of electricity are required, as well as 4.2 million Btu/h (1.2 million W) of steam and 300,000 gal/h (1,135,620 L/h) of cooling water (see table 96). A return on the investment of 109% is attained when selling KAc for $2.45/gal ($0.65/L) (see table 97).

Table 95. Fixed-Capital Investment for Base-Case Economics in Producing KAc From 500 Tons (454 Tonnes) of Sewage Sludge/Day

Section	**FCI ($)**
Gasifier	$8,000,000
Fermenter	3,936,000
Cell Recycle	14,131,000
Acetic Acid Extraction	4,011,000
KAc Production	2,418,000
Total	**$32,496,000**

Table 96. Utility Summary for Base-Case Economics in Producing KAc From 500 Tons (454 Tonnes) of Sewage Sludge/Day

Section	**Electricity (kW·h [GJ])**	**Steam (million Btu/h [million W])**	**Cooling Water (thousand gal/h [thousand L/h])**
Gasifier	1520.0 (5.5)	-	40.0 (151.4)
Fermenter	392.8 (1.4)	4.2 (1.2)	130.3 (493.2)
Cell Recycle	1622.1 (5.8)	-	-
HAc Extraction	626.4 (2.3)	-	-
KAc Production	102.2 (0.4)	-	132.9 (503.1)
Total	**4263.5 (15.3)**	**4.2 (1.2)**	**303.2 (1147.7)**

- = not required

Table 97. Economic Evaluation for Base-Case Economics in Producing KAc From 500 Tons (454 Tonnes) of Sewage Sludge/Day

Item	Annual Cost (in million $)
Revenue: 55,288.3 lb/h (25,078.8 kg/h) 50% KAc, $2.45/gal ($0.65/L)	**$107.281**
Medium, 1645 gal/h (6227 L/h), $0.028/gal ($0.007/L)	0.387
45% KOH, 17.552 tons/h (15.923 tonnes/h), $302/ton ($333/tonne)	44.525
Process Water, 39,957 lb/h (18,124 kg/h), $0.20/1000 gal ($0.05/1000 L)	0.009
Solvent Make-Up	0.028
Total Raw Materials Cost	**$44.949**
Electricity, 4263.5 kW•h (15.3 GJ), $0.04/kW•h ($11/GJ)	1.433
Steam, 4.2 million Btu/h (1.2 million W), $2.0/million Btu ($1.89/million KJ)	0.071
Cooling Water, 303.2 thousand gal/h (1147.7 thousand L/h), $0.05/thousand gal ($0.01/thousand L)	0.127
Total Utilities Cost	**$1.631**
Labor, 6 People/Shift, $30,000/Person/year	0.756
Supervision and Overhead, 100% of Labor	0.756
Maintenance, 5% of FCI	1.625
Insurance and Taxes, 2% of FCI	0.650
Total Direct Costs	**$50.367**
Depreciation, 10% of FCI	3.250
Total Costs	**$53.617**
Pretax Profit	53.664
Taxes, 40%	21.466
Net Profit	32.198
Cash Flow	35.448
Return on Investment	**109.08%**
Payout Period	0.92 years

The effect of KOH product form on the return on the investment is shown in table 98. KOH is available in either solid form as flakes, crystals, or briquettes, or in liquid form as a 40% to 45% solution. Although the product is the same, the costs of these two forms vary significantly, from $1040/ton ($1146/tonne) for the solids to $302/ton ($333/tonne) for the solution. If solid KOH is used in the process, the return on the investment falls to 64%. Clearly, the use of liquid KOH is a better choice for the process.

Table 98. Effect of KOH Product Form on KAc Economics

Caustic Potash (KOH) Product	% KOH	Cost ($/ton [$/tonne])	Return on Investment	
			MSW*	Sewage Sludge**
Flake, crystal, or briquette	100	$1040 ($1146)	63.7	63.9
45% (nominal) solution	45	302 (333)	108.6	109.8

* Based on process of tables 92 through 94 in processing 500 tons/day (454 tonnes/day) of MSW to KAc.

** Based on process of tables 95 through 97 in processing 500 tons/day (454 tonnes/day) of sewage sludge to KAc.

TASK 16. ACETIC ACID RECOVERY USING ZEOLITES

Zeolites are currently used in a variety of different chemical-processing applications. Most of the processing applications utilize the zeolites as catalysts, although some are used in the removal of volatile organic compounds from stack gases. The current processing market generally doesn't use zeolite in the refinement of liquid process streams — the main thrust of this research endeavor.

The initial zeolite tests were conducted using Zeochem's Zeocat PZ-2/400 hydrophobic zeolite. This zeolite has an Si-to-Al ratio of about 400 to 500:1. The zeolite particles were made as 0.16-cm and 0.32-cm extrudates.The initial tests were conducted using the 0.32-cm extrudates.

Zeolite Loading Curve

In an effort to understand the mechanisms of the zeolite, an experiment was initiated to construct a loading curve for acetic acid. Figure 30 presents the loading curve. In all of these experiments, essentially half of the acetic acid was in the acetate form. The free-acid concentrations were plotted vs. loading percent. As is noted in the figure, a 13% loading was obtained at a free-acid concentration of 20 g/L.

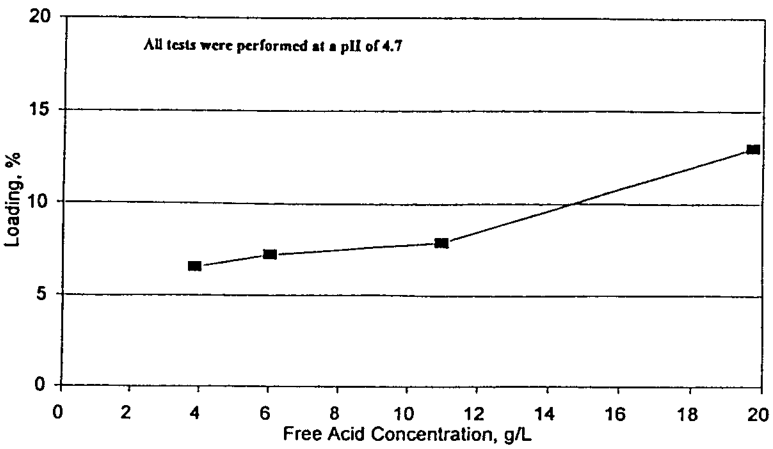

Figure 30. Zeolite Loading Curve

Acid Removal From Reactor Permeate Using Zeolites

Following the preparation of a loading curve, the next logical step was to use the zeolite in conjunction with permeate from a reactor. This test was conducted using a packed bed design, with the initial solution consisting of permeate collected from a reactor producing acetic acid using Isolate ERI2. This experiment was conducted three times using the same zeolite. Accurate data for the first of the three permeate runs were not collected. The second run yielded a 9.5% loading rate, and the final run yielded a 7.6% loading rate. Thus, the use of zeolites on reactor permeate containing acetic acid and acetate has been demonstrated.

Acid Removal From Reactor Culture Using Zeolites

The next step was to use culture from a reactor in conjunction with zeolite. This test was conducted following the same packed bed design. The difference in this experiment was that the initial solution consisted of culture collected from a CSTR producing acetic acid. Three tests were conducted to determine loading rate and performance loss in the zeolite. Loadings of 6.9% to 8.6% were achieved.

Zeolite Performance in Conjunction With a Bioreactor

The next step was to put a zeolite bed online with a healthy reactor. A new housing was made to hold approximately 40 g of zeolite. This bed was left online for approximately 28 h. The reactor conversions stayed above 90% the entire time that the zeolite bed was online. The zeolite bed was removed from the bioreactor and then allowed to air dry for about 2 weeks. The main point of this experiment was to show that the culture could interact with the zeolite without any harmful effects. Figure 31 shows the performance in the bioreactor for 24 h prior to the experiment and up to 24 h after being exposed to the zeolite bed. The performance did not seem to be impaired, even when the zeolite bed was left on for 28 h.

Acetic Acid Removal Using Hot-Air Stripping

A preliminary test was performed to attempt to remove the water trapped on the zeolite during loading using only a heated air stream. Figure 32 shows the apparatus used in the regenerative process. A flask with the loaded zeolite was placed in an oven. A silicon tube was run from the flask to a condenser (outside the oven). The temperature of the oven was slowly increased in an effort to drive off the acid water trapped on the zeolite. Samples were collected from the bottom of the condenser in alternating 1- and 5-mL aliquots. The recovery data are presented graphically in figure 33. According to the volume of material recovered, 81% of the loaded acid/water mixture was recovered. Attempts are being made to refine the recovery process to enable recovery of essentially all of the loaded material.

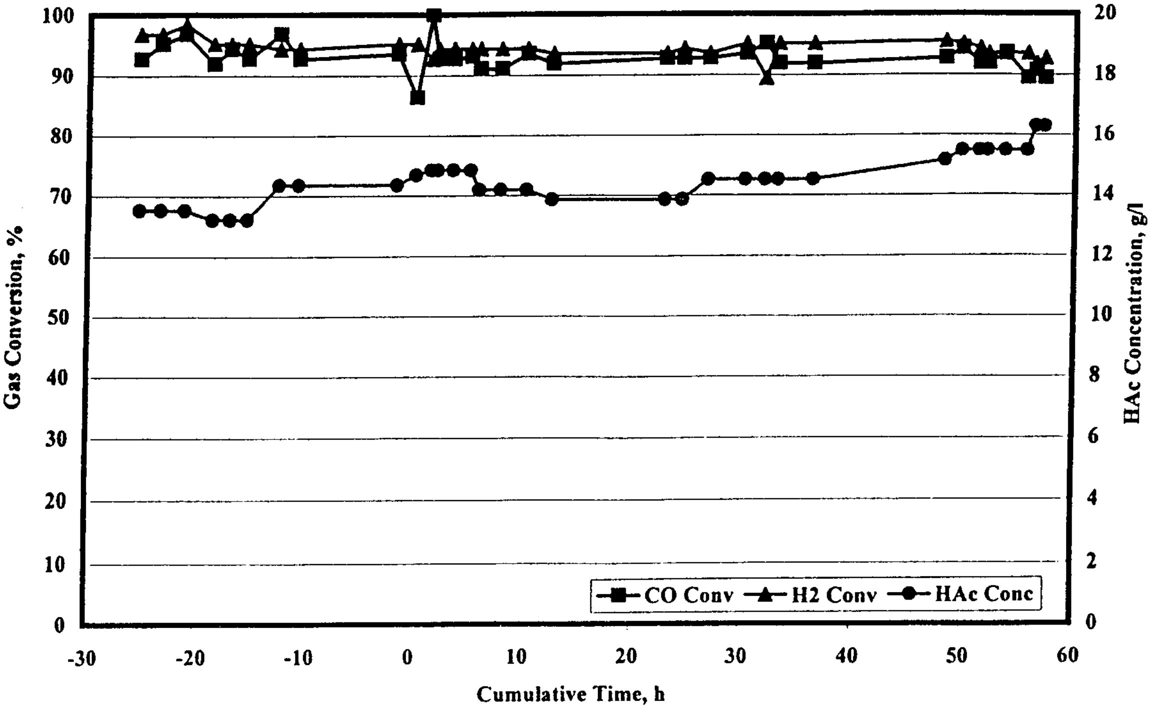

Figure 31. Bioreactor Performance with Zeolite Bed Present

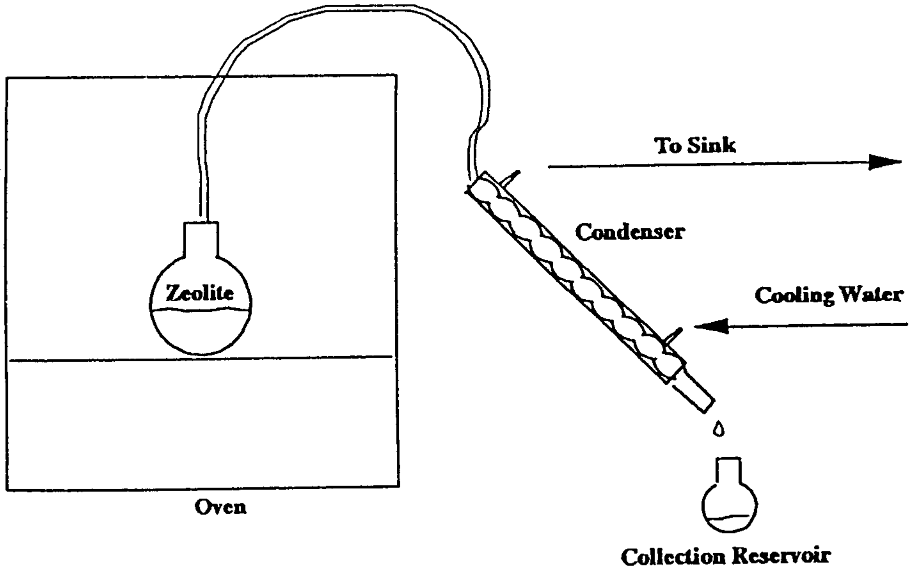

Figure 32. Zeolite Regeneration System

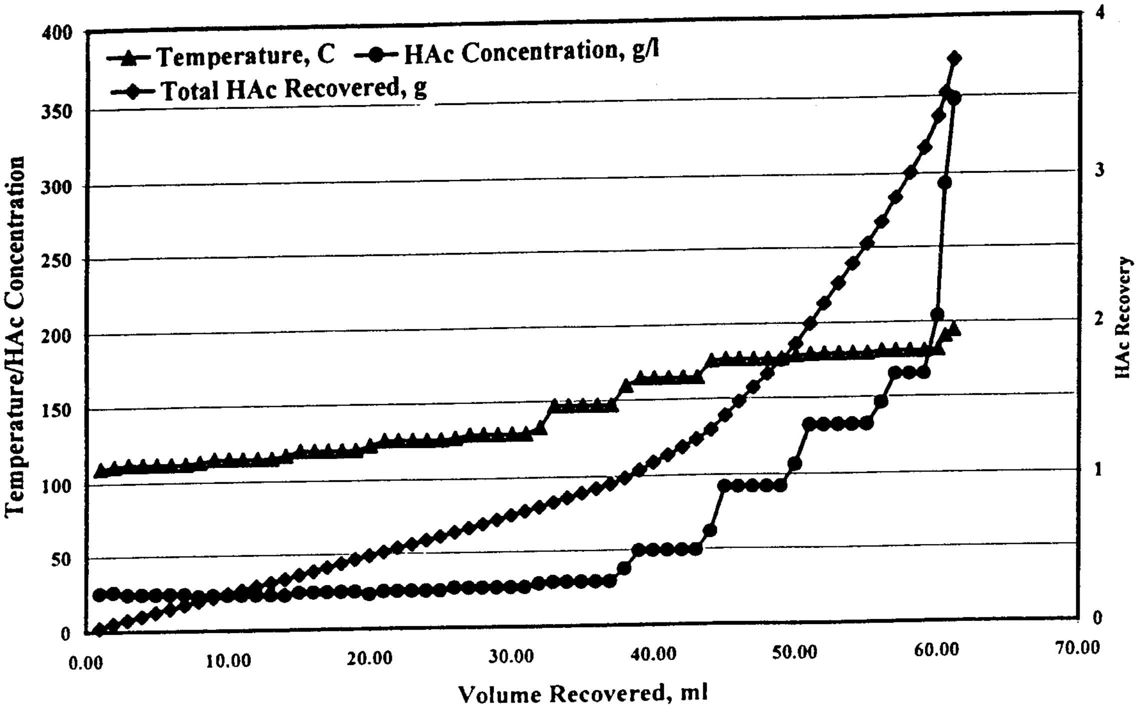

Figure 33. Acetic Acid Recovery From Zeolite

Preliminary Economic Evaluations

Preliminary economic projections have been prepared for CMA production from MSW and sewage sludge using zeolites as the method for acid recovery. In these economics, the use of zeolites helps cut the costs for cell recycle, product recovery, and CMA production. A summary of capital costs, utilities, and process economics in converting 500 tons/day (454 tonnes/day) of MSW to CMA using zeolites in the process is shown in tables 99 through 101, respectively. The fixed-capital investment totals $28 million, in comparison to $35.4 million in the base-case process (see tables 85 through 87). Overall utility usage is increased, requiring 2700 kW h (9.7 GJ) of electricity (in comparison to 5100 kW•h (18.4 GJ) in the base process), 2.4 million Btu/h (0.7 million W) of steam (compared to 3.5 million Btu/h [1.0 million W]), and 1.7 million gal/h (6.4 million L/h) of cooling water (compared to 280,000 million gal/h [1,059,912 million L/h]). The process economic projections show that the total operating costs are increased from $13.8 million/year to $15.8 million/year. However, the return on the investment is increased from 77.6% to 91.3%. Thus, the major advantage in using zeolites is the 21% decrease in the fixed-capital investment.

Tables 102 through 104 show similar results when using sewage sludge as the raw material. The fixed-capital investment is nearly the same at $27.7 million. Utility usage is slightly less, and the return on the investment is slightly decreased to 87.5%.

Table 99. Fixed-Capital Investment for a Process Producing CMA From 500 Tons (454 Tonnes) of MSW/Day When Using Zeolites for Acid Recovery

Section	FCI ($)
Gasifier	$8,000,000
Fermenter	3,695,000
Zeolite Bed	6,942,000
Zeolite Regeneration	7,104,000
CMA Production	2,235,000
Total	**$27,976,000**

Table 100. Utility Summary for a Process Producing CMA From 500 Tons (454 Tonnes) of MSW/Day When Using Zeolites for Acid Recovery

Section	Electricity (kW·h [GJ])	Steam (million Btu/h [million W])	Cooling Water (thousand gal/h [thousand L/h])
Gasifier	1520.0 (5.5)	-	40.0 (151.4)
Fermenter	357.9 (1.3)	3.5 (1.0)	125.5 (475.1)
Zeolite Bed	89.5 (0.3)	-	-
Regeneration	30.0 (0.1)	210.0 (61.5)	1425.0 (5394.2)
CMA Production	667.0 (2.4)	-	118.0 (446.7)
Total	**2664.4 (9.6)**	**213.5 (62.6)**	**1708.5 (6467.4)**

- = not required

Table 101. Economic Evaluation for a Process Producing CMA From 500 Tons [454 Tonnes] of MSW/Day When Using Zeolites for Acid Recovery

Item	Annual Cost (in million $)
Revenue: 18,256.1 lb/h (8281.0 kg/h) CMA, $700/ton ($772/tonne)	**$53.673**
Medium, 1733 gal/h (6560 L/h), $0.028/gal ($0.007/L)	0.408
Lime, 4616.1 lb/h (2093.9 kg/h), $40/ton ($44/tonne)	0.776
MgO, 2085.3 lb/h (945.9 kg/h), $355/ton ($391/tonne)	3.109
Process Water, 42,091 lb/h (19,092 kg/h), $0.02/1000 gal ($0.005/1000 L)	0.009
Total Raw Materials Cost	**$4.302**
Electricity, 2664.4 kW•h (9.6 GJ), $0.04/kW•h ($11/GJ)	0.895
Steam, 213.5 million Btu/h (62.6 million W), $2.0/million Btu ($1.89/million KJ)	3.587
Cooling Water, 1708.5 thousand gal/h (6467.4 thousand L/h), $0.05/thousand gal ($0.01/thousand L)	0.718
Total Utilities Cost	**$5.200**
Labor, 6 People/Shift, $30,000/Person/year	0.756
Supervision and Overhead, 100% of Labor	0.756
Maintenance, 5% of FCI	1.399
Insurance and Taxes, 2% of FCI	0.560
Total Direct Costs	**$12.973**
Depreciation, 10% of FCI	2.798
Total Costs	**$15.771**
Pretax Profit	37.902
Taxes, 40%	15.161
Net Profit	22.741
Cash Flow	25.539
Return on Investment	**91.29%**
Payout Period	1.10 years

Table 102. Fixed-Capital Investment for a Process Producing CMA From 500 Tons (454 Tonnes) of Sewage Sludge/Day When Using Zeolites for Acid Recovery

Section	FCI ($)
Gasifier	$8,000,000
Fermenter	3,936,000
Zeolite Bed	6,596,000
Zeolite Regeneration	7,017,000
CMA Production	2,145,000
Total	**$27,694,000**

Table 103. Utility Summary for a Process Producing CMA From 500 Tons (454 Tonnes) of Sewage Sludge/Day When Using Zeolites for Acid Recovery

Section	Electricity (kW h [GJ])	Steam (million Btu/h [million W])	Cooling Water (thousand gal/h [thousand L/h])
Gasifier	1520.0 (5.5)	-	40.0 (151.4)
Fermenter	392.8 (1.4)	4.2 (1.2)	130.3 (493.2)
Zeolite Bed	82.1 (0.3)	-	-
Regeneration	28.0 (0.1)	193.6 (56.7)	1321.1 (5000.9)
CMA Production	657.7 (2.4)	-	116.0 (439.1)
Total	**2680.6 (9.7)**	**197.8 (58.0)**	**1607.4 (6084.7)**

Table 104. Economic Evaluation for a Process Producing CMA From 500 Tons (454 Tonnes) of Sewage Sludge/Day When Using Zeolites for Acid Recovery

Item	Annual Cost (in million $)
Revenue: 17,330.5 lb/h (7861.1 kg/h) CMA, $700/ton ($772/tonne)	**$50.952**
Medium, 1645 gal/h (6227 L/h), $0.028/gal ($0.007/L)	0.387
Lime, 4382 lb/h (1988 kg/h), $40/ton ($44/tonne)	0.736
MgO, 1980 lb/h (898 kg/h), $355/ton ($391/tonne)	2.951
Process Water, 39,957 lb/h (18,124 kg/h), $0.02/1000 gal ($0.005/1000 L)	0.009
Total Raw Materials Cost	**$4.083**
Electricity, 2680.6 kW• h (9.7 GJ), $0.04/kW• h ($11/GJ)	0.901
Steam, 197.8 million Btu/h (58.0 million W), $2.0/million Btu ($1.89/million KJ)	3.323
Cooling Water, 1607.4 thousand gal/h (6084.7 thousand L/h), $0.05/thousand gal ($0.01/thousand L)	0.675
Total Utilities Cost	**$4.899**
Labor, 6 People/Shift, $30,000/Person/year	0.756
Supervision and Overhead, 100% of Labor	0.756
Maintenance, 5% of FCI	1.385
Insurance and Taxes, 2% of FCI	0.554
Total Direct Costs	**$12.433**
Depreciation, 10% of FCI	2.769
Total Costs	**$15.202**
Pretax Profit	35.750
Taxes, 40%	14.300
Net Profit	21.450
Cash Flow	24.219
Return on Investment	**87.45%**
Payout Period	1.14 years

CONCLUSIONS

A two-phase research and development program was performed in order to demonstrate the technical and economic viability of BRI's gasification/fermentation process, and to collect valuable design and scale-up information for later process demonstration. In Phase I, the feasibility of utilizing a biological process for the conversion of MSW, sewage sludge, and other waste materials to CMA has been demonstrated. Gasification, a technology well-developed in Europe, is used to convert the waste into a synthesis gas containing primarily CO, CO_2, and H_2. Synthesis gas is then converted to acetic acid/acetate using the BRI isolate ERI2. A 10-min GRT at atmospheric pressure is required in the CSTR with cell recycle for these oxygen-blown gasifier syngases, and the retention time decreases proportionally with increased pressure. Thus, retention times of seconds are possible at elevated pressures. The fermentation broth contains approximately 20 g/L acetic acid/acetate. The acetic acid is removed from the broth by solvent extraction using solvent A, co-solvent 11. A high distribution is obtained with this solvent system, and the separation factor shows that only negligible quantities of water are extracted along with the acid. CMA production occurs by reacting dolomitic lime/MgO with the acetic acid directly in the solvent phase. A first order rate constant of 0.258 min^{-1} is obtained. The CMA is then dried and pelletized using existing technology. The BRI-produced CMA was found to be essentially identical with industrial CMA in physical property and ice melting, ice penetration, and eutectic-point tests.

The economics of producing CMA from wastes by gasification/fermentation is quite attractive. In Phase I, the production costs from MSW and sewage sludge, without including tipping fees, were projected at $123 and $126/ton ($136 and $139/tonne), respectively. Preliminary market analyses indicate that, at this price, the potential market for CMA is 1 million tons/year (907,200 tonnes/year). Finally, an Industrial Advisory Committee (IAC) has been formed to advise in the development of a technical and marketing strategy for the commercialization of this technology. The IAC met on March 30, 1994, in Fayetteville, AR, to tour the carbon black waste gas to acetic acid pilot plant, and to review results from the Phase I research effort.

In the Phase II program, additional bench-scale research and development were carried out to yield design and scale-up data for process demonstration. Bench-scale fermentation experiments were carried out with air-blown, oxygen-blown, and steam-blown MSW syngas. The required GRTs for suitable conversions of CO and H_2 in the syngas ranged from 3 to 15 min, depending on the combined CO and H_2 content of the syngas. Typical gas phase contaminants such as chlorides, H_2S, COS, and metals were not found to be a problem in fermentation at levels above those expected in the MSW syngases.

The CMA production process was modified to form a breakable emulsion during extraction with the solvent system, which resulted in significant increases in the rate of CMA formation from acetic acid in the solvent phase. Also, a near-saturated solution of CMA is now produced in the CMA reactor, which enables inerts to be easily removed from the CMA product. This change permits the use of less expensive, lower grades of lime and MgO as feedstocks, since the inerts may simply be filtered out of the aqueous near-saturated solution. Chloride and sulfate were removed from the fermentation medium in order to essentially eliminate these environmentally unfriendly compounds from the CMA. With these changes, the CMA product remained high in quality and comparable to the industrial CMA.

Carbon bed adsorption was investigated as a method of enhancing the fermentation rate by removing cellular material from the water recycle stream prior to fermentation. However, fermentation tests showed that this operation is unnecessary, as long as the free-acid concentration in the reactor is kept below inhibitory levels. Zeolites were evaluated as an alternative and less expensive method of recovering acid from the fermenter permeate. These systems look very promising, with a potential to decrease the capital costs for the gasification/fermentation process by more than 20%. The economics of producing both CMA and KAc remain promising, with returns on the investment projected at 78% in producing CMA and 109% in producing KAc from MSW.

APPENDIX A. CALCULATIONS OF ALLOWABLE METAL CONCENTRATIONS IN SYNGAS

Assumptions:

1) The metals listed will be in an aerosol that will react with assumed available HCl in the gasified MSW.

2) All of the metals will be dissolved into the fermentation broth.

3) The metals will be washed out of the system with the liquid.

Calculations:

With the above assumptions and the maximum concentrations listed in Table 73, the metals concentration allowed in the gas phase becomes a simple mole balance calculation:

Moles in = Moles out

$$C_g \dot{V}_g = C_l \dot{V}_l \qquad (1)$$

$$C_g = \frac{C_l \dot{V}_l}{\dot{V}_g} \qquad (2)$$

Since

$$\dot{V}_g = \frac{V_l}{GRT}; \dot{V}_l = \frac{V_l}{LRT}$$

Equation 2 becomes:

$$C_g = \frac{C_l(GRT)}{LRT}$$

Where:

C_g ≡ Concentration in the gas phase

C_l ≡ Concentration in the liquid phase

GRT ≡ Gas Retention Time

LRT ≡ Liquid Retention Time

$\dot{V}$ ≡ Volummetric Flow Rate

V_l ≡ Liquid Volume

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