

Production of Low-Cost Acetate Deicers from Biomass and Industrial Wastes

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Calcium magnesium acetate (CMA), a mixture of calcium acetate and magnesium acetate, is used as an environmentally benign roadway deicer. The present commercial CMA deicer made from glacial acetic acid and dolomitic lime or limestone is more expensive than salt and other deicers. Also, a liquid potassium acetate deicer is used to replace urea and glycol in airport runway deicing. Two alternative low-cost methods to produce these acetate deicers from cheap feedstocks, such as biomass and industrial wastes, were studied. CMA deicers produced from cheese whey by fermentation and extraction were tested for their acetate content and deicing property. The CMA solid sample obtained from extraction of the acetic acid present in a dilute aqueous solution and then back-extracted with dolomitic lime to form CMA had about the same acetate content (70 percent acetic acid or 90 percent CMA) as the commercial CMA deicer. The sample from dried whey fermentation broth contained 50 percent acetic acid or 63 percent CMA, with the remaining solids being other organics and salts present in whey. Deicing tests showed that CMA samples from fermentation and extraction had an ice penetration rate equal to or slightly better than the commercial CMA. Cost analysis showed that CMA can be produced at a product cost of \$204 to \$328/ton, less than 30 percent of the current market price for the commercial CMA, for a plant size of 8,400 tons CMA per year. The lower CMA cost should dramatically increase CMA use in the deicing market.

From 10 million to 14 million tons of road salt are used annually in the United States and Canada. Salt is an extremely effective snow and ice control agent and is relatively inexpensive. However, a study in New York State showed that although 1 ton of road salt cost only \$25, it caused more than \$1,400 in damage (1). Salt is corrosive to concrete and metals used in the nation's infrastructure, is harmful to roadside vegetation, and poses serious threats to environment and ground-water quality in some regions (2). FHWA spends about \$12.5 billion annually, a substantial portion of which is used to rebuild and resurface highways and bridges damaged by salt corrosion. FHWA has long recognized this problem and has identified calcium magnesium acetate (CMA) as one alternative road deicer (3).

CMA is a mixture of calcium acetate and magnesium acetate. It is currently manufactured by reacting glacial acetic acid with dolomitic lime (CaO-MgO) or limestone (Ca/MgCO₃). CMA has a deicing ability comparable to salt but is noncorrosive and harmless to vehicles, highway concrete, bridges, and vegetation. It is biodegradable and associated with no identified environmental concerns (2). CMA is not simply noncorrosive; it inhibits corrosion (2). Thus, CMA can be used in mixture with salt to reduce corrosion caused by salt. The use of CMA for highway deicing should save millions of dollars each year just in highway and automobile main-

tenance costs. Detailed discussions of the comparison between salt and CMA for highway deicing can be found elsewhere (4,5).

At the present cost of \$1,000/ton, versus \$35/ton for salt, CMA is too expensive for widespread use, although some studies have shown that all its material costs may be offset by the savings in infrastructure replacement costs (1). Consequently, CMA is used only in limited areas where corrosion control is required or in environmentally sensitive areas to protect vegetation and ground water from salt contamination (6). The use of CMA as a deicer, however, will be cost-effective and better accepted if its price can be reduced to \$300 to \$400/ton (7). It is thus desirable to produce low-cost CMA deicers from alternative feedstocks such as biomass and industrial wastes (8).

Several alternative methods to produce acetic acid and CMA by fermentation of biomass and extraction of acetic acid from dilute aqueous solutions are reviewed. An anaerobic fermentation process to produce CMA from cheese whey, a dairy waste, is examined in detail. Deicing performance and cost analyses of this new, alternative CMA deicer from whey were also studied and are discussed.

PRODUCTION OF ACETIC ACID AND CMA

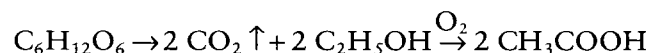
Acetic acid is an important raw material in the chemical industry. In the last several years, the yearly production of acetic acid in the United States has continuously increased to 1.8 million tons in 1995. Current commercial glacial acetic acid is exclusively produced from petrochemical routes (9,10) and costs \$0.7/kg. The high price of glacial acetic acid contributes to the major cost of CMA deicer. Thus, there has long been an interest in producing low-cost acetic acid and acetate from fermentation (11).

Production by Fermentation

Several fermentation routes have been widely studied for their potential to produce acetic acid or acetate from biomass. A comparison of various fermentation routes is given in Table 1.

Aerobic Acetic Acid Fermentation

Acetic acid (vinegar) traditionally has been produced from ethanol derived from sugar fermentation. This process generally involves two steps: (a) fermentation of sugar to ethanol by yeasts such as *Saccharomyces cerevisiae* and *Kluyveromyces fragilis*, and (b) oxidation of ethanol to acetic acid by species of *Acetobacter*. The reactions are as follows:



This process has two major disadvantages. First, the acetic acid yield is, at most, only two-thirds of the sugar source, since up to one-third of the organic carbon is lost as carbon dioxide (CO₂) during the ethanol fermentation. In practice, the yields of ethanol and acetic acid are rarely more than 90 percent and 85 percent of the theoretical value, respectively. With an overall efficiency of 75 percent, only 0.5 g of acetic acid can be produced per gram of sugar used. Second, strict aeration is required for the growth of *Acetobacter* to convert ethanol to acetic acid. Improper aeration may cause serious damage to the acetic acid bacteria or result in overoxidation of acetic acid to CO₂ and water. As a result, the conventional aerobic vinegar fermentation process suffers from low yield and high production cost, and thus cannot compete well with the natural gas-based synthetic process (9).

Earlier studies conducted by Stanford Research Institute concluded that CMA production via aerobic vinegar fermentation of glucose or hydrolyzed corn

TABLE 1 Comparison of Various Fermentation Routes for Producing Acetate from Biomass

	Aerobic Vinegar Fermentation ¹	Anaerobic Homoacetic Fermentation		Anaerobic Digestion ³
		<i>C. thermoaceticum</i>	<i>C. formicoaceticum</i> ²	
Substrate	Glucose / Ethanol	Glucose	Lactate	Cellulosics
Acetate yield	<60%	>80%	>95%	30% ~ 80%
Acetate conc. (w/v)	6% ~ 10%	2% ~ 10%	3% ~ 7.5%	<3%
Fermentation time	1 ~ 3 days	1 ~ 7 days	2 ~ 7 days	6 ~ 15 days
Energy requirement	high in fermentation	medium	low	high in product recovery

¹requires ethanol fermentation of glucose first; ethanol is the substrate for acetic acid fermentation.

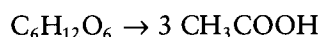
²lactate can be obtained from carbohydrates through homolactic acid fermentation.

³methanogenic activities are suppressed to allow acetate accumulation.

starch was not economically competitive and did not warrant further consideration (12). This prompted the search for anaerobic homoacetogens for acetic acid and CMA production.

Anaerobic Homoacetogenic Fermentation

There has been increasing interest in producing acetic acid from renewable resources by using anaerobic homoacetogens because of the high product yield from anaerobic fermentation. In contrast to the aerobic vinegar process, nearly 100 percent of the substrate carbon can be recovered in the product, acetic acid, by anaerobic fermentation. The reaction is as follows:



The actual acetic acid yield from glucose is usually greater than 80 percent (weight per weight). With a few exceptions, the final concentration of acetic acid produced from the anaerobic process is usually low, only about 2 percent, as compared with 6 to 10 percent obtained from the aerobic process. This low product concentration leads to a prohibitively high energy requirement for the recovery of the acetic acid produced in the anaerobic process (13), although the overall energy consumption is still lower than that for the aerobic process. To attain a viable, economical production, acetate concentration must exceed 4 percent and a low-cost feedstock should be used.

Table 2 presents some anaerobic bacteria that can convert carbohydrates and other carbon sources to acetic acid via homofermentation. *C. thermoaceticum* has been extensively studied for its ability to convert glucose, xylose, and cellulose to acetic acid at 60°C (11,14). Other known anaerobic homoacetogens include *C. formicoaceticum*, *C. aceticum*, *C. thermoautotrophicum*, *C. magnum*, *Acetobacterium woodii*, *A. carbinolicum*, and

Acetogenium kivui. Ljungdahl et al. (15) studied three thermophilic acetogens—*C. thermoaceticum*, *C. thermoautotrophicum*, and *A. kivui*—for their abilities to produce CMA from glucose. It was concluded that although *C. thermoaceticum* was the most desirable, none would have successful industrial applications.

Recently, Parekh and Cheryan (16) reported a mutant strain of *C. thermoaceticum* that could produce acetate concentration as high as 10 percent (weight per volume) in a fedbatch fermentation with cell recycle. The reactor productivity was 0.8 g/L/hr and the acetate yield from glucose was 80 percent. However, the results were obtained with a synthetic medium with a high yeast extract content. Efforts to use inexpensive industrial feedstocks for acetate production by using this strain have not been as successful.

None of the homoacetogenic bacteria can ferment lactose; however, several of them can readily convert lactate to an equal amount of acetate. Among all the homoacetogens, only *A. woodii*, *A. carbinolicum*, and *C. formicoaceticum* can ferment lactate to acetate. *A. woodii* can grow at temperatures below 32°C and at a pH between 4.5 and 6.8. *C. formicoaceticum* can grow at a temperature around 35°C and a pH between 6.6 and 9.6 (17). Both organisms are inhibited by acetic acid, but *C. formicoaceticum* can tolerate a higher concentration than can *A. woodii*. *C. formicoaceticum* is also more active than *A. woodii* when grown on lactate at neutral pH and mesophilic temperatures. *A. carbinolicum* is a new isolate similar to *A. woodii*. *C. formicoaceticum* is the most promising to convert lactate to acetate. Recent study with this organism obtained a high acetate concentration of 7.5 percent (weight per volume) in a fibrous bed bioreactor.

Homolactic fermentation has been widely applied in the dairy industry for producing lactic acid from lactose. It is feasible to produce acetic acid from whey permeate by converting lactose to lactic acid, and then to

TABLE 2 Optimal Growth Conditions and Substrates for Various Anaerobic Homoacetogens

Organism	Temp	pH	Growth Substrate
<i>Clostridium aceticum</i>	30°C	8.3	Fructose, Pyruvate, CO ₂ /H ₂ , CO/H ₂
<i>C. formicoaceticum</i>	37°C	7.6	Fructose, Pyruvate, Pectin, Lactate, Galacturonate
<i>C. thermoaceticum</i>	60°C	7.0	Fructose, Pyruvate, Glucose, Xylose, (Lactate)*
<i>C. thermoautotrophicum</i>	60°C	5.7	Fructose, Glucose, Galactose, Glycerate, Methanol, Formate, CO ₂ /H ₂ , CO/H ₂ , (Lactate)*
<i>C. magnum</i>	30°C	7.0	Fructose, Glucose, Sucrose, Xylose, Citrate, Malate
<i>Acetobacterium woodii</i>	30°C	6.7	Fructose, Glycerate, Glucose, Lactate, CO ₂ /H ₂ , Formate
<i>A. carbinolicum</i>	27°C	7.0	Fructose, Glucose, Pyruvate, Lactate, Formate, Aliphatic alcohols C ₁ -C ₅ , CO ₂ /H ₂
<i>Acetogenium kivui</i>	66°C	6.4	Fructose, Pyruvate, Formate, Mannose, Glucose, CO/H ₂

*only a few strains can utilize lactate for growth.

acetic acid by using homolactic and homoacetic bacteria, respectively (18). Since both lactate and lactose are abundant in many industrial waste streams (lactate in corn steep liquor from the corn wet milling process and lactose in whey from the cheese industry), it is promising to produce low-cost acetate from lactate and lactose fermentations (19,20).

Anaerobic Digestion

Anaerobic digestion of biomass as a means of producing CMA in a mixture of organic-acid salts was recently studied by Trantolo and others (21–23). In their processes, growth of methanogens was suppressed to allow acetate accumulation. Sewage sludge, woody biomass, and, in principle, any low-grade biomass such as cheese whey can be used in this process. However, the reaction rate is low and acetate yield is only 30 percent to 80 percent, depending on the fermentation condition. The acetate concentration obtained from this process was also very low, only 0.8 percent, although theoretically 3 percent is possible. Other organic acids present in the product stream include propionic and butyric acids. The major problem with this process is that the reactor performance is not stable because many undefined mixed cultures are involved and are difficult to control.

Other Bioprocesses

As shown in Table 2, some homoacetogens may use hydrogen gas and single-carbon compounds, such as carbon monoxide (CO), CO₂, methanol, and formate, to produce acetic acid. This provides a biological method to convert syn-gas (CO, CO₂, and H₂) to acetic acid, although the low solubilities and large volume associated with the gaseous feedstocks might limit their industrial applications. Engineering Resources, Inc. (Fayetteville, Ark.), is currently developing a process to produce acetic acid from biomass and industrial wastes through gasification followed with fermentation of the syn-gas.

Acetate Production from Whey Lactose

Whey is a byproduct from the manufacture of cheese and casein. It contains about 5 percent lactose, 1 percent protein, 1 percent salts, and 0.1–0.8 percent lactic acid. The biological oxygen demand of whey is high—40,000 mg/L. Currently, less than 50 percent of the total whey solids produced in the United States is used in human food or animal feed (24). The surplus whey must find a new use or be treated as a pollutant. Whey can be used for acetic acid production via fermentation.

There is no homoacetogen that can directly convert lactose to acetate. However, acetate can be produced efficiently from lactose via two anaerobic fermentation processes. The first is to use propionic bacteria to ferment lactose to propionate and acetate (25). Acetate is not the major product, but it may be economically recovered as a byproduct from this process. The second process is to use a coculture consisting of homolactic and homoacetic bacteria, which sequentially converts lactose to lactate and then to acetate. The feasibility of producing acetate from whey fermentation by using such a coculture has been studied in both free cell batch cultures and immobilized cell continuous cultures (19,20). The overall acetate yield from lactose was greater than 90 percent (weight per weight), and a high acetate concentration of up to 7.5 percent was obtained in recycle fedbatch fermentation by using immobilized cells and a fibrous bed bioreactor.

Acetic Acid Recovery from Fermentation Broth and Wastewater

Fermentatively produced acetic acid usually is recovered by solvent extraction or azeotropic dehydration. However, the acetic acid produced in the anaerobic fermentation at pH 7 is in the form of acetate salt. Conventional solvents can extract only free acid from the fermentation broth. Previous attempts to adapt the microbes to acidic pH and to acidify the broth before extraction failed to reduce production costs to a competitive level. Separation of acetic acid by adsorption with ion exchange resins is not feasible at present. Steam or gas stripping of the volatile acetic acid present in a dilute aqueous solution is not economically feasible, either. An energy-efficient steam stripper with caustic solution to improve stripping efficiency has been described recently (U.S. Patent 4,917,769, 1990). However, because of the low relative volatility of acetic acid to water (0.69), a large number of trays or equilibrium stages are required to obtain 90 percent recovery. Also, the tray design in this stripping tower is quite complicated. It is difficult to use high concentrations of lime slurry as the caustic in this stripper.

Recently, extractive recovery of carboxylic acids, including acetic acid, from dilute, aqueous solutions, such as fermentation broth and wastewater, having an acid concentration of 1 to 4 percent, has received increasing attention (26–28). The highest concentration of acetic acid that most anaerobic homoacetogens can tolerate is usually lower than 3 percent. Conventional extraction solvents require a concentration of acetic acid higher than 10 percent and, therefore, an evaporation process is usually recommended before solvent extraction. Nevertheless, if a highly efficient extractant is available, the

heating process can be reduced to a level sufficient only for killing the microbes in the liquor. Solvents with a high distribution coefficient can be used to extract acetic acid from a low concentration solution. These solvents include trioctylphosphine oxide (TOPO) and long-chain aliphatic amines (27).

In general, only the undissociated acid can be extracted by the solvent (28). Under basic conditions ($\text{pH} > 7$), the acetic acid is present as acetate salt and cannot be extracted. Therefore, the extraction is usually conducted at a pH value lower than 5 and the extractant can be regenerated by back-extraction with an alkaline solution at $\text{pH} > 10$. A two-step extraction process thus can be used to produce concentrated organic salts from a dilute acid solution. In this process, a solvent with a high distribution coefficient is used to extract organic acids from a fermentation broth with a pH value below 6 (preferably at 3). Back-extraction with an alkaline solution (with pH above 10) is then followed to regenerate the extractant and to form an organic salt in a concentrated solution. This two-step extraction method would provide an energy-efficient way to recover, separate, and concentrate organic acids from a dilute fermentation broth.

PROCESSES FOR CMA PRODUCTION FROM WHEY

Two potential processes to produce acetate and CMA from cheese whey based on the fermentation and extraction technologies discussed earlier are shown in Figure 1. The technical feasibilities of the fermentation and extraction to be used in the processes have been discussed in the previous sections and demonstrated in a recent laboratory study (19). Several CMA samples were prepared from whey following the process steps shown in Figure 1. They were then tested for their likeness to the present commercial CMA in their chemical composition and deicing performance. The purpose of this work was to evaluate the qualities and deicing ability of the CMA produced from cheese whey.

CMA Sample Preparation

CMA Samples from Process 1

The first sample (Sample 1) was prepared as follows. Three L synthetic media containing 4 percent lactate were fermented in a batch fermentor [37°C , $\text{pH} 7.6$,

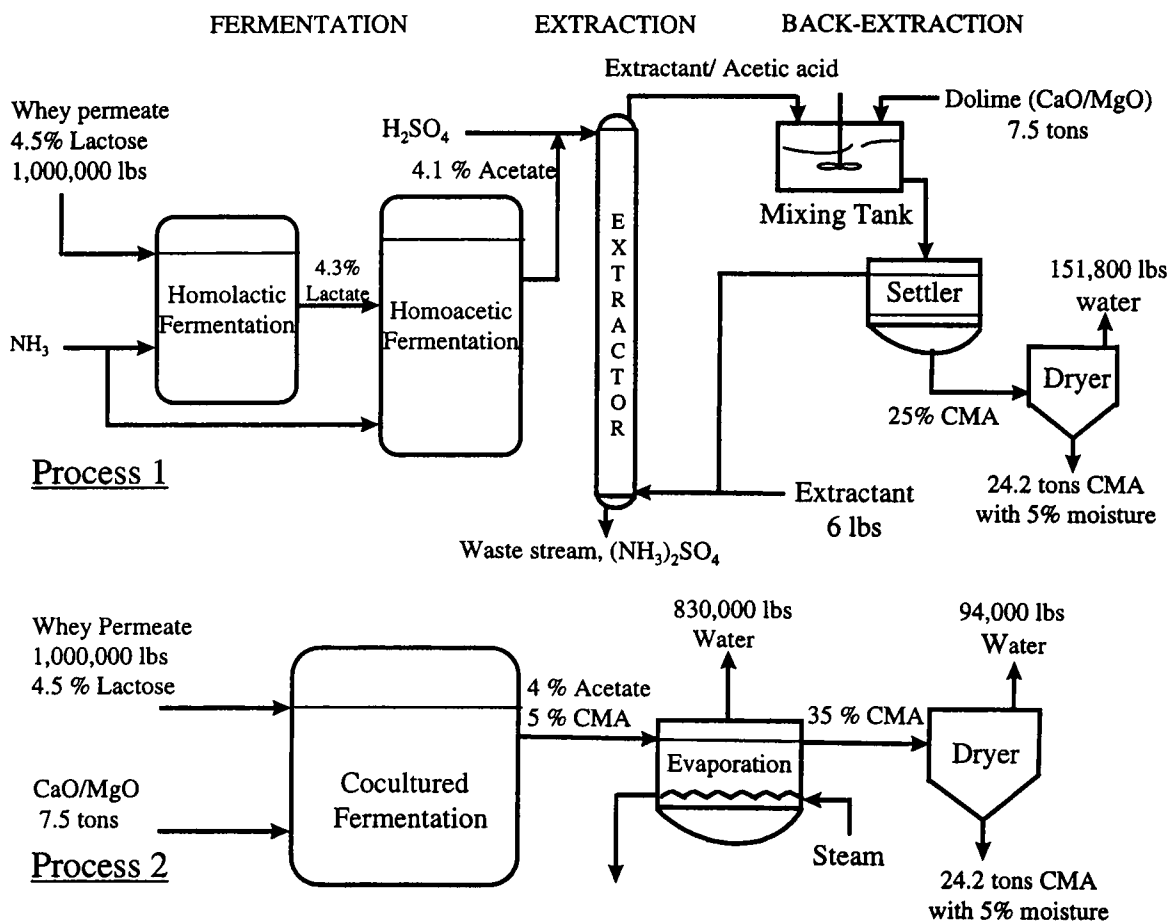


FIGURE 1 Two processes for CMA production from whey permeate.

with sodium hydroxide (NaOH)] for about 5 days. The broth containing 3.5 percent acetate was acidified to pH 3 with sulfuric acid, extracted with an amine extractant, and then back-extracted with CaO-MgO slurry. The CMA-containing solution was then dried and the solids were crushed to powder.

A second sample (Sample 2) was prepared from acid whey in a similar way. The acid whey was first fermented in a homolactic bioreactor to convert lactose to lactate. The broth was then added with some yeast extract and trypticase, autoclaved, and then fermented again in a homoacetic bioreactor to convert lactate to acetate. The final broth containing sodium acetate was then acidified with sulfuric acid, extracted with the amine extractant, and back-extracted with dolomitic limestone slurry. The three phases—organic, aqueous, and solid (unreacted dolime)—were then separated by centrifugation; the aqueous phase containing CMA was dried and crushed to obtain the powder product.

It was found later that these two CMA samples contained significant amounts of sulfate. Improved extraction methods were therefore used to prepare two more CMA samples. These two CMA samples were prepared from whey broth containing calcium acetate as follows. The broth containing 4 percent acetate was acidified to pH 3 with sulfuric acid. After the precipitate was removed, the broth was extracted with the amine extractant and then back-extracted with CaO-MgO slurry. One sample (Sample 3) was obtained from continuous extraction process by using the packed column extractor described previously and the other sample (Sample 4) was prepared from batch extraction. After the unreacted dolime was removed by centrifugation, the CMA-containing solution was dried and the solids were crushed to powder. These samples were then tested for acetate content and ice penetrating ability.

CMA Sample from Glacial Acetic Acid

For comparison purposes, a CMA sample (Sample 5) was prepared by directly reacting acetic acid with dolomitic lime (this is the present commercial production method for CMA deicer). After the unreacted solids were removed, the solution was dried and the solids were crushed to powder.

CMA Sample from Process 2

Another CMA sample (Sample 6) was prepared from the fermentation broth without extraction. Sweet whey permeate was fermented in a bioreactor containing both homolactic and homoacetic bacteria to convert lactose to acetate. CaO and MgO were used to neutralize the acetic acid during the fermentation. The initial lactose concentration in the whey medium was 3.5 percent and the final acetic acid concentration was 3 percent. After

cells and unreacted CaO and MgO were removed by sedimentation, the whole broth was dried to obtain an unrefined (crude) CMA sample.

CMA Sample Analysis and Testing

Composition Analysis

The first two CMA samples were tested for their CMA and insoluble contents and deicing ability. Weighted samples were dissolved in water. The solution was filtered to remove any insoluble and the filtrate was analyzed with high-performance liquid chromatography to determine acetate content. The filter paper used in filtration was washed and then dried. The dry weight difference of the filter paper before and after filtration was measured to determine the amount of insoluble in the CMA samples. Sample 1 had 60 percent CMA and 30 percent insoluble, Sample 2 had 75 percent CMA and 0 percent insoluble, and the commercial CMA product had 90 percent CMA and 7 percent insoluble. The large amount of insoluble in Sample 1 is believed to be CaO and MgO residues that were not reacted during back-extraction. This insoluble can be easily removed by filtration or centrifugation as evidenced in Sample 2, which does not have any insoluble. However, about 10 percent of Sample 1 and 25 percent of Sample 2 are believed to be magnesium sulfate ($MgSO_4$). This impurity was carried into the final CMA product by the sulfuric acid used to acidify the acetate broth during extraction. The product purity from the extraction process was later improved by avoiding sulfate contamination in the acetate broth.

Deicing Test

The ice penetration test described in SHRP H-205.3 was carried out to test the deicing ability of various CMA samples. The experiment was done at 0°C and -15°C. Salt and dolime were also tested for comparison purposes. A water-soluble blue dye and a deicer (in powder form) were spread to cover the surface of the ice formed in a well. The same weight of each deicer sample was used in this experiment. The color penetrating depth as a function of time after applying the deicer was recorded. Each sample test was duplicated and the average was plotted (Figure 2). Salt clearly is the fastest deicer and dolime does not work as a deicer. Sample 2 and commercial CMA have about the same deicing performance, and Sample 1 is slightly inferior because of its large insoluble content.

Comparison with Commercial CMA

The other four CMA samples were also tested for their acetate content and deicing ability. The ice penetrating

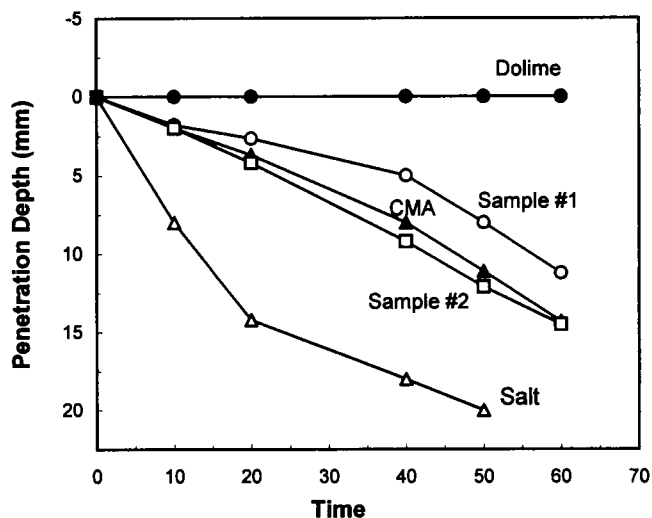


FIGURE 2 Ice penetration performance of various deicers at 0°C.

rate for each deicer was estimated from the ice penetration data, and the relative rate (with commercial CMA = 1) is reported in Table 3. Sample 3 has about the same acetate content as the commercial CMA deicer. The slightly lower acetic acid content per gram of the solid sample can be attributed to the higher calcium-magnesium ratio in this sample (the commercial CMA has a 3:7 ratio). The ice penetration experiment showed that this sample is at least as good as the commercial CMA deicer. Sample 4 is slightly inferior in its deicing ability. It is not clear why this sample did not perform as well as the other sample. There may have been some

procedural errors in preparing this sample by using batch extraction. Sample 6 is slightly better in its ice penetrating performance, probably because of the presence of other small molecular weight salts. Its acetate content is only 70 percent of the pure CMA sample. This is not unexpected since lactose makes up 70 percent of the total solids in whey. In summary, CMA samples from both processes showed an ice penetration rate similar to that of the commercial CMA. The CMA made from cheese whey should perform as well as the current CMA deicer made from glacial acetic acid.

ECONOMIC AND COST ANALYSES

An earlier study conducted by Stanford Research Institute (12) estimated that the CMA production costs from corn using *C. thermoaceticum* to ferment glucose to acetate were \$0.266/lb for a 100 ton/day plant and \$0.188/lb for a 1,000 ton/day plant. Depending on the plant size, the raw material costs associated with the feedstock used in the fermentations accounted for 30 to 50 percent of the total production costs. Any costs associated with the raw materials will presumably be transferred to the product cost on a one-to-one basis. It is thus compelling to use low-cost waste materials to produce CMA. Also, the CMA production costs were found to be more sensitive to the operating costs than to the capital costs. Increasing the acetate concentration from fermentation is especially important for reducing the operating costs when energy-intensive evaporation and distillation are used in product recovery. Similar conclusions were obtained in a more recent study (29).

TABLE 3 Comparison of Acetate Content and Ice-Penetrating Rate of Various CMA Samples

Sample	Composition (w/w %)			Relative Ice Penetrating Rate
	Acetate	Ca	Mg	
Commercial CMA deicer	67.2	8.38	10.62	1.0
Sample #1 synthetic medium	44.8	-	-	0.81 ± 0.11
Sample #2 acid whey	56.0	-	-	1.04 ± 0.02
Sample #3 continuous extraction	64.8	14.41	2.62	0.99 ± 0.01
Sample #4 batch extraction	70.1	21.34	0.095	0.88 ± 0.02
Sample #5 direct reaction	70.2	14.55	7.04	0.97 ± 0.03
Sample #6 whole fermentation broth	50.0	13.04	3.31	1.03 ± 0.02

Sample #1 also contained ~30% insolubles (mainly CaO and MgO)

Sample #2 also contained ~25% MgSO₄

Another recent study using either sewage sludge or woody biomass to produce CMA showed that the production costs would be \$0.117/lb if the residue biomass cost \$50/ton, or \$0.092/lb if the biomass were free (22). Anaerobic digestion with 6.5-day fermentation time to reach 3 percent acetate was assumed in this process evaluation. The product yield from fermentation was assumed to be 50 percent, and extraction with TOPO was used for acetate recovery and reaction with lime (CaO) to make calcium acetate. The plant capacity in this analysis was 500 tons/day CMA.

On the basis of cost relationships and financial analyses provided by these previous studies, the CMA production costs could be easily reduced to \$0.09 to \$0.15/lb or less by using zero-cost raw material such as sweet whey permeate and acid whey. Because the fermentation of whey performed either as well as or better than that in all the previous studies, it is conceivable that a low-cost CMA deicer could be produced from whey. The economics of the two CMA processes shown in Figure 1 were evaluated. Cost analysis for CMA production from whey permeate was based on a plant scale of processing 1 million lb whey permeate (4.5 percent lactose) per day, which is equivalent to a CMA production capacity of about 24 tons/day or 8,400 tons/year. This plant scale was chosen on the basis of present and immediate future market size for the CMA deicer and available cheese whey supplies from typical dairy plants. The product cost was estimated at \$328/ton for Process 1 and \$290/ton for Process 2. These costs are significantly lower than the present market price of \$1,000/ton. However, the CMA product from Process 2 also contains large amounts of other materials (30 percent in weight), which contribute to deicing performance. Thus, on a total solid basis, this product cost is only \$204/ton.

For these two CMA processes, the total direct production costs consist of 60 percent of the product cost. It is noted that CMA product costs would increase dramatically if the process scale were less than 25 percent of the one studied here. The economical process scale for CMA production from whey is 6 tons/day (2,200 tons/year) or more. This corresponds to a daily supply of 250,000 lb whey to the CMA plant. A cheese plant usually produces 250,000 to 1,000,000 lb whey per day. Therefore, producing CMA from whey should work well for both CMA manufacturing and whey disposal.

MARKET ANALYSIS

Comparison of CMA and Other Deicers

Although CMA has been proven to be as effective as rock salt in road deicing and is an effective anti-icing

agent, it is currently used only in limited areas because of its high price. A lower-cost CMA deicer (from cheese whey) should allow CMA to compete better with other chemical deicers (salt, calcium chloride, Cargill CG-90, and urea) and increase CMA use in deicing. It is noted that the demand for chemical deicers is very sensitive to winter weather and may vary by as much as a factor of two or three from year to year.

All solid chemical deicers, except salt, cost \$150/ton or more, but CMA at \$1,000/ton is the most expensive at present. However, all of these lower-cost deicers are more corrosive than CMA. Also, CMA is a corrosion inhibitor. The 20 percent CMA–80 percent salt mixture in solution has been shown to be almost as noncorrosive as the CMA solution. Thus, it is possible to make a deicer consisting of 20 percent CMA and 80 percent salt with a competitive price of \$150/ton. In addition, the federal government pays states for 80 percent of the CMA cost used in deicing new bridges and highways in environmentally sensitive areas. The costs for CMA users in these applications thus are only 20 percent of the purchasing price. When the low-cost CMA deicer from cheese whey is available, at a projected price of \$400/ton or lower, the CMA deicer will be much cheaper to use than most other low-corrosion deicers. However, federal cost sharing alone has not yet increased CMA use.

CMA Market Survey

Current Use of CMA in Highway Deicing

To determine CMA market size and price effects on its market acceptance, a CMA market survey of 10 state transportation departments was conducted in 1993. Only state transportation departments were surveyed because they are the major potential users of CMA and most current CMA use is for highway deicing. Of the 10 states surveyed, 8 had used CMA deicer in the past, but only 3 used CMA in the 1992–1993 winter season. Five states were planning to use CMA again in the 1997–1998 winter season. The amount of CMA used (or to be used) by each state ranged from 50 to 400 tons, depending on weather conditions. State transportation departments had used CMA in the past (*a*) to prevent corrosion (six responses), (*b*) to prevent environmental damage (two responses), (*c*) to support SHRP research (one response), and (*d*) to comply with laws banning the use of salt on new bridges (one response). The price of CMA was the most important factor affecting its future use. Other factors were deicing performance (six responses), followed by corrosion (two responses) and laws (one response). Environmental damage by salt was not considered as important to future decisions to use a CMA deicer.

Factors Affecting CMA Use

According to a 1991 report, the cost of salt use associated with infrastructure and automobile damage was \$555/ton (4). However, this information apparently did not encourage CMA use in highway deicing (four *no* responses, six *maybe* responses), especially at the CMA price of \$650/ton in 1993. Again, no respondents gave much attention to the environmental benefit of CMA use. The Intermodal Surface Transportation Efficiency Act of 1991, which provided states with 80 percent CMA costs, did not have a significant effect on CMA use either (eight *no* responses, one *yes*, one *maybe*), because federal funds were needed for highway reconstruction and rehabilitation. Also, the possible use of a 20 percent CMA and 80 percent salt mixture as a deicer to reduce both costs and corrosion did not appear to affect CMA use (six *maybe* responses, three *no*, one previous user). Only 50 percent of the respondents were interested in anti-icing using CMA (five *yes* responses, five *no*). However, this anti-icing application is likely to increase CMA use by 63 percent, based on the estimated CMA uses in anti-icing and in deicing.

The low-level interest in these potentially cost-effective applications may be attributed to a lack of education on the cost benefits of a CMA deicer, and a lack of a driving force for change. The high CMA price again was the major obstacle to CMA use in highway deicing. Price resistance may be much lower in the consumer product market if the CMA/salt blend works as effectively as salt. Laws banning salt use on new bridges and in environmentally sensitive areas have helped increase CMA use, but the effect is relatively small. It is clear that a much-lower-priced CMA is the only hope for increasing CMA use in highway deicing now and in the foreseeable future.

Effect of CMA Price on Market Size

Eight respondents provided their estimated CMA use at various price levels. Only one respondent indicated that price would have a slight effect for the range between \$400 and \$650. The price for CMA to start to break into the highway deicing market is most likely \$300/ton (six responses) or lower (\$200/ton, one response; \$100/ton, one response). Two respondents indicated that at the break-in price, the amount of CMA used could increase from zero or 200 tons to 50,000 to 100,000 tons. It is thus clear that the price effect on CMA use will not be significant until the price is \$300/ton or lower. On the basis of responses from this survey, CMA market size as affected by its price was estimated. Figure 3 illustrates the effect of CMA price on CMA market size normalized on either usage (tonnage) or market value (\$MM) with the \$650/ton price in 1993 at 1. Figure 3(a) gives a more conservative view

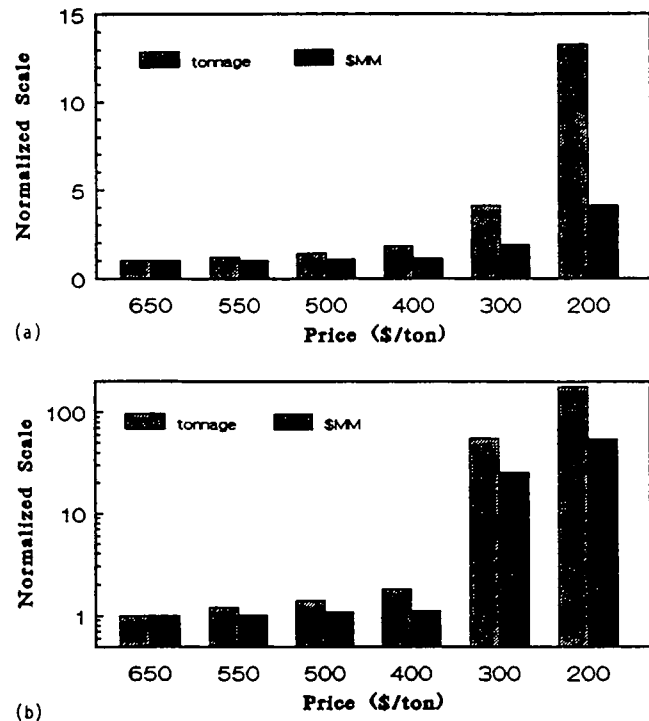


FIGURE 3 Effect of CMA price on projected market size: (a) conservative view; (b) aggressive view.

whereas Figure 3(b) provides a more aggressive view (based on a quantum jump in CMA use at the break-in price). It is clear that there is no commercial benefit to lowering the CMA price to \$400/ton, especially in the highway deicing market. This market survey did not cover other potential uses for CMA, such as for private property, airport, and municipality deicing, which may have a greater acceptance for a higher-priced CMA. These markets may provide better opportunities for small, local CMA producers.

CONCLUSIONS

Low-cost CMA deicers can be produced from cheese whey via anaerobic fermentation and extraction by using long-chain aliphatic amines. The CMA deicers produced from the two processes have deicing performance similar to that of the present commercial CMA deicer made from glacial acetic acid. The lowered CMA costs could dramatically increase CMA use in the deicing market.

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