A New Process for Producing Ca/Mg Acetate Deicer with Ca/Mg Waste and Acetic Acid Produced by Wet Oxidation of Organic Waste

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A new process for producing calcium magnesium acetate (CMA) deicer with acetic acid, produced by wet oxidation of organic wastes, and Ca/Mg wastes is proposed. Four kinds of representative organic waste were used as low-cost raw materials, for production of acetic acid, which was then converted to CMA by mixing with a Ca/Mg source such as oyster shells and industrial Mg wastes. The conversion efficiencies to acetic acid and from acetic acid to CMA achieved 14–16% and higher than 99%, respectively.

The most common chemicals used for roadway deicing are calcium chloride and sodium chloride. Widespread and massive use of these chloride salts, however, has serious corrosion and environmental problems.

Calcium magnesium acetate (CMA) has been proposed as a substitute for chloride salts, since it is relatively benign to the environment, besides it has acceptable ice-melting properties.[1,2] The cost, however, of manufacturing CMA, is a major drawback that limits its widespread application to a roadway deicer. CMA's high cost is mostly attributed to the production of acetic acid. Previous studies have indicated that wet oxidation is effective for treatment of organic waste of large water content, and that acetic acid is a stable intermediate product, whilst a high reaction temperature or catalyst is required for its complete decomposition.[3–7] Conversely, if the residual acetic acid can be utilized to produce acetate, rather than being decomposed, it should reduce the cost of manufacturing CMA.

In the experiment, rice hull as a representative of agricultural waste, Welsh onion as a representative of waste after extraction of valuable matters (anti-oxidant, in this case), and carrots and beef suet as representatives of food waste, were selected as low-cost raw materials for producing acetic acid by wet oxidation. Amounts of starting materials were limited to 0.07 g (dry base). Oyster shells, industrial wastes including MgO and $Mg(OH)_2$ (designated as Mg wastes hereafter), as well as reagent-grade $CaCO_3$, $Ca(OH)_2$ and $MgCO_3$/MgO, were used as sources of Ca and Mg. Liquid H_2O_2 was used as oxidant. A 100% H_2O_2 supply was defined on the basis of the stoichiometric demand of oxygen, for complete oxidation of carbon in the raw material to carbon dioxide. Previous studies have revealed that a H_2O_2 supply of 100% for vegetables and 150% for fats and meats was sufficient for their complete oxidation.[3]

Oxidation experiments for producing acetic acid were conducted using a batch reactor, with an internal volume of 5.7 cm^3, constructed of a piece of stainless steel 316. The typical procedure was as follows: the desired amount of test material and H_2O_2-water mixture were added to the batch reactor, which was then sealed. The reactor was put into a salt bath that had been preheated to a desired temperature. After the desired reaction time, the reactor was removed from the salt bath and put into a cold water bath to quench the reaction. The reaction time was defined as the duration at which the reactor was maintained in the salt bath. Experimental conditions for producing acetic acid are as follows: temperature 300–450 °C, reaction time 10–300 s, H_2O_2 supply 30–150%, pressure 12–33 MPa and water fill 30%.

After the oxidation reaction, solution samples were collected and analyzed by TOC (total organic carbon), ^{1}H-NMR, GC/MS, HPLC and/or CIA, and residual solids obtained by evaporating water after mixing with Ca/Mg sources were analyzed by XRD.

In order to attain economically viable acetate production, acetic acid concentration must be high. Experiments with food wastes, including the extracted onion waste, were performed over a wide range of conditions, to test if acetic acid can be produced in large quantity. Results show that a high acetic acid concentration can be obtained by controlling oxidation conditions. Case I in Table 1 shows the highest acetic acid yields and their respective experimental conditions. Acetic acid yield was relatively high, achieving 14–16% (wt/wt) of the starting materials. It should be mentioned that residual TOC concentration excluding acetic acid was also high in case I. Subsequently, the conditions for obtaining acetic acid with both high concentration and high purity were reassessed. Using conditions shown in case II of Table 1, high acetic acid yields were obtained, while the residual TOC decreased greatly. As such, these respective experimental conditions were selected, at the moment, as the optimum for producing acetic acid. A comparison of beef suet with vegetable (carrots, onion) shows that to obtain the same high acetic acid concentration using vegetable, as for the oxidation of beef suet, a decrease in oxygen supply is required, since it is readily oxidized. Carbon other than that in residual TOC including acetic acid is converted to carbon dioxide, with little carbon monoxide and residual solid in some case.

Based on this result, to obtain large-scale production of acetic

Table 1. Experimental conditions for production of acetic acid with highest concentration (Case I) and with both high concentration and purity (Case II), their yields, and residual TOC

	Temp. / °C	Time / s	O_2 / %	Yield / %[a]	Residual TOC/%[b]
Case I:					
Beef suet	400	30	100	15.7	20.4
Carrots	400	30	50	15.0	34.0
Welsh onion	400	30	50	14.8	33.5
Rice hull	300	60	70	14.1	30.0
Case II:					
Beef suet	400	30	150	15.5	7.0
Carrots	400	90	50	12.9	11.6
Welsh onion	400	90	50	12.5	10.9
Rice hull	330	60	110	12.3	6.9

[a] Acetic acid yield: wt/wt of starting material. [b] (Residual TOC excluding acetic acid/ initial TOC)×100%.

acid, rice hull was oxidized at a temperature between 300 and 400 °C. The highest acetic acid yield and the optimum condition for producing acetic acid are also shown in Table 1. Although the acetic acid yield (wt/wt) for rice hull shown in this table is slightly lower than those for carrots and onion, the acetic acid yield on the TOC/TOC basis is a little higher than those for carrots and onion because of the presence of inorganic material (about 20%) in the rice hull.

Residual intermediate products other than acetic acid were also identified. Results showed that (1) in the case of beef suet, other intermediate products were mainly low molecular weight mono-carboxylic acids with 3–4 carbon atoms in both cases I and II; (2) for vegetable (rice hull, carrots, onion), in case I, other intermediate products were not only low molecular weight carboxylic acids (both mono- and dicarboxylic acids) but also 5-hydroxymethyl-2-furaldehyde (HMF), 2-furaldehyde (2-FA) and 1-hydroxy-2-propanone, while in case II, residual intermediate products were almost low molecular weight carboxylic acids (mainly oxalic acid). HMF may come from dehydration decomposition of glucose and 1-hydroxy-2-propanone from thermal decomposition of polysaccharide.

In case of meat, ammonia may remain. An additional experiment with pork (nitrogen content: 13.1%) at the same condition as that for beef suet in case I in Table 1 showed 2200 ppm of residual concentration of ammonia (equivalent to about 40% of initial amount) as well as 7000 ppm of acetic acid. A pH of the solution was 7.7 instead of 3 to 4 for other cases.

Subsequently, experiments of production of calcium/magnesium acetate were carried out by mixing the Ca and Mg reagents into acetic acid solution produced in case II. Figure 1 shows the ^{1}H-NMR spectra of intermediate products, for mixing and non-mixing of $Ca(OH)_2$. In the case of mixing of $Ca(OH)_2$, a signal of methyl protons of calcium acetate at 1.91 ppm is observed (Figure 1(b)) for all testing materials. Similar results were obtained when using $CaCO_3$, $MgCO_3/MgO$, instead of $Ca(OH)_2$. The results indicate that acetic acid produced by wet oxidation can be easily converted into calcium/magnesium acetate by mixing with a Ca/Mg reagent.

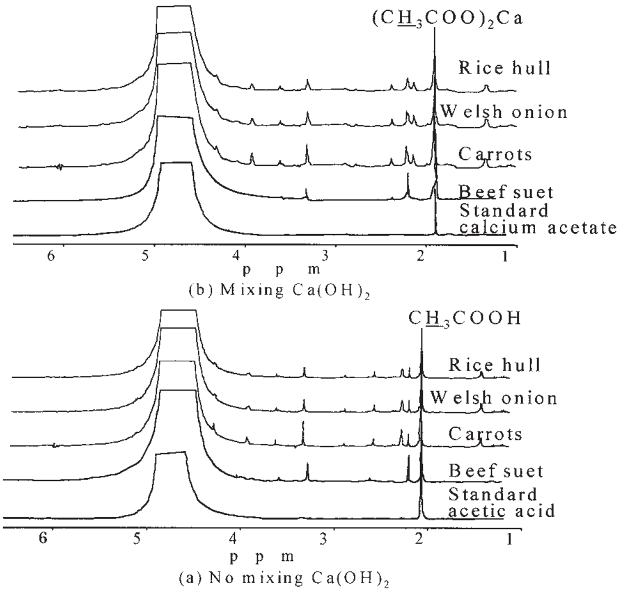

Figure 1. ^{1}H-NMR spectra of intermediate products in solution, after oxidation under the conditions used to produce the highest yield of acetic acid; with (a) no-mixing and (b) mixing of $Ca(OH)_2$.

The XRD analyses of residual solid, obtained by evaporating water after mixing with Ca/Mg sources, were carried out. As shown in Figure 2, calcium acetate crystals were found, but peaks for ammonium acetate, which might be seen at $2\theta = 18.76$, 21.94, 22.96, 24.14, were not detected, even when ammonia was added to a solution as much as making the pH 7.0. Magnesium acetate crystals were also obtained when using reagents $MgCO_3$/MgO (not shown).

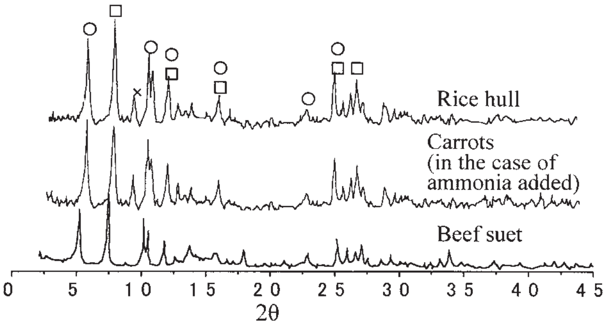

Figure 2. XRD patterns of solid product obtained (□: $(CH_3COO)_2Ca\cdot H_2O$, ○: $(CH_3COO)_2Ca\cdot 0.5H_2O$, ×: $(CH_3COO)_2Ca$).

Further, tests were undertaken to see if oyster shells and Mg wastes would react with acetic acid solutions. Ground oyster shells and Mg wastes were mixed with acetic acid solutions produced in case II, by wet oxidation of rice hull, carrot, beef suet. Similar results were obtained using oyster shells and Mg wastes as with reagent $CaCO_3$, and $MgCO_3/MgO$, which indicated a potential use of oyster shells and Mg wastes as low-cost source of Ca/Mg in the production of CMA.

The conversion efficiencies of acetic acid to Ca/Mg acetate were investigated using $CaCO_3$, $Ca(OH)_2$, $MgCO_3/MgO$ reagents, oyster shells, and Mg wastes, as sources of Ca and Mg. Results show that the relative efficiencies were (1) reagent $Ca(OH)_2$ = reagent $CaCO_3$ > (2) reagent $MgCO_3$ > (3) reagent $Mg(OH)_2$ > (4) Mg wastes > (5) oyster shells, considering the stoichiometric demand of Ca/Mg for complete neutralization of acetic acid. However, when using an excess of concentrated Ca and Mg, > 99% conversion efficiency was obtained within 10 minutes, using either the reagents, oyster shells or Mg wastes, although the reaction rate differed for various sources of Ca and Mg.

It should be added that residual organic compounds other than acetic acid are mostly low molecular weight carboxylic acids and ammonia in case of meat, that Ca/Mg salts of these acids except of oxalic acid may also be used as deicer, and that ammonia does not remain in solid compounds obtained by evaporation of water.

References and Notes

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