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Kinetics study of thermal decomposition of sodium carboxylate salts

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ABSTRACT

The MixAlco™ process ferments lignocellulosic biomass to carboxylate salts that are thermally decomposed into ketones, which are then chemically converted to a wide variety of chemicals and fuels. To perform these decompositions, suitable reaction models are necessary to properly design, scale, and optimize commercial reactors. For three salt types (sodium acetate, and two types of mixed sodium carboxylate salts), activation energy was determined using three isoconversional methods that employed TGA curves at different heating rates. For all three salt types, activation energy varied significantly with conversion. The average activation energy for sodium acetate was 226.65 kJ/mol, and the activation energies for the two mixed sodium carboxylate salts were 195.61, and 218.18 kJ/mol. In addition, three functions of conversion were employed to see which one best modeled the experimental data. The Sestak-Berggren model fits all three salt types best.

1. Introduction

Using the MixAlco™ process, the thermal decomposition of carboxylate salts is a critical step in converting biomass into useful chemicals and fuels. Kinetic models and parameters for these decompositions are necessary to design and size reactors on a commercial scale. The MixAlco™ process (Fig. 1) is a biorefinery that ferments lignocellulose into mixed carboxylate salts via anaerobic mixed-acid fermentation. The carboxylate salts are concentrated by evaporation and chemically converted into chemicals, solvents, and fuels (e.g., ketones, alcohols, and gasoline) [1–3].

Lignocellulosic biomass is first pretreated with calcium hydroxide (lime) to increase digestibility and is then fermented to carboxylic acids using a mixed culture. The fermentation broth is adjusted to pH 8–10 by adding hydroxide, which ensures that all of the carboxylic acids are neutralized. Then the fermentation broth is clarified and dewatered, which involves evaporating all volatiles in the broth, leaving precipitated solids. The solids remaining after dewatering are mostly carboxylate salts with small amounts of cells, extracellular proteins, and minerals.

The carboxylate salts are thermally decomposed to yield their corresponding ketones, as shown in Equation (1).

$$M^+(RCOO^-) + M^+(R'COO^-) \rightarrow RCOR' + M_2CO_3 \quad (1)$$

For purposes of this study, M^+ is a sodium ion, but generally can be any alkali metal or half of any alkaline earth metal.

The aim of this study is to first properly model the thermal decomposition of a simple carboxylate salt (sodium acetate) and then apply that model to the thermal decomposition of a mixture of reagent-grade carboxylate salts similar to that produced by the MixAlco™ process. Finally, the model is tested using actual carboxylate salts from a MixAlco™ fermentation. The first step was to determine the activation energy (E_A) for the thermal decomposition of all three salt types using three isoconversional methods. Next, functions of conversion were proposed to model each of the thermal decompositions using

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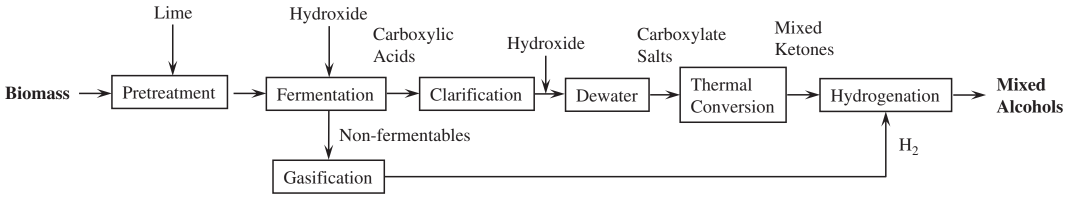

Fig. 1 – MixAlco™ process diagram.

three isothermal models. The use of reagent-grade salts eliminated reactions associated with impurities found in fermentation salts, allowing measured kinetics to be attributed solely to the thermal decomposition of the carboxylate salts.

2. Materials and methods

2.1. *Preparation of salts*

In this paper, any solid mixture of sodium carboxylate salts will be described as *salts*. Anhydrous sodium acetate (Mallinckrodt Chemicals, AR (ACS), 99.0%) was used for this study. It was ground with mortar and pestle and sieved into a particle size range of 150–212 μm. The sodium acetate was then dried at 105 °C for 24 h and placed in a desiccator.

Reagent-grade salts were prepared by mixing the corresponding reagent-grade carboxylic acids with equimolar amounts of reagent-grade sodium carbonate in deionized water, resulting in a solution of pH 8.5. These acid and corresponding salt profiles are typical of what has been reported for anaerobic mixed culture fermentation [4–6]. A 2-L aliquot of this solution was evaporated in a glass beaker. The reagent-grade precipitated salts were collected, weighed, and dried at 105 °C for at least 24 h. The salts were ground with mortar and pestle and washed with chloroform to remove any residual acids. The salts were separated into the same particle size range as sodium acetate and then dried at 105 °C for an additional 24 h and placed in a desiccator.

Fermentation salts were prepared using clarified broth from a MixAlco™ fermentation (Terrabon, Inc, Houston, TX). Clarification was performed using a proprietary process involving ultra-filtration and reverse osmosis. The broth was adjusted to pH 9 by adding excess sodium carbonate and was then evaporated to collect the fermentation salts. The fermentation salts were ground and separated into a particle range in the same manner as the reagent-grade salts. Acid and corresponding salt compositions were verified by gas chromatography (Table 1).

2.2. *Thermal decomposition*

Thermal gravimetric analysis (TGA) decompositions were performed in a Netzsch TG 209 C thermal analyzer. Samples were weighed (5–10 mg) into 100-μL aluminum sample pans. A purge gas of N_2 at a flow rate of 20 mL/min was used for all runs. For isothermal runs, the temperature was ramped up to the set temperature at a rate of 20 °C/min. Non-isothermal runs used heating rates of 1, 2, 4, 8, and 16 °C/min.

A Carbolite HTR 11/75 rotary reactor furnace with a viewing panel was used to visually inspect the decomposition reaction. Samples of 30 g were placed in the reaction vessel and a purge gas of N_2 at a flow rate of 50 mL/min was used for all runs. All runs in the rotary reactor furnace used a heating rate of 10 °C/min.

2.3. *Solid analysis*

Samples of reagent-grade and fermentation salts were weighed (0.3 g) and dissolved with 2 mL of 3-M phosphoric acid. The mixture was then diluted to 10 mL with deionized water. Solutions of dissolved salts were mixed with equal parts of a 1.162 g/L solution of 4-methyl-valeric acid (internal standard) and 3-M phosphoric acid. Acid analysis was performed using an Agilent 7890A gas chromatograph (GC) system equipped with a flame ionization detector (FID), and an Agilent DB-FFAP: J&W 123-3232 column. Injection volume was 0.2 μL and inlet temperature was 230 °C. Carrier gas was helium at 103 kPa (gauge) at a flow rate of 3.78 mL/min. The

Table 1 – Acid and corresponding salt profiles of reagent-grade and fermentation salts.

Carbon number	Acid	Reagent-grade salts		Fermentation salts	
		Acid (wt.%)	Salt (wt.%)	Acid (wt.%)	Salt (wt.%)
2	Acetic	37.48	40.46	45.13	47.68
3	Propionic	14.75	14.97	19.77	19.63
4	Isobutyric	1.43	1.39	1.33	1.27
4	Butyric	12.23	11.87	18.25	17.33
5	Isovaleric	2.60	2.44	3.22	2.95
5	Valeric	10.43	9.79	6.69	6.14
6	Caproic	13.44	12.28	4.20	3.75
7	Heptanoic	5.63	5.04	1.11	0.97
8	Octanoic	2.01	1.77	0.31	0.27