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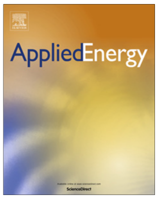

# The deleterious effect of inorganic salts on hydrocarbon yields from catalytic pyrolysis of lignocellulosic biomass and its mitigation

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## HIGHLIGHTS

- Alkali and alkali earth metals decreased hydrocarbon yields during catalytic pyrolysis of biomass.
- The effect on reducing hydrocarbon yields followed the order: $K^+ > Na^+ > Ca^{2+} > Mg^{2+}$.
- Metals enhanced cracking and dehydration reactions increasing thermally-derived $CO_x$.
- Both acid-infusion and acid-washing increased yields of aromatic hydrocarbons.

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## ABSTRACT

The effect of alkali and alkali earth metals (AAEMs) on yields of hydrocarbons from catalytic pyrolysis of biomass was investigated. Experiments were performed in a tandem micro-reactor that segregates the biomass from the zeolite catalyst (*ex-situ* catalytic pyrolysis). It was found that even trace amounts of AAEMs added to cellulose as acetate salts dramatically reduced the yields of hydrocarbons. Both the concentration and types of AAEM salts impacted product distribution. The yield of aromatics and olefins decreased monotonically with increasing concentration of AAEMs. The effect of AAEMs on reducing hydrocarbon yields followed the order: $K^+ > Na^+ > Ca^{2+} > Mg^{2+}$. Two pretreatments of biomass were investigated to alleviate the catalytic effects of AAEMs that naturally occurs in biomass: acid-washing and acid-infusion. It was found that pretreated biomass increased yields of hydrocarbons apparently by suppressing reactions that would otherwise convert carbohydrate to non-condensable gases and char.

## 1. Introduction

Catalytic pyrolysis is a promising pathway for production of aromatic and olefin hydrocarbons from biomass suitable for use in reformate gasoline and other energy products [1–6]. While several types of catalysts have been explored, HZSM-5 zeolite is attractive for its ability to produce gasoline-range aromatics and value-added olefins [4,5,7,8]. Catalytic pyrolysis using zeolites appears to occur in two stages: thermal decomposition of solid biomass followed by catalytic conversion of the resulting vapors over zeolite. Extensive research using individual components or model compounds has been conducted to understand the effect of biomass composition on product yields and to elucidate reaction mechanisms [9–12]. However, the effect of inorganic minerals found in biomass, mainly alkali and alkali earth metals (AAEMs), on catalytic pyrolysis remains relatively obscure. These metals are known to influence the thermal decomposition of polysaccharides, significantly affecting pyrolysis product distribution [13–15]. AAEMs are thought to form coordination bonds with the oxygen atoms of vicinal hydroxyl groups of the glucose ring, thereby making the ring unstable. This enhances the formation of low molecular weight oxygenates while suppressing the formation of levoglucosan. In practice, the catalytic activity of AAEMs can be mitigated by pretreatment of the biomass prior to pyrolysis by either washing out the metals [16–19] or convert them to thermally stable salts that prevent the metals from effectively interacting with the biomass [20,21].

Alkali and alkaline earth metals are important nutrients in plant growth. Often these remain in the harvested plant material and represent part of the ash content of feedstocks. It is well known to contribute to ash fouling during combustion and gasification of biomass, but it also represents a challenge in catalytic pyrolysis where it has been reported to accumulate on zeolite catalysts [22,23]. Accumulations of AAEM can lead to catalyst deactivation

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at a rate dependent upon AAEM content but even small amounts can be problematic over time.

We hypothesized that AAEMs, by changing the distribution of primary products of pyrolysis, will influence product distribution of catalytic pyrolysis. Experiments included tests with pure cellulose treated with acetate salts of AAEMs, which simulate the forms of AAEMs naturally occurring in biomass, and tests with real biomass that was either acid-washed or acid-infused.

## 2. Materials and methods

### 2.1. Feedstock

Microcrystalline cellulose (Sigma–Aldrich) with negligible amount of inorganic minerals was used to investigate the effect of minerals on catalytic pyrolysis of cellulose. Acetate salts used in this study were purchased from Fisher Scientific with >99.5% purity. The pure cellulose sample was impregnated separately with acetate salts of potassium (K), sodium (Na), calcium (Ca), and magnesium (Mg), using the method described in a previous study [13]. Briefly, a desired amount of acetate salt was dissolved in 25 ml deionized water and this solution added to 2.5 g of cellulose and stirred to obtain well-mixed slurry. The sample was dried in an oven at 110 °C overnight to obtain an acetate-impregnated cellulose sample.

Red oak purchased from Wood Residual Solutions (Montello, Wisconsin) was ground and screened to a size range of 250–400 μm. Acid-washed red oak samples were prepared by the method described by Patwardhan et al. [24]. In brief, the biomass samples were washed with 0.1 N $HNO_3$ for 15 min, followed by three subsequent washes with deionized water to remove the acid. Acid-infused red oak samples were prepared by the method described by Kuzhiyil et al. [20] using sufficient sulfuric acid to stoichiometrically react with the AAEMs in the biomass to form thermally stable salts. All the pretreated red oak was dried in an oven at 50 °C to the same moisture content as the original sample. Further information on the red oak used in these experiments can be found in previous studies [20,25].

### 2.2. Pyrolysis reactor

Catalytic pyrolysis experiments were conducted on a Tandem micro-scale reactor system (Rx-3050 TR, Frontier Laboratories, Japan) coupled with a gas chromatograph (GC) (7890A, Agilent Technologies, USA). A schematic diagram of the system is shown in Fig. 1. A detailed description of the system is found in previous publications [26,27]. Inorganic minerals found in biomass have been reported to accumulate on zeolite catalyst, which decreases the catalytic activity over time [22,23]. A previous study from our group suggested that *ex-situ* catalytic pyrolysis, by separating pyrolysis and catalytic conversion into two reactors, has several important advantages including reducing the frequency of catalyst regeneration and extending catalyst lifetime [27]. Accordingly, all catalytic pyrolysis experiments in the present study used an *ex-situ* configuration except where otherwise indicated. HZSM-5 catalyst (CBV2314, Zeolyst, USA) with particle size of 50–70 mesh was used in this study. Biomass was pyrolyzed in the first reactor at a prescribed temperature with pyrolysis vapors transported to the catalyst bed reactor that operated at an independently controlled temperature.

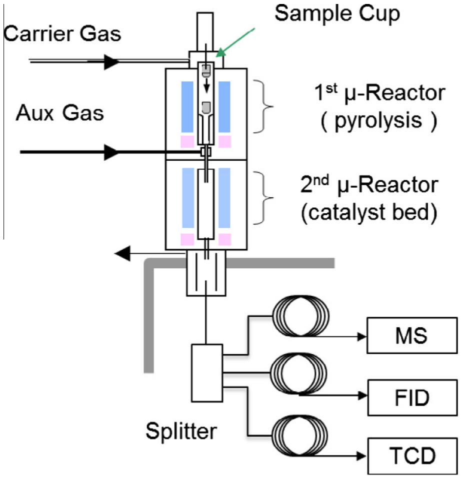

**Fig. 1.** Schematic diagram of Tandem micro-reactor system in this study.

The volatiles were analyzed by the Agilent GC installed with three GC columns and detectors. The GC oven program started with a 3-min hold at 40 °C, followed by ramping to 250 °C at a heating rate of 10 °C/min. The final temperature was held for 4 min. The injector temperature was set at 250 °C. A mass spectrometer detector (MSD) was used to identify the products while a flame ionization detector (FID) and a thermal conductivity detector (TCD) were used to quantify the condensable volatiles and non-condensable gas products. A Phenomenex ZB 1701 (60 m × 0.250 mm and 0.250 μm film thickness) and a Porous Layer Open Tubular (PLOT) column (60 m × 0.320 mm) (GS-GasPro, Agilent, USA) were connected to FID and TCD, respectively. Both columns are calibrated with standards. Details about quantification and calibration can be found in previous studies [18].

Non-catalytic pyrolysis experiments were also performed in the Tandem reactor with the catalytic reactor empty. The interface temperature was set to 350 °C to minimize condensation of products. At the end of an experiment the mass of thermally-derived char was calculated as the weight change of the sample using a microbalance. Condensable organic compounds were quantified by FID using method described in a previous study [28]. Thermally-derived carbon monoxide and carbon dioxide ($CO_x$) were quantified by TCD. Catalytically-derived $CO_x$ was calculated by subtracting the yield of $CO_x$ for non-catalytic pyrolysis from the total yield of $CO_x$ for catalytic pyrolysis under otherwise identical reaction conditions.

## 3. Results and discussion

### 3.1. Effect of calcium acetate on catalytic pyrolysis of cellulose

To investigate whether AAEMs influence the yield of products from catalytic pyrolysis that are suitable for fuels and other energy applications, pure cellulose was impregnated with $Ca(CH_3COO)_2$ (CaAc) at five different levels: 0.006, 0.02, 0.05, 0.15, and 0.3 mmol calcium acetate/g cellulose. The impact of CaAc on catalytic pyrolysis of cellulose is summarized in Fig. 2. Detailed product distributions for those samples are found in Table S1.

Presence of even small amounts of CaAc in cellulose noticeably decreased yields of both aromatic and olefin hydrocarbons. Carbon yield of aromatics decreased monotonically from 27.2% for pure cellulose to 18.5% as CaAc concentration increased to 0.3 mmol/g cellulose (approximately 4.7 wt%). Olefin yield from pure cellulose was 17.5%, decreasing to 13.7% in the presence of 0.3 mmol/g CaAc in cellulose.

Carbon yield of CO decreased monotonically from 29.2% to 19.0% while yield of $CO_2$ increased from 7.7% to 9.5% as CaAc increased to 0.3 mmol/g cellulose. To better understand the different trends for CO and $CO_2$, non-catalytic pyrolysis were also performed under identical reaction conditions. Thermally- and catalytically-derived $CO_x$ yields are summarized in Fig. 2.