



# Calcium-catalyzed pyrolysis of lignocellulosic biomass components



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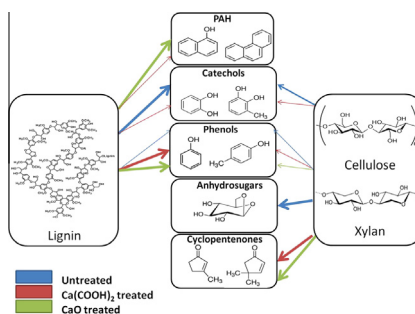
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## HIGHLIGHTS

- Individual biomass components are pretreated with calcium compounds and pyrolyzed.
- Oil characterization indicates that calcium compounds alter pyrolysis chemistry.
- Reactions, including deoxygenation and alkylation are observed.
- Reaction pathways are proposed based on experimental evidence.

## GRAPHICAL ABSTRACT



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## ABSTRACT

The present study examines the effect of calcium pretreatment on pyrolysis of individual lignocellulosic compounds. Previous work has demonstrated that the incorporation of calcium compounds with the feedstock prior to pyrolysis has a significant effect on the oxygen content and stability of the resulting oil. The aim of this work was to further explore the chemistry of calcium-catalyzed pyrolysis. Bench-scale pyrolysis of biomass constituents, including lignin, cellulose and xylan is performed and compared to the oils produced from pyrolysis of the same components after calcium pretreatment. The resulting oils were analyzed by quantitative GC–MS and SEC. These analyses, together with data collected from previous work provide evidence which was used to develop proposed reaction pathways for pyrolysis of calcium-pretreatment biomass.

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## 1. Introduction

For several decades, fast pyrolysis of lignocellulosic biomass has been a promising route to produce renewable fuels and chemicals because of the robustness of the process and the high liquid yields produced. Recently, however, it has become clear that there are significant issues with downstream processing of pyrolysis oil to produce a drop-in fuel. Pyrolysis oil is highly oxygenated, making it unstable during storage for any appreciable length of time. Upgrading processes to simultaneously hydrogenate and deoxygenate use moderately high temperatures which increase the rate

of polymerization of the oil. Because of this, a low-temperature stabilization step is required before hydrodeoxygenation can be performed (Mercader et al., 2011; Venderbosch et al., 2010). This creates a significant economic barrier to production of transportation fuels from pyrolysis. In order to overcome these issues, catalysts have been added directly to the pyrolysis reactor to directly produce oil with lower oxygen content (Agblevor et al., 2010; Carlson et al., 2009). Zeolite catalysts, specifically ZSM-5, are the typical choice for catalytic fast pyrolysis. This choice is based on the successful use of zeolites in the petroleum refining industry. While other types of catalysts have been studied (Di Blasi et al., 2008; Lu et al., 2009; Meesuk et al., 2011; Veses et al., 2014), zeolites are still used primarily.

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The proposed mechanism for zeolite pyrolysis is an acid-catalyzed “carbon pool” chemistry, similar to that observed for catalytic conversion of methanol to olefins (Wang et al., 2003). In this mechanism, oxygenated biomass intermediates (mainly anhydrosugars) are fragmented and oxygen is removed in the form of CO, CO<sub>2</sub>, and H<sub>2</sub>O. The remaining hydrocarbon fragments, such as short-chain olefins, then combine to produce thermodynamically-favorable aromatics. In the hydrogen-deficient, oxygen-rich pyrolysis environment, however, this chemistry also promotes formation of carbonaceous residues (“coke”) on the surface of the catalyst. This coke lowers the acidity of the catalyst surface resulting in deactivation (Du et al., 2013). The coke formed on the catalyst can be removed by combustion, and circulating fluidized bed reactors have been employed for continuous catalyst regeneration. This reactor design adds complexity to the pyrolysis system, increasing the capital and operating costs associated with the process.

In addition to catalyst coking, zeolite catalysts present other technical issues for biomass pyrolysis. The high temperatures for pyrolysis and regeneration, as well as the presence moisture from the biomass, can cause detrimental changes in the pore structure and surface composition of the zeolite (Vitolo et al., 2001). Also, perhaps most significantly, zeolite catalysts can be irreversibly fouled by alkali and alkaline earth metals present in biomass feedstocks. This fouling leads to loss of acidity and activity of the catalyst (Mullen and Boateng, 2013; Paasikallio et al., 2014).

In order to avoid the issues associated with solid-acid catalysts, such as zeolites, research has focused on the application of basic catalysts for fast pyrolysis. By employing cations such as alkali and alkaline earth metals (AAEM), synergy between the catalyst and naturally occurring ash components in the biomass can be achieved. In this approach, inorganic compounds which are always present in biomass do not foul or deactivate the catalysts, allowing for potential simplification of reactor design and improved economics.

Results have been reported previously on the effect of various calcium salts on the fast pyrolysis of pine, lignin, and tannins with a particular emphasis on calcium formate (Case et al., 2014a,b; Mukkamala et al., 2012). In this work, the effects of two calcium compounds, calcium oxide and calcium formate, are investigated for pyrolysis of lignin, cellulose and xylan. These two particular calcium compounds were chosen after studying several pretreatments because calcium formate showed particular action as a hydrogen donor and calcium oxide showed the most significant deoxygenation activity. The use of lignocellulosic model compounds in bench-scale pyrolysis experiments provides information about the origin of particular compounds observed during previous pyrolysis experiments and allows for elucidation of mechanistic pathways.

## 2. Methods

### 2.1. Feedstock preparation

Lignocellulosic compounds used were Indulin AT (sodium-free kraft lignin, MeadWestVaco), spray-dried nanocellulose produced mechanically from kraft pulp (UMaine Process Development Center), and xylan from beechwood (TCI chemicals).

The mass loading of calcium used was the same as in previous studies, 0.43 g calcium/g biomass component (Case et al., 2014a,b). This loading corresponds to the addition of 140 g calcium formate and 60 g calcium oxide, respectively, to 100 g biomass component. In all cases, the mixture of biomass component/calcium compound was oven dried to 5–10% moisture and sieved to achieve particles smaller than 1.5 mm.

### 2.2. Pyrolysis

The pretreated components were pyrolyzed with 40–60 mesh sand as heat transfer medium in a 3.5 cm × 30 cm entrained flow reactor described in detail elsewhere (DeSisto et al., 2010). The reactor temperature was measured using two K-type thermocouples located on the vertical axis measured 3.0 and 9.5 in. from the top of the reactor. The pine/calcium formate mixture was metered through a screw feeder and pneumatically fed into the reactor, using a nitrogen flow rate of 6 L/min. Feed rates varied somewhat depending on the material properties, but the vapor residence time was held constant by the nitrogen flow. The pyrolysis temperature was 500 °C for all experiments. Immediately downstream of the reactor, char was separated using a hot gas filter (HGF) also held constant at 500 °C. The total vapor residence time in the fluidized bed reactor and the HGF was 10–12 s, with about 90% of that time in the HGF. After the vapor passed through the hot gas filter, the liquid was collected in a condenser operated at 6 °C, followed by an electrostatic precipitator (ESP) to collect aerosols.

### 2.3. Product characterization

The organic phase of the bio-oil naturally phase-separated from water, however all analysis was conducted on oils collected from the electrostatic precipitator to ensure that there was no residual water.

#### 2.3.1. Size exclusion chromatography

Size exclusion chromatography (SEC) was performed using an Shimadzu HPLC–GPC equipped with two columns measuring 1–1 k Daltons and 1 k–20 k Daltons, respectively, with N,N-dimethylformamide (DMF)/Trichloroacetic acid/LiBr as the mobile phase. All of the oil samples were completely soluble in this solvent mixture, as well as the Indulin AT feedstock. The nanocellulose and xylan feedstocks were not soluble however, so no data for the molecular weight distributions of these feedstocks is presented. Due to the relatively low molecular weight of the oils produced with hot gas filtration, a large fraction of the sample elutes at the end of the calibration range with low resolution, making it difficult to quantitatively determine the molecular weight distribution and average molecular weight of an unknown sample. Therefore, results from this method were used for comparative purposes only.

#### 2.3.2. Quantitative analysis by GC/MS

Chemical composition was characterized using a Shimadzu Q2010 gas chromatograph–mass spectrometer (GC–MS). The samples were diluted with ethyl acetate and prepared by adding known amounts of butylated hydroxytoluene as a recovery standard and biphenyl as an internal standard. All of the samples were derivatized with N-methyl-N-(trimethylsilyl) trifluoroacetamide (MSTFA) for one hour before analysis. Compounds reported were verified by both mass spectral fragmentation pattern and retention time matches to genuine standards.

## 3. Results and discussion

### 3.1. Gas chromatography–mass spectrometry (GC–MS)

The organic fractions of the oil products were analyzed by GC–MS. While this technique provides valuable information about the chemical structure of oil components, it can identify only a small fraction of the pyrolysis oil (typically less than 20%). This is because of several factors. First, because of the diversity of compounds

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