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Synergism among biomass building blocks? Evolved gas and kinetics analysis of starch and cellulose co-pyrolysis

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ABSTRACT

Debate surrounds biomass co-pyrolysis: can thermal decomposition be modeled as the sum of individual components, or do synergistic reactions promote or hinder devolatilization? Activation energies of mixtures of starch and cellulose pyrolyzed at 10, 50 and 100 K/min were determined via the distributed activation energy model. Reaction kinetics suggest that blending may promote devolatilization, seen through lower activation energies. Yet, evolved gas analysis shows no evidence of synergism as a result of blending, at least at lower temperatures. As the percentage of cellulose increases, the temperature at which the peak mass loss rate occurs and peak evolved gases emerge are linearly related. As such, there is little evidence of chemical reaction synergism during the pyrolysis of these two biomass building blocks, but rather synergistic behavior is perhaps a result of the starch physically promoting the devolatilization of cellulose at lower temperatures when present in larger quantities.

1. Introduction

The 2007 United States Independence and Security Act mandates that 16 billion gallons of cellulosic biofuel be blended into traditional transportation fuels by 2022, a portion of which must be biodiesel produced from biomass [1]. The widespread use of biomass as a renewable feedstock for the production of liquid fuels and syngas depends on several factors. For the pyrolytic conversion of solids, these include the ability to design appropriate reaction systems, insure adequate supplies of feedstocks, standardize biomass-derived pyrolysis liquid products and, perhaps most importantly, develop a comprehensive understanding of the thermochemical pathways underlying the decomposition of solid biomass to liquid and gaseous fuels [2]. The ability to predict the behavior of mixed biomass streams during co-pyrolysis is imperative to insuring successful large-scale implementation of thermochemical conversion of biomass to biofuels.

A number of studies demonstrate the ability to alter bio-oil and pyrolysis gas composition and yield from pyrolysis, the thermal decomposition in the absence of oxygen, by changing reaction temperatures, pressures and heating rates [3,4] as well as exploiting reaction synergy among solid fuels to tailor the properties of the pyrolysis products by co-pyrolyzing biomasses [5]. This is critically important as we move forward with industrial scale production of bio-oils via thermal treatment. However, we require a deeper understanding as to the nature of these synergistic reactions. For example, does the physical compilation of solid fuels that devolatilize at lower temperatures than others cause changes in overall reaction rates and kinetics? Does blending fuel streams change the pyrolysis gas compositions evolving from solid blend pyrolysis? Can we predict the activation energies required to pyrolyze blended fuel streams from knowledge of their pure component characteristics, or does synergy impact activation energies? These and other questions must be answered on a fundamental level to better design industrial pyrolysis units and determine optimal feedstock blends. For that reason, here we investigate the kinetics and evolving gas compositions of two fundamental biomass building blocks with the same chemical formula but different molecular geometry: starch and cellulose.

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There is discord in the literature about the nature of blended solid fuel pyrolysis; some find that the yields and activation energies of co-pyrolyzed fuels are linearly proportional to the contributions of the individual components [6,7]. Others detect non-additive compositions and activation energies across heating rates and temperature ranges [8–10]. And yet still others, our group included, find both additive and synergistic behavior for the same samples, such as the peak mass loss reaction rates found via derivative thermogravimetric curves displaying additive behavior (linearly increasing reaction rate as biomass percentage in coal–biomass blends increases) whereas the activation energy and evolved gas compounds of the same blends may display synergistic behavior [11,12]. However, there is scant information in the literature concerning whether varying the composition of blends can induce reaction synergism. A survey of singular source biomass components (i.e. feed corn stover, nut shells, wood samples) indicates that this would be the case; each of these biomasses is comprised of different ratios of cellulose, hemicellulose, lignin, starch, proteins, etc., and each displays a different thermal decomposition profile. Despite this accepted generalizability, the specific contribution of different biomass constituents to the overall kinetic behavior has yet to be explored.

Cellulose and starch are polymers of glucose, and represent the carbohydrate building blocks of biomass [13]. They have the same unit molecular formula $[C_6H_{10}O_5]_n$, though different molecular orientations. Starch is comprised of repeating glucose units oriented in the same direction (alpha linkages), whereas in cellulose, neighboring units are rotated 180° around the axis of the polymer chain backbone (beta linkages). The hydroxyl group attached to carbon-1 is below the plane of the ring in starch, and above for cellulose. Hydrogen bonding in the β-linked polymer is what lends cellulose its structural advantage, yielding a strong, fibrous nature, as compared to starch, which solubilizes fairly easily in water. There are a number of studies in the literature that describe the thermal decomposition of pure starch [14–16] and pure cellulose [17]; we could not locate any that probe the potential synergistic relationship that occurs among blends of these compounds. Starch and cellulose are a model system to probe the potential synergism between biomass constituents; they have the same composition but vastly different structural characteristics and known decomposition profiles. They are both known to thermally decompose via a dehydration → depolymerization → devolatilization pathway, but these reactions occur at different temperatures and rates for each material [15,17]. As such, we query whether or not the decomposition of starch can synergistically impact the onset of cellulose decomposition. That is, if we note synergism between these two components, then the starch may promote decomposition of the hydrogen-bonded cellulose, which would indicate the possibility of producing pyrolysis bio-oil and syngas at lower temperatures by blending biomass materials with lower energy barriers to decomposition in the overall raw material mixture. However, the results presented herein apply beyond bio-fuel production; as we seek new sources of renewable materials such as thermoplastics and biopolymers, knowledge of how blended biomass building blocks such as starch and cellulose behave under various thermal environments may assist in renewable materials design [18–22].

2. Materials and methods

2.1. Materials

Microcrystalline Cellulose (CAS: 9004-34-6) was purchased from Fisher Scientific, supplied by Alfa Aesar, Lot #10179415. Soluble Starch (CAS: 9005-84-9) was supplied by Fisher Scientific, Lot #136971 as Certified ACS Regent Grade. Samples were used as received. Approximately 1 g of each mixture was fabricated by weighing the desired amount of cellulose and starch on a Sartorius semi-microbalance to ±0.1 mg and placed into a clean glass vial, as given in Table 1. Contents were homogenized by placing the vials on a vortex mixer for several minutes. Samples were stored at ambient conditions until used.

Table 1
Mixtures of starch and cellulose used in pyrolysis experiments.

Sample	Cellulose	Starch	Mixture 1	Mixture 2	Mixture 3
Cellulose mass fraction	1.0	0	0.75	0.50	0.25
Starch mass fraction	0	1.0	0.25	0.50	0.75

2.2. Thermogravimetric analysis-differential scanning calorimetry (TGA–DSC)

Each pure solid fuel and blend was pyrolyzed in a high purity nitrogen atmosphere (reactive + protective gas flow at 70 mL/min) in a 70 μL alumina crucible using a Mettler Toledo TGA/DSC1 with gas flow control, data output to the Mettler STARe Default DB V10.00 software. The DSC was calibrated with indium standard (Mettler Toledo) at 10 K/min. The mass is measured every second to the 10^{-9} g, along with temperature to ±0.1 K. All samples were heated to 383 K and held for 15 min to insure moisture removal. Then the sample was heated at 10, 50 or 100 K/min up to 1173 K and held for 30 min to obtain a stable mass reading. Every sample was run at 10 K/min three times to insure reproducibility; each sample at 50 K and 100 K/min was run once, with random samples run a second and third time to insure reproducibility.

There are multiple methods available to analyze the pyrolysis kinetics of solid carbonaceous fuels. Many are based off of the Arrhenius equation, expressed in the general form as:

$$k = Ae^{-E/RT} \tag{1}$$

where A is the frequency (or pre-exponential) factor, E the activation energy, T the absolute temperature, R the universal gas constant, and k is the reaction rate constant. It is often assumed that the thermal decomposition of carbonaceous fuels such as biomass occurs as an infinitely large set of first order reactions, allowing for the calculation of an overall, or apparent activation energy assuming an overall, or apparent, first order reaction. Nonisothermal TGA data are transformed by defining the extent of conversion, $x(t)$, as a function of initial mass, m_i, final mass, m_f, and mass at any time t, m_t:

$$x(t) = \frac{m_i - m_t}{m_i - m_f} \tag{2}$$

A large portion of the biomass pyrolysis literature calculates the activation energy using the reaction rate constant method (RRCM) (see, for example [12,23–25]). In this case, the rate of material reacted at any given time is expressed as a function of the rate constant:

$$\frac{dx(t)}{dt} = k(1 - x(t)) \tag{3}$$

A plot of ln k versus $1/T$, often referred to as an Arrhenius plot, will yield a straight line with a slope of E/R, if the reaction proceeds via an overall first order. Many biomasses, when subjected to analysis via the RRCM, show multiple devolatilization regimes – abrupt changes in slope of the Arrhenius plot at temperatures specific to a given biomass – with each region having its own activation energy. Dozens of biomass pyrolysis studies in the literature show a reaction order of approximately 1; this assumption is commonly applied to account for the simultaneous reactions [26,27].

However, the RRCM fails to capture the entire range of decomposition; for biomass pyrolysis we often see multiple mass loss