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Investigating the role of feedstock properties and process conditions on products formed during the hydrothermal carbonization of organics using regression techniques

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HIGHLIGHTS

- Hydrothermal carbonization data were collected from the literature.
- Regression techniques were used to build statistical models.
- Regression techniques used include multiple linear regression and regression trees.
- Process conditions are more influential on yield and liquid and gas-phase carbon.
- Feedstock type is more influential on solid carbon, energy, and normalized carbon.

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ABSTRACT

The purpose of this study is to develop regression models that describe the role of process conditions and feedstock chemical properties on carbonization product characteristics. Experimental data were collected and compiled from literature-reported carbonization studies and subsequently analyzed using two statistical approaches: multiple linear regression and regression trees. Results from these analyses indicate that both the multiple linear regression and regression tree models fit the product characteristics data well. The regression tree models provide valuable insight into parameter relationships. Relative weight analyses indicate that process conditions are more influential to the solid yields and liquid and gas-phase carbon contents, while feedstock properties are more influential on the hydrochar carbon content, energy content, and the normalized carbon content of the solid.

1. Introduction

Hydrothermal carbonization (HTC) is a thermal conversion technique that continues to gain significant attention as a sustainable and environmentally beneficial means for biomass and waste transformation to value-added products. HTC is a unique process in which wet feedstocks are thermally converted into value added products under relatively low temperatures (<350 °C) and with relatively low input energy requirements (Funke and Ziegler, 2010; Libra et al., 2011; Li et al., 2013; Lu et al., 2012; Titirici et al., 2012). Feedstock transformation during HTC occurs through a series of simultaneous reactions, including hydrolysis, dehydration, decarboxylation, aromatization, and recondenstation (Funke and Ziegler, 2010; Libra et al., 2011; Sevilla and Fuertes, 2009a, 2009b; Titirici et al., 2007, 2012), with degree of conversion depending on reaction time and temperature (e.g., reaction severity), as well as other process-related conditions and feedstock type. Carbon-rich, energy-dense carbonaceous materials, referred to as hydrochar, with attractive surface functionalization are ultimately generated and have garnered significant study, as they may be used in a variety of environmentally-relevant applications, including as a soil amendment (e.g., Libra et al., 2011), energy source (e.g., Berge et al., 2011; Heilmann et al., 2010), environmental sorbent (e.g., Román et al., 2012, 2013), and/or a material for energy and/or hydrogen storage (e.g., Falco et al., 2013). Several recent reviews have detailed different aspects of carbonization, including reaction mechanisms (e.g., Funke and Ziegler, 2010; Libra et al., 2011), recovery of valuable liquid and solid products (e.g., Reza et al., 2014), and material synthesis for various material and/or environmental applications (e.g., Libra et al., 2011; Titirici et al., 2007, 2012).

The number of published papers reporting on various aspects of HTC has increased significantly over the past ten years, with

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carbonization investigations performed on a variety of feedstocks, ranging from pure substances, such as glucose and cellulose, to more complex feedstocks, such as mixed municipal solid waste (MSW), food waste, and animal wastes, and over a range of process conditions (e.g., Berge et al., 2011; Falco et al., 2011; Kang et al., 2012; Li et al., 2013). Results from these individual studies indicate that carbonization product characteristics are greatly influenced by both feedstock properties and processing conditions. However, their specific influence/role on products formed from HTC remains unclear. Because these experimental results are often described with no reference to process kinetics, which likely vary with feedstock, reactor volumes, and reactor heating mechanisms/rates, reported conclusions and trends that detail the influence of specific feedstock properties and process conditions cannot be universally applied. Conflicting reports of the influence of specific process conditions, such as reaction time (e.g., Li et al., 2013; Lu et al., 2013; Roman et al., 2012; Mumme et al., 2011) and feedstock type (e.g., Hoekman et al., 2011; Wiedner et al., 2013), on carbonization product characteristics support this hypothesis.

Despite the large number of peer-reviewed carbonization studies, very few of these studies have focused on developing statistical models to understand parameter/reaction condition importance or to predict product characteristics given a specific feedstock and set of reaction conditions. Kinetic models have been developed to describe product disappearance and generation based on their specific experimental data/conditions (e.g., Knežević et al., 2009, 2010; Alenezi et al., 2009; Pinkowska et al., 2012; Reza et al., 2013b; Danso-Boateng et al., 2013). The applicability of these models is somewhat limited to specific study conditions (e.g., range of temperatures, times, reactor sizes, and types of feedstock) and the ability to expand their models to other feedstocks and process conditions has not been studied. Others have focused on modeling specific aspects of carbonization, such as particle liquefaction (e.g., Kamio et al., 2008). Mumme et al. (2011) conducted regression analyses of data obtained from the carbonization of anaerobic digestate and cellulose to evaluate the statistical significance of process related data. Because they added catalysts and adjusted their initial pH conditions and used only their experimental data in their regression analyses (<15 points), the universal use of their developed models may be limited.

To date, there has been no attempt to aggregate and subsequently analyze literature reported carbonization data with the intent of developing statistical models to elucidate the importance of feedstock properties and reaction conditions on the hydrothermal carbonization process and to predict product characteristics when carbonizing a variety of feedstocks over a range of reaction conditions. The purpose of the work presented in this manuscript is to use data collected from the literature to develop regression models that describe the role of process conditions (e.g., reaction time, reaction temperature) and feedstock chemical properties (e.g., elemental composition) on carbonization product characteristics (e.g., yields and composition). The specific objectives of this work are to: (1) collect and analyze carbonization data from previously published studies, (2) build parametric and non-parametric statistical models using literature-reported process conditions and feedstock properties and to compare their predictive performance, and (3) highlight the critical feedstock properties and carbonization process conditions by assessing parameter importance and relationships in these regression models. Data were analyzed using multiple linear regression (MLR) and regression trees (RT). These statistical approaches differ in that the MLR model assumes a linear relationship between variables, while no relationships between variables are assumed in the RT models. Results from these analyses were used to ultimately understand the relationships between process conditions, feedstock properties, and the characteristics of the generated products (e.g., solids recovery, solids energy content and normalized carbon content of the gas, liquid and solid-phases). In addition, a series of models were generated that may be used as a screening tool to meet a specific carbonization objective.

2. Methods

2.1. Data collection and extraction

A survey of existing HTC-related literature was conducted. Studies reporting on hydrothermal treatment processes occurring between 180 and 350 °C were collected. Literature searches were conducted in scientific databases (including Science Direct, Web of Knowledge, and Google Scholar) using key words including: hydrothermal carbonization, hydrothermal conversion, hydrothermal decomposition, subcritical water hydrolysis, hydrolysis, and hot compressed water. Literature available in these databases through May 2014 was collected. The purposes of these collected studies varied, ranging from recovery of liquid-phase intermediates (e.g., acid and/or 5-(Hydroxymethyl)furfural (HMF) recovery) to production of carbon-based materials for use as an energy source or adsorption media.

Process related data (e.g., reaction time, reaction temperature, solids concentration) and experimentally collected carbonization product information from each study were tabulated. The carbonization product information reviewed and assessed in this study includes: solid-phase carbon content (% carbon in the recovered solids), normalized carbon content of the hydrochar (mass of carbon per mass of initial dry feedstock), energy content of the hydrochar, hydrochar yield (mass of dry recovered solids per mass of initial dry feedstock), gas-phase carbon content (mass of carbon in the gas per mass of initial dry feedstock), and liquid-phase carbon content (mass of carbon in the liquid per mass of initial dry feedstock). These parameters were chosen because they are often reported and critical when carbonizing feedstocks with the purpose of waste and/or biomass conversion.

Data from all collected manuscripts were either extracted from published data tables, the text, or from published figures using Plot Digitizer (version 2.6.1). In some instances, calculations were performed to obtain desired information using data provided in the manuscripts. In this study, a reaction time equal to zero represents the time when reactor heating commences. If required, reported reaction times were corrected to reflect the heating period based on provided heating rate data or other provided temperature-related information. If not reported directly, heating rates were calculated based on provided information assuming a constant and linear rate. Reactor heating times are defined as the time it takes to heat the reactor from room temperature (assumed to be 25 °C) to the final desired temperature. All collected data were converted to a consistent set of units. Feedstock ultimate and proximate data were also collected from the published studies. If feedstock data were not reported, literature searches were conducted to obtain average initial feedstock properties.

2.2. Development of statistical models

MLR is an explicit and frequently used technique for developing predictive relationships between dependent and independent variables. An advantage associated with this technique is the generation of an equation that is easy to use and understand. However, this regression technique assumes a linear relationship between variables, potentially resulting in a model with modeling errors and limited ability to interpret important relationships. RT analyses differ from MLR in that they represent a non-parametric technique in which no *a priori* relationships between variables are assumed, allowing for the modeling of nonlinearities. This