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Quantifying the sensitivity of feedstock properties and process conditions on hydrochar yield, carbon content, and energy content

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ABSTRACT

Hydrothermal carbonization (HTC) is a wet, low temperature thermal conversion process that continues to gain attention for the generation of hydrochar. The importance of specific process conditions and feedstock properties on hydrochar characteristics is not well understood. To evaluate this, linear and non-linear models were developed to describe hydrochar characteristics based on data collected from HTC-related literature. A Sobol analysis was subsequently conducted to identify parameters that most influence hydrochar characteristics. Results from this analysis indicate that for each investigated hydrochar property, the model fit and predictive capability associated with the random forest models is superior to both the linear and regression tree models. Based on results from the Sobol analysis, the feedstock properties and process conditions most influential on hydrochar yield, carbon content, and energy content were identified. In addition, a variational process parameter sensitivity analysis was conducted to determine how feedstock property importance changes with process conditions.

1. Introduction

Hydrothermal carbonization (HTC) is a wet, low temperature thermal conversion process that continues to gain significant attention for the sustainable generation of value-added products from organics (e.g., Berge et al., 2011; Libra et al., 2011; Titirici et al., 2012; Idowu et al., 2017; Ro et al., 2017). Over 700 studies have been published over the past 20 years evaluating different aspects of the carbonization of a variety of feedstocks over a large range of process conditions. In addition, many review papers have been published that detail different aspects of the carbonization process, 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), material synthesis for various material and/or environmental applications (e.g., Libra et al., 2011; Titirici et al., 2012), and the role of process conditions on carbonization products (e.g., Fang et al., 2018; Nizamuddin et al., 2016; Román et al., 2018).

Of all the value-added products generated from the HTC process, hydrochar represents the most widely studied (e.g., Falco et al., 2011; Kang et al., 2012; Li et al., 2013; Hoekman et al., 2017). Hydrochar is a carbon-rich and energy-dense material. The high level of interest associated with hydrochar generation and its properties is because of its many potential applications, which include use as a soil amendment (Libra et al., 2011), solid fuel (Berge et al., 2011; Reza et al., 2014), media for adsorption of contaminants (Flora et al., 2013; Román et al., 2012), and energy storage (Titirici et al., 2012). It is well documented that feedstock properties and process conditions influence hydrochar properties. Changes in reaction temperature have been documented to influence hydrochar yield (Benavente et al., 2015; Basso et al., 2016), carbon content (Benavente et al., 2015; Lu et al., 2013) and energy content (Basso et al., 2016; Benavente et al., 2015). Feedstock initial solids concentration and reaction time have also been reported to influence the hydrochar properties (Heilmann et al., 2011; Li et al., 2013), as have changes in feedstock type (Berge et al., 2011; Kang et al., 2012; Lu and Berge, 2014). Despite this knowledge, the degree of influence of process conditions and feedstock properties on hydrochar properties has not been previously identified or quantified.

Linear and non-linear statistical models have been developed to describe and understand the relationships between process conditions and hydrochar properties (Kannan et al., 2017; Sabio et al., 2016; Tag et al., 2018; Volpe and Fiori, 2017). These models are generally developed based primarily on study conditions and rarely include feedstock properties. Li et al. (2015) developed linear and non-linear regression models based on data collected from the HTC literature and

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determined process conditions have greater influence on hydrochar yields than feedstock properties, while feedstock properties are more influential on the hydrochar carbon content and energy content. The feedstock properties used in the work described by Li et al. (2015) were somewhat limited, as only the ultimate and proximate properties of feedstocks were considered. The relative importance of specific process conditions and feedstock properties, however, remains unknown. Quantification of the importance of specific process conditions and feedstock properties is an important step towards the design of more informed and purposeful carbonization studies.

It is important to determine the feedstock and process conditions that universally influence hydrochar characteristics. To evaluate this, linear and non-linear models were developed to describe hydrochar characteristics based on data collected from HTC-related literature. A global sensitivity analysis was subsequently conducted to identify the parameters that most influence hydrochar characteristics. The specific objectives of this work were to: (1) develop linear and non-linear statistical models (regression tree and random forest models) predicting hydrochar yield, carbon content, and energy content as a function of feedstock properties and process conditions using data collected from the literature, (2) use Sobol analysis (a global sensitivity analysis) to evaluate and quantify the sensitivity of independent variables within the models that best fit the data, and (3) compare the performance of the different models and identify the most influential parameters on the studied hydrochar properties.

2. Materials and methods

2.1. Data collection and extraction

Methods for data collection and extraction are similar to that described in Li et al. (2015). Briefly, studies reporting on hydrothermal carbonization occurring between 180 and 350 °C were collected. Literature searches were conducted in scientific databases using key words including: hydrothermal carbonization, hydrothermal conversion, hydrothermal decomposition, subcritical water hydrolysis, hydrolysis, and hot compressed water. Literature available in these databases through August 2017 was collected. Feedstock properties, process conditions and carbonization product information from each study were tabulated. A list of the model parameters investigated in this study is provided in Table 1.

Feedstock properties collected from the literature include proximate analysis parameters (ash content, volatile matter and fixed carbon), ultimate analysis parameters (carbon, hydrogen and oxygen content), and chemical composition (cellulose, hemicellulose and lignin content). Feedstock lignin, cellulose, and hemicellulose contents are not routinely reported in HTC-related studies. If these properties were not reported, literature searches were conducted to obtain these properties for the specific feedstock. Feedstock lignin content was also collected and used as reported. No standard approach to reporting feedstock lignin content in these studies exists; feedstock lignin content was reported as either: (1) Klason lignin, (2) Acid detergent lignin (ADL), or (3) no reference to the technique used to determine the lignin content was provided. Conversion between these types of lignin is not possible, and was therefore used as collected. The collected data were also used to approximate feedstock polarity index, which was calculated as the mass ratio of O + N to C, as defined by Rutherford et al. (1992). Polarity index illustrates the hydrophobicity of the organic feedstocks (Wu et al., 2001); the smaller the polarity index, the more hydrophobic the feedstock.

Process conditions collected for this study include initial solids concentration, reaction temperature, and reaction time. In this study, reaction temperature is the final desired temperature. Reaction time includes the time it takes to heat the reactor to the desired temperature and the time maintained at the desired temperature. The time to cool the reactor is not considered. Initial solids concentration is defined as the percentage of dry solids present in the initial wet feedstock.

The hydrochar properties modeled in this work include hydrochar yield (mass of dry recovered solids per mass of initial dry feedstock, % dry basis), hydrochar carbon content (carbon content in the recovered solids, % dry basis), and hydrochar energy content (MJ/kg, dry basis). For hydrochar yield, carbon content and energy content, 649, 622, and 475 data points were collected, respectively, from the literature.

2.2. Development of statistical models

Both linear and non-linear models were developed to describe the relationship between independent and dependent parameters. A series of models representing all possible combinations of non-correlated parameters were developed. Correlated parameters were defined as those with a correlation coefficient greater than 0.8 (Beldjazia and Alatou, 2016). Correlated parameters associated with the linear models were determined using the Pearson correlation test. Distance correlation tests, which measure the dependence between two random variables, were used to evaluate correlations associated with nonlinear relationships (Székely and Rizzo, 2009).

Multiple linear regression (MLR) was used to describe linear relationships. MLR models were developed using the "lm" function in the statistical software package R (version 3.1.0, R Development Core Team). Non-linear relationships were described using regression tree

Table 1
Feedstock properties and process conditions investigated in this study.

Parameter	Unit	Abbreviation	% Papers Reporting Parameter[4]
Ash[2]	%, dry basis	Ash_{feed}	66
Volatile matter[2]	%, dry basis	VM_{feed}	44
Fixed carbon[2]	%, dry basis	FC_{feed}	44
Carbon[2]	%, dry basis	C_{feed}	70
Hydrogen[2]	%, dry basis	H_{feed}	67
Oxygen[2]	%, dry basis	O_{feed}	68
Polarity[3]	–[1]	Pol_{feed}	0
Cellulose[2]	%, dry basis	Cel_{feed}	26
Hemicellulose[2]	%, dry basis	Hem_{feed}	26
Lignin[2]	%, dry basis	Lig_{feed}	26
Initial solids concentration[2]	%, dry basis	$Solids_{initial}$	89
Temperature[2]	°C	T_{final}	100
time[2]	min	t	99

[1] Parameter is unit less;
[2] Values are based on those reported in the literature, taken from either each individual study or are based on average values associated with each feedstock;
[3] Calculated values;
[4] Percentage of the HTC-based papers reporting each parameter.