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Evaluation of Arrhenius-type overall kinetic equations for hydrothermal carbonization

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ABSTRACT

An Arrhenius-type overall kinetic equation was used to model hydrochar mass yield, carbon and oxygen content of hydrothermal carbonization experiments. The equation is based on the coalification model, which was earlier published, and is based on the assumptions of Arrhenius temperature behaviour. A dataset of 29 feedstock biomasses from previous studies was collected to evaluate the performance of the equation. The lowest mean absolute error (MAE) in the temperature range of 200–330 °C was found for hydrochar yield to be 1.76%, carbon content 1% and oxygen content 1.01%, respectively. It was demonstrated that not all parameters of the equation need to be specified for every feedstock. Based on this fact, a method to predict the outcome of HTC based on the lignin content of a feedstock was proposed and validated. Comparisons to other equations were performed, and the results revealed that a dose-response curve was the most accurate model for representing the experimental data.

1. Introduction

Hydrothermal carbonization (HTC) is a thermochemical conversion process in which carbon-containing material, such as biomass, can be converted into so-called hydrochars. This product is characterised by an increased carbon content and, according to its elemental composition and heating value, similar to fossil lignite. Recently L'vov discussed thermodynamic and kinetic approaches for thermal decomposition of solids [1]. In view of the use of an Arrhenius-type equation here for HTC, some general information about this "wet" conversions are given. In HTC, carbohydrates are hydrolysed and the intermediates show further reaction. As water is inside and outside the feedstock particle, heat transfer limitations and water transport for hydrolysis are not an issue. Due to the hydrolysis of carbohydrates and the fast splitting of polar bonds during HTC, temperatures around 200 °C are sufficient, compared to dry pyrolysis with much higher temperatures. The hydrolysis products are dissolved and show further reactions, namely water elimination. This is the main carbonization step, increasing the carbon content. The consecutive products polymerize, leading to the solid product hydrochar [2–4].

A model connecting input and output variables is required to implement such a process within a pilot or industrial plant. Facing this objective, experimental data from HTC are subject to mathematical evaluation, aiming to work out significant factors and optimal process conditions and to predict output streams. Regarding chemical reactions, parameters such as temperature, time and concentration can be related to the yield by means of the reaction rate and, for the temperature dependence, the Arrhenius equation. As long as the reaction is known and the participating intermediates can be monitored a mechanistic modelling is possible. This has been conducted for the case of HTC by Kruse et Grandl [5], with different degrees of accuracy among a variation of feedstock biomasses. Empirical modelling in the field of HTC was performed using linear and polynomial regression [6–12]. Li et al. fitted a linear regression line to a literature based dataset, with the aim of determining significant input parameters influencing HTC [7]. The model was able to fit the elemental composition of the hydrochar, but produced high error rates concerning the solid mass yield. The challenge may be behind the different structural quantities (cellulose, hemicellulose, and lignin) of the feedstock material, which were not represented in the model equation. In contrast to purely empirical models, Ruyter developed a coalification model to represent the oxygen conversion during HTC based on Eq. (1.1) [13].

$$50t^{0.2}\exp\left[\frac{-3500}{T}\right] = \frac{O_{feed} - O_t}{O_{feed} - 6} \tag{1.1}$$

Where t is the reaction time, T the reaction temperature, O_{feed} the oxygen content of the feedstock and O_t the oxygen content after t reaction time. Funke and Ziegler demonstrated the change of the carbon

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content of cellulose, lignin and wood with increasing oxygen conversion according to Eq. (1.1) [2]. Kruse fitted experimental results from spent brewer grains to the coalification model by adjusting the parameters A, B and C (Eq. (1.2)) [14].

$$A t^{B} \exp\left[\frac{-C}{T}\right] = \frac{O_{feed} - O_t}{O_{feed} - 6} \tag{1.2}$$

Motivated by this approach, this study evaluates Eq. (1.2) regarding its ability to model carbon content, oxygen content and hydrochar mass yield for a variety of feedstock biomasses. To the best of the authors' knowledge, this has never been applied to these response variables. It represents an approach to model hydrothermal carbonization by a lumped equation, which assumes Arrhenius temperature behaviour. As mentioned above, limitations of mass and heat transfer are of no importance during the degradation of the solid and carbonization, in contrast to dry processes. Or in other words: It is very likely that the rate determining steps are chemical reactions or strongly related to chemical reactions, showing an Arrhenius-like behaviour.

The evaluation is performed with a dataset collected from literature. The resulting mean absolute error (MAE) is compared to three alternative equations, which were previously proposed to correlate HTC data. Even though a satisfactory fitting was reported for those approaches, none of the authors compared their model with others.

2. Material & methods

2.1. Dataset

The dataset is collected from a variety of publications in the field of HTC [15–31] (Supplementary material Table 1). The origin of the feedstocks covers lignocellulosic biomass, cellulose, algae, compost residues and agricultural residues from a total of 29 feedstock biomasses. The data contains 166 HTC runs where hydrochar yield was reported and 152 with the carbon and oxygen content. The reaction temperature ranges from 150 to 330 °C, where 90% of the runs lay between 180 − 294.9 °C.

2.2. Coalification model

In the present work, the coalification model (Eq. (1.2)) is used to model carbon, oxygen and hydrochar yield. The equation was linearized (Eq. (2.1)) in order to perform linear least square fitting.

$$\ln A + B \ln(t) - \frac{C}{T} \tag{2.1}$$

Different variants of the equation were developed to enable the fitting of parameter A, B and C to every feedstock individually or only once to the entire dataset. The motivation of this approach is to analyse, if parameter A, B and C need to be fitted to every feedstock, or if any of them can be regarded as constant values, therefore enabling modelling of HTC with a lower amount of parameters.

2.3. Reference models

To assess the accuracy of the coalification model, three alternative models were applied for comparison. The comparisons were evaluated by the MAE, which resulted from fitting the model parameters to every feedstock individually. The first reference model was a linear regression according to Eq. (2.2). This approach was used by Mumme et al. [6] including the pH as extra addend, and by Heilmann et al. with the solid load as extra addend [10,11].

$$f = a \cdot T + b \cdot t + c \tag{2.2}$$

The other two reference models included the severity factor R_0 (Eq. (2.3)).

$$R_0 = t \exp\left[\frac{T - T_{Ref}}{\omega}\right] \tag{2.3}$$

The severity factor was linearized and implemented in a linear equation (Eq. (2.4)) following the approach of Suwelack et al. [32,33].

$$f = a \ln(R_0) + b \tag{2.4}$$

The model is referred as *severity model* in this article. Guo et al. implemented the severity factor into the dose-response curve (Eq. (2.5)) [34]. The curve is characterised by an upper and lower barrier (b and a, respectively).

$$f = a + \frac{b - a}{1 + 10^{(c - \ln(R_0))d}} \tag{2.5}$$

The severity model was applied with $T_{ref} = 100$ and the dose-response model was used with $d = 1$, $\omega = 14.5$ and $T_{ref} = 100$ to obtain equations with the same number of parameters.

2.4. Statistics

The estimation of the parameters was performed with the statistical analysis software SAS 9.4. The linear, severity and linearized coalification models were fitted by linear least squares with PROC GLM. The dose-response model was fitted by non-linear least squares using the Gauss-Newton method in PROC NLIN; starting values were a = 0.5, b = 0.5 and c = 8 for carbon content and oxygen, and c = 10 for yield.

With the CLASS statement, a variable is denoted as a categorical variable. Different parameter settings for the coalification model were constructed by implementing a categorical feedstock variable in the regression procedure. This is done by merging the categorical feedstock variable within the continuous variables. The linear least squares procedure, therefore, estimates the parameter for every group of the categorical variable. SAS codes are given in the supplementary material.

The explanatory variables time and temperature were used with the units seconds and Kelvin, respectively. The response variables carbon, oxygen and hydrochar yield were expressed as fractional numbers between 0 and 1.

2.5. Validation

The validation of the model is evaluated by its mean absolute error (MAE):

$$MAE = \frac{\sum |y_i - \hat{y}_i|}{n} \tag{2.6}$$

Were y_i is the measured value, $\hat{y}_i$ is the calculated or predicted value by the model and n is the number of observations.

3. Results

The performance of the models has been evaluated for the temperature ranges of 200–330 °C and 150–330 °C, because hydrothermal carbonization occurs at very slow rates below 200 °C. The MAE values for the different models are presented in Table 1. Solutions for the parameter estimates are listed in the supplementary material.

The subscript i indicates that every feedstock has its own value for the corresponding parameter. The absence of the subscript indicates that the value of the parameter is identical for every feedstock. Obviously, model 1 has the highest MAE because no parameter was fitted to a particular feedstock. The MAE is remarkably reduced when one parameter (A, B or C) is fitted to every feedstock (model 2, 3 and 4). Within these variants model 2, where the pre-exponential factor is fitted to every feedstock, has the lowest MAE in most cases. However, the differences are very low within the three variants. For model 5, 6 and 7 an additional parameter is fitted to every feedstock, further reducing the MAE compared to model 2, 3 and 4. Model 5 and 6, where