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Novel kinetic studies on biomass hydrothermal carbonization

Alberto Gallifuoco*, Gabriele Di Giacomo

University of L'Aquila, Department of Industrial and Information Engineering & Economics, Via G. Gronchi, 18, 67100 L'Aquila, Italy

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ABSTRACT

This work aims to study kinetic data on biomass hydrothermal carbonization by a new point of view. The time course of essential properties signaling hydrochar evolution is found to be sigmoidal ubiquitously. The logistic curve here proposed, attributable to the Hill equation, furnished near-perfect regressions (R^2 as high as 0.999) in all cases studied. The broad applicability and the excellent correlations stimulated the research heuristically and routed process optimization. The evidence is reported that the success of fittings bases on profound mechanistic reasons. Arguments are discussed supporting the hypothesis that hydrochar formation is a stochastic phenomenon. The method deduces the Hill equation by applying statistical methods to the hydrothermal carbonization, modeled as a discrete Markov-chain process. The role of the model equation parameters is also discussed. The potentiality of the method proposed in this pioneering work could pave the way for a new paradigm in the modeling of hydrothermal carbonization.

1. Introduction

The current conditions of the planet and the growing needs of humanity make it imperative to frame the energy supply chain within precise paradigms: renewability, efficiency, optimization, intensification, sustainability.

Biomass plays a pivotal role in these strategic issues, not just as a raw material to convert into energy carriers for replacing fossil fuels progressively. In fact, the potential that biomass has as a source of high value-added products, such as super performing materials and devices, is becoming increasingly clear (Fang et al., 2018; Titirici et al., 2012).

Not all biomass conversion routes are sustainable and environmental-friendly *per se*. Some of these methods could require harmful chemicals, or costly pretreatments, while other biomass exploitation techniques would require high transportation expenses. With these limitations, it could be difficult to reach the goal of full sustainability. On the contrary, hydrothermal carbonization (HTC) deserves the increasing attention of worldwide laboratories as a process capable of overcoming the drawbacks mentioned above (Roman et al., 2018). It is common opinion between authoritative researchers that HTC not only meets all the requirements to support the expectations it has generated but potentially could lead to unexpected results and encourage the more extensive use of waste biomass in all countries.

Sustainability is a keyword that appears pervasively in all contemporary studies on the exploitation of biomass, and there is the sound reason for things to be so. One point deserves significant attention. Sustainability depends not only on choosing the production paths wisely, but it is also a matter of optimization and intensification of processes. There is more than one condition to achieve to ensure the development of advanced hydrothermal carbonization processes and plants. It is necessary to master the operational conditions for obtaining char with the required characteristics. It is essential to provide useful information for the correct design of industrial plants. The overall efficiency of the process should be improved to increase its attractiveness compared to that of other techniques.

The correct modeling of the phenomena occurring in the reactors during the HTC is a prerequisite for achieving the conditions described above. Mathematical models available In the literature represent the kinetics of the process using different methodological approaches. Nevertheless, it is a prevailing opinion of the scientists that, given the complexity of the system, a description adequately suitable for the needs of the designers is not yet available. This statement seems right regardless of the approach adopted, mainly because most of the models developed so far do not possess the generality required for advanced industrial HTC processes (Roman et al., 2018).

HTC is often described using a lumped reaction network which comprises a few elementary pseudo-first-order steps. Upon integration of the resulting differential equations, one obtains the yield in hydrochar as a function of time (Reza et al., 2013; Valdez et al., 2014; Cai et al., 2016).

Another approach dense of useful applications is to effort the modeling with response surface methodology and a proper design of experiments. This statistical methodology pervades somewhat the literature because, provided that a suitable data fitting be available, it

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* Corresponding author.
E-mail address: alberto.gallifuoco@univaq.it (A. Gallifuoco).

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predicts the system behavior as a response to changes in the operational parameters (Alvarez-Murillo et al., 2015; Mäkelä et al., 2016). Previous works illustrated the application of an entirely different approach, which can be successfully doable as long as one has excellent correlations with the experimental data set (Gallifuoco et al., 2017, 2018). In this case, one could set up by intuition empirical equations for describing the evolution of solid and liquid phases during batch HTC. Provided that the accordance between equations and experimental evidence be profound and ubiquitous, and this is not so easy to accomplish, one gets a powerful instrument for predicting the proceeding of the process. This achievement could constitute a valuable starting point for searching the mechanistic bases of the hydrothermal carbonization heuristically.

Data of the literature on hydrothermal carbonization of both model substrates and waste biomasses show that the time progress of more than one process parameter features a sigmoidal behavior (Alvarez-Murillo et al., 2016; Reza et al., 2013; Möller et al., 2011; Relvas et al., 2015). In some cases the sigmoidal aspect is very slight, but the careful inspection of the diagrams highlights it anyway. S-shaped curves are frequent in plots of char yield or higher heating value (HHV) *versus* time. This peculiarity also appears when the severity factor is the independent variable of the batch reaction progress and whatever the source of the substrate is (municipal waste, agro-food scrapes, forestry residuals and so on). The reason for this universal behavior lies in the autocatalytic character of the overall carbonization reaction. The progressive accumulation of chemicals in the liquid and their recombination accelerate the solid phase transformation. At long reaction times, the native biomass depletes, all the available solid has converted into hydrochar, and the rate of the conversion must necessarily reduce asymptotically to zero. Parameters which trace the system evolution, such as carbon content and HHV, echo this process dynamics. The analysis which follows aims to give a novel explanation of this behavior, based on the exploitation of similarity between apparently very different phenomena. To the best of authors' knowledge, the approach this paper deals with appears for the very first time in the literature.

2. Methods

The central idea behind the methods of this paper is to leverage the excellent fitting of an equation to data for trying to infer the kinetic model heuristically. The results obtained by several authors which used logistic equations for fittings are satisfactory. In a study on hydrothermal carbonization of corn stalk, the amount of hydrochar was decreasing with the increasing severity parameter, both in single- and two-stage tests. (Guo et al., 2015). Those authors adopted the following dose-response function:

$$S = A_1 + \frac{A_2 - A_1}{1 + 10^{(\log x_0 - \log R_0)B}} \tag{1}$$

In Eq. (1), S is the solid yield, $\log R_0$ the severity factor. A_1, A_2, B, and $\log(x_0)$ are bare constants. The regression coefficient was fully satisfactory ($R^2 = 0.980$). The fitting between HHV and $\log R_0$ was a somewhat worse ($R^2 = 0.958$), but indeed far more satisfying than those generally found for other models studied in the literature. The higher the severity, the higher was the HHV, as predictable, since the hydrochar energetic value was computed using a linear function of the carbon content (Channiwala and Parikh, 2002). The same equation was tested for the present paper. The fitting resulted entirely satisfactory ($R^2 > 0.9$), but not sufficient for to develop the modeling reliably, and consequently Eq. (1) was discharged.

The general ability of logistic functions to fit data of HTC using lumped parameters as the independent variable manifests spontaneously in many settings, even when the independent variable is, in turn, a lumped experimental measure (Gallifuoco et al., 2017, 2018). So is the case when studying the time evolution of the coordinates on the van Krevelen plane. During the reaction time, the hydrochar atomic ratios described trajectories following a sigmoidal function of the corresponding electrical conductivity of the liquid phase (data not shown, paper submitted).

A previous article (Gallifuoco et al., 2017) studied the carbon content of the forming char as a function of the batch process time. The HTC of lignocellulosic biomass occurred at temperatures from 200 to 300 °C. The correlations were even better than those discussed before, regardless of the temperature (R^2 between 0.996 and 0.998). The equation was as follows:

$$C(t) = C_0 + \Delta C \frac{\left(\frac{t}{t_h}\right)^p}{1 + \left(\frac{t}{t_h}\right)^p} \tag{2}$$

In Eq. (2) t is the process time, C_0 is the initial carbon percentage, ΔC is its endpoint increase, t_h the time corresponding to half of this increase and p is a parameter. The method here presented pivots on Eq. (2), which comes from the practice of pharmacology as a frequently used dose-response function. To the best of authors' knowledge, the only other application of a model that can be traced back to Eq. (2) does not appear in the context of HTC, but in a paper concerning the pyrolysis of a wide range of residual materials (Xiao et al., 2016). In this last paper, the pyrolysis temperature replaces the process time as the independent variable, and the logistic function correlates with the atomic ratio H/C. Regression coefficient was $R^2 = 0.974$, which is a full success, considering that the analysis concerns data obtaining with dissimilar materials, from chicken manure to rice bran. So one has both dry and wet processes that, although considerably different from each other, seem to obey quite a similar underlying degradation mechanisms. This last observation strengthens the belief that it is worth taking a unifying effort in the matter of modeling.

3. Results and discussion

It is noteworthy that Eq. (2) modeled not only hydrochar carbon content, but the trajectory described by the solid on the van Krevelen diagram as a function of isothermal batch reaction time (R^2 as high as 0.999). Also, Eq. (2) resulted decidedly connected to the single H/C and O/C ratios, the HHV and the yield of the hydrochar, and so on. The fittings remained almost perfect also when extending the analysis to the HTC of non-lignocellulosic biomasses (Gallifuoco et al., 2018).

In the presence of such a variety of applications, it is more convenient to put Eq. (2) in a general form, introducing a generic property y(t) that may vary over time during the HTC from the initial value y_0 to the endpoint one y_∞.

$$y(t) = y_\infty + \frac{(y_0 - y_\infty)}{1 + \left(\frac{t}{t_h}\right)^p} \tag{3}$$

Eq. (3) is connected to the Hill equation, developed empirically long ago for modeling the kinetics of biochemical reactions with a co-operative binding of more ligands to the same enzyme (Hill, 1910). For the sake of generality, let introduce a dimensionless variable which measures the extent of a generic transformation in the HTC system:

$$X = \frac{y_0 - y(t)}{y_0 - y_\infty} \tag{4}$$

X is, therefore, the ratio between the extent of transformation attained by y at time t and the maximum one attainable at the end of the process. Upon substitution into Eq. (2) one gets:

$$X = \frac{(t/t_h)^p}{1 + (t/t_h)^p} \tag{5}$$

The parameter t_h is now recognizable as the half-way time, i.e., the time required for accomplishing $X = 1/2$. Eq. (5) is appropriately in the form of Hill's.