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CVR - Centro para a Valorização de Residuos
Campus de Azurém da Universidade do Minho
4800-058 Guimarães
PORTUGAL

Telef.: +351 253 510 020
Fax: +351 253 510 029
http://www.cvresiduos.pt
e-mail: geral@cvresiduos.pt

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EDITORS
Fernando Castro, Cândida Vilarinho,
Joana Carvalho

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PRODUCTION OF LOW-COST HYDROCHARS BY HYDROTHERMAL CARBONIZATION OF COMPOST: KINETIC MODELING AND TREATMENT OF THE GENERATED LIQUID EFFLUENT BY FENTON

F.F. Roman[1], J.L Diaz de Tuesta[2], P. Praça[3], A.M.T. Silva[4], J.L. Faria[5], and H.T. Gomes[6]
1 Centro de Investigação da Montanha (CIMO), Instituto Politécnico de Bragança, 5300-253 Bragança, Portugal, and Laboratory of Separation and Reaction Engineering – Laboratory of Catalysis and Materials (LSRE-LCM), Faculdade de Engenharia, Universidade do Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal, roman@ipb.pt
2 Centro de Investigação da Montanha (CIMO), Instituto Politécnico de Bragança, 5300-253 Bragança, Portugal, and Laboratory of Separation and Reaction Engineering – Laboratory of Catalysis and Materials (LSRE-LCM), Faculdade de Engenharia, Universidade do Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal, jl.diazdetuesta@ipb.pt
3 Resíduos do Nordeste, EIM, S.A. Empresa Intermunicipal, Mirandela, 5370-340, Portugal, paulopraca@residuosdonordeste.pt
4 Laboratory of Separation and Reaction Engineering – Laboratory of Catalysis and Materials (LSRE-LCM), Faculdade de Engenharia, Universidade do Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal, adrian@fe.up.pt
5 Laboratory of Separation and Reaction Engineering – Laboratory of Catalysis and Materials (LSRE-LCM), Faculdade de Engenharia, Universidade do Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal, jlfaria@fe.up.pt
6 Centro de Investigação da Montanha (CIMO), Instituto Politécnico de Bragança, 5300-253 Bragança, Portugal, and Laboratory of Separation and Reaction Engineering – Laboratory of Catalysis and Materials (LSRE-LCM), Faculdade de Engenharia, Universidade do Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal, htgomes@ipb.pt

ABSTRACT

The production of hydrochars from compost through hydrothermal carbonization (HTC) was studied as valorization alternative against organic waste accumulation. Temperature, time and load of compost were varied in the HTC process and the carbon content of the solid and the liquid effluent were used as dataset to develop a kinetic model able to predict the carbon content in the hydrochars and in the effluent at different operating conditions. Furthermore, the treatment of the liquid effluent resulting from the HTC process was assessed by Fenton reaction.

Keywords: Valorization, Compost, Hydrothermal Carbonization, Kinetic Study, Fenton.

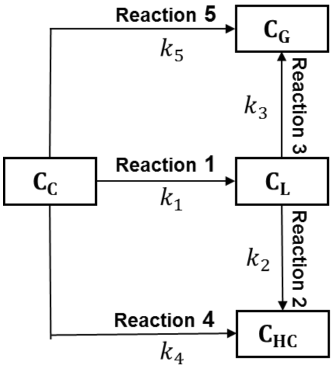
INTRODUCTION

Hydrothermal Carbonization (HTC) is a thermochemical conversion technique that mimics the natural coalification process, where the feedstock is submerged in water and heated in a confined space, under autogenous pressure [1]. Lately, this technique has been explored as a suitable technology to produce functional carbonaceous materials from biomass [2]. In this regard, the use of waste precursors to synthesize carbonaceous materials is quite advantageous, since they are cheap and highly available. Nowadays, municipal solid waste management commonly includes a mechanical and biological treatment process, resulting in a solid stream, further processed to compost, which can be used as fertilizer. Compost production is higher than the existing demand, and the expected developments on up-coming directives ruling "End-of-waste" criteria are leading to barriers on the use of waste-derived fertilizers [3]. Thus, the development of new alternatives for the treatment of organic wastes are necessary. In this context, this work deals with the valorization of compost, through the production of low-cost materials by HTC. Furthermore, to achieve truly sustainable processes, the knowledge of reaction mechanisms that allow predicting system behaviors is crucial

[4],.thus the development of a suitable kinetic model to predict the HTC behavior of compost and the treatment of the liquid effluent obtained from the HTC process by Fenton was also considered.

METHODOLOGIES

The compost was provided by the waste management company Resíduos do Nordeste, S.A. The HTC of compost was carried out in a Teflon vessel inserted in a stainless-steel body (Parr Instrument co., USA) at previous selected operating conditions (150-230 ºC,1-5 h, 1-4 g of compost, 30 mL) using a Doehlert Matrix to plan the experiments. The carbon material was separated from the liquid matrix by filtration. The carbon balance and the kinetic equations were evaluated from experimental data of the carbon content in the liquid phase, estimated by TOC analysis (Shimadzu Equipment TOC-L CSH/CSN) and the carbon content in the solid phase, estimated by elemental analysis (Carlo Erba Instrument EA 1108). A lumped kinetic model based on the elemental carbon content was assumed, anticipating that the compost (C) undergoes reactions that originate liquid intermediates (L), while it can undergo solid-solid reactions in a pyrolysis-type reaction, giving rise to hydrochar (HC) and gases (G). Liquid intermediates further react and generate hydrochar and gases. The proposed model is illustrated on Fig. 1, alongside with the equations that describe the system. The temperature dependence (Arrhenius equation) is then incorporated on the power-law kinetic model and it is solved analytically. The values of the adjustable variables, *viz.* the pre-exponential factors (k_0) and activation energies (E_a), were obtained using ProOrigin v8.0.



$$\frac{dC_{c(t)}}{dt} = -C_{c(t)}(k_1 + k_4 + k_5)$$

$$\frac{dC_{L(t)}}{dt} = k_1 C_{C(t)} - C_{L(t)}(k_2 + k_3)$$

$$\frac{dC_{G(t)}}{dt} = k_3 C_{L(t)} + k_5 C_{c(t)}$$

$$\frac{dC_{HC(t)}}{dt} = k_4 C_{C(t)} + k_2 C_{L(t)}$$

Fig. 6. Proposed mechanism for the thermochemical conversion of compost to hydrochar.

For the liquid effluents resulting from the HTC process, obtained under different reaction conditions, Fenton runs were performed in a 250 mL well stirred round flask reactor considering an iron(II) concentration of 100 mg·L^{-1}, pH set at 3.0 by means of H_2SO_4, 50 ºC and the stoichiometric amount of H_2O_2 to completely mineralize TOC.

RESULTS AND DISCUSSION

Kinetic modeling

Table 1 summarizes the values found for the adjusted variables of the developed kinetic model. The R^2 is 0.964, whereas the adj. R^2 is 0.949. The *p-value* obtained *via* ANOVA is 6.87·10^{-4}, values that indicate well-adjusted parameters.

Table 8. Activation Energies and pre-exponential factors obtained from fitting of the kinetic model to the experimental data.

Reaction	k [min^{-1}] at 190 ºC	E_a [kJ·mol^{-1}]	k_0 [min^{-1}]
1	8.69·10^{-4}	51	4.91·10^{2}
2	9.06·10^{-19}	238	6.31·10^{8}
3	1.43·10^{-5}	164	4.49·10^{13}
4	1.24·10^{-4}	226	3.83·10^{21}
5	2.69·10^{-4}	66	7.47·10^{3}

The highest kinetic constant at 190 ºC was found for the formation of liquid soluble intermediates from compost (reaction 1), whereas the production of hydrochar from liquid intermediates (reaction 2) shows the lowest kinetic constant. The lowest activation energy was estimated for the 1st reaction, while the reactions related to the formation of hydrochar resulted in the highest value (Reactions 2 and 4), meaning that the production of hydrochar depends strongly on the temperature.

Treatment of the effluent obtained in the HTC process

The Fenton process was assessed in the treatment of the liquid effluents resulting from the HTC of compost, that displays TOC values from 1000 to 5000 mg·L^{-1}. Fig. 2 shows TOC and H_2O_2 concentration evolution upon time of reaction performed with 2 effluents obtained in the HTC of compost at (1) HTC Reaction 2: 3 h, 2.5 g of compost, 190 ºC, with initial TOC of 2086 mg·L^{-1} and (2) HTC Reaction 11: 2 h, 3 g of compost, 230 ºC, with initial TOC of 2750 mg·L^{-1}.

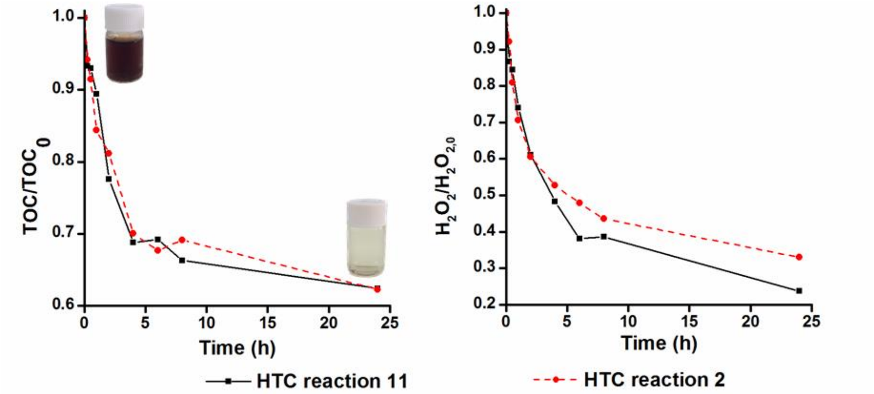


Fig. 7. Normalized TOC and hydrogen peroxide concentration upon reaction time.

A removal of TOC of 30% after 4 h can be verified for both runs. On Fig. 2 it is also possible to observe the color change in the effluent before and after the reaction (small vials on the figure).

CONCLUSIONS

HTC of compost is a suitable approach to its valorization and to produce carbon-based materials. The kinetic model developed can predict the quantity of hydrochar produced and the loss of elemental carbon transferred to the liquid phase under different operating conditions. Fenton reaction was able to reduce the color and the TOC of the liquid waste water effluent obtained from HTC of compost.

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