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Activation of Pyrolytic Bio-Char from Olive Residues: A Predictive Model for Yield and Surface Area

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Highlights

- Pyrolytic bio-char produced from olive residues and activated with carbon dioxide shows a linear trade-off between yield and surface area.
- A simple model is proposed to predict the relationship between yield and surface area during activation.
- The model is validated with experimental results.

1. Introduction

A great amount of work in the literature is dedicated to the kinetic modelling of gasification reactions, while a limited number of authors have paid attention to the evolution of physical parameters, which are very important in the case in which the reaction is applied to the production of activated carbons. The Volume reaction model (VRM) [1], the Shrinking core model (SCM) [2], and the Random pore model (RPM) [3] are unable to provide a relationship between kinetics and the physical properties of the activated carbon and, particularly, between yield and surface area.

2. Methods

Experimental CO_2 activation of pyrolytic bio-char produced from olive residues has demonstrated that both yield and surface area vary linearly with time (Figure 1). Moreover, a unique relationship between increases in surface area and reduction of yield is observed (Figure 2).

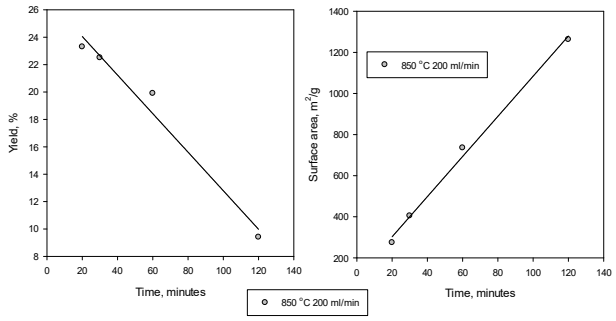

Figure 1. Effect of activation time on yield and surface area

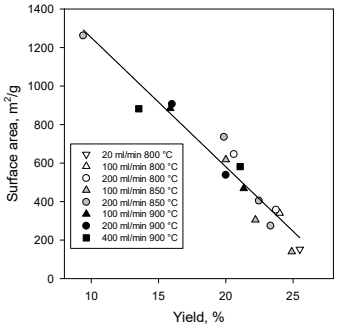

Figure 2. Relationship between yield and surface area

Based on the experimental observations, an empirical kinetic expression for the yield of activated carbon is proposed, $Y_{AC} = Y_C - k_y t$, where Y_C is the yield of initial bio-char and $k_y = k_{y0} e^{\left(\frac{-E_{ay}}{RT}\right)}$, with k_{y0} = 121 min^{-1} and E_{ay} = 61,207 J/mol. Similarly, the specific surface area evolution is described by $a = a_0 + k_s t$, with a_0 as the specific area of the initial bio-char and k_{s0} = 2,001 m^2/g min^{-1}and E_{as} = 48,166 J/mol.

A simplified bio-char activation model is proposed, as illustrated in Figure 3, with the following assumptions: (i) no external mass transfer limitations; (ii) formation of cylindrical pores ([3] and [4]); (iii) particle shrinking rate negligible with respect to the pore evolution rate; (iv) increase in pore diameter with time is negligible compared to the increase in pore length (the reaction is stopped before pores start to collapse); (v) the activation rate is independent of the CO_2 partial pressure.

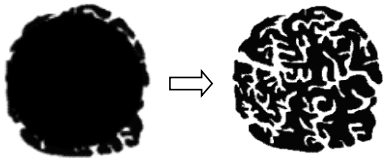

Figure 3. Illustration of activation model

As a result, the surface area of a single activated char particle is $A_{AC} = n_p \pi d_0 y = n_p \pi d_0 k t$ where n_p is the number of pores in a single particle, d_0 is the pore diameter and k is the kinetic constant for the pore propagation. The volume of an activated particle is $V_{AC} = V_C - (\pi/4) n_p d_0^2 k t$, where V_C is the volume of a particle of original bio-char. Based on the assumptions above, the activated bio-char yield can be predicted as:

$$Y_{AC} = Y_C \left(\frac{V_C - V_{AC}}{V} \right) = \left(\frac{\frac{4}{3}\pi R_{p0}^3 - \frac{\pi}{4} d_0^2 (n_p k}{4 \quad R3} \right.$$

which is analogous to the expression empirically derived from the experimental results. Therefore, for any temperature, knowing k_y, the value of $n_p k$ can be calculated. Given that the particle size does not change with the activation, the specific surface area can also be evaluated at any given time as:

$$a = A_{AC} P_{AC} = A_{AC} P_C (Y_C/Y_{AC}) = n_p k \pi d_0 t P_C (Y_C/Y_{AC}) = C^* n_p k \pi d_0 t$$

where P_{AC} is the number of activated bio-char particles per unit mass, and P_C is the number of original bio-char particles per unit mass, and C^* is a constant. The equation predicts, for any given temperature, the expected linear relationship between specific surface area and time, illustrated in Figure 1.

3. Results and discussion

The experimental and predicted yields and specific surface areas are successfully compared in Figures 4 and 5 for a value of the empirical parameter $C^* = 8.2\ 10^3\ g^{-1}$, characteristic of the olive residue bio-char activation.

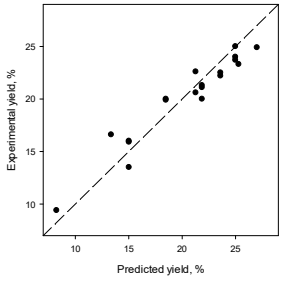

Figure 4. Yield model predictions

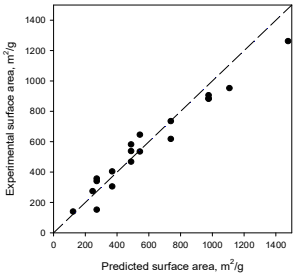

Figure 5. Specific surface area model predictions

4. Conclusions

A simple model is proposed and validated, able to predict the relationship between yield and surface area of bio-char from olive residues, activated with carbon dioxide.

References

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Keywords: Bio-char; Activation; Modelling.