Hydrothermal Carbonization: A Renewable Alternative to Fossil Fuels and Respective Evaluation

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Introduction: Hydrothermal carbonization (HTC), emulates the natural process of coalification. Biomass in the presence of subcritical water is heated in a closed environment. The main product is hydrochar a solid carbon-rich material with a calorific value comparable to that of lignite.

Computational Methods: The hydrothermal carbonization of grape marc can be described accurately with a two-step reaction mechanism according to which, the initial feedstock A forms an intermediate compound B which, in turn, forms the final product C. At each step the formation of the volatiles V_1 and V_2 takes place in parallel to the A-B-C transformation.

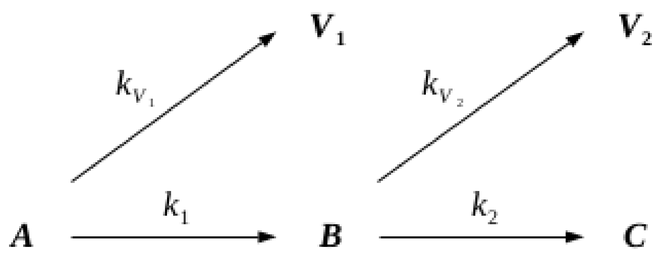

Figure 1. Two-step reaction mechanism for the hydrothermal carbonization of grape marc.

Assuming that the temperature dependence of the kinetic constant is expressed by the classical Arrhenius equation and that all involved reactions are of the first order, the equations that describe the model are:

$$\frac{\partial m_A}{\partial t} = -k_1 m_A - k_{V_1} m_A$$

$$\frac{\partial m_B}{\partial t} = k_1 m_A - k_2 m_B - k_{V_2} m_B$$

$$\frac{\partial m_C}{\partial t} = k_2 m_B$$

$$\frac{\partial m_{V_1}}{\partial t} = k_{V_1} m_A$$

$$\frac{\partial m_{V_2}}{\partial t} = k_{V_2} m_B$$

where m represents the mass yield of each chemical species involved. The above system of coupled PDEs was solved by using COMSOL reaction engineering module with reaction temperature, kinetic parameters (table 1) and residence time as inputs.

Table 1. Values of the Arrhenius parameters (k_0, E_a).

$k_{0,1}$ [s^{-1}]	$k_{0,2}$ [s^{-1}]	$k_{0,V1}$ [s^{-1}]	$k_{0,V2}$ [s^{-1}]
$3.34 \cdot 10^7$	$1.10 \cdot 10^{10}$	$9.15 \cdot 10^6$	$1.55 \cdot 10^{10}$
$E_{a,1}$ [kJ/mol]	**$E_{a,2}$ [kJ/mol]**	**$E_{a,V1}$ [kJ/mol]**	**$E_{a,V2}$ [kJ/mol]**
94.5	139.7	93.7	146.2

Results: The solution of the system for known Arrhenius parameters (Table 1) leads to the distribution of mass yield versus time for two experimental temperatures (180 and 250 ^oC) and for residence times up to 8 hours.

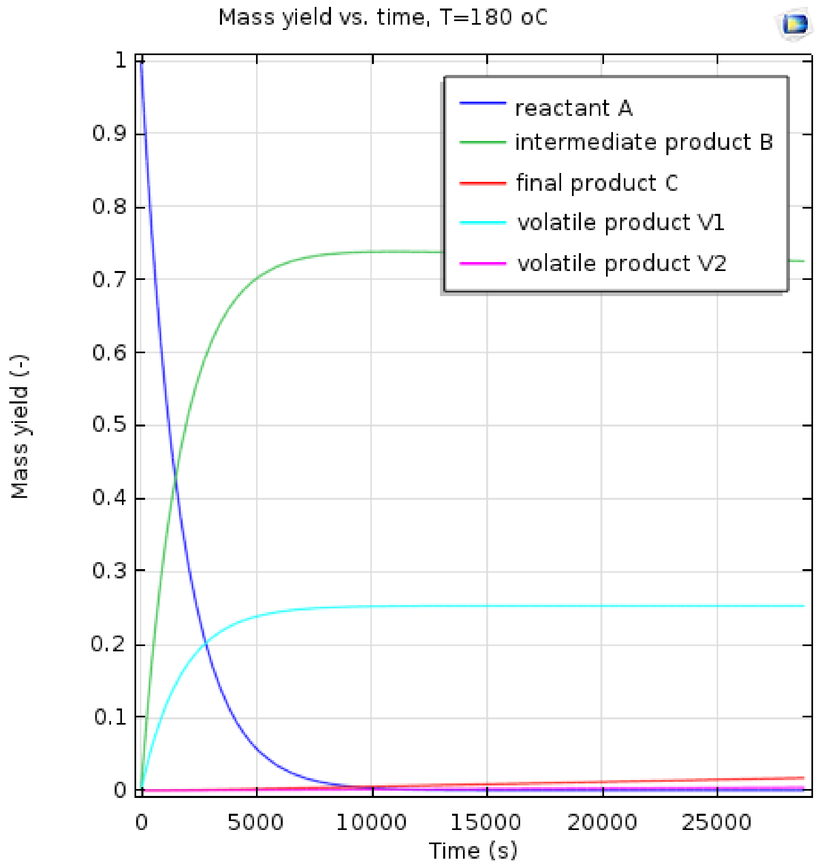

Figure 2. Mass yield versus time, T=180 ^oC.

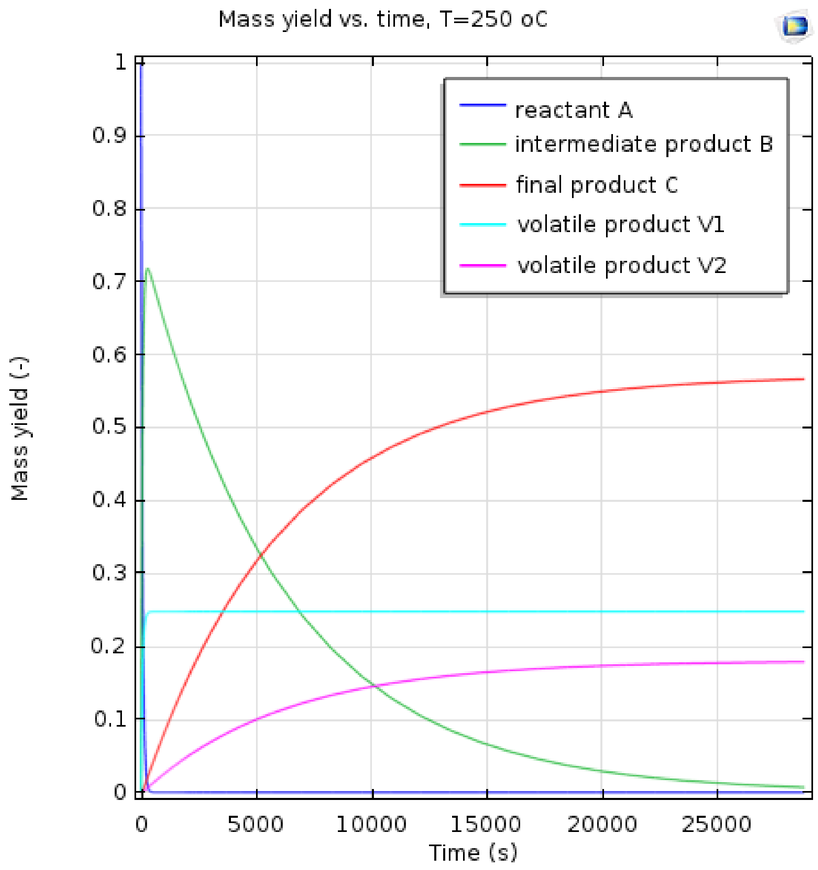

Figure 3. Mass yield versus time, T=250 ^oC.

Conclusions: •Reaction temperature is the dominant parameter. As temperature increases, the effect of residence time diminishes. •Elevated temperatures promote the production of the volatile byproducts. •The low temperature of 180 ^oC proves to be insufficient to facilitate the second-step reactions (negligible amount of produced hydrochar). •The first-step reactions occur faster (lower activation energies). •Accurate kinetics models are necessary for process optimization •HTC is an overall attractive process due to its simplicity, hydrochar properties and lack of initial drying step.

References:

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