

## S1. Hess' Law

To establish a balance on the heat of hydrothermal liquefaction reaction, Hess' law can be used. For a given temperature, the resulting enthalpy of the reaction corresponds to the difference of standard enthalpy of formation of reactants and products (Equation 2):

A reaction can be described as follow:

$$0 = \sum_i \vartheta_i A_i \quad (\text{Equation 1})$$

Where  $A_i$  are the compounds involved in the reaction.

$\vartheta_i > 0$  if the compound  $A_i$  is a product

$\vartheta_i < 0$  if the compound  $A_i$  is a reactant

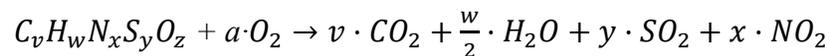
$$\Delta H_{r(T)}^0 = \sum_i \vartheta_i \Delta H_{f(T)}^0 \quad (\text{Equation 2})$$

The standard enthalpies of formation of biomasses and liquefaction products  $\Delta H_{f(T)}^0$  are not known but can be calculated thanks to the measurement of enthalpy of the combustion reaction. The measurement or the calculation of the enthalpy of the combustion reaction, their initial elemental composition and the known enthalpy of formation of combustion products such as  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{SO}_2$  and  $\text{NO}_2$  (presented in Table S1) allow the calculation of the standard enthalpy of formation of the product of interests.

Table S1. : Enthalpy of formation of combustion products.

Combustion products	Standard enthalpies of formation $\Delta H_f^0$ (kJ/mol)
$\text{CO}_2(\text{g})$	-393.5
$\text{H}_2\text{O}(\text{l})$	-285.8
$\text{SO}_2(\text{g})$	-296.8
$\text{NO}_2(\text{g})$	33.8

The enthalpy of formation of biocrude and the organic fraction dissolved in the aqueous phase can be calculated from the enthalpy of formation of combustion products and from the enthalpy of combustion  $\Delta H_{combustion}$ . The equation of full combustion is given by:



with  $a = v + \frac{w}{4} + y + x \frac{z}{2}$

The enthalpies of formation of the biocrude and the organic fraction are then given by :

$$\Delta H_{formation} = v \cdot \Delta H_{f,CO_2(g)}^0 + \frac{w}{2} \cdot \Delta H_{f,H_2O(l)}^0 + y \cdot \Delta H_{f,SO_2(g)}^0 + z \cdot \Delta H_{f,NO_2(g)}^0 - \Delta H_{combustion}$$

Finally, the global enthalpy of reaction can be calculated with Hess' law from the difference of the enthalpies of formation between the products and the reactants