



# Biomass torrefaction: Modeling of reaction thermochemistry



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## HIGHLIGHTS

- ▶ Model developed to describe the energy balance during willow torrefaction.
- ▶ First stage is exothermic releasing 40–280 kJ/kg.
- ▶ Second stage is either exothermic or endothermic.
- ▶ Higher torrefaction temperatures result in increased reaction rate and heat release rate.

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## ABSTRACT

Based on the evolution of volatile and solid products predicted by a previous model for willow torrefaction (Bates and Ghoniem, 2012) a thermochemical model has been developed to describe their thermal, chemical, and physical properties as well as the rates of heat release. The first stage of torrefaction, associated with hemicellulose decomposition, is exothermic releasing between 40 and 280 kJ/kg<sub>initial</sub>. The second stage is associated with the decomposition of the remaining lignocellulosic components, completes over a longer period, and is predicted to be either endothermic or exothermic depending on the temperature and assumed solid properties. Cumulative heat release increases with the degree of torrefaction quantified by the mass loss. The rate of mass loss and rate of heat release increase with higher temperatures. The higher heating value of volatiles produced during torrefaction was estimated to be between 4.4 and 16 MJ/kg increasing with the level of mass loss.

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## 1. Introduction

Raw biomass faces utilization challenges due to its low bulk energy density, hydrophobicity, propensity to decay during storage, and high grinding energy requirement. Torrefaction has been proposed as thermal pretreatment to improve these characteristics (Arias et al., 2008; Bergman et al., 2005; Ohliger et al., 2012). Torrefaction is a mild pyrolysis occurring between 200 and 300 °C for a residence time between several minutes to about an hour which results in partial devolatilization (0–60 wt.%) of the solid biomass (Prins, 2005). Pyrolysis broadly refers to partial to complete devolatilization (70–90 wt.%) occurring over a wide temperature range (200–1000 °C) though typically between 400 and 700 °C (Neves et al., 2011).

Multi-scale (e.g. particle, reactor, flowsheet) models of torrefaction require quantification of the physical and chemical properties

of torrefaction products in order to describe the process energy balance. At the particle scale, the heat of torrefaction may act as a local source or sink of thermal energy and therefore affect temperature and conversion profiles significantly. As Turner et al. (2010) note, the heat release is a crucial mechanism through which chemical reaction and heat transfer phenomena are coupled at the particle scale. Another important level of coupling occurs between the particle temperature and the solid physical properties, such as specific heat, density, and conductivity, which determine the rate at which heat diffuses through the particle. Description of the evolution of these properties requires accurate kinetics and thermochemical models.

At the reactor scale, an accurate estimate of the reaction enthalpy is necessary for process design and control. For example, process conditions which lead to excessive heat release could potentially cause runaway thermal reactions in the absence of active thermal management.

For the development of flowsheet models, it is necessary to quantify the thermal energy input required during torrefaction to assess the overall process efficiency. In particular, the feasibility of autothermal torrefaction as originally described by (Bergman et al., 2005), which combusts the volatile products released during

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torrefaction to provide heat for the process itself, depends on the accurate estimation of their composition and heating value.

The present work describes a model for the energy balance and thermochemistry of torrefaction based on a previous kinetics model (Bates and Ghoniem, 2012) for the evolution of volatile matter during willow torrefaction. The parameters of the two models are linked. While the volatile composition parameters from are specific to willow torrefaction, this work outlines a general framework for relating these feedstock-specific parameters to the energy balance of the reactions.

A variety of experimental studies have examined the effect of torrefaction conditions on the mass and energy yield of the solid product (Almeida et al., 2010; Arias et al., 2008; Bridgeman et al., 2008; Medic et al., 2012). Lee et al. (2012) and Medic et al. (2012) performed multiple regressions relating process parameters (such as initial moisture content, temperature, and residence time) to the solid product energy and mass yield. (Almeida et al., 2010) showed that the solid mass loss could be used as a quantitative indicator for the extent of torrefaction. Several product characteristics including solid energy yield, heating value, and chemical composition were linearly regressed against the solid mass loss. The validity of these empirical regressions beyond the thermal conditions tested is unknown. Additionally they cannot predict the energy content of liberated volatiles or the reaction thermochemistry. The latter are the objectives of this work.

### 1.1. Previous estimates for the heat of torrefaction

Estimates for the heat of torrefaction and pyrolysis as measured or deduced by a variety methods are summarized in Table 1. The main methods include (1) estimation from the heating value of the products, (2) differential scanning calorimetry (DSC), (3) fitting of coupled single particle models with experimental data and, (4) measurement of heat release using custom reactor systems.

Experimental attempts to assess the heat of willow and beech torrefaction through measuring (or estimating) the heating values of the initial biomass, solid, and volatile products have been unable to precisely classify it as either exothermic or endothermic (Prins, 2005; van der Stelt, 2011). Overall heat of torrefaction estimates based on this method vary widely and from 87–124 ( $\pm 449$ ) kJ/kg willow (Prins, 2005) and –1200 to 1500 kJ/kg beech (van der Stelt, 2011). Significant uncertainties arise from the measurement/estimation of the heating value of solid products and assumptions regarding leaked products.

van der Stelt (2011) also used a fixed bed reactor setup to torrefy a single 10 cm long, 28 mm diameter cylindrical beech particle in order to deduce the enthalpy of reaction. Six thermocouples enabled measurement of the particle temperature at positions between the centerline and surface. Based on the intraparticle temperature profile and a simplified single particle model, the reaction heat was estimated to be between 0 and –220 kJ/kg beech for torrefaction temperatures between 200 and 280 °C.

Ohliger et al. (2012) utilized a continuous screw reactor system to measure heat release during the torrefaction of beech wood. Though sensitive to the assumed physical properties of the biomass such as the specific heat capacity, it was concluded that the heat of torrefaction was between –199 and 148 kJ/kg beech.

### 1.2. Previous estimates for the heat of pyrolysis

Pyrolysis refers to devolatilization occurring over a broader range of thermal conditions than torrefaction; however, given the greater number of investigations examining the heat of wood pyrolysis, it is also worth summarizing these efforts. Literature estimates for the heat of wood pyrolysis range widely from –2300 kJ/kg biomass (exothermic) to 418 kJ/kg biomass (endothermic) (Turner et al., 2010). The differences have been attributed to the small sample sizes (ranging from milligrams to grams), the presence of impurities, and experimental conditions (Turner et al., 2010).

During differential scanning calorimetry (DSC) wood pyrolysis experiments ramping from 100 up to 500 °C at 10 °C min<sup>-1</sup> (Rath et al., 2003) found wide variations in the heat of primary wood pyrolysis depending on the sample mass, feedstock, and conditions. Observing an apparent shift from endothermic to exothermic behavior, it was concluded that the overall heat of pyrolysis depended on the competition between an exothermic char formation process (–3525 to –3827 kJ/kg<sub>char</sub>) and an endothermic (936 to 1277 kJ/kg<sub>gas+volatiles</sub>) volatile formation process. The overall heat of pyrolysis expressed as a linear superposition of an exothermic char formation and endothermic volatile formation weighted by mass fractions (obtained experimentally or from kinetic expressions) (Rath et al., 2003):

$$\Delta H_{\text{total}} = \Delta H_{\text{exo}} Y_{\text{char}} + \Delta H_{\text{endo}} (1 - Y_{\text{char}}) \quad (1)$$

where  $\Delta H_{\text{total}}$  has units of kJ kg<sub>biomass</sub><sup>-1</sup>,  $Y_{\text{char}}$  is a product mass fraction with units of (kg<sub>char</sub> kg<sub>biomass</sub><sup>-1</sup>),  $\Delta H_{\text{exo}}$  and  $\Delta H_{\text{endo}}$  are the apparent exothermic and endothermic heats of pyrolysis (see Table 1) for the reported values.

**Table 1**

Experimentally measured or deduced enthalpy of reaction for torrefaction and pyrolysis (–) exothermic, (+) endothermic.

Enthalpy of reaction	Temperature range (°C)	Feedstock	Method	Source
87 ± 449 kJ/kg <sub>biomass</sub>	250	Willow	ASTM bomb calorimetry	Prins (2005)
150 ± 1350 kJ/kg <sub>biomass</sub>	230–280	Beech	Estimated through analysis of products and reactant	van der Stelt (2011)
0 to –200 kJ/kg <sub>biomass</sub>	200–280	Beech	Deduced from experimental data with simplified single particle model	van der Stelt (2011)
–199 to 148 kJ/kg <sub>biomass</sub>	270–300	Beech	Deduced from experimental data with continuous screw reactor	Ohliger et al. (2012)
936–1277 kJ/kg <sub>gas+volatiles</sub>	100–500	Spruce, Beech	Differential scanning calorimetry	Rath et al. (2003)
–3525 to –3827 kJ/kg <sub>char</sub>				
–293 to –1673 kJ/kg <sub>mass loss</sub>	275–470	Beech	Deduced from experimental data with single particle model	Roberts and Clough (1963)
200.8 kJ/kg <sub>mass loss</sub>	470	Beech	Deduced from experimental data with single particle model	Kung and Kalelkar (1973)
255 to –20 kJ/kg <sub>mass loss</sub>	300–600	Wood sawdust	Deduced from experimental data with single particle model	Koufopoulos et al. (1991)
25 kJ/kg <sub>char,tar,gas</sub>	200–850	(Various)	Deduced from experimental data with single particle model	Haseli et al. (2011)
–55.3 to –176 kJ/kg <sub>biomass</sub>	100–600	Pine, oak sawdust	Deduced from experimental data with model of packed sawdust reactor	Strezov et al. (2004)

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