

Torrefaction Kinetics of Norwegian Biomass Fuels

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Torrefaction kinetics of Norwegian biomass fuels, including spruce (softwood) and birch (hardwood) was studied using a thermogravimetric analyser. Small samples of approximately 10 mg and particle size of 63–125 μm were heated at a constant heating rate of 5 $^{\circ}\text{C}/\text{min}$ and kept afterwards for 4 hours in isothermal conditions at different temperatures (230, 240, 250, 260, 270 and 280 $^{\circ}\text{C}$). A two-step kinetic model was employed to simulate the recorded mass loss curves. The results showed that the decomposition of the initial biomass in the first step, to form an intermediate solid and volatiles, exhibited a higher conversion rate compared with the second step. The rate constants (in s^{-1}) for two steps are: $k_1 = 21.2 \times \exp\left(\frac{-48109.7}{RT}\right)$, $k_2 = 4.74 \times 10^9 \exp\left(\frac{-149639.9}{RT}\right)$ for spruce and $k_1 = 106.6 \times \exp\left(\frac{-55112.8}{RT}\right)$, $k_2 = 2.80 \times 10^{10} \exp\left(\frac{-163263.7}{RT}\right)$ for birch. Moreover, the final solid yield, which decreased gradually with increasing torrefaction temperature, reproduced the experimental results well.

1. Introduction

Torrefaction is a thermochemical process for upgrading cellulosic biomass into a more homogeneous fuel which can be utilised in other conversion processes for energy purposes. The main idea is to try to modify the feedstock properties towards a more predictable fuel during energy conversion without taking out much of its energy content. Many research studies have been performed in the past decade in order to assess properties of torrefied fuel. A nice overview over the past findings can be found in the review prepared by (Chew and Doshi, 2011). The energy situation in Norway is quite different to other European countries as most of the electricity and the residential heating energy consumption is acquired through sustainable and green alternatives mainly in the form of hydropower or biomass. Major reductions in greenhouse gas emissions have to be therefore achieved through adjustments in other polluting sectors.

Currently, changes in the transport sectors for both land and air traffic are being considered for the mitigation of the greenhouse gas emissions in Norway. One topic is the production of biofuels through biomass gasification and Fischer–Tropsch processes. Torrefaction could play an important role for this type of technology since untreated biomass is difficult to gasify in an entrained flow reactor, which is one of the gasification reactor alternatives for production of syngas suitable for upgrading to biofuels through Fischer–Tropsch processes. The importance of torrefaction in this particular field has been reviewed by (van der Stelt et al., 2011).

Torrefaction as a means for achieving stable operating conditions in processes for power and heat production through combustion has also been a major drive for the authors of this manuscript to work on torrefaction. The fuel properties of typical Norwegian woods, birch (hardwood) and spruce (softwood), after dry and wet torrefaction have been assessed in the respective works of (Tapasvi et al., 2012) and (Bach et al., 2013). The same fuels have been used in this study although the current focus is to look into the thermal degradation kinetics under dry torrefaction conditions. Determining the torrefaction kinetic parameters of typical Norwegian fuels is important for the prediction of their behaviour under different pre-treatment conditions. It is also useful for design and optimization of torrefaction reactors.

2. Mechanism and kinetic model

For torrefaction it is more relevant to perform the kinetic study under isothermal conditions. The history for performing kinetic studies on pyrolysis is quite rich and spans over several decades. The review prepared by (Lede, 2012) on pyrolysis kinetics of cellulose might give the readers a historical overview of the topic. For torrefaction, the list of kinetic studies is much shorter but has been growing steadily in the past couple of years.

This study uses a two-step reaction in series model to simulate the mass loss on the basis of the data collected from a series of thermogravimetric analysis (TGA) experiments. The model has been used for pyrolysis and was described in the work of (Agrawal, 1988) as the modified Kilzer-Broido Model. The same model has been later adopted by (Di Blasi and Lanzetta, 1997) for modelling the degradation of xylan in an inert atmosphere and for the temperature range 200–340°C. For torrefaction, (Prins et al., 2006) also adopted this model for willow and lately (Shang et al., 2013) used it for modelling the weight loss characteristics of straw. (Repellin et al., 2010) relied on literature data for the activation energy and adjusted the other kinetic constants to predict the anhydrous weight loss of wood chips in a pilot kiln. Two models were used in their curve fitting, the modified Kilzer-Broido model and the Rousset model (Rousset et al., 2006). They neglected heat transfer limitations in their study and only compared the model to the final weight loss of the experiments.

The mechanism adopted for kinetic modelling in this study is presented in Equation (1) (Agrawal, 1988, Di Blasi and Lanzetta, 1997). It is assumed that biomass A is converted to an intermediate solid B and volatiles V_1 . The intermediate solid B reacts afterwards to form the final solid C and the additional volatiles V_2 .



Assuming first order kinetics, the rate equations for the solid compounds can be written as (2-4).

$$\frac{d[A]}{dt} = -(k_B + k_{V1})[A] \quad (2)$$

$$\frac{d[B]}{dt} = k_B[A] - (k_C + k_{V2})[B] \quad (3)$$

$$\frac{d[C]}{dt} = k_C[B] \quad (4)$$

The rate constants of the component steps are dependent on the activation energy and the pre-exponential factor in the Arrhenius' equation $k_i(T) = A_i e^{-\frac{E_i}{RT}}$, $i=A, B, V_1, V_2, C$.

For the kinetic modelling and simulation, the relative sample mass (M_t/M_0) defined by (5) is introduced.

$$\left(\frac{M_t}{M_0}\right) = \frac{m_t - m_{ash}}{m_0 - m_{ash}} \quad (5)$$

where m_t = sample mass at time t , m_{ash} = mass of ash in the initial sample, m_0 is the initial sample mass, $M_t = m_t - m_{ash}$, and $M_0 = m_0 - m_{ash}$.

The relative sample mass can be experimentally determined, called $(M_t/M_0)_{exp}$, via a thermogravimetric analysis. On the other hand, it can be calculated and called $(M_t/M_0)_{cal}$. Indeed, the relative sample mass can be expressed as the mass sum of the three pseudo compounds A , B and C in (6), or can be obtained through the integration of the differential equations (2-4) with the initial conditions $A = 1$ and $B, C = 0$ as in (7):

$$\left(\frac{M_t}{M_0}\right)_{cal} = [A] + [B] + [C] \quad (6)$$

or

$$\left(\frac{M_t}{M_0}\right)_{cal} = \left[1 + \left(\frac{k_B \cdot K_1 - k_B \cdot k_C}{K_1 \cdot (K_2 - K_1)}\right)\right] e^{-K_1 t} + \left(\frac{-k_B \cdot K_2 + k_B \cdot k_C}{K_2 \cdot (K_2 - K_1)}\right) e^{-K_2 t} + \frac{k_B \cdot k_C}{K_1 \cdot K_2} \quad (7)$$

where:

$$K_1 = (k_B + k_{V1}); \text{ and } K_2 = (k_C + k_{V2}) \quad (8)$$

3. Materials and methods

Norway spruce and birch woods were used as feedstock in this study. The fuel properties of the raw materials are given in Table 1, which is adopted from (Tapasvi et al., 2012). The biomass samples were first ground with an IKA MF 10 cutting mill. Particles having size of 63–125 μm were selected for thermogravimetric analysis in a METTLER Toledo TGA/SDTA 851e.

Table 1. Fuel properties of the feedstock

Type of biomass	Proximate analysis			Ultimate analysis					HHV ^b
	Ash ^a	VM ^a	Fixed C ^a	C ^a	H ^a	O ^a	N ^a	S ^a	
Norway birch	0.22	89.43	10.35	48.62	6.34	44.90	0.09	0.05	19.80
Norway spruce	0.23	86.34	13.43	50.10	6.36	43.52	0.07	0.05	20.45

^a wt%; ^b Higher heating value, in MJ/kg and ash free

Prior to the TGA experiments, the samples were dried at 100 °C for 24 h. For each of the experiments, an amount of 10 mg of the feedstock powder was spread in the 150 μL alumina crucible of the TGA. The sample was heated from room temperature and held at 100 °C for 30 min to remove the moisture and then heated with a heating rate of 5 °C/min to the torrefaction temperature (230, 240, 250, 260, 270 and 280 °C), at which the sample was isothermally held for 4 hours. A flow rate of 100 mL/min of nitrogen was supplied for all experiments.

The kinetic parameters (k , E , A in the Arrhenius equation) for torrefaction of the wood samples were determined by analysing the experimental data and model (7) using the nonlinear least square method, which minimizes the sum S of the squares in Equation (9):

$$S = \sum_i \left[\left(\frac{M_t}{M_0}\right)_{exp,i} - \left(\frac{M_t}{M_0}\right)_{cal,i} \right]^2 \quad (9)$$

where i denotes the different data points of the sample mass that can be respectively collected and calculated as time progresses.

4. Results and discussion

4.1 Thermogravimetric analysis of woods during torrefaction

Figure 1A and 1B respectively presents results from the thermogravimetric analysis of the Norway spruce and birch wood samples during torrefaction at different temperatures. In these figures, the TGA curves were constructed by plotting the data of remaining solid mass fraction (or relative sample mass, M_t/M_0) against (holding) time. Note that the remaining sample mass at 200 °C was normalized as the initial mass, m_0 , at $t = 0$, considering that dry torrefaction process is assumed to start at 200 °C (Bergman et al., 2005).

As can be seen from Figure 1, the trends of the TGA curves for the two woods are similar: increasing either the torrefaction temperature or holding time increased the mass loss. In addition, when the torrefaction temperature was increased from 230 to 280 °C, the slope of the TG curves increased, which indicates that the effect of holding time on the mass loss increased. Moreover, the effect of torrefaction conditions on the birch wood was stronger than that on the spruce because at a same torrefaction temperature and holding time, the birch had more mass loss than the spruce. This is presumably due to the fact that birch (hardwood) contains more hemicellulose than spruce (softwood) (Sjöström, 1981). Other possible causes should include the higher content of volatile matter for birch (89.4%) than spruce (86.3%) as given in Table 1.

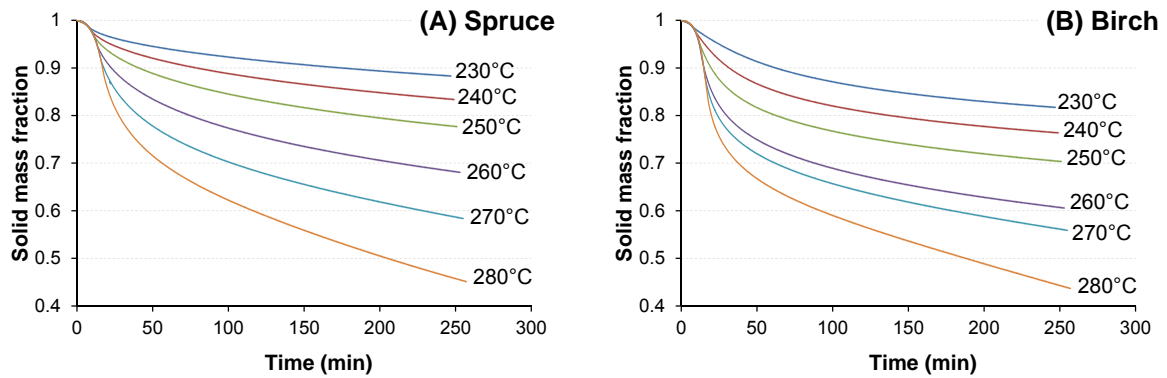


Figure 1. TGA curves for torrefaction of spruce (A) and birch (B) at different temperatures

4.2 Simulation details

Simulations on the basis of analysing model (7) using the nonlinear least square method were performed for all the collected data presented in Figure 1. Results from all of the simulations will be presented later in Section 4.3. In this section, the simulations for the spruce torrefaction at three different temperatures (230, 250 and 280 °C) will be discussed in detail for a demonstration and understanding of the fate of the intermediate (B) during torrefaction. Figure 2 graphically presents results from the selected simulations, in which A , B , and C denotes the mass of initial biomass (A), intermediate product (B) and final solid (C), respectively. The experimental and calculated data are represented by *exp* and *cal*, respectively. The calculated curve (*cal*) is the sum of three partial curves (A , B , and C), i.e. $cal=A+B+C$.

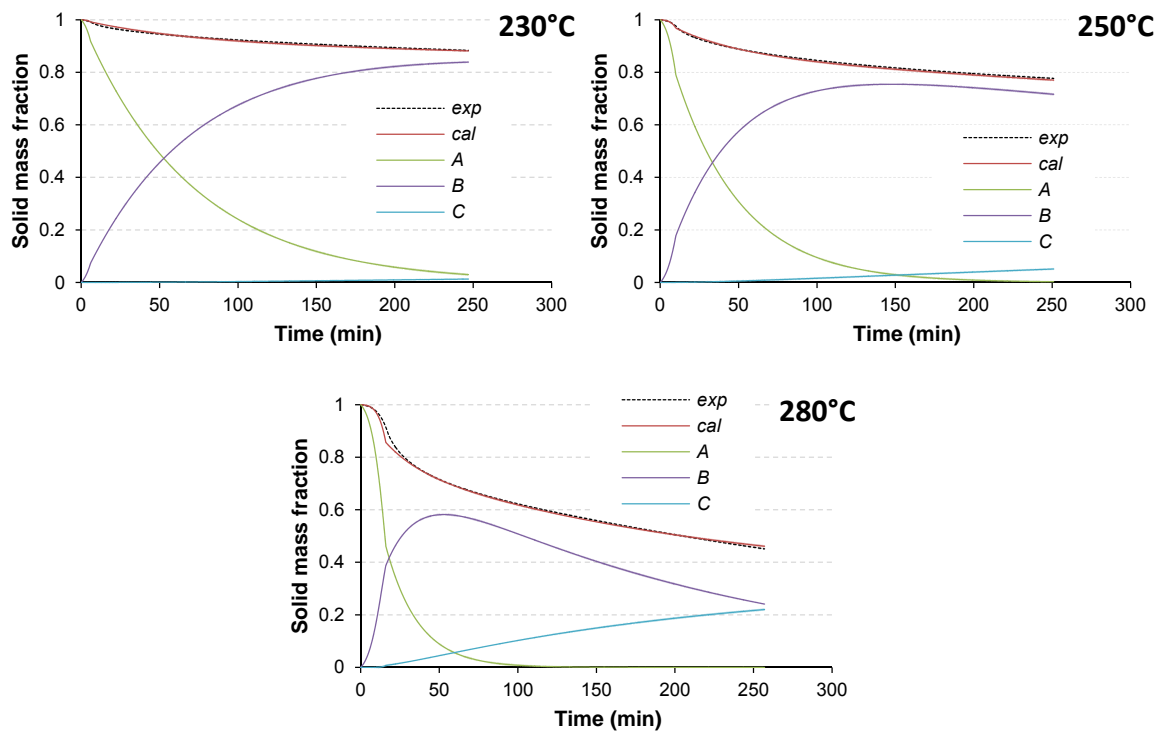


Figure 2. Simulation for spruce torrefaction of at 230, 250 and 280 °C

From Figure 2 it is observed for all of the three cases that, at time $t = 0$ when $T = 200$ °C, the initial spruce A started degrading to form its intermediate B . The formation of B was coupled with its degradation to form the final solid C . The simultaneous formation and decomposition of B competed to each other. This competition was dependent on torrefaction temperature, resulting in the different shapes of B curves. At 230 °C the intermediate B was quite thermally stable. B formation rates were greater than its decomposition rates. Only a small fraction of B was converted to C at a given time. Consequently, the B

curve increased consistently with time. However, at higher torrefaction temperatures (from 250 °C), B curves had a peak at which B decomposition became faster than B formation. The higher torrefaction temperatures, the earlier the peaks occurred and the sharper the peaks were. Overall, the decomposition of A was strongly dependent on the torrefaction temperature: at 230 °C, it took more than 250 min (~4.2 h) to convert the virgin biomass completely, but this gradually reduces to 230 and 100 min (~3.8 and 1.7 h) at 250 and 280 °C, respectively. In addition, the higher torrefaction temperatures, the more final solid (C) were formed.

4.3 Kinetic data extraction

Figure 3 graphically presents results from all of the simulations performed for the collected data presented in Figure 1. Relatively good fits between the simulated and experimental data are observed. In addition, the fits for the spruce are slightly better than that for the birch. It should be noted that the simulations with the curve fitting approach aimed to obtain the best overall fit for the all data sets, not for a single set of data collected from the torrefaction at one temperature. Therefore, certain individual fits may look better than the others.

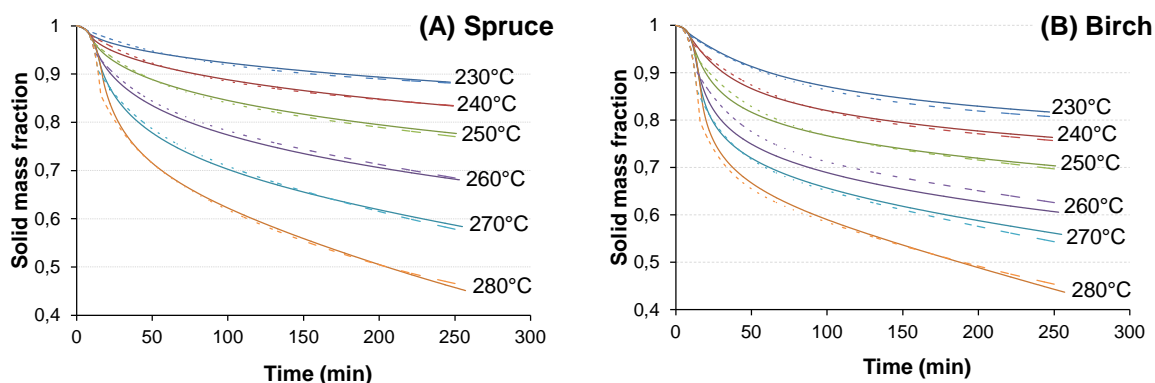


Figure 3. Simulations and curve fittings between experimental data (solid lines) and simulated data (dashed lines) for torrefaction of spruce (A) and birch (B) at different temperatures

From the simulations, the kinetic parameters were extracted, which are shown in Table 2. In this table the rate constant $k_i(T) = A_i \exp\left(-\frac{E_i}{RT}\right)$ ($i = B, V_1, C$ or V_2) in s^{-1} , the pre-exponential factor (A_i) in s^{-1} , the activation energy (E_i) in J/mol , the gas constant (R) in $J.mol^{-1}.K^{-1}$, and the absolute temperature (T) in K . The obtained kinetic parameters are in a reasonable range compared with kinetic parameters for the degradation of hemicellulose and cellulose, which has been reported in the literature (White et al., 2011). It can be seen from the table that the activation energy values in the first step are lower than those in the second step, but the pre-exponential factors in the second step are much higher than those in the first step. However, the constant rate in the first step ($K_1 = k_B + k_{V_1}$) is higher than that in the second step ($K_2 = k_C + k_{V_2}$).

Table 1. Extracted kinetic parameters for spruce and birch torrefaction

Rate constants (s^{-1})	Spruce	Birch
k_B	$21.2 \times \exp\left(\frac{-48109.7}{RT}\right)$	$106.6 \times \exp\left(\frac{-55112.8}{RT}\right)$
k_{V_1}	$4.74 \times 10^5 \exp\left(\frac{-99238.5}{RT}\right)$	$2.61 \times 10^5 \exp\left(\frac{-94428.0}{RT}\right)$
k_C	$4.74 \times 10^9 \exp\left(\frac{-149639.9}{RT}\right)$	$2.80 \times 10^{10} \exp\left(\frac{-163263.7}{RT}\right)$
k_{V_2}	$3.40 \times 10^8 \exp\left(\frac{-136254.3}{RT}\right)$	$2.3 \times 10^5 \exp\left(\frac{-104431.5}{RT}\right)$

$$R=8.314 \text{ J } K^{-1} \text{ mol}^{-1}, T: \text{ absolute temperature (K)}$$

This observation is also in agreement with the literature (Prins et al., 2006, Di Blasi and Lanzetta, 1997) and thus confirms that the conversion is much faster in the first step than in the second step, which was graphically demonstrated in Section 4.2. According to (Prins et al., 2006), the first step (degradation of the initial biomass to form the intermediate) is addressed to hemicellulose degradation and the second step

(further decomposition of the intermediate to produce the final solid) is due to cellulose decomposition. The significant difference in the reaction rates of two steps is because that hemicellulose has much poorer thermal resistant than cellulose (Prabir, 2010).

5. Conclusions

Torrefaction kinetics of Norway spruce and birch has been studied by TGA experiments followed by a kinetic modelling using a two-step model. The results showed that the decomposition of the initial biomass in the first step had much higher conversion rate compared to the second step. The solid obtained from the torrefaction contained not only the final solid but also some unreacted intermediate solid. The model exhibited high overall fits and the produced solid yields were well predicted. The rate constants (in s^{-1}) for two steps are: $k_1 = 21.2 \times \exp\left(\frac{-48109.7}{RT}\right)$, $k_2 = 4.74 \times 10^9 \exp\left(\frac{-149639.9}{RT}\right)$ for spruce and $k_1 = 106.6 \times \exp\left(\frac{-55112.8}{RT}\right)$, $k_2 = 2.80 \times 10^{10} \exp\left(\frac{-163263.7}{RT}\right)$ for birch. In addition, the effect of torrefaction temperature and holding time on the degradation of the initial biomass and the intermediate solid was significant.

Acknowledgments

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