CHEMICAL ENGINEERING TRANSACTIONS

VOL. 50, 2016

A publication of AIDIC

The Italian Association
of Chemical Engineering
Online at www.aidic.it/cet

Guest Editors: Katharina Kohse-Höinghaus, Eliseo Ranzi

ISBN 978-88-95608-41-9; **ISSN** 2283-9216

DOI: 10.3303/CET1650018

Thermal Decomposition of Biochar from Oxidative Spruce Torrefaction - A Kinetic Study

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In this work, biochar produced via torrefaction of Norwegian spruce at different temperatures (250, 275, or 300°C) in a simulated oxy-fuel combustion flue gas (CO_2/H_2O=1:0.7 mole/mole, O_2/CO_2=10 % v/v) for 30 minutes was examined by means of a thermogravimetric analyser (TGA) operated non-isothermally in an N_2 environment. A distributed activation energy model (DAEM) was applied for a kinetic analysis of the TGA data, assuming three pseudo-components. The results showed that the model closely described the pyrolysis of the biochar obtained from spruce torrefied at 250 or 275°C, but not 300°C. The effect of the torrefaction temperature on pyrolysis kinetics of the Norway spruce is stronger than that of the carrier gas composition. Oxidative torrefaction increases the activation energy of hemicellulose and lignin, but decreases the activation energy of cellulose.

1. Introduction

Torrefaction, which may be defined as mild pyrolysis at temperatures within 200-300oC is an advanced pretreatment technique for improving the fuel quality of lignocellulosic biomass materials (Couhert, Salvador et al. 2009, Chen, Du et al. 2012, Tran, Trinh et al. 2016). During the process of torrefaction mainly hemicelluloses and extractives of biomass are thermally decomposed resulting in a high quality solid fuel, called biochar, and combustible volatiles. Biochar is a hydrophobic fuel with lower moisture content, better grindability, and superior heating value, compared to the native biomass, which is just suitable for combustion and gasification. In the usual industrial torrefaction practices, the produced volatiles are burned with air to produce and supply part of the heat required for the pre-drying and torrefaction process itself. Direct contact of the hot flue gas with biomass during torrefaction could be an efficient way for the heat to transfer to the biomass. However, air consisting overwhelmingly of inert N2 results in the handling of large flue gas volumes which would translate into increased investments in terms of piping and ancillary equipment. This shortcoming will be eliminated if oxy-fuel combustion technology is applied. It is just because, in the process of oxy-fuel combustion, pure oxygen is employed as oxidizer instead of air (oxygen + nitrogen). In addition, the oxy-fuel combustion flue gas is enriched with CO2 compared to conventional air-fuel combustion. Consequently, it is easier and more economically to capture CO2 from oxy-fuel combustion flue gases. Oxy-fuel combustion is also considered as a method for increasing the combustion efficiency and reducing the NOx emission due to the absence of air nitrogen. So, a combination of oxy-fuel combustion with torrefaction would offer a multiple benefits including 1) improved the overall efficiency; 2) reduced volume of flue gas enriched with CO2 for CCS (Carbon Capture and Storage), and reduced NOx emission.

Since the flue gas from oxy-fuel combustion mainly consists of CO2, water and O2, the process of biomass torrefaction and fuel properties of biochar may be different from biomass torrefaction in an inert environment such as N2 (Bridgeman, Jones et al. 2008, Eseltine, Thanapal et al. 2013, Sarvaramini and Larachi 2014). Recently, we have reported some results from our study on biomass torrefaction in conditions relevant for integration with oxy-fuel-combustion. In this work, effects of torrefaction temperature and carrier gas composition on mass and energy yields of the torrefaction process, and fuel properties of biochar were investigated in comparison with biomass torrefaction in N_2. As a follow-up, the work presented in the present

Please cite this article as: Tran K.Q., Bui H.H., 2016, Thermal decomposition of biochar from oxidative spruce torrefaction - a kinetic study, Chemical Engineering Transactions, 50, 103-108 DOI: 10.3303/CET1650018

paper was carried out to look at the pyrolysis kinetics of biochar obtained from our previous work, considering the importance of combustion and pyrolysis (or devitalization, forming char) in solid fuel combustion for heat and power generation (Lakshmanan and White 1994, Ledakowicz and Stolarek 2002). Indeed, combustion is currently contributing to 90% of the global bioenergy consumption (Bain, Overend et al. 1998, Al-Mansour and Zuwala 2010, Saidur, Abdelaziz et al. 2011, Míguez, Morán et al. 2012); The combustion and gasification (partial combustion) characteristics of char (char burn-off) is known to be strongly affected and determined by the devitalization step. For this reason, the pyrolysis kinetics of biomass and torrefied biomass have been extensively studied (Broström, Nordin et al. 2012, Tapasvi, Khalil et al. 2013, Bach, Tran et al. 2014, Tran, Bach et al. 2014, Bach, Tran et al. 2015, Bui, Tran et al. 2016). However, no similar work has been reported so far for biochar produced via oxidative torrefaction, which suggests a need of the present work. The objective of the study presented in this paper was to evaluate the reactivity and to generate kinetic data for pyrolysis of biochar produced via biomass torrefaction in simulated oxy-fuel combustion flue gases. In addition, influences of different torrefaction conditions including temperature and flue gas composition on the kinetics are also discussed.

2. Materials and Methods

2.1 Material and experimental methods

The samples of Norway spruce and its biochar used in this study were characterized and received from the previous work on development of a biomass process integrated with oxy-fuel combustion (Tran, Trinh et al. 2016). Table 1, imported from the previous work, presents one sample of native spruce and seven samples of biochar produced in different torrefaction conditions. The flue gas was simulated by mixing CO_2, O_2 and steam. The investigations of oxygen effect were carried out at oxygen concentrations of 0–10% v/v (dry flue gas) and a temperature of 275^{o}C while the investigations of temperature effect were carried out at temperatures of 250–300^{o}C and an oxygen concentration of 10% v/v (dry flue gas). A total flow rate of the simulated dry flue gas (CO_2 and O_2) was 500 ml/min. The effect of water vapour was studied by adding steam with a CO_2/steam ratio of 1/0.7 (mole/mole). The ratio was approximated based on the data available in the literature (Wang, Peng et al. 2013). The torrefaction in N_2 and CO_2 were performed as a reference cases. A consistent holding time of 30 min was applied for various torrefaction conditions.

Table 1. Torrefaction conditions

Case	Sample ID	Torrefaction conditions	
		Temperature, °C	Inlet gas composition
0	Raw spruce	None	
1	N_2-275°C	275	N_2
2	CO_2-275°C	275	CO_2
3	CO_2-H_2O-275°C	275	CO_2 and H_2O CO_2/H_2O=1:0.7 mole/mole
4	CO_2-H_2O-5%O_2-275°C	275	CO_2 , O_2 and H_2O CO_2/H_2O=1:0.7 mole/mole, O_2/CO_2=5% v/v
5	CO_2-H_2O-10%O_2-275°C	275	CO_2 , O_2 and H_2O CO_2/H_2O=1:0.7 mole/mole, O_2/CO_2=10% v/v
6	CO_2-H_2O-10%O_2-250°C	250	CO_2 , O_2 and H_2O CO_2/H_2O=1:0.7 mole/mole, O_2/CO_2=10 % v/v
7	CO_2-H_2O-10%O_2-300°C	300	CO_2 , O_2 and H_2O CO_2/H_2O=1:0.7 mole/mole, O_2/CO_2=10 % v/v

Among seven cases of torrefaction under investigation, Cases 1-5 share the common torrefaction temperature of 275^{o}C and differ from one another in the carrier gas composition. In the meantime, Cases 5-7 are designed to study the effect of torrefaction temperature. Results from the fuel characterization of the samples are presented in Table 2. The analyses of moisture content, volatile matter and ash content were conducted adopting ASTM standards: E871, E872 and D1102, respectively. The pyrolysis experiments were carried out in N_2, using a thermogravimetric analyzer (TGA) (Netzsch STA 449 F1) operated no-isothermally. For every TGA experiment, approx. 2 mg of one sample at a time with particle sizes smaller than 250 μm was deposited in an alumina cup of the TGA reactor. The samples were heated to 105^{o}C for an hour, followed by heating up to 700^{o}C at a constant heating rate of 10^{o}C/min in N_2 environment.

Table 2. Proximate analsyis of the samples.

Sample ID (Case)	VM	FC	Ash	MC
0 (Raw spruce)	85.18	14.32	0.50	49.96
1	77.14	22.56	0.60	0
2	74.55	24.83	0.61	0
3	77.99	21.41	0.60	0
4	76.97	23.42	0.61	0
5	75.81	23.54	0.65	0
6	80.89	18.55	0.56	0
7	63.337	35.83	0.80	0

VM: Volatile matter, FC: Fixed carbon, MC: moisture content

2.2 Kinetic modelling and numerical method

In general, the pyrolysis of lignocellulosic biomass materials can be represented by the global reaction scheme (Coats and Redfern 1964, Vlaev, Markovska et al. 2003): Solid biomass -- > char + volatile. For this scheme, the kinetic equation is the general form of Eq. (1).

$$\frac{d\alpha}{dt} = A.e^{\frac{-E_a}{RT}}.f(\alpha) \qquad (1)$$

where A, E_a, and T stand for the pre-exponential factor, activation energy and absolute temperature, respectively. R is the universal gas constant, 8.314 J.mol^{-1}K^{-1}. In addition, $f(\alpha)$ is the conversion function of the conversion degree, α, and t is the reaction time. The conversion degree (α) is determined in term of the mass fraction of decomposed solid or released volatiles of samples, expressed as Eq. (2) (Ren, Lei et al. 2013, Bach, Tran et al. 2014)

$$\alpha = \frac{m_o - m_t}{m_o - m_f} \qquad (2)$$

where m_0, m_f , and m_t is the initial mass, final mass, and the mass at time t, respectively, of the sample under investigation. Recently, a multi parallel-reaction scheme has been proposed and successfully applied for kinetic modelling of biomass pyrolysis (Hu, Jess et al. 2007, Tapasvi, Khalil et al. 2013, Tran, Bach et al. 2014, Bach, Tran et al. 2015). The model is based on the assumption that different chemical compounds with similar thermal behaviors are grouped as a pseudo-component. Lignocellulosic biomass materials are mainly consisted of hemicellulose, cellulose and lignin. Therefore, the three pseudo-components model is commonly employed for pyrolysis kinetic modelling. Following this assumption, the pyrolysis is presented kinetically by Eq. (3) and Eq. (4), in which c_i is the contribution factor of the i^{th} component.

$$\frac{d\alpha_i}{dt} = A_i.e^{\frac{-E_{a,i}}{RT}} f(1-\alpha_i) \qquad i = 1,2,3 \qquad (3)$$

$$\frac{d\alpha}{dt} = \sum_1^3 c_i \frac{d\alpha_i}{dt} \qquad (4)$$

For each of the pseudo-components, the distributed activation energy model (DAEM) with first order reaction was applied. The general equation of DAEM is Eq. (5) (Anthony and Howard 1976), where *f(E)* stands for the distribution function of activation energy. Among several form of *f(E),* the Gaussian (Eq. 6) presenting a mean activation energy (E_0) and its standard deviation (σ) is wildly used (de Caprariis, De Filippis et al. 2012).

$$1-\alpha = \int_0^\infty \exp\left[-\int_0^t A\,exp\left(\frac{-E}{RT}\right)dt\right] f(E)dE \qquad n = 1 \qquad (5)$$

$$f(E) = \frac{1}{\sigma\sqrt{2\pi}}\exp\left[-\frac{(E-E_0)^2}{2\sigma^2}\right] \qquad (6)$$

For the present study, non-linear least square technique was applied for the optimization of kinetic simulation which aims to minimize the objective function as given in Eq. 7 (Orfão, Antunes et al. 1999).

$$S = \sum_{i=1}^{n}[\left(\frac{d\alpha_i}{dt}\right)_{exp} - \left(\frac{d\alpha_i}{dt}\right)_{model}]^2 \qquad (7)$$

$\left(\frac{d\alpha_i}{dt}\right)_{exp}$ and $\left(\frac{d\alpha_i}{dt}\right)_{model}$ stands for the experiment and modelled conversion rate, respectively, n is the number of experimental points. The quality of curve fitting is evaluated by Eq. (12) (Branca and Di Blasi 2003)

$$Fit\ (\%) = \left(1 - \frac{\sqrt{\frac{S}{N}}}{[\left(\frac{d\alpha_i}{dt}\right)_{exp}]_{max}}\right).100\% \qquad (12)$$

3. Result and discussion

3.1 Thermogravimetric analysis

Fig.1 represents DTG (derivative thermogavimetric) curves derived from the collected TGA data for raw spruce sample and its biochar products. Fig. 1A demonstrates the effect of flue gas composition. The raw spruce sample exhibits a clear shoulder at the temperature of about 583oC. This was attributed by the main degradation of hemicellulose (Sarvaramini and Larachi 2014). The shoulder is less pronounced, even disappeared from the DTG curves if bio-char. This indicates that torrefaction removed significantly the content of hemicellulose from spruce. On the other hand, the DTG curves for biochar, produced in simulated flue gases with different compositions, are similar one another. The peak at about 340oC, mainly accounting for the decomposition of cellulose shifted slightly to lower temperature compared to the raw sample. It means that the thermal resistivity of cellulose was negatively affected by torrefaction.

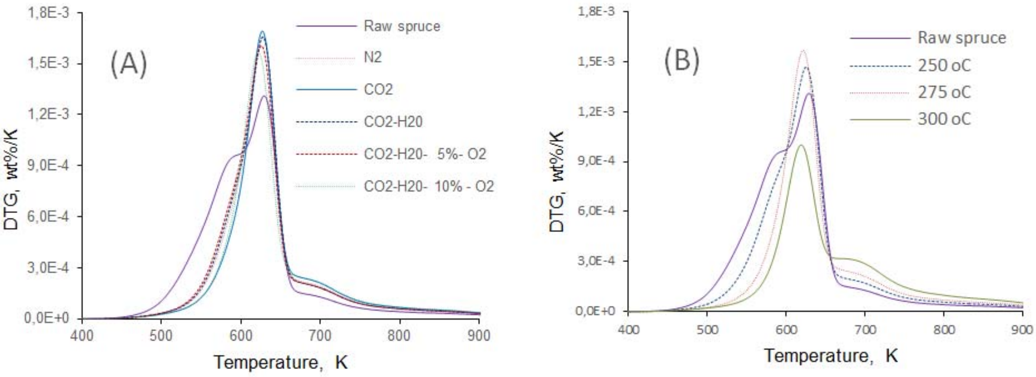

Figure 1 TG analysis. (A) Effect of torrefaction atmosphere at 275 oC, (B) Effect of torrefaction temperature

The effect of torrefaction temperature is presented in Fig. 1B. Overall, the trend was similar to the effect of carrier gas composition. However, the differences between the curves of different temperatures are much more significant. Interestingly, when the torrefaction temperature increased, the height of the second shoulder on the right hand side of the curves, representing the decomposition of lignin also increased noticeably.

3.2 Kinetic analysis

Chapter 2 The data presented in Fig. 1B was used for a kinetic analysis assuming the three pseudo-components model. The simulated DTG curves of the three pseudo-components model for untreated and samples torrefied at 250 ^{o}c, 275 ^{o}C and 300 ^{o}C are presented in Fig. 2 whereas the extracted kinetic parameters are shown in Table 3. As can be seen from Fig. 2, in the case of raw spruce (Case 0), the predicted curve fits very well the experimental data, with a fit quality of about 99% (Table 3). The fit quality decreases slightly with increased torrefaction temperatures up to 275^{o}, but still remains at a satisfactory level (higher than 98%). When torrefaction temperature is increased further to 300^{o}C, Case 7, the fit quality decreases significantly down to 96.64%. This poor fit quality can also be observed in Fig. 2. Indeed, the simulated curve does not describe the pyrolysis, especially for the tail of the DTG curve, of biochar produced via the oxidative torrefaction at 300^{o}C.

Chapter 3 Table 3 shows that, except for Case 7, oxidative torrefaction increases the activation energy of hemicellulose and lignin, but decreases the activation energy of cellulose. The standard deviation (σ) of the predicted activation energy for cellulose in all cases is relatively higher for the other component. These trends are also valid when torrefaction temperature is increased from 250^{o}C to 275^{o}C, except for the activation energy of hemicellulose, being decreased slightly from 109.83 KJ/mol to 101.93 KJ/mol (with a relatively higher σ).

Table 3. Extracted kinetic data from three pseudo-components model

Torrefaction temperature, °C	Fit quality (%)	Component	E_a (KJ/mol)	σ (KJ/mol)	A (min^{-1})	c
Raw spruce (Case 0)	98.73	Hemicellulose	90.74	0.32	5.32E+07	0.25
		Cellulose	209.09	2.29	4.40E+17	0.62
		Lignin	36.40	0.11	8.41E+01	0.13
250 (Case 6)	98.47	Hemicellulose	109.83	0.49	2.76E+09	0.20
		Cellulose	208.28	2.17	4.41E+17	0.65
		Lignin	40.85	0.11	1.89E+02	0.15
275 (Case 5)	98.34	Hemicellulose	101.93	1.55	1.25E+09	0.10
		Cellulose	173.84	1.37	4.70E+16	0.67
		Lignin	45.83	0.19	4.30E+02	0.23
300 (Case 7)	96.64	Hemicellulose	-	-	-	-
		Cellulose	186.42	2.56	1.35E+16	0.60
		Lignin	43.61	0.23	2.81E+02	0.40

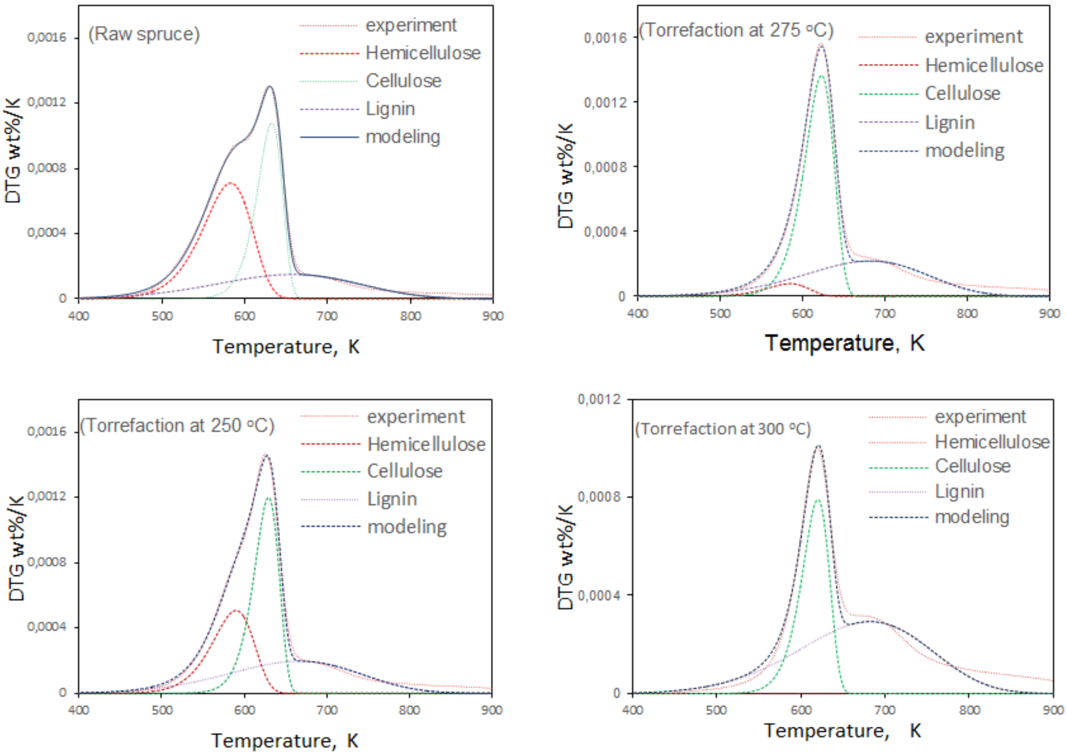

Figure 2 Simulation and curve fitting for pyrolysis of samples from Case 0, Case 6, Case 5, Case 7

4. Conclusions

A three pseudo-components DAEM was employed for kinetic modeling and analysis of raw spruce and its biochar produced via torrefaction of Norwegian spruce at different temperatures (250, 275, or 300oC) in a simulated oxy-fuel combustion flue gas (CO2/H2O=1:0.7 mole/mole, O2/CO2=10 % v/v) for 30 minutes. The results showed that the model closely described the pyrolysis of the biochar obtained from spruce torrefied at 250 or 275oC, but not 300oC. The effect of the torrefaction temperature on pyrolysis kinetics of the Norway spruce is stronger than that of the carrier gas composition. Oxidative torrefaction increases the activation energy of hemicellulose and lignin, but decreases the activation energy of cellulose.

Acknowledgments

This work is financially supported by the Research Council of Norway and industry partners through CenBio and the KMB projects STOP (STable OPerating conditions for biomass combustion plants) and BioCarb+ (Enabling the biocarbon value chain for energy), which are gratefully acknowledged.

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