



The 8th International Conference on Applied Energy – ICAE2016

Simultaneously boosting the mass and fixed-carbon yields of charcoal from forest residue via atmospheric carbonization

Khanh-Quang Tran^{a,*}, Maria Zabalo Alonso^a, Liang Wang^b, Øyvind Skreiberg^b

^aDepartment of Energy and Process Engineering, Norwegian University of Science and Technology, NO-7491 Trondheim, Norway

^bSINTEF Energy Research, P.O. Box 4761 Sluppen, NO-7465 Trondheim, Norway

Abstract

The carbonization of various forest residues in comparison with their stem wood was studied by means of thermogravimetric analyzer operated non-isothermally at atmospheric pressure with a heating rate of 10K/min and a final temperature of 800°C. GROT (tops and branches) and stem wood samples of Norway spruce and birch trees collected from forests in Southern Norway were used as feedstock. The work focused on analyzing the effect of process parameters (feedstock particle size, initial mass, and the residence time of gas released during the devolatilization) on the mass and fixed carbon yields of charcoal produced. The results show that it is possible to simultaneously improve the mass and fixed carbon yield of biochar produced by controlling the fate of gas released during devolatilization to promote the formation of secondary char. Differences between forest residues and their stem wood with regards to the effect of the investigated process parameters were observed.

© 2017 The Authors. Published by Elsevier Ltd. This is an open access article under the CC BY-NC-ND license

(<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

Peer-review under responsibility of the scientific committee of the 8th International Conference on Applied Energy.

"Keywords: Forest residues; carbonization; fixed-carbon; charcoal."

1. Introduction

Charcoal, the main product from carbonization (slow pyrolysis) of biomass, has a wide range of applications in various industries, which among others include direct combustion of charcoal as solid fuel, gasification of charcoal for synthesis gas production, and use as reductant alternative to fossil carbon in metallurgical industry [1, 2]. For the application as metallurgical reductant, it is required that the fixed carbon content of charcoal is higher than 80 wt%. This requirement can normally be achieved by increasing the severity of carbonization (higher temperatures and/or longer carbonization times). As a result, more volatile matters of the feedstock will be released into the gas phase, which is translated to more material and energy losses. Combustion of this pyrolysis gas for energy recovery is possible, but

* Corresponding author. Tel.: +47-73-59-36-25; fax: +47-73-59-35-80

E-mail address: khanh-quang.tran@ntnu.no

requires extra investment, which is rarely feasible for small and decentralized carbonization units. High-pressure carbonization of biomass has been proposed for improving the mass and fixed carbon yield at the same time [4, 5]. However, the high-pressure requirement also leads to extra cost and is not that feasible for small carbonization units. On the other hand, the mass and fixed carbon yield can be improved simply by promoting the secondary char formation from the pyrolysis gas via increasing the particle size of the feedstock [4, 5]. It is because of the catalytic cracking effect, of the char formed in the outer layers of the fuel particle, on the nascent pyrolysis gas on its way diffusing outward. Alternatively, similar effects can be achieved by simply confining the pyrolysis gas in the reactor. The work presented in this paper aims to study the effect of prolonged contact time between nascent pyrolysis gas and char during carbonization on the mass and fixed carbon yields of charcoal produced. The contact time is prolonged by varying process parameters (feedstock particle size, initial mass) and pyrolysis gas confinement. In addition to this, the work focuses on the use of forest residues as feedstock, which is a promising and low-cost renewable resource.

2. Experimental methods

2.1. Material

The biomass materials used as feedstock for the present study are forest residues or GROT (tops and branches) and stem wood of Norway spruce and birch trees from forests in Southern Norway. The collected samples were chipped and dried at 105°C for 24 hours. The pre-dried samples were then milled and sieved to obtain powder samples of two particle ranges: $d < 1\text{mm}$ and $63\mu\text{m} < d < 100\mu\text{m}$. Fixed carbon content and ash content of the tested samples were analyzed according to procedures described in ASTM E872 and D1102. Element compositions of the samples were analyzed by means of an Eurovector EA 3000 CHNS-O Elemental Analyzer. The higher heating value of the samples was measured by a bomb calorimeter (IKA C5010/5012 model), following the procedure described in ASTM E711-87(2004).

2.2. Thermogravimetric method

A thermogravimetric analyzer (TGA), SDT Q600 model from TA Instrument, was used for studying the non-isothermal decomposition of the samples during the pyrolysis process. Two different initial masses of sample were used, being 1 mg and 10 mg. Experiments with 1mg samples were run for small particles only ($63\mu\text{m} < d < 100\mu\text{m}$), whereas experiments with 10mg were run for the samples with both particle sizes ($63\mu\text{m} < d < 100\mu\text{m}$ and $d < 1\text{mm}$). For each TGA run, a sample of either 10 mg or 1 mg was loaded in an alumina crucible that was then placed into the TGA furnace. Nitrogen (purity 99.999%) was used as purging gas through the TGA reactor, with a volumetric flowrate of 100mL/min, for 30 minutes before starting the heating up of the furnace. After this purging at room temperature, the furnace was heated to 105°C and kept at this temperature for 30 minutes, followed by a heating program up to 800°C with a heating rate of 10 K/min. For experiments with 10 mg of sample as initial mass, the crucible was operated in two modes: 1) open crucible (no lid), and 2) closed crucible (with lid), for studying the effect of the gas released from the sample during devolatilization on the char and fixed carbon yields. The lid has small pinholes on it to avoid possible pressure increase.

2.3. Evaluation methods for char yield and fixed carbon yield

In this work, the term of char yield (y_{char}) is defined according Eq. 1 [4, 5]:

$$y_{\text{char}} = M_{\text{char}} / M_{\text{feed}} \quad (1)$$

where M_{char} is the dry mass of char produced in the process at its final temperature and M_{feed} is the mass of the feedstock measured at the end of the 105°C heating stage [3,4]. In addition to the char yield, the

fixed carbon yield of one sample is also calculated. The fixed carbon yield (y_{char}) is a meaningful indication of carbonization efficiency and defined according to Eq. 2 [4, 5]:

$$y_{\text{fc}} = y_{\text{char}} * (\% \text{ FC}) / (100 - \% \text{ feed ash}) \quad (2)$$

where (% FC) refers to the fixed carbon content of the charcoal, and (% feed ash) is the ash content of the dry feedstock [4, 5]. For calculation of the fixed carbon yield, the charcoal produced after the pyrolysis process needs to undergo a proximate analysis (following the standard ASTM D1762-84 procedure) in order to determine its fixed carbon content.

3. Results and discussion

3.1. Fuel characterization

Table 1. Fuel characterization of the feedstocks (dry basis)

Feedstock ID	Proximate analysis, wt%			Ultimate analysis, wt%					HHV (MJ/kg)
	VM	FC	Ash	C	H	N	S	O	
Spruce GROT	72.1	25.4	2.5	51.7	6.1	0.7	0.0	41.5	20.63
Spruce wood	78.0	21.4	0.6	49.6	6.4	0.1	0.0	43.8	19.64
Birch GROT	73.8	23.5	2.7	50.7	6.3	0.8	0.0	42.1	20.84
Birch wood	81.4	17.8	0.8	49.9	6.7	0.4	0.0	43.1	19.57

VM: Volatile matter; FC: Fixed carbon

Table 1 presents results from the proximate and ultimate analysis of the GROT and woody biomass samples, together with their HHV values. Overall, the GROT have higher HHV than their stem wood. This is mainly due to the higher C and lower O content of the GROT compared to their stem wood. On the other hand, the GROT have lower volatile matter (VM) but higher fixed carbon (FC) content than their stem wood, of which the later would be better for GROT as start material to produce charcoal for use as metallurgical reductant, considering the high FC content requirement. However, the ash content of the GROT is also higher than that of their stem wood, which is not desirable by metallurgists especially for the silicon production.

3.2. Thermogravimetric analysis

The behavior of the samples tested during decomposing in a pure nitrogen atmosphere (open crucible) were studied by means of analyzing the weight loss curves (TGA curves) and the first derivative of the weight loss curves (DTG curves) as function of temperature. Figure 1 shows TGA and DTG curves obtained from stem wood and GROT samples of 1 mg and small particle size ($63 \mu\text{m} < d < 100 \mu\text{m}$). Three main regions of the DTG curves can be distinguished, which is in agreement with the literature [7, 10, 11]. The first region corresponding to the degradation of hemicellulose is visible by the shoulder at low temperature (in the range of 560-600K for all types of experiments). The second region which corresponds to the degradation of the cellulose component can be distinguished, characterized by the maximum value (or peak) of the DTG curve, which is mainly associated with the intensive cellulose decomposition rate. The third region characterized by a flat, long tail corresponds to the decomposition of lignin, which takes place in a very wide range of temperatures. It can be observed that the shoulder is much more prominent for hardwood (birch) than for softwood (spruce). For spruce samples, there is a visual overlap between hemicellulose and cellulose decomposition regions, due to the relatively low hemicellulose content in spruce, softening the effect that the peak associated with the maximum

hemicellulose devolatilization rate has in the global DTG curve [6, 12, 13]. These differences between hardwood and softwood are equally observed for both, stem wood and forest residue samples.

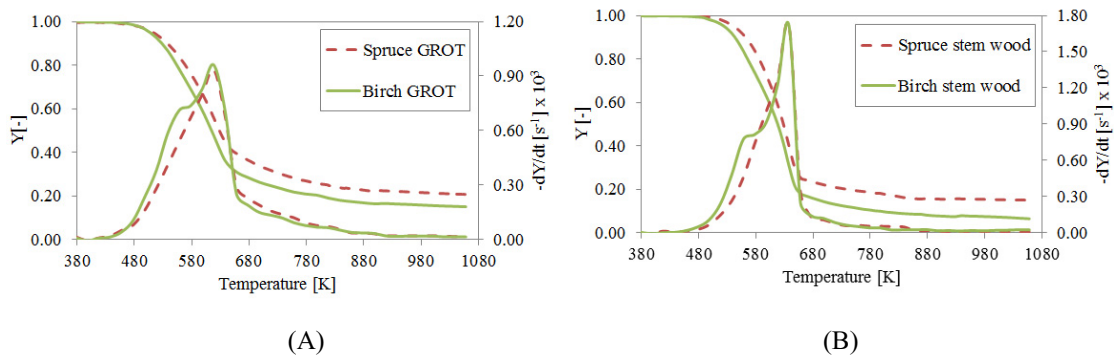


Fig. 1. TGA and DTG curves of: (A) forest residue (GROT) samples; (B) stem wood (Initial mass: 1mg; particle size: $63\mu\text{m} < d < 100\mu\text{m}$; no lid)

Differences in devolatilization behavior between the samples are observed in combination with an examination of the devolatilization parameters presented in Table 2 [6, 7]. These parameters include the remaining mass fraction, Y (wt% on dry basis), and decomposition rate, $R = -dY/dt$ (s^{-1}) at some key decomposition points of the process. The subscript “*shoulder*” refers to the shoulder caused by hemicellulose decomposition and marks its maximum devolatilization rate. This point is defined as the point at which the value of the second derivative of the mass loss curve, $-d^2Y/dt^2$, is nearest to zero in the region around the shoulder [6, 8]. The subscript “*peak*” refers to the point at which the highest devolatilization rate is achieved. This point is directly associated with the maximum decomposition rate of the cellulose component.

Table 2. Devolatilization characteristics of the tested samples in pure nitrogen atmosphere.

Species	10mg; $63\mu\text{m} < d < 100\mu\text{m}$			10mg; $d < 1\text{mm}$			1mg; $63\mu\text{m} < d < 100\mu\text{m}$		
	Y_{peak} (wt%)	R_{shoulder} ($10^3 \cdot \text{s}^{-1}$)	R_{peak} ($10^3 \cdot \text{s}^{-1}$)	Y_{peak} (wt%)	R_{shoulder} ($10^3 \cdot \text{s}^{-1}$)	R_{peak} ($10^3 \cdot \text{s}^{-1}$)	Y_{peak} (wt%)	R_{shoulder} ($10^3 \cdot \text{s}^{-1}$)	R_{peak} ($10^3 \cdot \text{s}^{-1}$)
Spruce GROT	60.18	0.6303	0.8984	56.63	0.6859	0.9850	55.25	0.7139	0.9738
Spruce wood	42.71	0.9606	1.7890	45.07	0.9070	1.7510	40.73	1.0310	1.7140
Birch GROT	53.25	0.6357	0.8942	51.91	0.6287	1.0790	46.00	0.7231	0.9883
Birch wood	40.71	0.7373	1.6340	42.62	0.7488	1.6830	33.50	0.8047	1.7370

Among the forest residue samples, very different behaviors were observed for experiments under different conditions of sample mass and particle size. Higher values of decomposition rates (R_{shoulder} and R_{peak}) were registered for stem wood samples than for forest residue samples for spruce and birch species. This is justified by the higher amount of ash forming components that forest residue samples have in comparison with stem wood samples, which of some have a catalytic effect favoring char formation, in addition to the ash lowering the volatiles content and hence the devolatilization rate. As can be seen in Table 1, also the fixed carbon content is significantly higher and the volatiles content significantly lower for the forest residue samples. As for the stem wood samples, spruce is the species with the highest maximum devolatilization rate, followed by birch.

3.3. Char yield and fixed carbon yield

Char yields and fixed carbon yields calculated from the experimental data are presented in Table 3. The influence of the initial mass on char and FC yield can be clearly observed by comparing the data between columns 1 and 2 with columns 3 and 4, respectively. In the case of spruce GROT for example, the char and FC yield significantly increased by 39.1% from 20.59 % (column 1) to 28.64 % (column 3) and from 18.03% (column 2) to 25.08 % (column 4), respectively. Similar trends are observed for the birch GROT with lower increase percentages of 32.81 % and 32.79 % for the char and FC yields, respectively. The trends are also valid for the case of spruce stem wood, but not birch stem wood. The positive effect of increasing initial mass of feedstock on the yields can be attributed to catalytic formation of secondary char due to longer contact time between pyrolysis gas and char during carbonization, except for the unexpected results of the birch wood case, of which the reason is not known. Similar to the case of birch wood tests with different initial masses, no consistent trend was observed as expected when increasing the feedstock particle size from ($63 \mu\text{m} < d < 100 \mu\text{m}$) to ($d < 1 \text{ mm}$). This can be examined by comparing the (no lid) data of column 3 versus 7, and column 4 versus 8 (no lid), as well as even the (with lid) data of column 5 versus 9, and column 6 versus 10. It is to say the yield changes from case to case varied up and down within $\pm 13\%$, and the reason is unknown.

Table 3. Char yield and fixed carbon yields (wt%) determined according to ASTM D1762-84.

Sample	Initial mass: 1mg $63\mu\text{m} < d < 100\mu\text{m}$		Initial mass: 10mg $63\mu\text{m} < d < 100\mu\text{m}$				Initial mass: 10mg $d < 1\text{mm}$			
	No lid		No lid		With lid		No lid		With lid	
	1	2	3	4	5	6	7	8	9	10
	y_{char}	y_{fc}	y_{char}	y_{fc}	$y_{\text{char r}}$	y_{fc}	y_{char}	y_{fc}	$y_{\text{char r}}$	y_{fc}
Spruce GROT	20.59	18.03	28.64	25.08	30.44	26.56	26.65	23.34	30.24	26.38
Spruce wood	14.93	14.26	17.74	16.94	23.90	22.33	19.52	18.64	22.21	20.75
Birch GROT	18.93	16.47	25.14	21.87	32.89	28.22	21.96	19.10	29.39	25.22
Birch wood	16.78	15.68	16.04	14.98	20.56	18.71	17.68	16.52	20.49	18.65

Let us now compare the data of columns 3 versus 5, and columns 4 versus 6 for the small particle size ($63 \mu\text{m} < d < 100 \mu\text{m}$) and columns 7 versus 9, and columns 8 versus 10 for the large particle size ($d < 1 \text{ mm}$) to evaluate the effect of the pyrolysis gas confinement in the reactor. Interestingly, for all cases the effect is positive. The most significant improvements in char and FC yields are observed for the test of birch GROT with the large particle size ($d < 1 \text{ mm}$). Indeed, the char and FC yields increased by 33.83% and 32.04%, respectively, from 21.96% (column 7) to 29.39% (column 9) and 19.10% (column 8) to 25.22% (column 10).

In general, the result from the lid tests can be explained by the fact that the escape of nascent pyrolysis gas from the sample was hindered by the lid and the residence time of the gas in the matrix and vicinity of the solid carbon residues was increased. It has been reported beneficial effects of increased vapor-phase residence times and increased vapor concentrations on favoring char formation and char yields [4, 7]. The reason for this happening is that keeping the released pyrolysis gas in contact with both the decomposing solid biomass and the solid mass products has the effect of secondary tar reactions taking place inside the crucible, forming secondary char and increasing the char yield.

4. Conclusions

The following conclusions are drawn from the present study: 1) the confinement of the pyrolysis gas released during devolatilization in the carbonization reactor helps improve the char and fixed carbon yield

of charcoal produced via carbonization of from forest residues and wood. 2) Different char yield trends between GROT and wood samples were observed. In addition to this, while the decomposition rate during devolatilization of the stem wood samples varied consistently with changes in the sample mass and particle size, that for the forest residue samples was inconsistent.

References

- [1] Altun NE, Hicyilmaz C, Kk MV. Effect of particle size and heating rate on the pyrolysis of Silopi asphaltite. *Journal of Analytical Applied Pyrolysis* 2003;**67**:369-79.
- [2] Shuping Z, Tulong W, Minde Y, Chun L. and Junmao, T. Pyrolysis characteristics and kinetics of the marine microalgae *Dunaliella tertiolecta* using thermogravimetric analyzer. *Bioresurce Technology* 2010;**101**:359-65.
- [3] Monsen B, Grnli M, Nygaard L, Tveit H. The use of biocarbon in Norwegian ferroalloy production. Available at: https://www.researchgate.net/publication/259572787_The_Use_of_Biocarbon_in_Norwegian_Ferroalloy_Production
- [4] Wang L, Skreiberg Ø, Grnli M, Specht P, Antal Jr MJ. Is elevated pressure required to achieve a high fixed-carbon yield of charcoal from biomass? Part 2: The importance of particle size. *Energy Fuels* 2013;**27**:2146-56.
- [5] Wesenbeeck SV, Higashi C, Legarra M, Wang L, Antal Jr MJ. Biomass pyrolysis in sealed vessels. Fixed-carbon yields from avicel Cellulose That Realize the Theoretical Limit. *Energy-Fuels* 2016;**30**:480-91.
- [6] Grnli MG, Vrhegyi G. Thermogravimetric Analysis and Devolatilization Kinetics of Wood. *Ind. Eng. Chem. Res.* 2002;**1**:4201-08.
- [7] Di Blasi C. Modeling chemical and physical processes of wood and biomass pyrolysis. *Progress in Energy and Combustion Science* 2008;**34**:47–90.
- [8] Branca C, Albano A, Di Blasi C. Critical evaluation of global mechanisms of wood devolatilization. *Thermochimica Acta* 2005;**429**:133-41.
- [9] Pattanotai T, Watanabe H, Okazaki K. Experimental investigation of intraparticle secondary reactions of tar during wood pyrolysis. *Fuel* 2013;**104**:468-75.
- [10] Bennadji H, Smith K, Serapiglia MJ, Fisher EM. Effect of particle size on low-temperature pyrolysis of woody biomass. *Energy Fuels* 2014;**28**:7527-37.
- [11] Tran K-Q, Bach Q-V, Trinh TT, Seisenbaeva G. Non-isothermal pyrolysis of torrefied stump – A comparative kinetic evaluation. *Applied Energy* 2014;**136**:759-66.
- [12] Vrhegyi G, Antal MJ Jr, Jakab E, Szab E. Kinetic modelling of biomass pyrolysis. *Journal of Analytical and Applied Pyrolysis* 1997;**42**:73-87.
- [13] Tapasvi D, Vrhegyi G, Tran K-Q, Grnli, M, Skreiberg Ø. Thermal Decomposition Kinetics of woods with emphasis on torrefaction. *Energy Fuels* 2013;**27**:6134-45.