



9th International Conference on Applied Energy, ICAE2017, 21-24 August 2017, Cardiff, UK

## Study of CO<sub>2</sub> gasification reactivity of biocarbon produced at different conditions

Liang Wang<sup>a\*</sup>, Przemysław Maziarka<sup>b,c</sup>, Øyvind Skreiberg<sup>a</sup>, Terese Løvås<sup>b</sup>, Mariusz Wądrzyk<sup>b</sup>, Alexis Sevault<sup>a</sup>

<sup>a</sup>*SINTEF Energy Research, Trondheim, Norway*

<sup>b</sup>*Norwegian University of Science and Technology, Trondheim, Norway*

<sup>c</sup>*AGH University of Science and Technology, Krakow, Poland*

---

### Abstract

Biocarbon has a great potential to replace fossil reductants and help reduce greenhouse gas emissions from carbon intensive metallurgical industries. In this work, biocarbon samples were produced from Norway spruce under different final temperatures (550, 650 and 800 °C) and holding times (10 and 30 minutes). The CO<sub>2</sub> gasification reactivity of the biocarbon, or biomass char, samples was investigated in a thermogravimetric analyser at different gasification temperatures (850, 900 and 950 °C). The results show that the gasification reactivity of the spruce wood char produced at higher carbonization temperature is lower than of those produced at lower temperatures. The time of half conversion (t<sub>50</sub>) of spruce wood char produced at 800 °C was 334 seconds, while only 290 seconds was needed for that produced at 550 °C. In addition, the CO<sub>2</sub> gasification reactivity of spruce wood char produced at longer holding time (i.e., 30 minutes) is also lower than those prepared at shorter holding time (i.e., 10 minutes). All the spruce wood char samples showed significantly higher reactivity as they were gasified at a higher temperature. The time needed for half conversion of the tested char samples at a gasification temperature of 950 °C was only one fourth of those at a gasification temperature of 850 °C.

© 2017 The Authors. Published by Elsevier Ltd.

Peer-review under responsibility of the scientific committee of the 9th International Conference on Applied Energy.

*Keywords:* Biocarbon; carbonization; CO<sub>2</sub> gasification; reactivity

---

### 1. Introduction

Gasification reactions for biomass have been investigated extensively during the past decades in order to realize efficient and economical biomass conversion processes to produce energy and fuel. Gasification of biomass is a

---

\* Corresponding author. Tel.: +47 48064531

E-mail address: [liang.wang@sintef.no](mailto:liang.wang@sintef.no)

complex thermochemical process including drying, pyrolysis and char gasification. The char gasification is the step determining both fuel and energy conversion efficiency. On the other hand, gasification of biomass char, or biocarbon, can be a separate process to produce fuel gases and chemicals. Compared to direct biomass gasification, gasification of biocarbon has several advantages including minimum effects from tar and high reactivity of the porous char structure. Besides its direct use in thermal energy and fuel gases production, biocarbon has great potential to replace fossilized carbonaceous materials in metallurgical industry as reductant. The metal production is an energy intensive production process with consumption of significant amounts of fossilized carbonaceous materials and causing emission of a vast amount greenhouse gases (GHG) consequently [1]. Biocarbon can be produced from a wide range of biomass materials with low cost and in large amount. Therefore, use of biocarbon is in many cases economically feasible and attractive for the metallurgical industry. In addition, biocarbon normally has low contents of ash and some undesired inorganic elements that are abundant in fossil coal and coke. These elements might negatively affect a metal production process and properties of the metal products as well. In brief, utilization of renewable biocarbon is a promising way to reduce consumption of fossil carbon and GHG emissions in metal production processes.

The physicochemical properties of biocarbon is very important as it is used in metallurgical production processes. Reactivity of biocarbon towards  $\text{CO}_2$  is one of the key properties that give strong effects on productivity and specific energy consumption of a metal production process. Compared to fossilized carbon reductants, the biocarbon has considerably higher reactivity due to its highly porous structure and large surface area. As biocarbon is used as reductant, intensive reaction of biocarbon with  $\text{CO}_2$  in the pre-reduction zone in a manganese process production process occurs. It can result in significant increase of carbon and energy consumption and affects the reaction of manganese ore with the carbon reductant as well [1]. From this point of view, carbon reductants with lower reactivity is wanted to ensure a high energy efficiency of the manganese production process. Compared to coal and coke, the biocarbon has higher content of volatile matter that also affects the reactivity of biocarbon towards  $\text{CO}_2$  through interactions between volatile matter and the carbon matrix [2]. Additionally, the volatile matter will release and further combust after the biocarbon is fed into the furnace. The intensive heat generated due to combustion of volatile matter results in severe heating of the upper structure of the furnace by radiation and also possible water leakage in pipe joints. The physicochemical properties of biocarbon are heavily related to production conditions and properties of raw biomass materials. Woody biomasses are the main raw feedstock to produce the biocarbon that is currently used in metallurgical production processes. For the woody biomasses, the physicochemical properties and conversion behaviours of them during a carbonization process can be considerably different. Consequently, the biocarbon produced from different woody biomasses have different properties. Furthermore, carbonization conditions give significant effects on both yield and properties of the biocarbon produced from a certain biomass material. The most influential carbonization conditions on biocarbon properties include carbonization peak temperature, residence time, heating rate, pressure etc. In view of the potential of biocarbon to be a substitute for fossil reductants, there is a need to gain better understanding of effects of carbonization conditions on the  $\text{CO}_2$  gasification reactivity of produced biocarbons. Such understandings are important to ensure proper and efficient utilization of the biocarbon in metal production processes. Furthermore, the study results are valuable for tuning and optimizing carbonization process parameters to produce biocarbon with desired properties.

In this paper, a study is reported on the assessment of  $\text{CO}_2$  gasification reactivity of spruce wood biocarbon produced under different carbonization conditions, i.e. temperature and residence time. In addition, conversion behaviours of the spruce biocarbon under different gasification temperatures are also studied and presented.

## 2. Experiment setup and methods

Four kinds of biocarbon produced under different conditions were used in this study. The Norwegian spruce wood chips were first ground to particles with size smaller than 1 mm. Around 100 mg ground spruce wood were then loaded in an alumina crucible and pyrolysed in a thermogravimetric analyser (TGA, Mettler Toledo TGA 851e). After the crucible was loaded into the TGA furnace, 100 ml/min nitrogen flow was continuously purged through the furnace at room temperature for half an hour in order to remove residual oxygen. Afterwards, the ground spruce wood was heated up to a predetermined carbonization temperature of 550, 650 or 800 °C at a heating rate of 13 °C min<sup>-1</sup>. Soaking time at these temperatures was 10 minutes and the produced char sample was then cooled to room temperature. To study the effect of soaking time, the spruce wood sample was also carbonized at 550 °C for 30 minutes. The  $\text{CO}_2$

gasification of char was carried out in the same TGA. In a typical run, around 2 mg char sample was first loaded into an alumina crucible and spread evenly on the crucible bottom as a thin layer. The crucible with sample in was loaded into furnace and then purged with 100 ml/min nitrogen for half an hour, where after it was heated up at a heating rate  $13\text{ }^{\circ}\text{C min}^{-1}$  to a predetermined gasification temperature. As the temperature reached the desired gasification temperature, the  $\text{N}_2$  gas flow was shifted to  $\text{CO}_2$ . One sample was isothermally heated at this temperature in presence of  $\text{CO}_2$  with continuous recording of sample weight loss against reaction time. After the isothermal heating stage, the gas flow was shifted back to  $\text{N}_2$  and the TGA cooled down to room temperature. The fractional weight loss of one sample along increasing of temperature is displayed. Effect of gasification temperature on  $\text{CO}_2$  gasification reactivity of biocarbon was also studied. The biocarbon sample was gasified at 850, 900 and 950  $^{\circ}\text{C}$ .

### 3. Results and discussion

Fig. 1 shows fractional weight loss as function of time for  $\text{CO}_2$  gasification of spruce wood char samples at temperatures of 850, 900 and 950  $^{\circ}\text{C}$ . As can be seen from Fig. 1, the  $\text{CO}_2$  gasification conversion of 550  $^{\circ}\text{C}$  wood biocarbon is evidently faster than the two biocarbons produced at higher temperatures. The relative positions of the weight loss curves of the three biocarbon samples are in good agreement with the results reported in previous work. It is generally concluded that biocarbon produced at a low carbonization temperature normally has higher reactivity than those produced at higher temperatures. Similar findings have been reported, that chars produced from Acacia wood and Eucalyptus wood at increasing carbonization temperatures are less reactive and have higher activation energy [2]. Fig. 1 also shows that the differences in  $\text{CO}_2$  gasification reactivity of the three biocarbon samples are more evident as they are gasified at 950  $^{\circ}\text{C}$ . Fig. 2 shows the effect of soaking time on the gasification conversion behaviours of the chars produced at 550  $^{\circ}\text{C}$ . As evidenced by the figure, the reactivity of char produced at 550  $^{\circ}\text{C}$  with 30 minutes soaking time is generally lower than that produced with 10 minutes soaking time. Again it is interesting to see that at a higher gasification temperature, the conversion of 550  $^{\circ}\text{C}$  char produced with 10 minutes soaking time is evidently shorter in comparison to the one produced with longer soaking time. Fig. 3 shows effects of gasification temperature on fractional weight loss of char produced at 550 and 800  $^{\circ}\text{C}$ . Fig. 3 clearly shows that the 550 and 800  $^{\circ}\text{C}$  char samples conversion versus time curve shifted to a higher conversion rate as the gasification temperature increased. In Table 1, the time used for 50% conversion of the studied char samples at the three gasification temperatures are listed. Similar as the results displayed in Figs. 1-3, longer time is required to realize 50% conversion of char samples produced at higher carbonization temperature and longer soaking time. Additionally, the gasification temperature has a pronounced effect on the conversion rate of the studied samples. For gasification measurement performed at 950  $^{\circ}\text{C}$ , the time for realizing 50% conversion of the samples are significantly shorter than for gasification at 850  $^{\circ}\text{C}$ . It can partially explain that the carbon  $\text{CO}_2$  gasification reaction (Boudouard reaction) is an endothermic reaction. It means that increase of gasification temperature results in a shift in reaction equilibrium, promoting increased conversion of carbon consequently. Furthermore, according to the Arrhenius equation, an increase of gasification temperature favours faster reaction kinetics [2].

The reactivity of biocarbon towards  $\text{CO}_2$  are affected by many factors, including physicochemical properties of biocarbon, gasification reaction conditions and heat and mass transfer of gas and solid products during gasification processes, etc. The gasification reactivity studies in the present work were performed in the TGA under well controlled conditions. The gasification condition parameters such as purge gas flow rate, heating rate and gaseous reactant concentration are the same for all measurements. In addition, only about 2 mg char sample was used for each gasification experiment in order to minimize influence of heat and mass transfer limitations. Therefore, the different gasification reactivities observed from the studied samples are mainly associated to the different properties of them.

It was possible in this work to investigate and link these properties with the gasification reactivities of the biocarbon samples. The carbonization conditions give crucial effects on chemical properties of biocarbon. Upon high carbonization temperature and longer soaking time, more heteroatoms, such as oxygen and hydrogen, will be lost from the carbon structure due to release of gases [3]. In addition, amorphous carbon structure transfer into larger aromatic ring systems since the bond-breaking and bond-reforming reactions will be more intensive at severe carbonization conditions [3]. It causes reduction of heterogeneity of the carbon structure and leads to formation of more ordered carbonaceous structure.

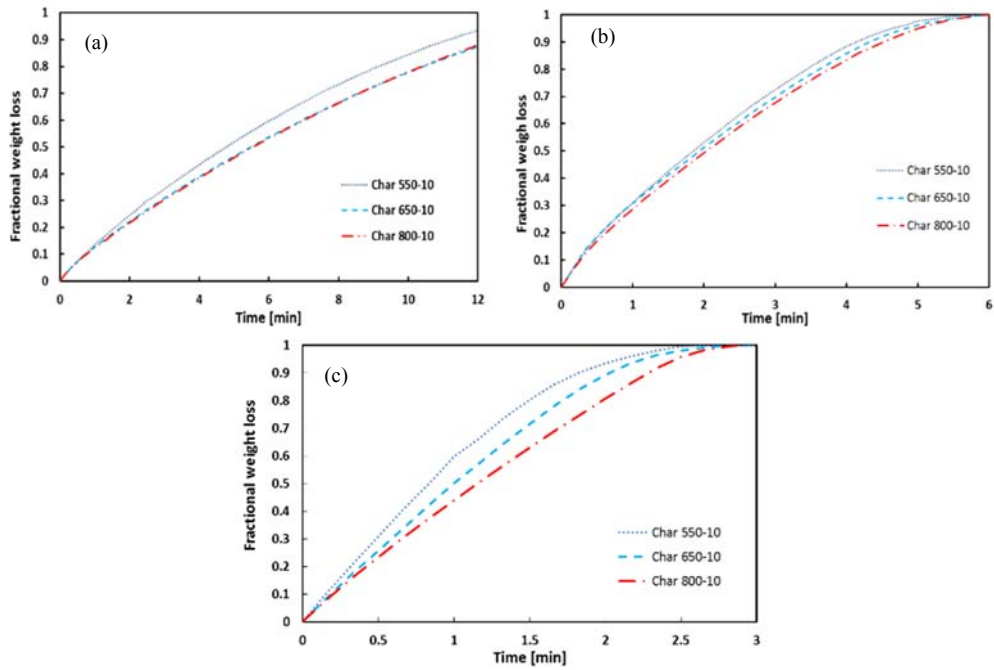


Fig. 1. Weight loss as function of time for CO<sub>2</sub> gasification of spruce wood biocarbon samples at temperatures of (a) 850 °C, (b) 900 °C and (c) 950 °C

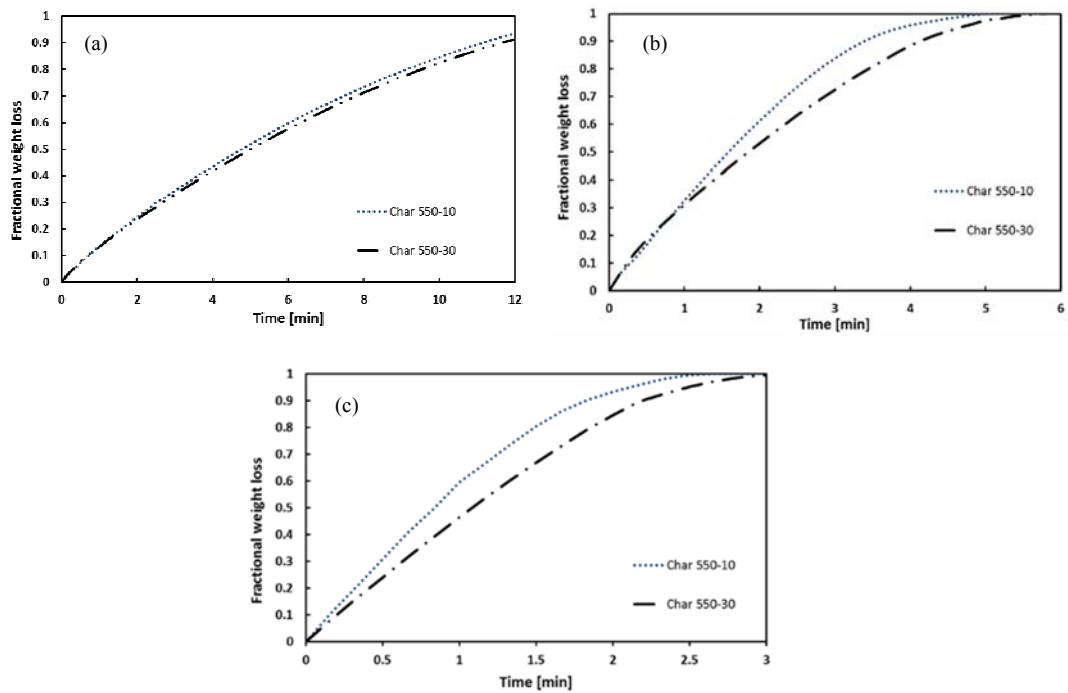


Fig. 2. Effect of carbonization time on fractional weight loss as a function of time for CO<sub>2</sub> gasification of spruce wood char samples at (a) 850 °C, (b) 900 °C and (c) 950 °C

For the more ordered/condensed carbon structure, a higher activation energy is needed to overcome for the gasification reactions to occur. Similar findings about effects of carbonization temperature and soaking time on biocarbon gasification reactivity have been reported previously [3,4]. It was reported that reduction of biocarbon reactivity coincide with changes of its carbon structure due to thermal annealing at higher temperature and longer holding time [3,4]. The content of inorganic elements and volatile matter will decrease as the biocarbon is produced at increasing carbonization temperature. It is well known that the CO<sub>2</sub> gasification reactivity of biocarbon is heavily associated with concentration and form of catalytic inorganic elements remaining after the carbonization process [5]. At increasing carbonization temperature, more inorganic elements will release from the biocarbon, especially for the alkali and alkali earth metals with high volatility. In addition, more reactions of the catalytic alkali and alkali earth metals with other mineral matters will occur at higher carbonisation temperature. It causes loss of these catalytic inorganic elements due to formation of non-volatile composites and/or other catalytically inactive species like silicates and aluminosilicates. Furthermore, the biocarbon volatile matter content will be considerably reduced as the carbonization temperature and soaking time increase. It has been reported that the reactivity of biocarbon can be much lower if intensive volatile-char reactions take place around and inside biocarbon particles [6]. This is because formation of reactive species/radicals, like H<sub>2</sub>, as the volatiles release from the biocarbon particles during the gasification process. These species/radicals might react with biocarbon to cause loss of catalytic alkali and alkali metal elements in the biocarbon [6]. Moreover, reactions between these species/radicals with biocarbon can lead to conversion of the carbon structure, from small aromatic ring systems to large and less reactive ones. Therefore, the gasification reactivity of biocarbon with higher volatile matter content is expected to be lower. In the present work, the devolatilization of around 2 mg biocarbon sample took place as it was heated up to a desired gasification temperature with purging of N<sub>2</sub>. Therefore, the residual volatile matter in the biocarbon sample after the devolatilization stage is expected to be very low. The effect of volatile-biocarbon reactions on the biocarbon gasification reactivity can therefore be omitted.

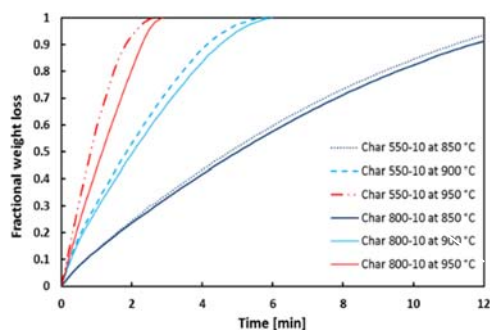


Fig. 3. Effect of gasification temperature on fractional weight loss of spruce char produced at 550 and 800 °C

Table 1. Time used for 50% conversion of the studied char samples

Sample	Temperature of gasification reactivity measurement		
	850 °C	900 °C	950 °C
Spruce wood 550-10	290	111	52
Spruce wood 650-10	329	115	61
Spruce wood 800-10	334	123	70
Spruce wood 550-30	302	97	65

#### 4. Conclusions

In the present work, CO<sub>2</sub> gasification reactivity of biocarbon produced under different temperatures and soaking times were investigated. It was found that biocarbon produced at higher carbonization temperatures have lower

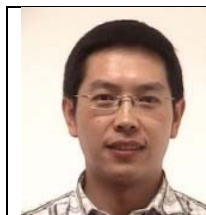
gasification reactivity. Reduction of gasification reactivity was also observed for the biocarbon produced with longer soaking time. At higher carbonization temperature and prolonged soaking time, the physicochemical properties of biocarbon can be considerably altered. It causes conversion of the carbon structure to an increasingly ordered and less reactive one, with loss of catalytic inorganic elements as well. Because of this, reduction of gasification reactivity of biocarbon upon increasing carbonization temperature and soaking time were observed in the present work. The present findings have important implications for the use of biocarbon as reductant for metal production and for energy production. Carbonization conditions can induce significant effects on biocarbon properties and reactivity consequently. Such effects should be carefully considered for producing biocarbon with desired qualities dedicated for special applications.

## Acknowledgements

The authors acknowledge the financial support from The Research Council of Norway and the BioCarb+ project industry partners: Elkem AS – Department Elkem Technology, Norsk Biobrensel AS, AT Biovarme AS, Eydenettverket, Saint Gobain Ceramic Materials AS, Eramet Norway AS, and Alcoa Norway ANS.

## References

- [1] Wang L, Hovd B, Bui HH, Valderhaug A, Buø TV, Birkeland RG, et al. CO<sub>2</sub> reactivity assessment of woody biomass biocarbons for metallurgical purposes. *Chemical Engineering Transactions*; 2016. p. 55-60.
- [2] Kumar M, Gupta RC, Sharma T. Effects of carbonisation conditions on the yield and chemical composition of Acacia and Eucalyptus wood chars. *Biomass and Bioenergy*; 1992;3(6):411-7.
- [3] Asadullah M, Zhang S, Min Z, Yimsiri P, Li C-Z. Effects of biomass char structure on its gasification reactivity. *Bioresource Technology*. 2010;101(20):7935-43.
- [4] Yip K, Xu M, Li C-Z, Jiang SP, Wu H. Biochar as a Fuel: 3. Mechanistic Understanding on Biochar Thermal Annealing at Mild Temperatures and Its Effect on Biochar Reactivity. *Energy & Fuels*. 2011;25(1):406-14.
- [5] Wang L, Sandquist J, Varhegyi G, Matas Güell B. CO<sub>2</sub> Gasification of Chars Prepared from Wood and Forest Residue: A Kinetic Study. *Energy & Fuels*; 2013;27(10):6098-107.
- [6] Li C-Z. Importance of volatile–char interactions during the pyrolysis and gasification of low-rank fuels – A review. *Fuel*. 2013;112(0):609-23.



### Biography

Liang Wang is a research scientist at SINTEF Energy Research in Trondheim Norway. His research focus on characterization of biomass and wastes using combined analytical instruments and techniques, advanced biomass carbonization technology, experimental and kinetic study of torrefaction, pyrolysis, gasification and combustion, of biomass and charcoal, ash chemistry during biomass and waste thermal conversion.