

Characterization of Residues from Entrained Flow Gasification of Wood

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Entrained flow gasification is a promising way to convert biomass into valuable fuels and chemicals. Residues formed during gasification of biomass have considerable effects on process efficiency and syngas quality. In the current work, residues from wood powder gasification were collected from two syngas coolers at different temperature levels in an electrically heated small-scale 15 kW entrained flow gasification reactor setup operating with air as gasification agent at a stoichiometry of 0.55 and a setpoint temperature of 1160 °C. The residues were characterized by thermogravimetric analysis to study general decomposition properties and their reactivity toward CO₂. The morphology, microstructure and chemical composition of the collected residues were examined by scanning electron microscopy (SEM)/energy dispersive X-ray spectrometry (EDS). It was found that the properties of the residues collected from the two coolers are very different. The differences are mainly related to the transformation and fate of products from decomposition and gasification of the wood particles at local temperature and concentrations conditions in the two coolers, and partly related to flow conditions and deposition history at the different physical locations. SEM/EDS analysis results show that the residues mainly contain a mixture of partially unconverted fuel particles, carbon rich chars and condensed organic and inorganic compounds, which have different visual appearance, structures and compositions in the residues collected from the two coolers. The general reactivity of the residues from the two coolers were in the same order. But, because of mainly different temperature histories and physical locations, their reactivities are still evidently different, which is associated to their resulting different physio-chemical properties.

1. Introduction

Gasification of biomass is a promising pathway for utilization of this renewable energy source for producing synthesis gas (syngas). The syngas can be used for further production of synthetic fuels, valuable chemicals as well as heat and power. Entrained flow gasification (EFG) is one of the gasification technologies, having several advantages. While EFG of coal powder is a proven technology [Breault et al., 2010], EFG of biomass powder is considered to be in a development stage. Compared to other gasification technologies, EFG can realize high carbon conversion efficiency due to its high operational temperature, with production of high-quality and hydrogen rich syngas. At high enough temperature, depending on the fuel used, slagging EFG operation can be carried out, protecting the reactor core inner surfaces. A high operational temperature, and especially at oxygen enriched or/and pressurised conditions, allows for compact reactor design and a high throughput, with a modest residence time needed to gasify the powdered fuel. Biomass fuels have high content of volatile matter that causes release of a large amount of tar during the gasification process, which if not completely converted will end up as an undesired by-product. However, owing to the high temperature during the EFG process, a tar-free syngas with a high CO and H₂ content and a low CH₄ content can be obtained. In the EFG process, the small fuel particles fed into the reactor are rapidly heated, causing devolatilization, release of tars and formation of a range of gaseous compounds as well as carbon rich char and soot [Qin and Jensen et al., 2012]. Gasification of char and soot are the main conversion limiting steps since these heterogeneous reactions are much slower than the initial devolatilization, tar cracking and gas forming reactions. Soot is normally observed in the syngas in the temperature range 1000-1400 °C, naturally

originating from light hydrocarbons in the burner section of the EFG reactor, and its concentration in the syngas is a direct result of incomplete combustion or gasification of the formed soot. In comparison to the char, soot has more ordered and dense structure, which results in a lower gasification reactivity and considerably affect the overall fuel conversion efficiency of the gasification process and as well the syngas quality. During operation of an entrained flow gasifier, the syngas needs to be cooled down and cleaned before utilization. Carbon rich residues in the syngas will then be carried out and pass through a critical temperature range and can deposit on different surfaces, to a degree dependent on several factors, including particle size and stickiness. The physical and chemical properties of these carbon rich residues are affected by local conditions (e.g. temperature and concentrations) inside the gasifier, which also influence their gasification reactivity. More knowledge of their morphology, physical and chemical properties and reactivity is needed, to increase the understanding of formation mechanisms and identify ways to reduce the residue amount and hence improve carbon conversion efficiency. Collection and characterization of carbon rich residues from EFG of biomass with presence of steam and O₂ have been reported [Li et al., 2015; Wiinikka et al., 2018]. However, the properties and reactivity of carbon rich residues produced from biomass EFG when using air as a gasifying agent needs further attention, especially in small-scale reactors where residence time can become a limiting factor for the gasification reactions and hence other operational or feedstock parameters need to be adjusted in order to obtain high conversion efficiencies. The EFG reactor used in this study, due to its modest scale and gasification chamber dimensions, could also due to a limited residence time, influence on the carbon conversion efficiency at the selected conservative operating conditions. Hence, it becomes interesting to investigate at what conditions gasification with air is enough to reach a good carbon conversion efficiency, and when the gasification process should be operated at more elevated temperature and/or with a more effective gasification agent and/or at pressurised conditions. The EFG reactor used in this study can operate with a pressure of up to 8 bar, a temperature of up to 1400 °C and with various gasification agents.

The objective of the present work is to study the residual particles obtained from EFG of wood powder and, particularly, their properties, morphology and reactivity. Thermogravimetric analysis (TGA) was employed to study sample properties and reactivity with respect to devolatilization and CO₂ gasification. SEM with EDS was used to examine the size, morphology, and elemental composition of the solid particles.

2. Experimental Section

Pellets manufactured from a mixture of pine and spruce wood sawdust were gasified in this work in a 15 kW electrically heated EFG reactor located in the SINTEF Energy Research Laboratory in Trondheim, Norway. The received fuel pellets were first milled in a hammer mill (MAFA EU-4B) with a 0.63 mm sieve installed, giving a reduced particle size distribution. The prepared wood powder fuel was further subjected to proximate, ultimate and ash analyses. Prior to one gasification experiment, the reactor core was heated up slowly to 1160 °C overnight. The chosen temperature with wood powder as fuel did not allow for slagging operation of the gasifier. The gasification process was started by feeding wood powder and air as gasifying agent to the reactor, at a stoichiometry of 0.55. The raw syngas and other products from the reactor (i.e. gas, tar, partially unconverted fuel particles, soot and ash/char) were cooled in two different coolers (radiative followed by convective) located downstream the gasification chamber, to reduce gas temperatures to close to room temperature. Residues in the coolers (i.e. ash and possibly tar, partially unconverted fuel particles, soot and char) settled primarily at the inlet and the outlet of the coolers; at the cooler #1 outlet (at about 28 °C), the cooler #2 inlet (at about 28 °C) and the cooler #2 outlet (at about 26 °C). The residues were collected after first cooling the reactor down to room temperature overnight after ending the gasification experiment, which was carried out during one working day. At the selected operating conditions, the temperature differences at the locations where the residues were collected became minor due to the effectiveness of the first and radiative cooler, meaning that it is mainly residence time, concentrations and flow conditions that influence on the different characteristics of the different residues. Pressurized air was used to extract the loose particles while the sticky ones were brushed off. All samples were collected in zip-type plastic bags and marked with the date, sampling point, and operating conditions. The solid residues collected after the EFG were analysed by TGA for examining their properties and reactivity. SEM with EDS was employed to obtain the size, morphology and inorganic elemental composition of the collected solid residues.

3. Results and Discussion

Wood sawdust is a typical fuel from woody biomass. The proximate, ultimate and ash analysis of the pine and spruce wood mixture used in this study are shown in Table 1 and Table 2. Properties of the collected solid residues were analysed by TGA in order to determine the moisture, volatile matter, ash and fixed carbon

content, see Table 3. Both the moisture and the fixed carbon content of the residue collected from the outlet of cooler #2 is much higher than those of the other two samples. The high fixed carbon content might be due to entrainment of smaller (e.g. soot) and partially gasified fuel particles that to a larger degree follow the flow and end up in the second, and lowest temperature (about 28-26 °C) cooler. Tarry vapours in the syngas can condense on the surface of the small particles and they can stick to the cooler surfaces, especially at the cooler outlet, due to the flow pattern. Additionally, water vapour can condense on these small particles and this can explain the higher moisture content at the cooler #2 outlet. A certain effect of the cooling can also be seen at the cooler #2 inlet, with higher moisture content and fixed carbon content compared to the cooler #1 outlet, which is operating at a higher temperature (about 204-28 °C measured, but the temperature at the inlet is much higher, close to the gasifier operating temperature, as the thermocouple is located well below the cooler inlet, in a cooled location). In addition, the ash content of the residues collected from the first and second cooler are different, and with higher ash content in the residue collected in the second cooler, especially at its inlet. This may be related to different flow patterns, and particle size and shape dependent impaction history and frequency and as well particle stickiness, at the inlet and outlets of the coolers, with more smaller char/ash particles depositing in the second cooler, especially at its inlet.

Table 1: Proximate and ultimate analysis of the fuel (on %dry basis, except Moisture content)

Sample	Moisture content	Ash content	Volatile matter	Fixed carbon	C	H	N	O	S	Cl
Fuel powder	5.4	0.5	84.9	14.6	50.8	6.1	<0.1	42.5	0.034	<0.01

Moisture content on %wet basis

Table 2: Ash analysis of the fuel (on mg/kg dry basis)

Sample	Ca	K	Mg	Na	Mn	Si	Al	P	Fe
Fuel powder	1020	454	161	102	95.2	81.7	25.7	81.7	13.6

Table 3: Properties of collected fuel residues after entrained flow gasification

Sample	Residue from cooler #1 outlet	Residue from cooler #2 inlet	Residue from cooler #2 outlet
Moisture (wt%, as received)	1.18	2.88	7.79
Volatile matter (wt%, dry basis)	92.35	82.13	83.47
Ash content (wt%, dry basis)	3.89	10.27	4.75
Fixed carbon (wt%, dry basis)	3.76	7.60	11.78

The weight loss curves (TG) and the corresponding differential weight loss curves (DTG) for the gasification of the residues collected from the cooler #1 outlet and the cooler #2 inlet in 5 vol% CO₂ in N₂ are shown in Figure 1.

The TG and DTG curves show that the two residue samples start to decompose in a similar temperature range. There are two reaction stages, as indicated by two DTG signal peaks, in the temperature range of 200-500 °C and 700-950 °C. The reactions in the temperature range 200-500 °C likely is related to release of compounds with high volatility, due to partially unconverted fuel particles and rerelease of condensed tars. The reaction rate of the residue sample from the first cooler is much higher in this temperature region, which might be due to the presence of more partially unconverted fuel particles and condensed tars in the residue collected from the outlet of this first and higher temperature cooler. A large mass loss was realized for the residue collected from the first cooler, having lost about 60% of its mass already at 400 °C. It indicates that the residue sample contains a larger fraction of compounds that are more reactive and ready to decompose at a low temperature, i.e. volatiles in partially unconverted fuel particles and condensed tar.

The reactions at high temperatures are mainly gasification of residual carbon and some release of remaining inorganic elements and volatile matter. The reaction rate of the residue from the cooler #2 inlet is higher in the temperature range 600-900 °C, with a peak value at a temperature of about 870 °C, compared with the reaction rate of the residue from the cooler #1 outlet, with a peak value at a slightly higher temperature of about 900 °C. The different behaviour can be attributed to compositional and property differences of the residues, including a catalytic gasification effect due to catalytic elements in the ash, enhancing the gasification rate and lowering the temperature where the peak value occurs. A higher amount of ash in the residue from the cooler #2 inlet can explain the lower temperature of the peak value and partly the higher gasification rate, as well as the extent of the gasification reaction, which is significantly lower than from the

cooler #1 outlet. In addition, there could be a hard to convert carbonaceous part remaining together with the ash that is not gasified further in the TGA at the chosen gasification conditions, with only 5 vol% CO₂ in N₂.

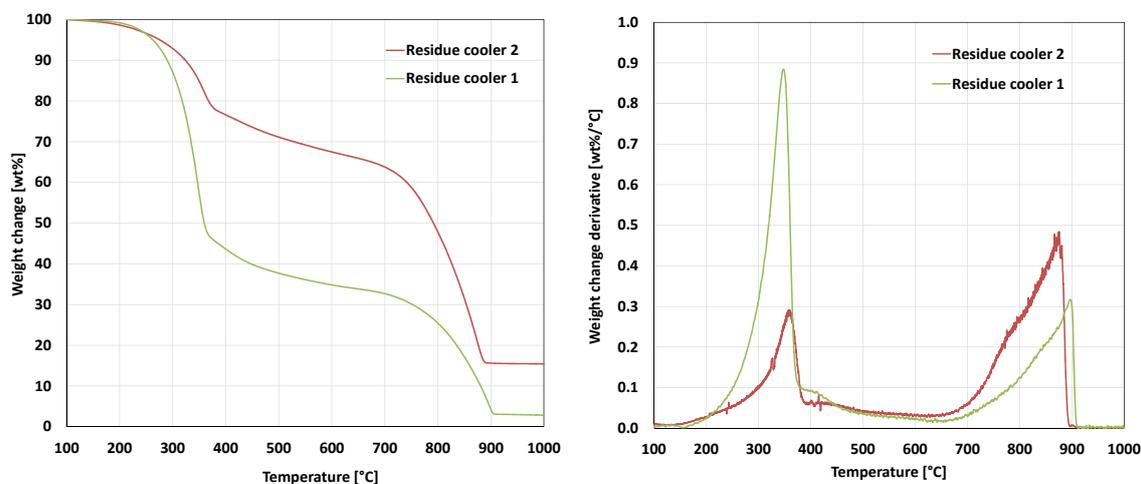


Figure 1: TG and DTG curves for the devolatilization and gasification (5 vol% CO₂ in N₂) of the carbon rich residues collected from entrained flow gasification at 1160 °C

Figure 2 shows SEM images of the residue collected from the cooler #1 outlet, the cooler #2 inlet and the cooler #2 outlet. Figure 2 (a) shows that there is variation in the degree of fuel conversion in the residue from the cooler #1 outlet, showing different degrees of converted fuel particles and ash/char/soot particles. A large fuel particle grain (indicated with an arrow) in the left corner of Figure 2 (a) can be seen, which still retains its initial wood fibre structure, i.e. it has only gone through a partial conversion. The major fraction of particles collected at the cooler #1 outlet have a size in the range of 80-120 µm and a nearly round and spherical shape with a few large holes (~10-20 µm) and many small holes (<1-5 µm), which can be clearly seen in Figure 2 (b) at a higher magnification. The formation of solid residues (mainly char) with similar morphology has been reported in other works [Trubetskaya et al., 2016]. At a high heating rate and temperature, as in an EFG reactor, the wood particles can pass through a plastic stage with loss of cell structure. During this stage, volatiles are generated and are very fast released from inside the solid particles to the exterior gas phase, causing rupture and formation of holes of different sizes.

Different than those collected from the cooler #1 outlet, there is a considerable number of small particles (down to 10 µm) that can be seen in the residue from the cooler #2 inlet in Figure 2 (c), and with a section shown with a higher magnification in Figure 2 (d). However, some of the particles are significantly larger, in the same size range as at the cooler #1 outlet. The small and flaky particles can be formed due to fragmentation of larger particles as they are transported from the first to the second cooler, or as they are brushed off when sampled. On the other hand, there are a few grains that have more porous structure, which is formed due to aggregating particles of different sizes. In addition, there are also many small particles on the surface of large spherical grains. SEM/EDS analyses showed that the grains consist of mainly minerals such as Mg, Fe, K and Ca, i.e. ash elements. The temperature in the second cooler is about 28-26 °C and significantly lower than the 204-28 °C in the first cooler, where the higher temperature is much underestimated due to the location of the thermocouple, i.e. well below the cooler inlet and in a cooled position. During this considerable decrease of temperature, minerals in vapour form condense from the gas flow and stick on the surfaces of large particles or aggregate together into large size clusters. As shown in Table 3, the ash content of the residue from the cooler #2 inlet is much higher than from the cooler #1 outlet, supporting the SEM/EDS analyses results. Observation of these grains indicates abundance of ash in the residue from the cooler #2 inlet, while on the other hand, only partially unconverted biomass and char particles were observed in the residue from the cooler #1 outlet. A higher conversion rate of the residue from the cooler #2 inlet compared to the cooler #1 outlet could be seen in the temperature range from 650-870°C in Figure 1, which can be attributed to release of high volatility inorganic elements together with gasification of fixed carbon.

Figure 2 (e) and (f) likewise show the structure and morphology of particles collected from the cooler #2 outlet. Figure 2 (f) clearly shows a large grain that is formed due to aggregating and sintering of small particles. The particles shown in Figure 2 (e) and with a section magnified in Figure 2 (f) are evidently of larger size and exhibit a more solid structure compared to those shown in Figure (a)-(d). It indicates that they have gone

through a further aggregation process and hence become heavier and are less prone to be carried out by the gas flow, hence depositing at the cooler #2 outlet.

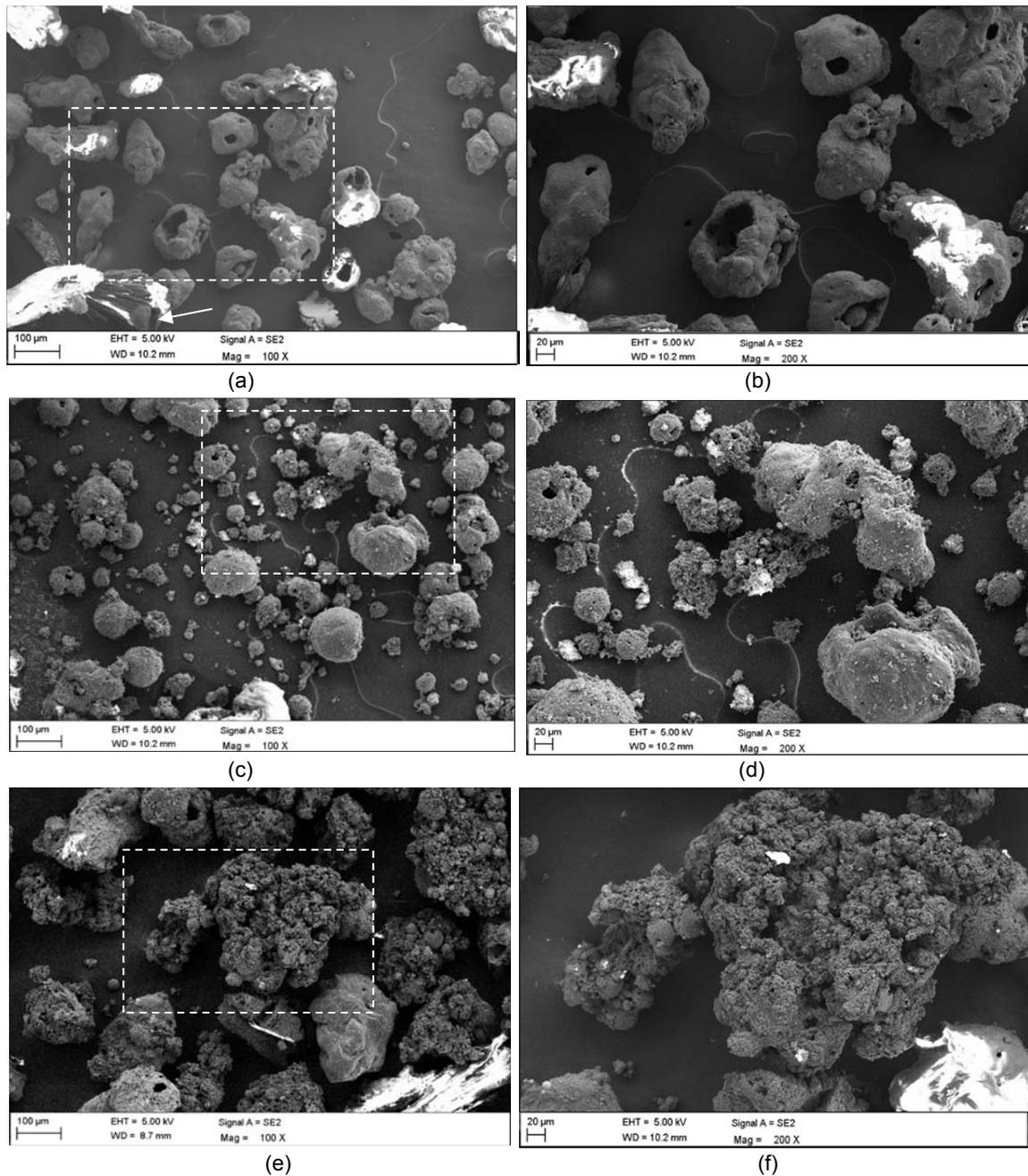


Figure 2: SEM images of residues collected from the cooler #1 outlet (a-b), the cooler #2 inlet (c-d) and the cooler #2 outlet (e-f). Left-side figures with a magnification of 100 X, while a section of those is magnified further at 200 X in the right-side figures

Regarding carbon conversion efficiency, the characteristics of the collected residues indicates a too low carbon conversion efficiency due to the clear presence of partially unconverted fuel particles. The main reason is a too short residence time, about 2 s, for achieving a high gasification degree for the wood powder particles. Hence, the gasification conditions have not enabled a good enough gasification process, which is supported by additional continuous gas measurements. Based on the flows in and out of the reactor, a modest carbon conversion efficiency of 70% was calculated. A similar carbon conversion efficiency was obtained by Schneider et al. [2016], achieving a carbon conversion efficiency of around 73% at a gasification temperature

of 1100 °C and particle size of 0.5-1 mm, and which increased to 80% when reducing the particle size to 0.2-0.25 mm. However, at 2 s residence time for beech wood particles of 0.08-0.2 mm it is possible to achieve full carbon conversion applying steam gasification environment and a gasification temperature of 1400 °C [Qin and Lin et al., 2012].

Hence, the gasification conditions must be enhanced in the direction of a higher carbon conversion efficiency, by increasing the gasification rate. This can be achieved by increasing the gasification temperature, changing the gasification agent (to e.g. oxygen enriched air) and operating at pressurised conditions. Reducing the feedstock particle size and operating with a reduced throughput will also enhance the carbon conversion efficiency, the former reducing the required residence time and the latter increasing the residence time. These are actions that makes sense from a research point of view to investigate the limits of a specific EFG reactor setup with respect to at which combination of particle size and residence time a high carbon conversion efficiency can be achieved. However, from a commercial and cost point of view a normal particle size and a high reactor throughput is wanted.

4. Conclusions

The properties, morphology and microstructure of residues from EFG of woody biomass are considerably different, as they are collected at different cooler levels. The differences are mainly related to gasification conditions and transformation behaviours of fuel and intermediate products at certain local conditions, involving mainly temperature, concentrations, flow conditions and their histories. The residue collected from the first of two coolers, in a higher temperature range, contains mainly large char particles with clear sign of melting. On the other hand, the residues collected from the second cooler in a lower temperature range are a mixture of large size and partly aggregated particles and smaller ones that are probably formed due to condensation of both organic and inorganic matters, giving a higher ash content. The gasification reactivity of the collected residues in different temperature ranges, toward CO₂, are therefore rather different, and is influenced by the ash content and its catalytic elements. A modest carbon conversion efficiency of 70% was reached in this work at the conservative gasification conditions chosen, showing that the small-scale 15 kW EFG reactor due to limited residence time needs to be operated at enhanced gasification conditions to achieve a needed carbon conversion efficiency of above 90%. This can be achieved by increasing the temperature, pressure or/and using a more effective gasification agent. In further work, the gasification conditions will be tuned to achieve a high carbon conversion efficiency and syngas quality. In a research perspective, the effect of reducing the feedstock particle size will also be investigated.

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