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Oxy-combustion of biomass in a circulating fluidized bed

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Abstract The objective of this study was to investigate combustion characteristics of biomass (willow, *Salix viminalis*) burnt in air and O₂/CO₂ mixtures in a circulating fluidized bed (CFB). Air and oxy-combustion characteristics of wooden biomass in CFB were supplemented by the thermogravimetric and differential thermal analyses (TGA/DTA). The results of conducted CFB and TGA tests show that the composition of the oxidizing atmosphere strongly influences the combustion process of biomass fuels. Replacing N₂ in the combustion environment by CO₂ caused slight delay (higher ignition temperature and lower maximum mass loss rate) in the combustion of wooden biomass. The combustion process in O₂/CO₂ mixtures at 30% and 40% O₂ is faster and shorter than that at lower O₂ concentrations.

Keywords: Biomass; *Salix viminalis*; Oxy-fuel combustion; CFB; TG/DTA

1 Introduction

Nowadays many countries around the world are taking initiatives to counteract global warming by reducing the greenhouse gas emissions. The Euro-

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pean Union is playing a leading role by setting targets to reduce its greenhouse gas emissions by 20% (from 1990 level), to increase the share of renewable energy to 20% in its primary energy consumption, and to improve energy efficiency by 20%. All three targets will be met by the year 2020. Efforts to increase boiler efficiency and the use of biomass and other solid renewable fuels are well in line with these objectives. Circulating fluidized bed (CFB) boilers are ideal for efficient power generation. They are capable of firing a broad variety of solid biomass fuels in small combined heat and power plants and large utility power plants. Biomass is considered as a carbon-neutral fuel in many countries, and its utilization for power generation can result in reduction in CO₂ emission since green plants capture atmospheric carbon dioxide during their growth cycle [1]. Biomass firing and co-firing coupled with oxy-fuel and carbon capture and storage (CCS) could be a ‘carbon negative’ technology. In the oxy-fuel combustion, biomass particles are burnt in a mixture of oxygen and recycled flue gas. Because nitrogen is almost completely eliminated from the oxidizing gas, the flue gas leaving the combustion chamber is highly enriched in CO₂ which means that the combustion process takes place in the O₂/CO₂ environment.

Wooden biomass such as willow (*Salix viminalis*) is a suitable energy crop for Northern and Eastern European climate conditions. It can be used as a raw material for energy production especially in fluidized bed boilers.

The objective of this study was to investigate combustion characteristics of wooden biomass burnt in air and O₂/CO₂ mixtures in a laboratory-scale CFB combustor. Detailed comparisons of ignition and devolatilization times and temperature profiles in the centre and at the surface of the particle have been made. To understand the thermal behavior of wooden biomass during air and oxy-combustion, a thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were also performed.

2 Experimental

2.1 Circulating fluidized bed combustor

Air and oxy-fuel combustion tests were conducted in a 12 kW bench-scale circulating fluidized bed combustor shown schematically in Fig. 1. The facility consists of a combustion chamber (1), a cyclone (2), a downcomer (3) and a loop seal (4). The electrically-heated rectangular combustion chamber (riser), 680×75×35 mm, is the main component of the unit. The

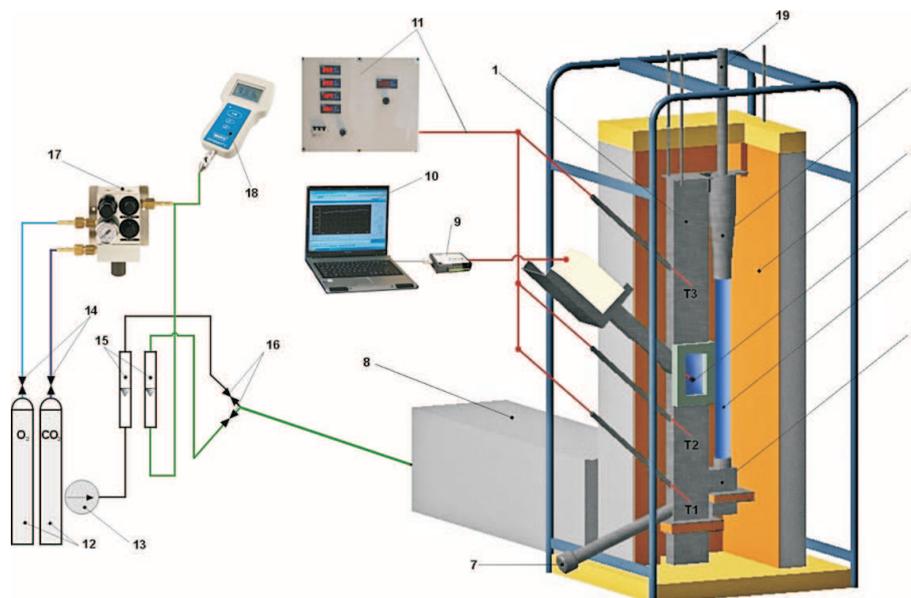


Figure 1: Schematic diagram of the experimental apparatus [2]: 1 – combustion chamber, 2 – cyclone, 3 – downcomer, 4 – loop seal, 5 – biomass particle, 6 – insulation, 7 – drain valve, 8 – preheater, 9 – card, 10 – computer, 11 – temperature control system, 12 – gas cylinders, 13 – air compressor, 14 – pressure regulators, 15 – rotameters, 16 – valves, 17 – mixer, 18 – gas analyser, 19 – ventilation duct, T1–T3 – S-type thermocouples.

front wall of the riser is made of transparent quartz through which the combustion process can be directly observed. Silica sand (particles smaller than $400\ \mu\text{m}$) to a mass of $0.3\ \text{kg}$ constituted the inert bed. The gases to make up gas mixtures are supplied from cylinders (12) to a mixer (17) and then transferred via a preheater (8) directly into the combustion chamber. Flow rates of gases are controlled by valves (16) and measured by rotameters (15). During combustion tests, the superficial gas velocity was kept at a constant level of about $5\ \text{m/s}$. The temperature was held at $850\ ^\circ\text{C}$ by means of a microprocessor controller (1). S-type thermocouples (T1–T3) measured the temperature at three different levels inside the combustion chamber with an accuracy of $\pm 2\ ^\circ\text{C}$.

A single biomass particle (5) was introduced into the combustion chamber and positioned stationary in the bed. To measure the temperatures in the centre and at the surface of the biomass particle a special stand was constructed. It provided a support for two S-type thermocouples. The tip

of the first thermocouple was located inside the particle, while the second thermocouple measured the surface temperature and served as a basket in which the biomass particle was placed. The thermocouples were connected via a card (9) to a computer (10) in order to record the temperature measurements. Ignition time and devolatilization time were measured by stopwatch with an accuracy of 0.1 s. The intraparticle temperature, the surface temperature, ignition time and devolatilization time were measured simultaneously.

The experiments were carried out in air (base case) and mixtures of O₂/CO₂ with oxygen concentrations in the range from 21% to 40% vol. Video and digital cameras were used to record the progress of combustion.

Spherical 8-mm particles of wooden biomass (willow, *Salix viminalis*) were used in this study. The proximate and ultimate analyses of wooden biomass are presented in Tab. 1.

Table 1: Proximate and ultimate analyses of wooden biomass (willow, *Salix viminalis*).

Proximate analysis (<i>air-dried basis</i>)	
Moisture (M), %	6.9
Ash (A), %	1.4
Volatile matter (VM), %	76.3
Fixed carbon (FC), %	15.4
Higher heating value (HHV), MJ/kg	18.2
Ultimate analysis (<i>dry, ash-free basis</i>)	
Carbon (C), %	49.6
Sulphur (S), %	6.0
Hydrogen (H), %	0.3
Nitrogen (N), %	0.1
Chlorine (Cl), %	0.02
Oxygen (O), % (by difference)	43.98

3 Thermogravimetric analysis

The combustion characteristic of wooden biomass was studied using a simultaneous TGA/DTA analyser (TA Instruments STD 2960). About 10 mg of fuel sample with size less than 100 μm was heated with a heating rate of 50 °C/min from the ambient temperature to 1200 °C during each exper-

iment. A total gas flow rate of 10 dm³/h was used in all the experiments. The following gas atmospheres were used in the experiments:

- air-combustion: 21% O₂ + 79% N₂,
- oxy-combustion: 21% O₂ + 79% CO₂,
30% O₂ + 70% CO₂,
40% O₂ + 60% CO₂,
- pyrolysis: 100% N₂ and 100% CO₂.

Thermogravimetric (TG) and differential thermogravimetric (DTG) profiles obtained during combustion and pyrolysis experiments were used to determine combustion behaviour and some characteristic temperatures such as ignition temperature, T_{ig} , peak temperature, T_{max} , and burnout temperature, T_b of the tested biomass. Ignition temperature is defined as the temperature at which fuel starts to burn. It is taken as the temperature at which the mass loss curves in the oxidation and pyrolysis experiments diverge. Peak temperature, T_{max} , is the point at which maximum reaction rate occurs. The last characteristic temperature considered is the burnout temperature which represents temperature when sample oxidation is completed. It is taken as the point immediately before reaction ceases when the rate of mass loss is 1%/min.

4 Results and discussion

4.1 CFB combustion tests

Each biomass sample introduced to the combustion chamber undergoes several characteristic stages namely:

- heating and drying,
- ignition and combustion of volatiles,
- combustion of remaining char.

Almost all solid fuels experience these processes but the duration of each process depends on the fuel type and its composition (moisture and volatile matter contents, total carbon content), temperature in the combustion chamber, heating rate and oxidizing atmosphere.

Figure 2 shows pictures of a willow sample burning in different oxidizing atmospheres. After rapid heating, the ignition of volatiles follows. Burning volatiles form a distinctive long flame. Differences in combustion times that

are related to the composition of oxidizing atmospheres can be noticed. At higher oxygen concentrations, the combustion process is more intense and, therefore, the total combustion time is shorter.

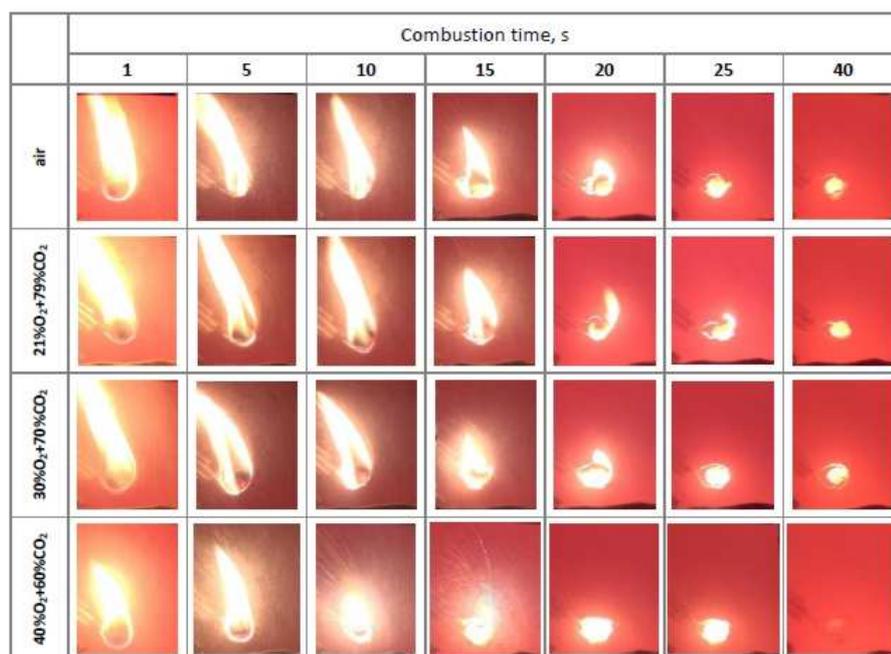


Figure 2: Combustion of biomass particles in air and O₂/CO₂ mixtures at 850 °C.

The ignition time was below 1 s in all atmospheres tested. Volatile matter combustion times and total combustion times are shown in Fig. 3. The volatile matter combustion time decreases slightly whereas the total combustion time decreases significantly with the increase in oxygen concentration. The total combustion time in a 40% O₂ + 60% CO₂ mixture is approximately 42% shorter than that for combustion in air.

Figure 4 shows temperatures measured at the surface and in the centre of wooden biomass particle burned at 850 °C in various atmospheres. In both cases, after an initial delay, the centre temperature exceeds the surface temperature and is approximately 100 °C higher during the course of combustion. Lower surface temperatures can be explained by intensive heat transfer between burning coal particles and bed material. Combustion in air proceeded at slightly higher temperatures and was slightly shorter in time compared to combustion in O₂/CO₂ mixture with 21% vol. O₂.

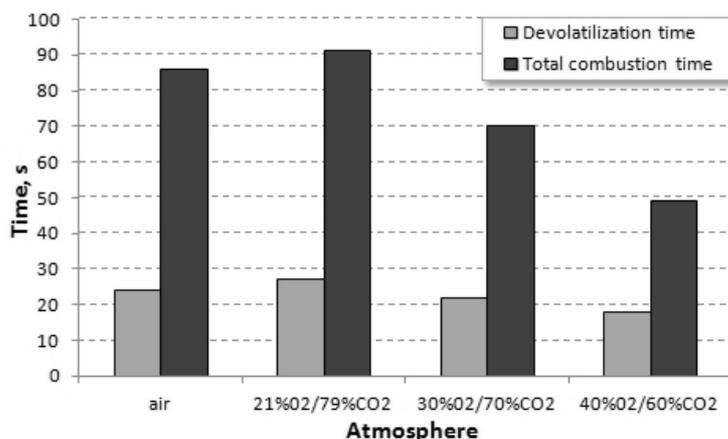


Figure 3: Devolatilization time and total combustion time for biomass particles burned in various atmospheres at 850 °C.

When the flame approaches its point of extinction, the surface temperature reaches its maximum value. This maximum value varies from ~ 1080 °C, for combustion in air, to ~ 1180 °C for combustion in the mixture of 40% O₂ + 60% CO₂. In the next stage, i.e., char combustion, the centre temperature was higher than the surface temperature. The maximum centre temperature was ~ 70 °C higher during combustion in the 40% O₂ + 60% CO₂ mixture than during combustion in air.

Combustion in a O₂/CO₂ mixture at 21% O₂ resulted in the centre temperature being ~ 40 °C lower than that for combustion in air. Higher specific heat capacity of CO₂ lowers the heating rate of the biomass particle. The diffusion coefficient of O₂ in CO₂ is smaller than that in N₂. These two factors influence negatively the kinetics of the combustion process and are responsible for observed decrease in the centre temperature.

Graphs shown in Fig. 4 can be used to determine, with good accuracy, the total time of combustion. When the char combustion process is completed, the surface temperature and the centre temperature drop to value corresponding to temperature in the combustion chamber.

4.2 TGA/DTA tests

The experimental variations of the mass loss versus temperature in the dynamic runs carried out in the oxidative atmosphere (combustion) and in

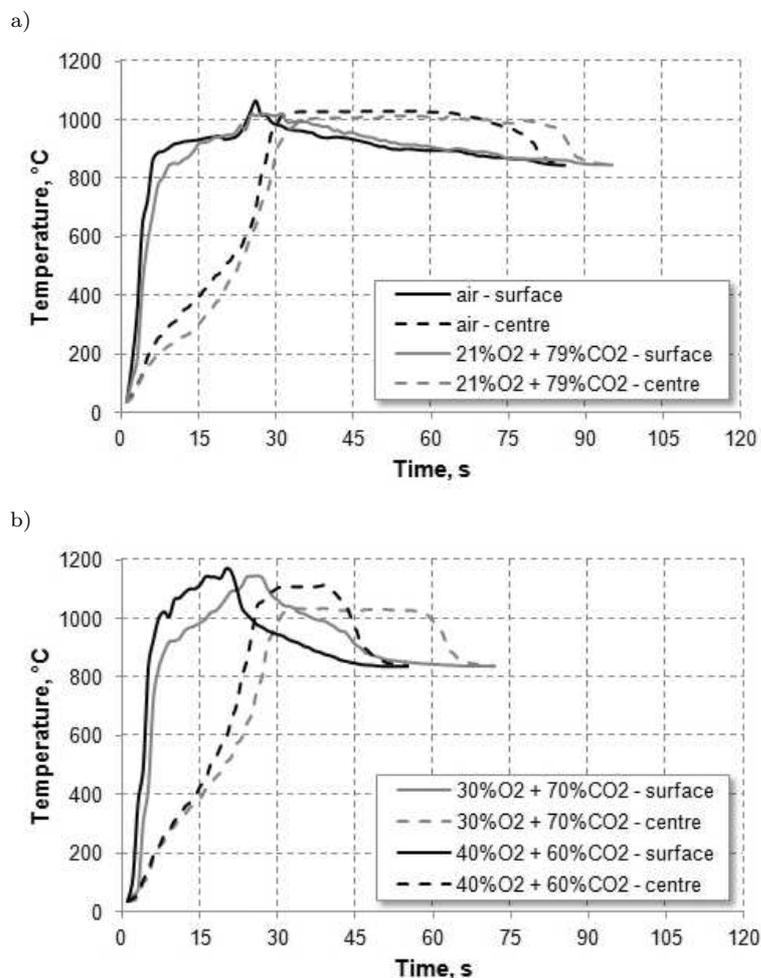


Figure 4: Temperature profiles for wooden biomass particle burned at 850 °C in various atmospheres: a) air and 21%O₂/79%CO₂, b) 30%O₂/70%CO₂ and 40%O₂/60%CO₂.

inert atmosphere (pyrolysis) were obtained. Figure 5 shows TG and DTG curves for wooden biomass in all atmospheres studied. The TG curves for combustion in air and oxy atmospheres (O₂/CO₂) show rapid mass loss in comparison to the pyrolysis curves. The end of combustion is marked by the constant mass of the incombustible ash. The rate of mass loss is higher in atmospheres containing more than 30% O₂ (Fig. 5a). The DTG curves of wooden biomass in all atmospheres are compared in Fig. 5b. In the case of combustion three peaks are visible in the DTG curve. The first one, within

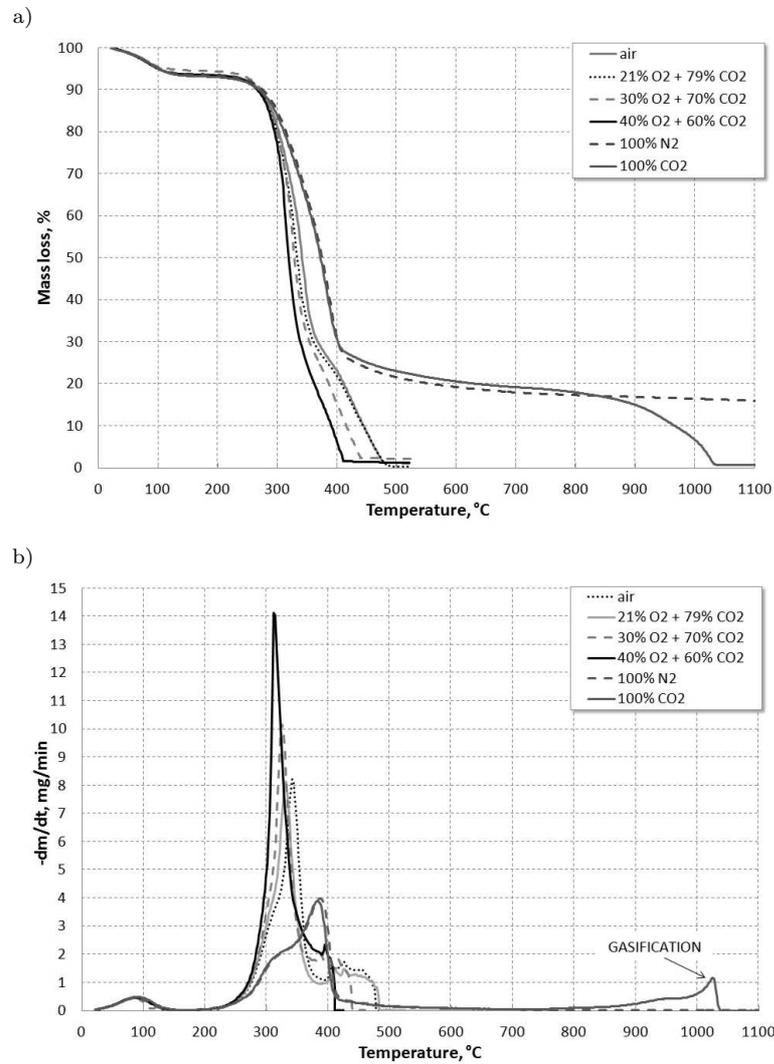


Figure 5: Thermogravimetric, TG, (a) and differential thermogravimetric, DTG, (b) curves for wooden biomass combustion and pyrolysis.

25–150°C temperature range, accounts for moisture release. The second peak between 210 and 380 °C is attributed to the release of volatiles and their burning. The last peak within about 400–480 °C temperature range in air and 385–410 °C in the 40%O₂ + 60%CO₂ mixture is considered to be due to combustion of char. The pyrolysis TG and DTG curves show similar

trend in N₂ and in CO₂ till they reach a critical temperature. On reaching this critical temperature, around 780 °C, a drastic mass loss occurs. This mass loss is attributed to the char-CO₂ gasification reaction. The gasification rate is so high that the wooden biomass even attains a total conversion in CO₂ atmosphere. This is marked by a constant mass at the end of 100% CO₂ curve. We are unable to see any effect of the gasification reaction in the oxy experiments because the oxidation reaction is completed before the char reaches the critical gasification temperature.

The temperature at which the combustion TG curve deviates from the pyrolysis TG curve was taken as the ignition temperature. This technique for the measurement of ignition temperature has been used by many researchers [3]. Burnout temperature is the temperature at which the final conversion is reached. Table 2 shows the ignition and burnout temperatures of wooden biomass in air and oxy-fuel atmospheres. The ignition temperature of *Salix viminalis* was determined to be 265 °C in the atmosphere of air. The relationship between the fuel volatile matter content (dry basis) and TG ignition temperature for solid fuels is shown in Fig. 6.

Table 2: Characteristic parameters for combustion and pyrolysis of wooden biomass.

Parameter	Atmosphere					
	Combustion				Pyrolysis	
	air	21% O ₂ 79% CO ₂	30% O ₂ 70% CO ₂	40% O ₂ 60% CO ₂	100% N ₂	100% CO ₂
Ignition temperature, T_{ig} , °C	265	268	263	258	–	–
Peak temperature, T_{max} , °C	332	342	324	312	379	386
Burnout temperature, T_b , °C	484	488	440	411	–	–
Burnout time, t_b , s	574	584	528	478	–	–
Maximum mass loss rate, DTG_{max} , mg/min	8.21	8.13	10.17	14.14	3.98	3.89
Maximum DTA, DTA_{max} , °C/mg	2.02	1.95	2.55	3.29	0.14	0.28

Generally, the ignition temperature decreases with the increase in volatile matter content. Replacing N₂ in the combustion environment by CO₂ causes slight delay (higher ignition temperature, burnout temperature and lower maximum mass loss rate) in the combustion of wooden biomass. However, when the concentration of oxygen in O₂/CO₂ mixtures is larger than

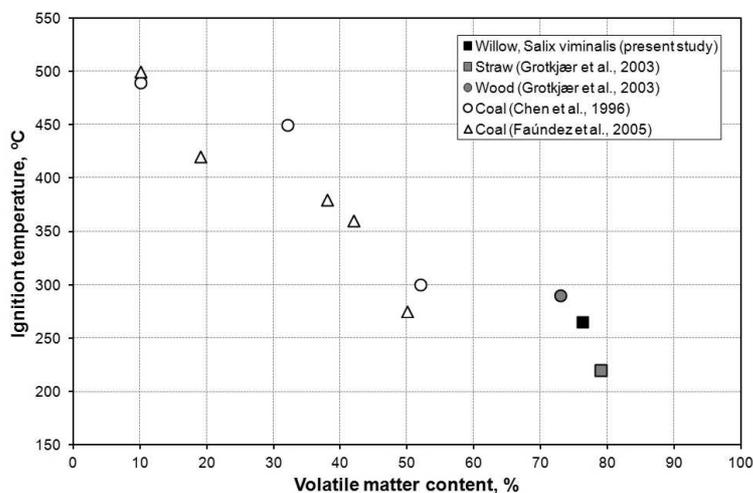


Figure 6: Relationship between fuel volatile matter content (dry basis) and TG ignition temperature for various solid fuels.

30%, the ignition and burnout temperatures decrease with increasing O_2 content. The ignition temperature of wooden biomass decreases by $10^\circ C$ and the burnout temperature is $77^\circ C$ lower when the O_2 concentration increases from 21% to 40%. The maximum mass loss temperature, T_{max} , also decreases by $30^\circ C$. The trends are consistent with those found in the literature [4,5]. TGA combustion tests show similar trends to those observed during CFB combustion tests. The combustion time decreases with an increase in O_2 concentration. The combustion time in the $40\%O_2 + 60\%CO_2$ mixture was approximately 17% shorter than that for combustion in air.

DTA curves show the difference in temperature between a tested sample and the reference material, which reflects exothermic or endothermic condition. Figure 7 shows the DTA curves during combustion and pyrolysis. The DTA curves clearly show the exothermic oxidation reaction and the endothermic gasification reaction. The char- CO_2 gasification reaction in the 100% CO_2 atmosphere is highly endothermic and may lower the particle temperature. The oxidation reaction, on the other hand, releases energy. Area under the oxidation curve is considered as a measure of the heating value of the fuel.

The maximum DTA of *Salix viminalis* was determined to be about $2^\circ C/mg$ in the air atmosphere. It is found that the peak heat release increases with

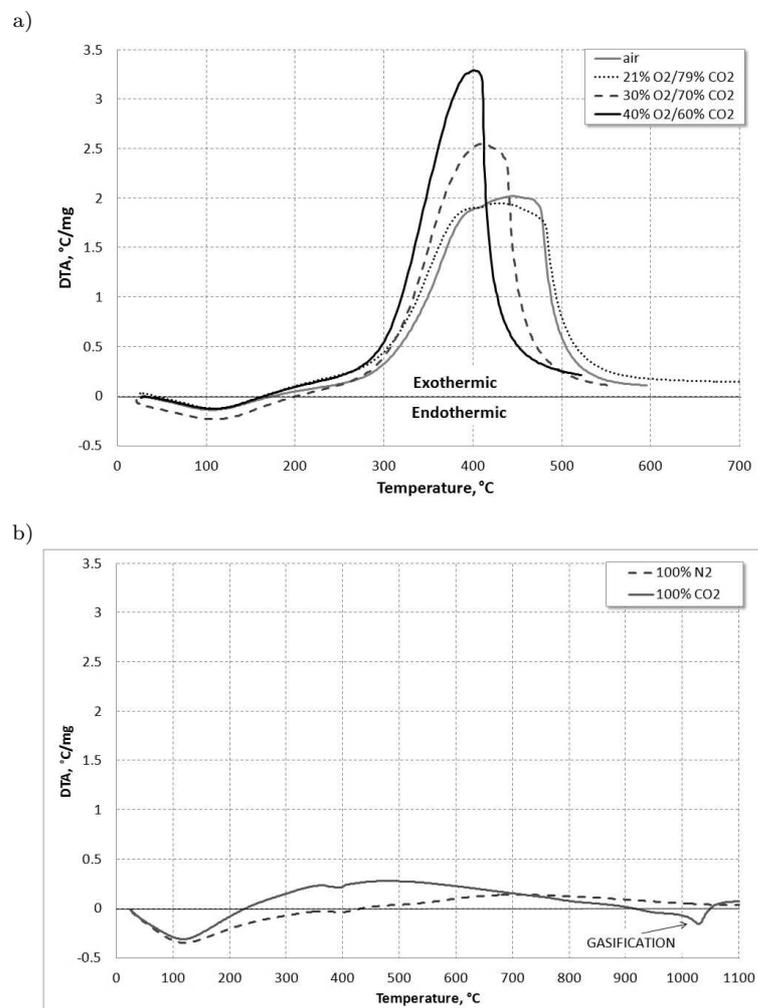


Figure 7: DTA curves of wooden biomass during combustion (a) and pyrolysis (b).

increasing oxygen concentration. The maximum DTA of wooden biomass increases to 3.34 °C/mg when the O₂ concentration increases from 21% to 40%. The peak heat release during combustion in 21%O₂ + 79%CO₂ was slightly less than in the air atmosphere. This may be attributed to high specific heat capacity of CO₂ in comparison to N₂.

5 Conclusions

The results of conducted CFB tests show that the composition of the oxidizing atmosphere strongly influences the combustion process of biomass fuels. The combustion process in O₂/CO₂ mixtures at 30% and 40% O₂ is faster and shorter than that at lower O₂ concentrations. The total combustion time (volatiles + char) in the 40%O₂ + 60%CO₂ mixture was approximately 42% shorter than that for combustion in air. Due to thermal properties of CO₂, the combustion rate in O₂/CO₂ mixtures at 21% O₂ was lower than that in air and the combustion process proceeded at lower temperatures.

The ignition and combustion characteristics of wooden biomass in O₂/N₂ and O₂/CO₂ atmospheres were also investigated using the TGA and DTA techniques. The ignition temperature and the burnout temperature of *Salix viminalis* were determined to be 265 °C and 484 °C, respectively, in the air atmosphere. Replacing N₂ in the combustion environment by CO₂ caused slight delay (higher ignition temperature, burnout temperature and lower maximum mass loss rate) in the combustion of wooden biomass. However, when the concentration of oxygen in O₂/CO₂ mixtures was larger than 30%, the ignition and burnout temperatures decreased with increasing O₂ content. The ignition temperature of wooden biomass decreased by 10 °C and the burnout temperature was 77 °C lower when the O₂ concentration increased from 21% to 40%. The DTA curves of wooden biomass clearly showed the exothermic oxidation reaction and the endothermic gasification reaction. The char-CO₂ gasification reaction in the 100% CO₂ atmosphere was highly endothermic and may lower the particle temperature.

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