

## Article

# Composition of Flue Gases during Oxy-Combustion of Energy Crops in a Circulating Fluidized Bed

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**Abstract:** In recent years, global warming and climate change associated with emissions of CO<sub>2</sub> from fossil fuel-fired power systems are a big worry for authorities in many countries worldwide. The utilization of biomass as an alternative, carbon-neutral fuel can reduce emissions of CO<sub>2</sub> and other greenhouse gases. Furthermore, the coupling of oxy-combustion of biomass with CO<sub>2</sub> capture is an option for carbon-negative power generation technology. In this study, emissions of NO<sub>x</sub>, SO<sub>2</sub>, and CO from the air- and oxy-combustion of three energy crops (*Miscanthus giganteus*, *Sida hermaphrodita*, and *Salix viminalis*) are presented and compared with emissions from other biomass fuels and reference coal. Combustion tests in air and O<sub>2</sub>/CO<sub>2</sub> mixtures were conducted in a 12-kW bench-scale CFB combustor at 850 °C. Measurements of flue gas compositions were taken using an FTIR spectrometer. In all tested atmospheres, emissions of SO<sub>2</sub>, N<sub>2</sub>O, and CO for biomass were lower than those for the reference coal. The oxidation of volatile nitrogen compounds was behind high emissions of NO<sub>x</sub> from biomass burned in air and O<sub>2</sub>/CO<sub>2</sub> mixtures. The lowest concentrations of NO were found in the 21% O<sub>2</sub>/70% CO<sub>2</sub> mixture. Combustion in mixtures containing more oxygen (30% and 40% O<sub>2</sub>) led to a decrease in emissions of N<sub>2</sub>O and CO and an increase in emissions of NO and SO<sub>2</sub>.

**Keywords:** biomass; oxy-fuel combustion; fluidized bed; *Miscanthus giganteus*; *Sida hermaphrodita*; *Salix viminalis*; wheat straw; Scots pine; bituminous coal



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## 1. Introduction

Various human activities related to the use of fossil fuels such as electricity generation, agriculture, and transport release large quantities of CO<sub>2</sub> into the atmosphere. Carbon dioxide as a greenhouse gas (GHG) is a major contributor to global warming. In the transition to a low-carbon economy, i.e., in the next few decades, the world will still be heavily dependent on fossil fuels as primary energy sources despite unprecedented progress in solar and wind energy generation. Therefore, the utilization of advanced systems for CO<sub>2</sub> capture, utilization, and sequestration (CCUS) becomes vital to abate emissions and lessen the impact of CO<sub>2</sub> emissions on climate change. Coupling CCUS with renewables should help to reach the 2 °C temperature rise limit recommended by the Paris Agreement.

The contribution of biomass to global primary energy consumption is the largest among all sources of renewable energy [1]. Biomass is carbon neutral because, unlike fossil fuels, it is a part of the natural carbon cycle. Carbon dioxide released during the combustion of biomass is absorbed by plants during their life cycles.

The basic characteristics of biomass as a fuel include moisture content, ash yield and composition, carbon content, and higher heating value (HHV). Vassilev and co-workers [2] reviewed the chemical composition of many biomass crops and found large variability

in moisture content, ash yield, and types of inorganic matter (minerals) in raw materials. However, the results of proximate and ultimate analyses when reported on a daf (dry, ash-free) basis were in a narrow range.

Among various biomass sources, dedicated energy crops (non-food crops, mostly perennial grasses, and fast-growing trees) are grown solely to provide renewable feedstock for the generation of electricity and heat and the production of biofuels [3]. These high biomass yield crops can be cultivated on marginal or reclaimed land; they are non-invasive and have low water and fertilizer needs. Herbaceous energy crops, e.g., miscanthus and switchgrass, can store approximately two times more CO<sub>2</sub> per 1 hectare of cultivation than woody crops such as poplar and willow.

Among CCUS technologies, oxy-fuel combustion is a promising process because it uses almost pure oxygen instead of air and generates a high-purity stream of CO<sub>2</sub> (95% or more) that can be stored or utilized to produce carbon-based fuels or chemicals. Biomass firing or co-firing in oxy-fuel systems integrated with CO<sub>2</sub> capture can be considered a carbon-negative technology.

Fluidized bed boilers, both stationary and circulating, are the best choice for firing low-quality coals, refuse-derived fuels, and biomass [4–6]. The well-known benefits of fluidized-bed combustion technology include high fuel flexibility and turndown ratio, low emissions of NO<sub>x</sub>, and high availability. Today, circulating fluidized-bed (CFB) boilers firing 100% biomass fuels are available commercially. Units at Konin (55 MW<sub>e</sub>) and Połaniec (205 MW<sub>e</sub>) power plants in Poland [7], and the 299 MW<sub>e</sub> Tees unit in the UK (the largest bio CFB in the world) [8], can be mentioned as examples.

Oxy-fuel CFB boilers are better than their pulverized-fuel (PF) counterparts. They do not require sophisticated burners and fuel preparation and feeding systems. Because the combustion temperature in oxy-CFB systems is lower than in PF units, oxy-CFB boilers can meet current NO<sub>x</sub> and SO<sub>x</sub> emission limits without additional de-NO<sub>x</sub> and de-SO<sub>x</sub> equipment. The combustion temperature can be controlled by cooling a part of the circulating particles in an external heat exchanger and recirculating them back to the combustion chamber [9]. This allows for using higher initial O<sub>2</sub> concentrations in smaller streams of recirculated flue gas, which results in units with reduced dimensions, higher thermal efficiency, and lower capital costs. Energy losses in oxy-fuel systems caused by air separation and CO<sub>2</sub> purification systems working at high pressures can be reduced in oxy-CFB units operating at elevated pressure. The latent heat in flue gases can be recovered and air infiltration can be eliminated in pressurized systems, which can improve the purity of CO<sub>2</sub> and reduce the cost of its capture [10,11].

Carbon dioxide utilization and storage require a gas stream with a concentration of CO<sub>2</sub> of 95% or more. The presence of impurities such as N<sub>2</sub>, O<sub>2</sub>, NO<sub>x</sub>, SO<sub>2</sub>, and other N- and S-containing gases affects the design, energy consumption, and costs of the CO<sub>2</sub> processing unit (CPU). Knowledge of pollutant formation and their concentration is, therefore, important for the design, performance, and cost of the CPU [12].

Several publications on the combustion of biomass in oxy-CFB systems are available in the open literature. A few of them provide some information on emissions of NO<sub>x</sub>, SO<sub>2</sub>, and other pollutants. The main observations drawn from these studies are presented in Table 1.

In this study, combustion tests of three dedicated energy crops, namely miscanthus (*Miscanthus giganteus*—a perennial grass with bamboo-like stems), Virginia mallow (*Sida hermaphrodita*—a perennial forb native to the eastern U.S.), and basket willow (*Salix viminalis*—a multi-stemmed shrub) were conducted in the bench-scale oxy-CFB reactor at 850 °C. On-line measurements of NO, NO<sub>2</sub>, N<sub>2</sub>O, NH<sub>3</sub>, HCN, SO<sub>2</sub>, and CO concentrations were taken during air- and oxy-fuel combustion. The influence of the chemical composition of oxidizing gas and biomass fuels on the emissions of above-mentioned pollutants was assessed. The results were compared to the emissions from wheat straw (agricultural biomass), Scots pine (woody biomass), and bituminous coal (reference fuel).

**Table 1.** Pollutant emissions from oxy-CFB combustion—a summary.

Reference	Test Facility and Operating Conditions	Fuels	Oxidizing Medium	Emissions Reported	Remarks
Tan et al. [13]	CFB, 800 kW <sub>th</sub> , ~900 °C, limestone, Ca/S = 3	Wood pellets, different coals, fraction of biomass in fuel blends 20–50%wt.	O <sub>2</sub> /CO <sub>2</sub> mixtures, 24–25% O <sub>2</sub> , recycled flue gas	NO <sub>x</sub> , SO <sub>2</sub> , CO, CO <sub>2</sub> , O <sub>2</sub>	The addition of wood pellets did not have a notable impact on the combustion characteristics of tested fuels. Emissions of NO (per unit of energy (higher heating value) in the fuel) were in the range of 14–20 ng/J, and emissions of SO <sub>2</sub> varied from 35 to 95 ng/J. When the O <sub>2</sub> concentration in the flue gas exceeded 3.5%, emissions of CO dropped below 200 ppm.
Duan et al. [14]	CFB, 10 kW <sub>th</sub> , 850 ± 10 °C	Rice husk, wood chips, dry wood flour, coal, biomass fraction in fuel 0–100%wt.	Air, 70% O <sub>2</sub> /30% CO <sub>2</sub> mixture	NO, NO <sub>2</sub> , CO, CO <sub>2</sub> , O <sub>2</sub> , SO <sub>2</sub>	Emissions of NO were higher for biomass fuels than for coal. Oxy-combustion produced less NO than combustion in air. NO emissions in the air and oxy-fuel atmosphere increased with an increasing fraction of biomass in the fuel blend.
Wang et al. [15]	CFB, 10 kW <sub>th</sub> , 800–900 °C	Corn straw, wheat straw, coal, 30% biomass in fuel blend	50% O <sub>2</sub> /50% CO <sub>2</sub> , 50% O <sub>2</sub> /50% recycled flue gas	NO, N <sub>2</sub> O, CO, CO <sub>2</sub> , O <sub>2</sub> , HCN	NO and N <sub>2</sub> O emissions increased with an increasing excess O <sub>2</sub> . An increase in the fraction of corn straw in the fuel blend caused an increase in emission factors of NO, N <sub>2</sub> O, and HCN.
Varol et al. [16]	CFB, 850 and 915 °C, limestone, Ca/S = 2	Wood pellets, high-sulphur lignite, biomass/lignite ratio up to 60%	25, 30% O <sub>2</sub> , CO <sub>2</sub>	NO <sub>x</sub> , SO <sub>2</sub> , CO, CO <sub>2</sub>	Increasing biomass share in the fuel blend had a negligible effect on NO <sub>x</sub> emissions. Emissions of CO and SO <sub>2</sub> decreased with an increasing fraction of biomass in the fuel blend.
Sung et al. [17]	CFB, 30 kW <sub>th</sub> , 750–840 °C	Sewage sludge, wood pellets	O <sub>2</sub> with recirculated flue gas	CO, NO	The lowest concentrations of CO (0.91%) and NO (14 ppm) were at 60% flue gas recirculation.
Nguyen et al. [18]	CFB, 100 kW <sub>th</sub> , 845–905 °C, flue gas recirculation	Wood pellets, lignite, biomass fraction in fuel blend 50–100%wt.	21–29% O <sub>2</sub> , CO <sub>2</sub>	NO, SO <sub>2</sub> , CO	An increase in biomass share caused a decrease in NO, SO <sub>2</sub> and CO concentrations. Oxy-combustion of pure biomass can produce negative CO <sub>2</sub> emissions of, approximately, −647 g/kW <sub>th</sub> .
Moreno et al. [19]	CFB, 200 kW <sub>th</sub> , 910 ± 10 °C, 835–852 °C, limestone	Coal, wheat straw, solid recovered fuel	O <sub>2</sub> , recirculated flue gas	NO <sub>x</sub> , SO <sub>2</sub> , HCl	NO <sub>x</sub> emissions of 359 mg/MJ <sub>th</sub> for combustion of coal and 203 mg/MJ <sub>th</sub> for co-combustion of coal with biomass. Emissions of SO <sub>2</sub> were 1.9–2.0 mg/MJ <sub>th</sub> . Emissions of HCl were 1.8 mg/MJ <sub>th</sub> for tests with no wheat straw and 3.9 mg/MJ <sub>th</sub> for combustion of pure biomass.

While there are several publications on NO<sub>x</sub> emissions from the oxy-combustion of coal, relevant publications on the oxy-combustion of biomass are scarce [20]. There are

no studies in the open literature on pollutant emissions during oxy-CFB combustion of energy crops such as *Miscanthus giganteus* and *Sida hermaphrodita*. This paper fills a gap in this field. This manuscript provides a comparative analysis of pollutant emissions during the combustion of energy crops and other fuels such as woody- and agro-biomass and bituminous coal. So, in this respect, it is similar to our previous work [12]. The test apparatus and methodology were the same to make sure the results can be compared.

## 2. Materials and Methods

### 2.1. Fuel Tested

Three different energy crops were selected for this study, *Miscanthus giganteus*, *Sida hermaphrodita*, and *Salix viminalis*, all originating from plantations in Poland. Agricultural biomass (wheat straw), woody biomass (Scots pine), and Polish bituminous coal were used as the reference fuels; the results of their combustion tests were already presented in reference [12]. Samples of tested fuels were milled and sieved to less than 0.2 mm for proximate and ultimate analyses. The basic characteristics of these fuels are summarized in Table 2. The ash yields for *Miscanthus giganteus* and *Sida hermaphrodita* are significantly higher than that for *Salix viminalis*. The energy crops tested in this study are characterized by a high content of volatile matter (VM). Their higher heating values (HHV) are in the range of 17.5 to 18.2 MJ/kg, typical for biomass fuels. Contents of sulphur and nitrogen in these crops are lower than in agricultural biomass (wheat straw) and coal. An additional advantage of these energy crops is a very low content of chlorine (less than 0.1%).

**Table 2.** Characteristics of tested fuels.

	<i>Miscanthus giganteus</i>	<i>Sida hermaphrodita</i>	<i>Salix viminalis</i>	Wheat Straw [12]	Scots Pine [12]	Bituminous Coal [12]
<b>Proximate analysis (wt.%, db)</b>						
Moisture	6.0	6.3	6.9	8.4	7.0	8.7
Ash	12.4	9.4	1.4	6.1	0.6	18.9
Volatile matter	75.8	76.7	76.3	68.3	76.8	26.8
Fixed carbon *	5.8	7.6	15.4	17.2	15.6	45.6
<b>Higher heating value, MJ/kg</b>	17.73	17.53	18.20	17.84	18.90	22.75
<b>Ultimate analysis (wt.%, daf)</b>						
Carbon	46.02	44.78	49.60	50.20	50.90	73.30
Hydrogen	5.38	5.19	6.00	5.80	5.70	4.30
Sulphur	0.03	0.02	0.03	0.08	0.01	2.30
Nitrogen	0.15	0.08	0.30	0.80	0.10	1.10
Chlorine	0.08	0.01	0.01	0.15	0.01	0.70
Oxygen *	48.34	49.92	44.06	42.97	43.28	18.30

Note: db—dry basis, daf—dry, ash free, \* by difference to 100%.

### 2.2. Experimental Apparatus and Procedure

The experiments were conducted in the 12-kW bench-scale test apparatus under conditions similar to those experienced in a real CFB boiler at the Department of Thermal Machinery at the Czestochowa University of Technology. The apparatus consists of a combustion chamber (riser), a down-comer, a cyclone, and a loop-seal, and has been described in detail in references [21–25]. In this section, only the experimental conditions are briefly mentioned.

Mixtures of O<sub>2</sub> and CO<sub>2</sub> mixtures from gas cylinders were used to simulate the oxy-fuel combustion conditions. The concentrations of oxygen varied from 21% to 40%vol. All tests were carried out at a temperature of 850 °C without the addition of a sorbent for the capture of SO<sub>2</sub>.

A 0.5 g sample of fuel was entered into the combustion chamber and burnt in the fluidized bed consisting of silica sand and ash particles. All fuel samples were prepared as pellets. The technique of pellets preparation is described in papers [23,24].

The composition of flue gases during the air and oxy-fuel combustion was measured by a portable FTIR spectrometer (Gaset DX-4000) while O<sub>2</sub> was measured using a zirconium sensor analyzer (AMS Oxitrace). The volume fractions of NO, NO<sub>2</sub>, N<sub>2</sub>O, SO<sub>2</sub>, CO, and other compounds were recorded every three seconds. The maximum error was less than 2%. Each experiment was repeated thrice minimum to guarantee a relative standard deviation below 5%.

In this study, temperature (850 °C), the superficial gas velocity (5 m/s), the mass of the fuel sample (0.5 g), and the mass of the inert material (0.3 kg) were constant. Only fuels and oxidizing atmospheres were different. Information collected during tests with a single fuel particle is sufficient to compare the influence of the combustion atmosphere on pollutant emissions. Our transient experiments with single biomass particles allowed us to collect data on instantaneous concentrations of emitted pollutants. These results are useful in assessing the behavior of biomass fuels in different combustion systems.

### 3. Results and Discussion

In this study, compositions of flue gases (NO<sub>x</sub>, SO<sub>2</sub>, and CO) during the air- and oxy-combustion of energy crops and reference biomass fuels and bituminous coal are reported and discussed.

#### 3.1. Composition of Flue Gases during Air-Combustion

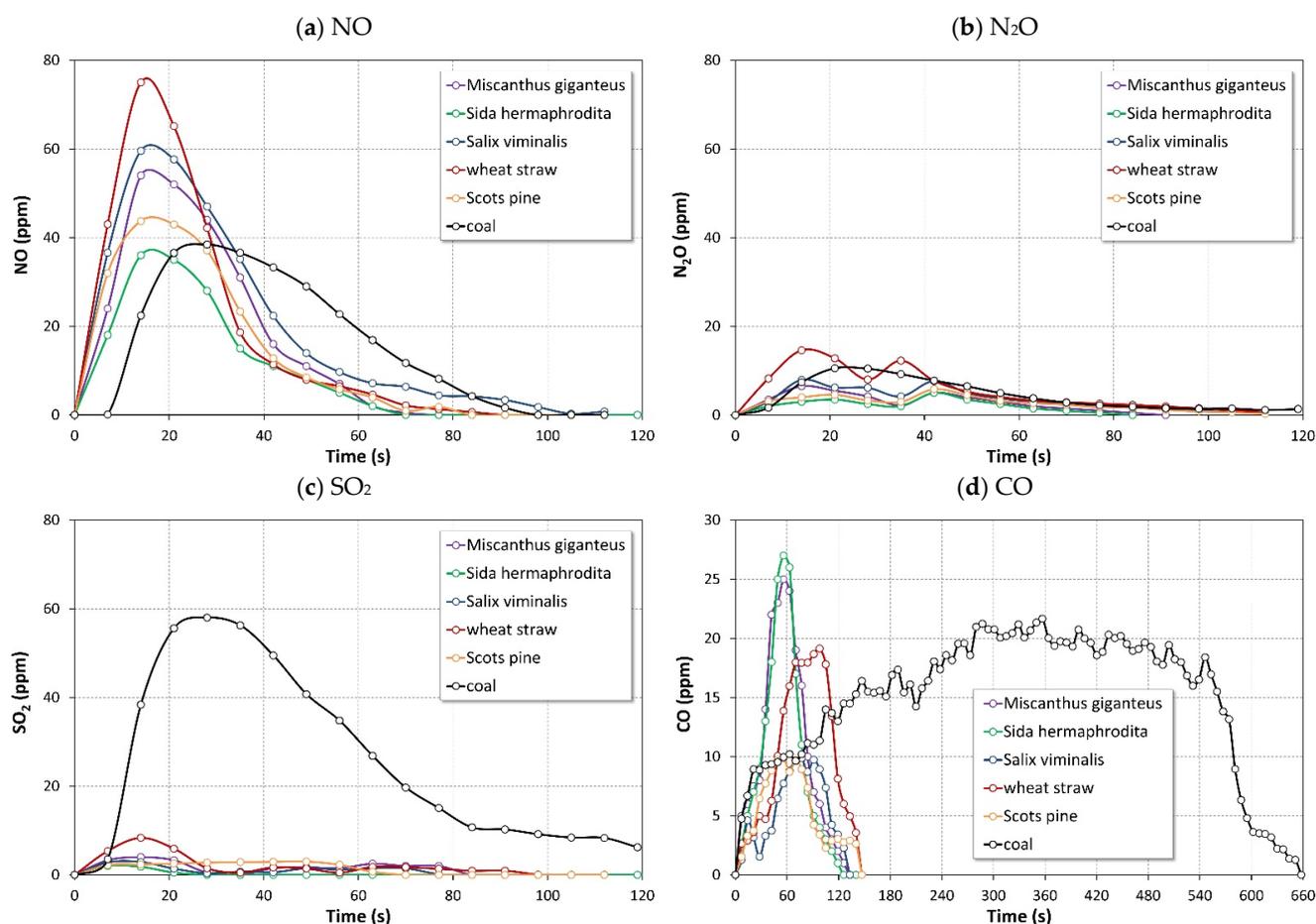
The effect of the fuel type on the instantaneous concentrations of NO, N<sub>2</sub>O, SO<sub>2</sub>, and CO during combustion in air is shown in Figure 1. The shapes of NO curves (Figure 1a) are similar for all energy crops, and their numerical values depend on the content of nitrogen and VM in the fuel. The highest emission of NO, approximately 60 ppm, was recorded for *Salix viminalis*. On the other hand, the lowest NO emission among all tested fuels was measured for *Sida hermaphrodita*, which is associated with the lowest nitrogen content in this fuel (see Table 2).

Emissions of N<sub>2</sub>O (Figure 1b) were much lower than emissions of NO. Two peaks of N<sub>2</sub>O concentration were observed during the combustion of biomass fuels. The first peak was seen during the combustion of VM and the second during the combustion of remaining char. Emissions of N<sub>2</sub>O for energy crops did not exceed 8 ppm. The highest emissions of N<sub>2</sub>O were recorded for wheat straw and the lowest for *Sida hermaphrodita*.

Nitrogen dioxide (NO<sub>2</sub>) concentrations were below the detection limit for all tested fuels.

The concentration of SO<sub>2</sub> (Figure 1c) from the combustion of coal was much higher than that from the combustion of biomass. The highest value of the SO<sub>2</sub> instantaneous concentration was observed during the combustion of VM, and it was approximately 58 ppm. The highest SO<sub>2</sub> emissions for biomass fuels were detected for wheat straw. Concentrations of SO<sub>2</sub> for energy crops were below 4 ppm. The lowest SO<sub>2</sub> emission among all tested fuels was measured for *Sida hermaphrodita*, which is associated with the lowest sulphur content in this fuel (see Table 2).

Concentrations of CO in the flue gas during conventional combustion are shown in Figure 1d. The highest values of CO emissions were noticed during the char combustion, both for coal and biomass. The highest values of the instantaneous concentrations of CO were 27 ppm and 25 ppm for *Sida hermaphrodita* and *Miscanthus giganteus*, respectively. The release of CO lasted for 120–140 s for biomass, and 650 s for coal. Overall CO emissions were much higher for bituminous coal, which is associated with a higher content of carbon.

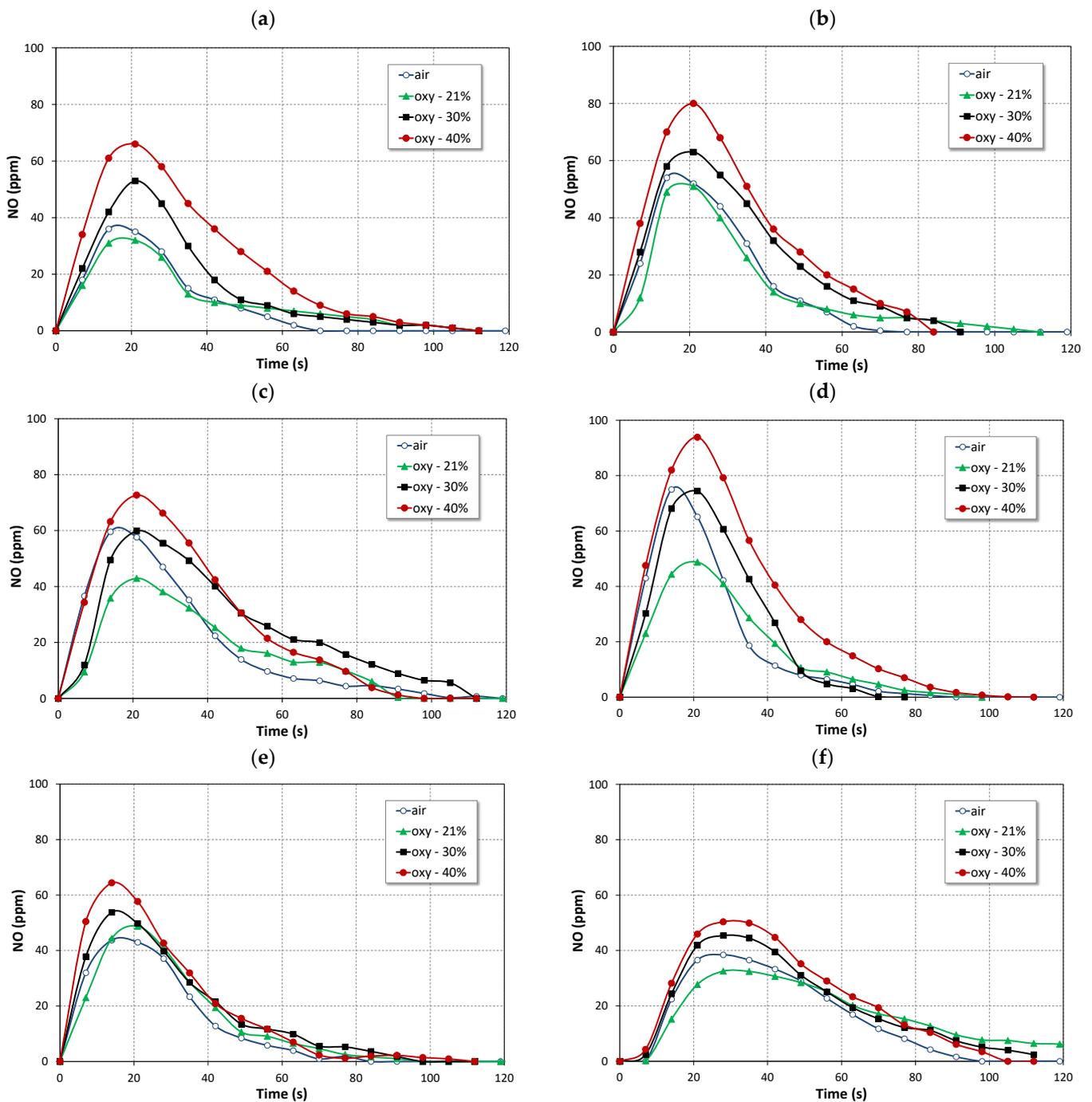


**Figure 1.** Effect of fuel type on instantaneous concentration of pollutants during air-combustion.

### 3.2. Composition of Flue Gases during Oxy-Combustion

The effect of the oxidizing atmosphere on the instantaneous concentrations of NO for all tested fuels is shown in Figure 2. The oxidizing atmosphere and type of fuel have a large influence on NO emissions. Concentrations of NO increased with increasing initial O<sub>2</sub> content in the O<sub>2</sub>/CO<sub>2</sub> mixture. The highest values of NO concentrations were measured in the 40%O<sub>2</sub>/60%CO<sub>2</sub> atmosphere and the lowest in the 21%O<sub>2</sub>/79%CO<sub>2</sub> mixture. This is associated with the temperature of fuel particles [21]. A higher temperature of the fuel sample causes higher emissions of NO [12]. Additionally, a higher concentration of O<sub>2</sub> in the combustion chamber enhances the combustion of VM and leads to a rise in NO formation. This finding has been also confirmed by the results presented in previous papers [26,27].

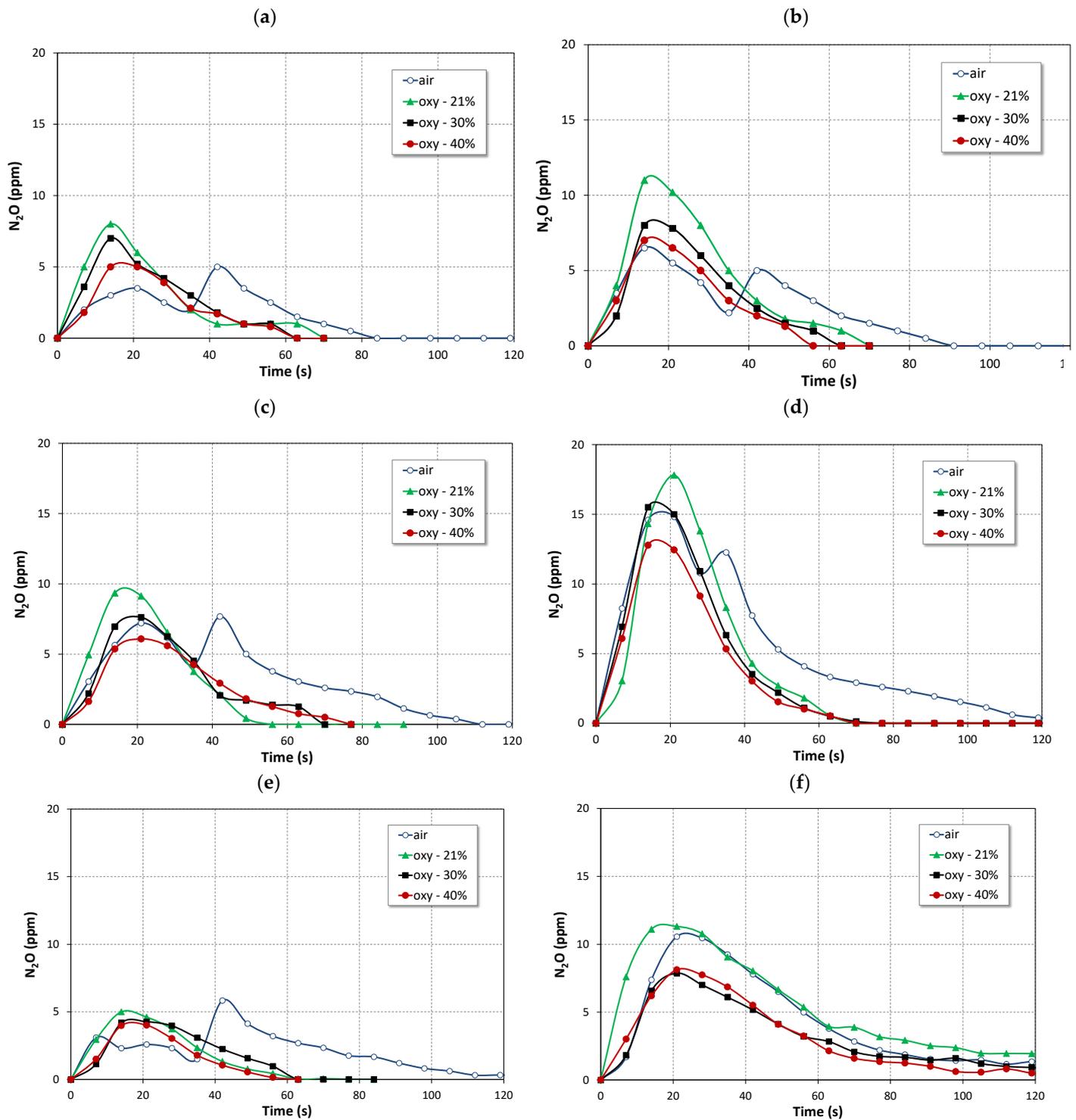
The highest NO concentrations were observed in the combustion of VM, especially for biomass fuels. The highest values of the instantaneous NO emissions in the oxy-combustion of energy crops were detected for *Miscanthus giganteus* and the lowest for *Sida hermaphrodita*. During combustion of *Miscanthus giganteus* in the 40%O<sub>2</sub>/60%CO<sub>2</sub> atmosphere, the highest value of the NO concentration was 80 ppm, and it was approximately 30 ppm higher than that in the 21%O<sub>2</sub>/79%CO<sub>2</sub> atmosphere (Figure 2b). The maximum amount of NO for *Sida hermaphrodita* and wheat straw was approximately twice as high in the 40% O<sub>2</sub> mixture than that in the 21% O<sub>2</sub> mixture. The highest instantaneous concentrations of NO during air-combustion were similar to those in the 30%O<sub>2</sub>/70%CO<sub>2</sub> atmosphere for *Salix viminalis* and wheat straw. In other cases, combustion in the 30% O<sub>2</sub> mixture caused higher emissions of NO. The lowest emissions of NO during oxy-combustion were detected for the reference coal due to the lowest VM content in this fuel.



**Figure 2.** Effect of oxidizing atmosphere on instantaneous concentrations of NO for all tested fuels. (a) *Sida hemaphrodita*. (b) *Miscanthus giganteus*. (c) *Salix viminalis*. (d) Wheat straw [12]. (e) Scots pine [12]. (f) Bituminous coal [12].

Emissions of  $N_2O$  in the air- and oxy-combustion for all tested fuels are shown in Figure 3. Nitrous oxide concentrations were much lower in comparison with NO emissions.  $N_2O$  was formed at the same time as NO, which suggests that the formation of  $N_2O$  was proceeded by the direct oxidation of fuel-N instead of the reduction of NO [12]. The shapes of  $N_2O$  curves in air combustion are bimodal. The highest  $N_2O$  emissions were detected in the combustion of VM in the 21% $O_2$ /79% $CO_2$  atmosphere. The highest value of  $N_2O$  concentration for energy crops, approximately 11 ppm, was observed for the combustion of *Miscanthus giganteus* (Figure 3b). As the oxygen concentration in the  $O_2/CO_2$  atmosphere

increased,  $N_2O$  concentrations decreased. The lowest  $N_2O$  emissions (below 8 ppm) for energy crops were observed for the combustion of *Sida hermaphrodita* both for air and oxy-combustion.



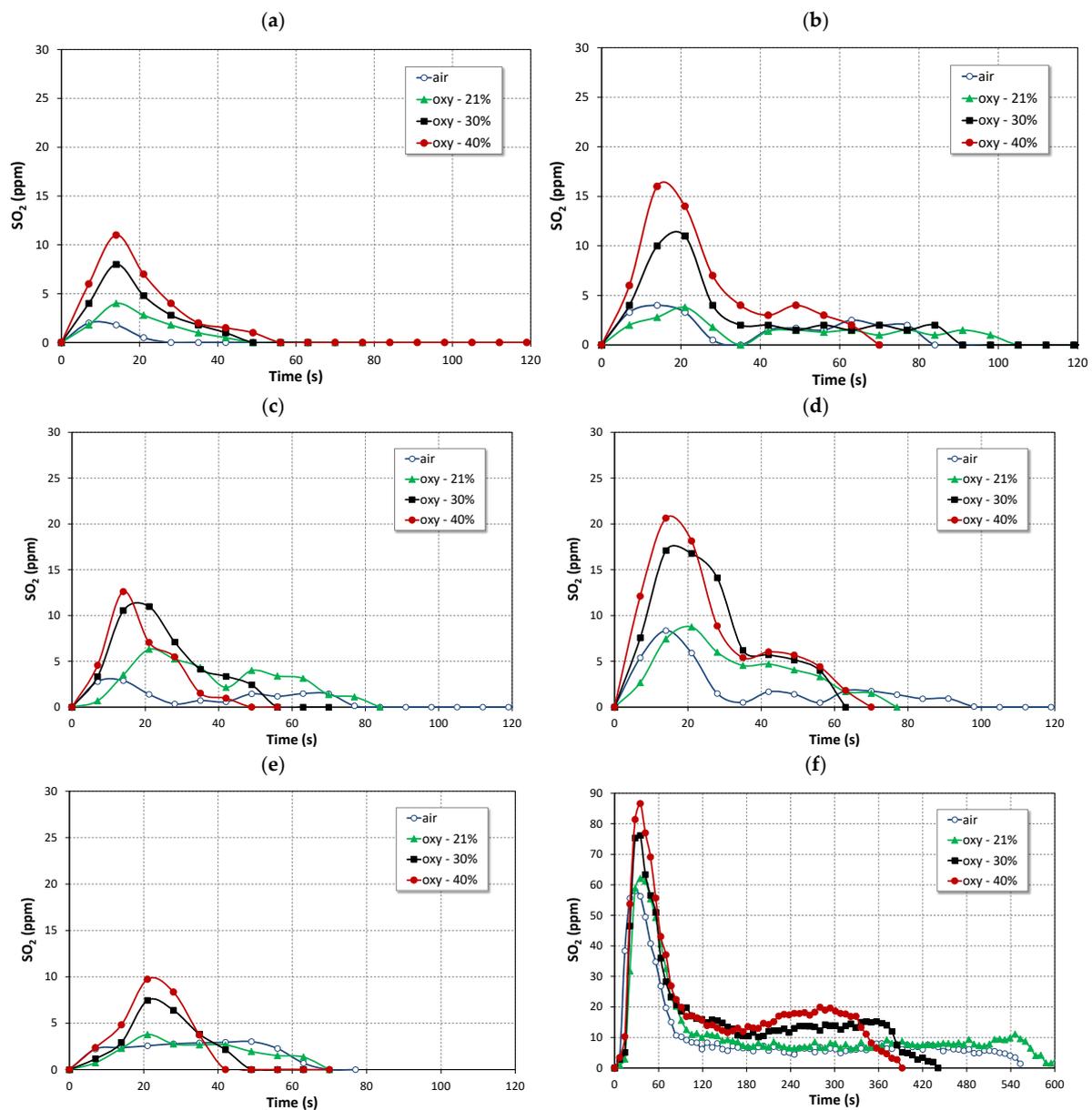
**Figure 3.** Effect of oxidizing atmosphere on instantaneous concentrations of  $N_2O$  for all tested fuels. (a) *Sida hermaphrodita*. (b) *Miscanthus giganteus*. (c) *Salix viminalis*. (d) Wheat straw [12]. (e) Scots pine [12]. (f) Bituminous coal [12].

HCN and  $NH_3$  are the most important precursors of  $NO_x$  formation. Higher concentrations of HCN were generated in oxy-fuel combustion. The highest emissions of HCN

were observed in 21%O<sub>2</sub>/79%CO<sub>2</sub>, mainly in the combustion of char. However, the highest values of the instantaneous HCN concentrations did not exceed 6 ppm for both energy crops and reference fuels. Analogous findings were reported in our previous study [23] and in reference [28]. The maximum ammonia emissions were observed during combustion in the mixture of 30%O<sub>2</sub> and 70%CO<sub>2</sub>, but the values of the instantaneous concentrations were very low, below 3 ppm, for all samples. Large amounts of CO<sub>2</sub> inhibited the oxidation of NH<sub>3</sub> and HCN to NO<sub>x</sub> [12].

Emissions of NO<sub>2</sub> were noted during the combustion of char only in the 21%O<sub>2</sub>/79%CO<sub>2</sub> mixture. The maximum values of NO<sub>2</sub> concentration did not exceed 3 ppm for energy plants. This observation is consistent with the results obtained in references [25,28].

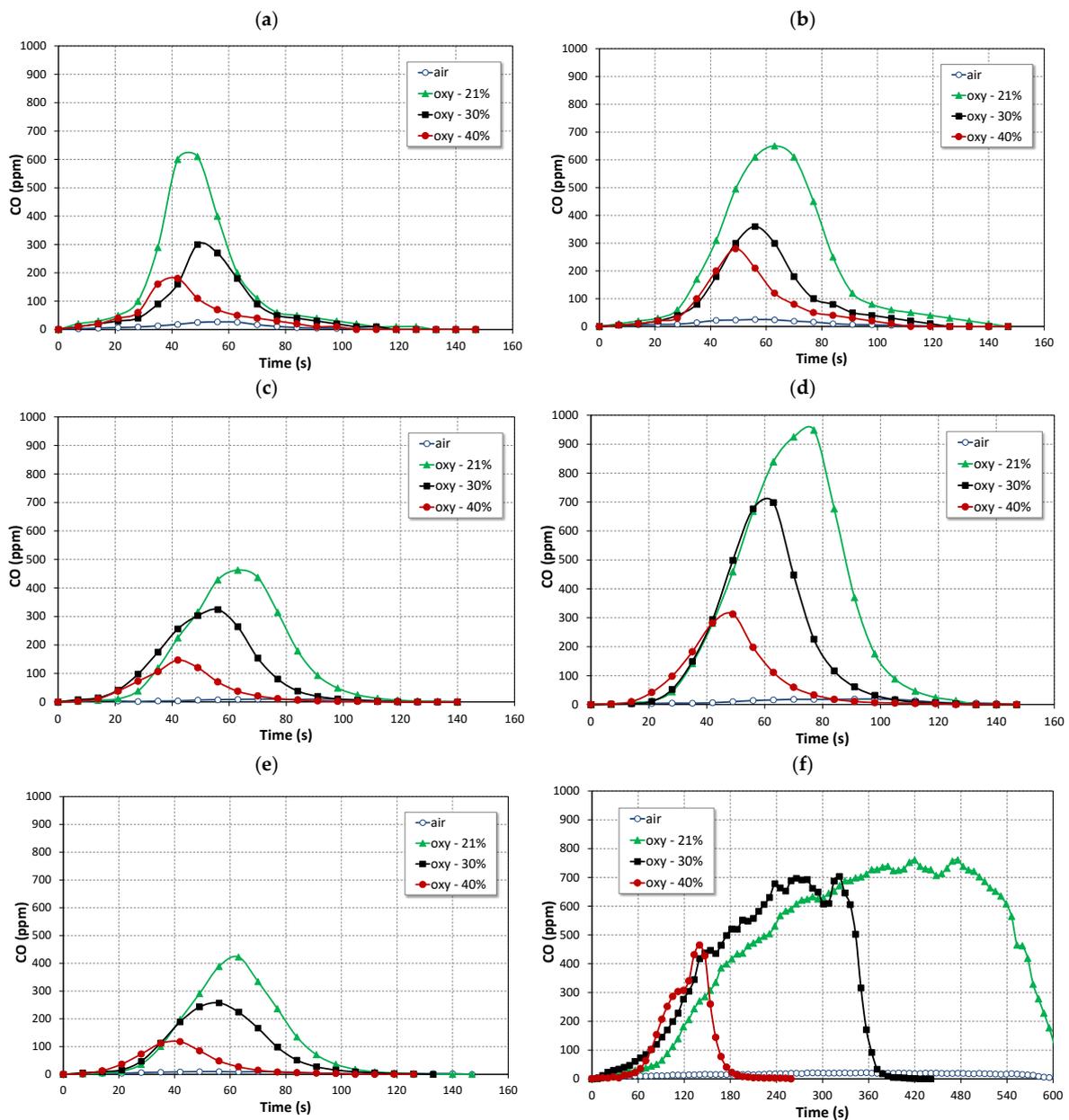
Figure 4 shows the influence of the oxidizing atmosphere on concentrations of SO<sub>2</sub> for energy crops and reference fuels.



**Figure 4.** Effect of oxidizing atmosphere on instantaneous concentrations of SO<sub>2</sub> for all tested fuels. (a) *Sida hemaphrodita*. (b) *Miscanthus giganteus*. (c) *Salix viminalis*. (d) Wheat straw [12]. (e) Scots pine [12]. (f) Bituminous coal [12].

The amount of  $\text{SO}_2$  formed during oxy-combustion of energy crops was much lower than that for the reference coal. For all tested samples, the maximum values of  $\text{SO}_2$  were detected for the VM combustion period. An increase in  $\text{SO}_2$  emissions was caused by an increase in the inlet concentration of  $\text{O}_2$ . The maximum value of  $\text{SO}_2$  for energy crops was 16 ppm for *Miscanthus giganteus* in the oxy-40% atmosphere. However, the highest  $\text{SO}_2$  concentration in the oxy-40% atmosphere was 68 ppm for coal. Oxy-combustion of *Miscanthus giganteus* in the mixture of 40%  $\text{O}_2$  resulted in three times as high emissions of  $\text{SO}_2$  than that in the mixture of 21%  $\text{O}_2$ . Comparable results for biomass and fossil fuels are reported in reference [28].

The effect of the oxidizing atmosphere on concentrations of CO during the combustion of energy crops and reference fuels is shown in Figure 5.



**Figure 5.** Effect of oxidizing atmosphere on instantaneous concentrations of CO for all tested fuels. (a) *Sida hemaphrodita*. (b) *Miscanthus giganteus*. (c) *Salix viminalis*. (d) Wheat straw [12]. (e) Scots pine [12]. (f) Bituminous coal [12].

The charts show the great influence of the oxidizing atmosphere on the amount of CO in exhaust gas. The oxy-combustion of energy crops in the mixture of 21% O<sub>2</sub> and 79 CO<sub>2</sub> caused a drastic increase in CO emissions compared to conventional combustion. The maximum values of the instantaneous CO concentrations in the oxy-21% atmosphere for energy crops were 650 ppm and 610 ppm, for *Miscanthus giganteus* and *Sida hermaphrodita*, respectively. This phenomenon could be described by the impact of the following reactions [12,28]:



The first reaction, called Boudouard's reaction, appears to be predominant in the conversion of carbon monoxide under characteristic conditions for fluidized combustion [12,28]. The amount of CO in the flue gases decreased with an increase in the initial concentration of O<sub>2</sub>. During combustion in the mixture of 40% O<sub>2</sub> and 60% CO<sub>2</sub>, the maximum values of CO concentrations were thrice lower for *Sida hermaphrodita* and *Salix viminalis* than those in the oxy-21% mixture. Similar trends for biomass fuels were reported in references [25,28].

#### 4. Conclusions

Three energy crops and reference fuels (agricultural and woody biomass and bituminous coal) were combusted in a bench-scale CFB, and the effect of the oxidizing atmosphere and fuel type on the composition of flue gases was studied. The most important conclusions from our study are as follows:

1. *Sida hermaphrodita* is the most environmentally friendly energy crop for both air and oxy-CFB combustion.
2. The instantaneous emissions of NO, N<sub>2</sub>O, CO, and SO<sub>2</sub> for the combustion of energy crops in O<sub>2</sub>/CO<sub>2</sub> environments are lower than those for combustion of agricultural biomass (wheat straw) and higher than those for combustion of woody biomass (Scots pine).
3. The instantaneous NO emissions during the combustion of energy crops in all atmospheres are higher than those of hard coal, which is due to the much higher content of volatile matter in renewable fuels.
4. The oxidation of volatile nitrogen compounds is behind high emissions of NO<sub>x</sub> from energy crops burned in air and O<sub>2</sub>/CO<sub>2</sub> mixtures.
5. The highest values of the instantaneous concentrations of NO and N<sub>2</sub>O for energy crops during oxy-combustion are observed for *Miscanthus giganteus* and during air-combustion for *Salix viminalis*.
6. Combustion of energy crops in the oxy-21% atmosphere causes the lowest NO emissions and the highest N<sub>2</sub>O emissions, which is associated with a lower temperature of burning fuel samples.
7. Emissions of CO for the combustion of energy crops in all atmospheres are much lower than those for the combustion of reference coal. It can be attributed to the higher content of carbon in fossil fuel.
8. Combustion of energy crops in the mixture of 21%O<sub>2</sub> and 79%CO<sub>2</sub> results in a very large increase in CO concentrations in the exhaust gas compared to conventional combustion.
9. As the initial concentration of oxygen in the O<sub>2</sub>/CO<sub>2</sub> mixture increases, emissions of SO<sub>2</sub> and NO increase even though emissions of CO and N<sub>2</sub>O decrease for energy crops and reference fuels.
10. Considering all emitted pollutants, the optimal atmosphere for the oxy-CFB combustion of energy crops should contain oxygen in the range of 21–30%vol.

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