

Co-firing coal and biomass blends and their influence on the post-combustion CO₂ capture installation

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Abstract. Co-firing of biomass with coal for energy production is a well-known technology and plays an important role in the electricity sector. The post-combustion capture integrated with biomass-fired power plants (Bio-CCS) seems to be a new alternative for reducing greenhouse gas emissions.

This study refers to the best known and advanced technology for post-combustion CO₂ capture (PCC) based on a chemical absorption in monoethanolamine (MEA). The co-firing of hard coal with four types of biomass was investigated using a laboratory fixed bed reactor system. The comparison of gaseous products emitted from the combustion of coal and different biomass blends were determined using gas chromatography.

Research proved that co-firing of biomass in fossil fuel power plants is beneficial for PCC process. It may also reduce the corrosion of CO₂ capture installation. The oxygen concentration in the flue gases from hard coal combustion was comparable with the respective value for a fuel blend of biomass content of 20% w/w. It was also noted that an increase in biomass content in a sample from 20 to 40 % w/w increased the concentration of oxygen in the flue gas streams. However, this concentration should not have a significant impact on the rate of amine oxidative degradation.

1 Introduction

Combustion of biomass and coal for power production helps to reduce greenhouse gas (GHG) emissions from the existing coal-fired power plants. Carbon dioxide, methane, nitrous oxide and perfluorocarbons are the main anthropogenic sources of GHG. For the electricity sector, co-firing of biomass with fossil fuels has a positive impact on CO₂ reduction since it is counted as neutral. Biomass has quite different chemical composition in comparison with hard coal, that is why burning it with coal blends also reduces NO_x and SO_x levels. Co-firing has a positive influence on the environment and economy depending on the chemical composition of the biomass used [1]. It minimizes the amount of waste, soil and water pollution and may also reduce fuel costs.

Recent studies [2, 3] have shown that integrated CO₂ capture and storage (CCS) with biomass-fired power plant is also considered. Enforcing CCS in combination with biomass co-firing power plants provides a further possibility of reducing CO₂ emissions for the electricity [4]. Nowadays, there is an on-going discussion about positive and negative aspects of incorporating CCS into biomass-fired power plants. One of the reasons behind current studies is to find the answer to the following question: “Would the incorporated CCS with biomass fired power plant be an attractive option to further

minimalize the cost of CO₂ and generate an additional revenue as CO₂ credit?” [3].

In 2014, greenhouse gas emissions were reduced by 22.9 % compared with the ones in 1990 in 28 Member States of the European Union (EU-28). The overall highest GHG emissions of the EU-28 were in Germany (21.9%) and the lowest in Malta 0.08%. Poland was 24th in terms of the amount of GHG emissions (8.64%) and it overtook Italy (9.69%), France (10.76%), the United Kingdom (12.6%) and aforementioned Germany. The greenhouse gas emissions in Poland in 2014 were reduced by 19.3% when compared with 1990 [5]. After the recent ratification, the EU target is to reduce GHG levels by at least 20% until 2020 and 40% until 2030. The proposed legislation includes tightening the EU Emissions Trading System (ETS) for the period after 2020.

At present, CO₂ fees and ETS credit to cover its CO₂ emissions allows EU-28 to stabilize energy price. From 2008 to 2014, the cost of unit CO₂ emission increased by 21% and stayed at the same level for the last two years [6]. However, calculation of CO₂ emissions and Green Certificates shows that the price may increase significantly in the future. One of the theoretical price scenarios of the U.S. Environmental Protection Agency’s (EPA) set Low, Mid, and High case forecasts for CO₂ prices. The CO₂ price per ton according to forecast will increase from \$15 to \$25 in 2022, from \$21 to \$43 in 2030 and from \$36 to \$110 in 2050. In order to avoid paying such high fees, it seems to be effective to carry

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out further research on CCS incorporated into biofuels. The IEA confirms that the cost of reducing GHG without CCS would be over 70% [2]. The combination of CO₂ capture with sustainable biomass conversion (Bio-CCS) seems to be the only large scale and the most promising technology that can remove CO₂ from the atmosphere. It has already been raised in the discussion over the EU Energy Roadmap 2050.

It was presented that currently carbon capture and storage (CCS) is at a phase of demonstration but in the future it could be applied to various energy plants, especially incorporating co-firing or co-gasification of sustainable biomass feedstock, or 100% biomass energy plants, biofuel production facilities or bio refineries.

The aim of this study is to analyse and describe the co-firing process of biomass with coal and to present its influence on capturing CO₂ from the flue gases by chemical absorption.

2 Biomass combustion with CO₂ capture

Combustion of biomass with fossil fuels has a good influence on the environment and the economy of power generation. Carbon dioxide is emitted into the atmosphere during biomass fuels burning, yet CO₂ is also absorbed during its growth thus the combustion of biomass is considered to be CO₂-neutral.

The main components of biomass are carbon, oxygen and hydrogen but they also contain nitrogen, sulphur and small amounts of chlorides. Biomass fuels may differ from each other and the composition of flue gas depends on the type of biomass during combustion. The main component of ash is Ca, K, Si, Mg, Mn, Al, Fe, P, Na and Zn. Due to the fact that biomass fuels have little concentration of sulphur in comparison to hard coal they emit lower amounts of SO₂ when they are fired and co-fired as blends. Co-firing of biomass with coal allows us also to pay less carbon tax due to lower CO₂ emission [4].

The IEA Greenhouse Gas R&D Programme (IEAGHG) [3] estimated the potential advantage of biomass fired power plant with post-combustion capture of CO₂. The study focused on techno-economic evaluation of different cases of biomass combustion and biomass co-firing power plants with and without CO₂ capture. The economic analysis of electric power production was based on the following cost: total investment, coal and biomass, Green Certificates and the ETS. The analysis showed that in case the ETS value rises according to the forecasts from 2030 [7], the existing biomass-fired or co-fired power plant with CO₂ capture will be comparable to power plants without CO₂ capture.

The use of biomass for energy production and conversion to other products plays an important role in Bio-CCS technology nowadays. Bio-CCS is used in many different facilities from the power, industrial and fuel sectors. It delivers power and heat, helps the atmospheric carbon dioxide recycling and does not contribute to negative emissions technologies (NETs).

Moreover, biomass allows thermo-chemical and biochemical production of biofuels such as biomethane, bioethane or lignocellulosis.

The IEAGHG studies [8] estimated a technical and economic potential of Bio-CCS about 10 GtCO₂/yr in 2050. The following Bio-CCS routes included: biomass integrated gasification combined cycle with CCS (BIGCC-CCS), circulating fluidised bed combustion with CCS (CFB-CCS), integrated gasification combined cycle with CCS (IGCC-CCS), and pulverised coal fired power plant with CCS (PC-CCS). Post-combustion capture with chemical absorption is very extended technology for removing CO₂ from industrial flue gases. The most popular absorbent used in this process is aqueous solution of monoethanolamine (MEA). This technology is well-known and advanced but requires high regeneration energy. The MEA-based CO₂ capture presents also many problems such as equipment corrosion and amine degradation [9].

Oxygen and impurities contained in flue gas: acid gases (SO_x, NO_x, H₂S), heavy metals, dust particulates [10] as well as hydrocarbons [11] can react with the solvent and lead to many degradation products. Oxidative degradation is the dominant type of amine degradation in the post-combustion capture process (PCC) based on MEA [12]. It mainly takes place in the absorber section where oxygen concentration is more than 5%_{vol} [13].

The most common amine degradation products are ammonia, formaldehyde and carboxylic acids such as acetic or oxalic one [14, 15]. All of them reduce the pH of amine solution and lead to equipment corrosion or technological problems like amine losses or foaming [16]. Oxygen is also well-known source of amine oxidative degradation products [17, 18, 19]. The reactions of MEA and an organic or inorganic acids lead to formation the Heat Stable Amine Salts (HSAS) [20, 21]. According to [22] even a small amount of HSS may lead to amine degradation so the concentration of them in MEA solution should not be more than 500 ppm. To avoid amine degradation and losing expensive solvent the concentration of SO_x in the flue gases should not exceed 10 ppm [23].

The study of flue gas composition during biomass combustion and co-firing has not been widely published yet, but may show the advantages and disadvantages of the Bio-CCS and its influence on CO₂ post-combustion capture system.

Although no post-combustion capture units have been installed yet at full scale, large demonstration projects based on amine scrubbing are being prepared. Combining biomass with CCS technologies (Bio-CCS), gasification for power production and conversion to biofuels are the promising technology routes in the power and transport sectors up to 2030 and 2050.

3 Material and methods

3.1 Material

One Polish hard coal (samples nos. C) provided by Ziemowit coal mine and the following biomass samples:

Helianthus Tuberosus, *Salix Viminalis*, olive residues (*Olea europaea.*), and *Sida Hermaphrodita* – denoted as samples nos. CB1, CB2, CB3 and CB4, respectively were used in the study presented. A sample of 10g of hard coal or its blends were prepared in accordance with the PN-G-04506:1996 standard. Prior to the analysis, the fuels were grounded using mill with a particle size between 1 and 3 mm and dried in the oven at 105°C for 24h in order to remove moisture.

The physico-chemical parameters included: total moisture, ash, volatiles and elemental composition such as total sulphur, carbon, hydrogen, nitrogen and oxygen were determined by the accredited Laboratory of the Department of Solid Fuels Quality Assessment of the Central Mining Institute. The results were shown in Table 1. The elemental composition of coal and biomass was the same but biomass contained more oxygen, total moisture, volatiles, hydrogen and nitrogen compared to coal samples. The amount of biomass total sulfur was almost four times lower than a coal sample.

Table 1. Physical and chemical characteristics of the studied fuels.

Parameter	Fuel sample				
	C	B1	B2	B3	B4
Moisture content, W^a , %wt	11.49	8.37	4.74	7.54	8.76
Ash content, A^a , % wt	5.42	5.93	1.51	4.11	2.63
Volatiles content, V^a , % wt	32.31	66.81	73.16	77.50	71.47
Total sulphur content, S_t^a , % wt	1.32	0.26	0.05	0.05	0.04
Carbon content, C_t^a , % wt	64.90	46.16	52.19	49.93	47.18
Hydrogen content, H_t^a , % wt	3.63	5.55	6.22	6.21	5.68
Nitrogen content, N^a , % wt	0.96	1.71	<LD	1.59	<LD
Oxygen content, O^a , % wt	13.24	32.28	35.29	42.04	35.73

C-hard coal, Biomass: B1-*Helianthus Tuberosus*, B2-*Salix Viminalis*, B3-*Olea europaea*, B4-*Sida Hermaphrodita*; ^a- analytical state, <LD-below the limit of detection.

A 10 g sample of hard coal and its biomass blends was placed at the bottom of the reactor at a ratio of 10, 20, 30 and 40 % w/w for B1 and 20 % w/w for B2, B3 and B4 respectively.

3.2 Methods

The tests were conducted in the laboratory scale fixed bed reactor set-up of the Laboratory of Advanced Energy Technologies, the Department of Energy Saving and Air Protection of the Central Mining Institute [24, 25] (Fig. 1).

The compositions of dry and clean samples of synthesis gas were analysed automatically via the two-channel gas chromatograph, Agilent 3000A included in two thermal conductivity detectors (TDC). The PLOT U

column with TCD1A detector was applied for separation of CO₂, C₂H₆ and H₂S. The MS5A PLOT column with TCD2A detector was applied for separation of H₂, O₂, N₂, CH₄ and CO. Helium and argon were used as the carrier gases in two columns, respectively.

To protect the sample against an entrainment by the gaseous media and for the better temperature distribution, coal and coal blends samples was placed at the bottom of the reactor between quartz wool.

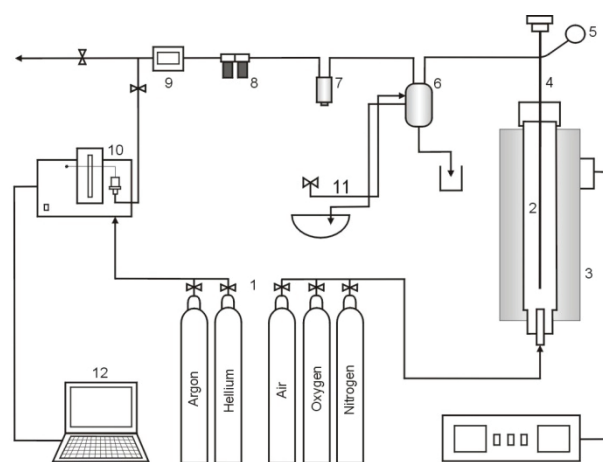


Fig.1. The laboratory-scale fixed bed reactor installation for coal combustion and gasification: 1-gases inlets, 2-fixed bed reactor, 3-resistance furnace, 4-thermocouple, 5-manometer, 6- water trap,7-solid particles filter, 8-gas dehumidifier, 9-mass flow meter, 10-gas chromatograph, 11- gas cooling water system, 12-computer.

The reactor was heated up at a rate of 1.33°C/s to the temperature of 900°C in the air atmosphere and with flow $(90\pm 6)\times 10^{-3} \text{ cm s}^{-1}$.

The amount of air required for the complete combustion of the selected carbon sample and its biomass blends was calculated stoichiometrically.

The oxygen concentration is closely related to the flow rate of air supplied to the coal boiler and the excess air fuel ratio (AFR). The value of the excess AFR depends primarily on the type of fuel combusted, the combustion process as well as the design of the boiler. Changing the excess AFR results in the amount of gas products combustion. Insufficient amount of air causes the formation of carbon monoxide and hydrocarbon, whereas excess of air leads to nitrogen oxides emission. For the total combustion, the tested samples of the AFR ratio was within the range 1.3-1.4.

Before the gas composition was analysed with the GC, the outlet gas was cooled and dried from liquid products in the water trap. The amount of gaseous products mixture (O₂, H₂, CO, CO₂, CH₄, C₂H₆, H₂S) was measured with the mass flow meter. Time-interval length resulting from the settings of the chromatographic method was 240s. The number of time intervals during the experiment for each sample was 16.

The volume values of the individual gas components of in the co-firing process of coal with biomass V_c was calculated from the equation (1):

$$V_c = \sum_{i=1}^n \frac{c_{ci} F_i}{100} t_i \quad (1)$$

where:

V_c – value of i_{th} gas component obtained during the experiment, m^3

C_{ci} – volume concentration of c_{th} gas component in i_{th} time interval, % vol.

F_i – gas flow rate in i_{th} time interval, $m^3 s^{-1}$

t_i – length of i_{th} time interval, s

n – number of time intervals during the experiment.

4 RESULTS AND DISCUSSION

4.1 Influence of biomass type on gaseous product in co-firing process

The temperature inside the reactor measured for each tested fuel sample was comparable and was within the range of 70-930°C. The first flue-gas samples were determined 240 seconds after the start of the combustion process and contained significant amounts of airborne oxygen. Therefore, for a comparative analysis of flue-gas composition, a time interval of 720-2880s was adopted, corresponding to the combustion temperature of about 250-850°C. The temperature increase during the experiment for each examined sample was comparable as shown in Fig. 2.

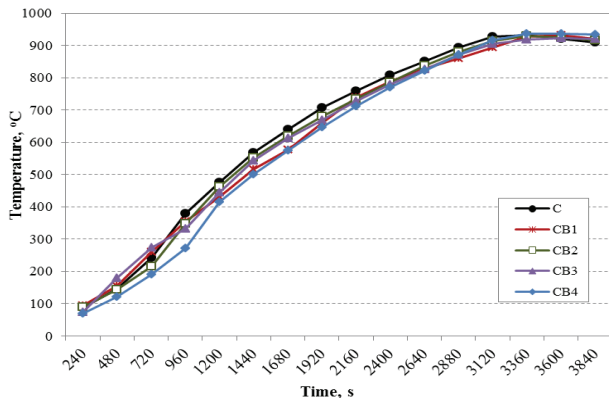


Fig.2. Temperature increase inside the reactor during the experiment for the tested fuel samples.

The main components of the gases released during the co-firing of coal and biomass blends were CO_2 , CO , O_2 and N_2 . There was also less C_2H_6 and H_2 , H_2S and other components, i.e. hydrocarbons, sulphur and nitrogen oxides. The measured maximum concentration of CO_2 for the pure carbon sample during the tested time interval was up to 16.8% vol., and it was close to the maximum concentration of CO_2 emitted during combustion of coal blends with biomass CB1, CB2, CB3 and CB4, that is 15.4% vol., 17.0% vol., 18.2% vol. and 16.8% vol., respectively. The change in CO_2 concentration during the experiment is shown in Fig. 3. In the CO_2 capture process using post-combustion method, the oxygen content in the flue gas has the greatest impact on the MEA degradation process.

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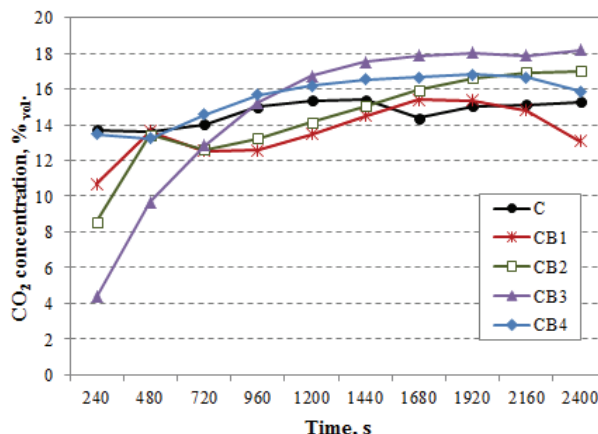


Fig. 3. Change in carbon dioxide concentration over time for the tested fuel samples.

The analysis of oxygen concentration during the experiment showed its slight increase during the combustion of coal and biomass blends in comparison with the coal sample. Most of the oxygen in the range of 250-850°C was obtained for BC3 mixture. It was related to the chemical composition of biomass as well as its ash and moisture contents. As shown in Fig. 4, all biomass blends burned more slowly, and the loss of oxygen was slower.

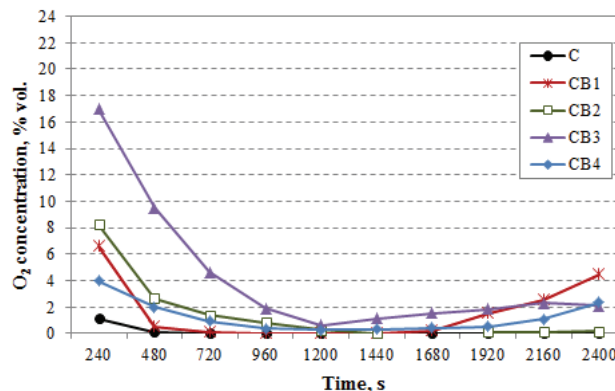


Fig. 4. Change in oxygen concentration over time for the tested fuel samples.

Taking into account the fact that the degradation of the MEA solution in the post-combustion process starts only with the oxygen content in the flue gases above 5% vol., it can be stated that the combustion of the coal-biomass blends will not affect significantly the increase in the rate of amine oxidative degradation of amine solution. The mean concentration of gaseous products, excluding nitrogen, is shown in Fig. 5, and the volume of all gaseous products and the total volume of gas blends V_c calculated from the equation (1) are shown in Table 2.

The analysis showed that methane content in the combusted coal sample was 1.9% vol, and the presence of this component in the gases after combustion of coal and biomass blends was within the range of 1.8-2.5%.

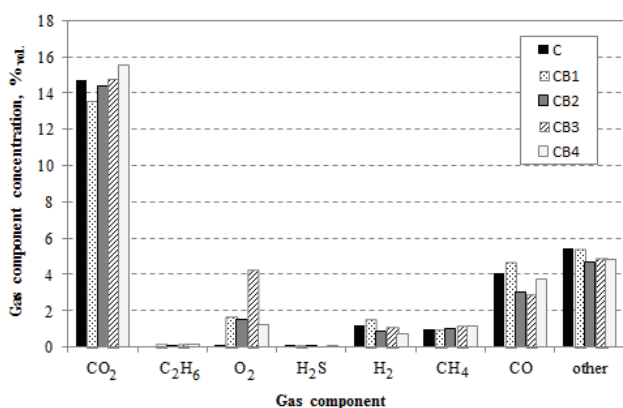


Fig. 5. Average concentration of gas components for the tested coal and biomass blends.

The content of C₂H₆ in all combusted samples was close to zero.

In the combustion processes of solid fuels, its sulphur content is converted into hydrogen sulphide and sulphur oxides. The technology of CO₂ capture process using amine method is very sensitive to the sulphur content in flue gases and the permissible SO_x level should not exceed 10ppm. Because of the low share of sulphur in the chemical composition of biomass compared to the pure carbon sample, the concentration of H₂S in biomass blends flue gas (0.03-0.04% vol.) was three times lower than in the sample of the combusted coal (0.13% vol.). Based on this analysis, it can be stated that the biomass content in the tested fuel blends will also have an impact on the reduction of sulphur oxides whose presence above 10ppm is one of the main causes of MEA degradation.

Table 2. Volume of individual gas components and total volume of gas for the tested coal and biomass blends.

Gas component	Volume, 10 ⁻³ m ³				
	C	CB1	CB2	CB3	CB4
CO ₂	4.99	5.22	4.85	5.41	5.78
C ₂ H ₆	0.01	0.01	0.01	0.02	0.01
O ₂	0.04	0.56	0.49	1.60	0.46
N ₂	25.15	28.45	25.88	27.11	28.04
H ₂ S	0.03	0.00	0.00	0.00	0.00
H ₂	0.42	0.36	0.24	0.2	0.18
CH ₄	0.14	0.11	0.13	0.17	0.18
CO	1.37	1.16	0.95	0.33	0.29
other	1.86	2.05	1.60	1.78	2.24
V _c , m ³	34.00	37.88	34.20	36.60	37.16

Due to the fact that H₂ and CO do not affect amine degradation process, they were not analysed more extensively. It was noted, however, that the presence of biomass in fuel blends reduced their content in flue gases.

For most biomass and coal blends, the increase in the total volume of flue gas was observed. The relative increase in total volume of gas for CB1, CB3 and CB4

samples in relation to pure carbon sample C was 11%, 8% and 9%, respectively. For the sample CB2, the total volume of gas was comparable.

4.2 Influence of biomass concentration on gaseous product in co-firing process

The research results of co-firing the selected coal and biomass type (*Helianthus Tuberosus*) with 20, 30 and 40% w/w are presented in Fig. 6. For a better comparison of the obtained results, only flue gas samples were analysed within the temperature range of 350-850°C when the amount of gaseous products was the highest.

The differences in concentrations of individual gas components were observed regarding the amount of combusted biomass. The average concentration and volume of carbon dioxide for all fuel blends were comparable. It was noted, however, that the share of other gaseous products increased or decreased depending on the biomass concentration. The biggest upward trend has been visible in the case of oxygen. The mean concentration of this component in the analysed time interval was 1.61% vol. for the sample with a biomass content of 20% w/w and 3.10 and 4.98% vol. for the remaining samples respectively. With the increase in the amount of biomass in the sample, the amount of hydrocarbons in the flue gas decreased. The average concentration of CH₄ was 0.96, 0.32 and 0.00% vol. and the concentration of C₂H₆ was 0.10, 0.03 and 0.00% vol., respectively. The downward concentration trend was also observed for H₂S (0.04, 0.02, 0.00% vol.), H₂ (1.50, 0.46, 0.02% vol.), CO (4.70, 1.11, 0.15% vol.) and the remaining gases (5.38, 4.77, 2.25% vol.).

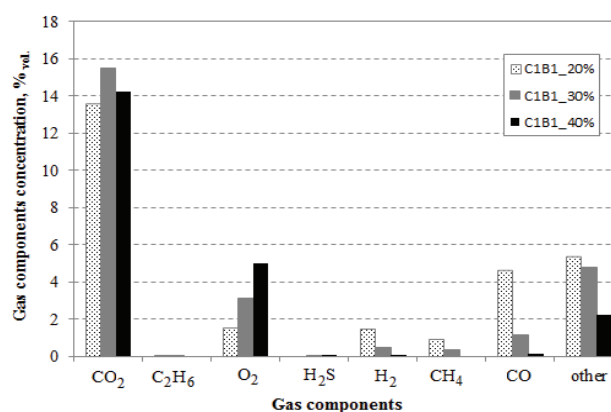


Fig. 6. Average concentration of gas components for the analysed coal and biomass blends.

The volume of the individual gas components and the total volume are shown in Table 3.

As shown in the Table 3, the increase in the percentage share of biomass in the fuel resulted in a decrease in the total volume of the separated gas. Compared to the CB1_20% sample, the volume decrease was 11% for CB1_30% and 18% for CB1_40%.

Table 3. Volume of individual gas components and total volume of gas for the tested coal and biomass blends.

Gas component	Volume, 10 ⁻³ m ³		
	CBI 20%	CBI 30%	CBI 40%
CO ₂	5.22	5.21	4.39
C ₂ H ₆	0.01	0.01	0.00
O ₂	0.56	1.04	1.52
N ₂	28.45	25.06	24,17
H ₂ S	0.00	0.00	0.00
H ₂	0.36	0.15	0.01
CH ₄	0.11	0.11	0.00
CO	1.16	0.37	0.05
other	2.05	1.59	0.07
V _c	37.88	33.60	30.84

5 Conclusions

The conducted studies showed no increased impact of amine solvent degradation on CO₂ capture process using post-combustion method.

During co-firing of coal with biomass energy crops in the amount up to 20% w/w, there is a similar percentage of gaseous products as in the case of pure coal combustion. The oxygen content which contributes to amine degradation is comparable to the various types of biomass and safe for the process to be conducted properly. With an increase in the share of biomass in fuel mixtures, the average oxygen concentration and its volume in the total gas increases proportionately to the amount of biomass. Such flue gas blends subjected to carbon dioxide capture process should be controlled for the risk of oxidative degradation.

The advantage of using an increased amount of biomass is the low emission of sulphur-containing gases as well as the reduced amount of hydrocarbons. All these compounds also have an effect on amine degradation, that is why their reduced content in flue gases has a beneficial effect on the CO₂ capture. The conducted studies also showed that the increase in the share of biomass to coal in the range of 30-40% w/w results in an increase in the total volume of flue gas by 11-18% compared to blends containing 20% w/w of biomass, with similar CO₂ emission.

The results of this research indicate the beneficial effect of the post-combustion method integrated with a biomass-fired power plant.

Acknowledgments

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