# Experimental approach of co-firing and anaerobic fermentation of biomass and coal, and their thermochemical properties

A. E. Cioablă · G. Trif Tordai · P. Rotaru ·
Margareta Socaciu · Ioana Ionel

**Abstract** This article studied two sorts of biomass (corn and beech sawdust) and two varieties of coal (bituminous coal and lignite), which can produce energy using two different technologies: co-firing and anaerobic fermentation in pilot installations, in order to determine the future perspectives of those materials for large scale applications. By thermal analysis, the thermochemical characteristics of biomass (corn and beech sawdust) and of coal (bituminous coal from Jiu Valley and lignite from Oltenia basin) were determined. The co-firing tests have been achieved at a ratio of 15 % biomass, the rest being coal. At biomass–coal co-firing, the $SO_2$, $NO_x$, CO, $CO_2$ and fly ash concentrations in the flue gases is lower than the burning of fossil fuels. In the anaerobic fermentation of biomass, the maximum concentration of methane inside the produced biogas was 50–55 % by volume in the beech sawdust batch and 67–68 % by volume in the corn batch.

**Keywords** Biomass · Biogas · Co-firing · Anaerobic fermentation · Thermal analysis

A. E. Cioablă · G. T. Tordai · I. Ionel
Department of Mechanical Machines, Faculty of Mechanical
Engineering, Technology and Transportation, "Politehnica"
University of Timisoara, 1 Mihai Viteazu Street, 300222
Timisoara, Timis, Romania

P. Rotaru (✉) · M. Socaciu
Department of Physics, Faculty of Exact Sciences, University of
Craiova, 13 AI Cuza Street, 200585 Craiova, Dolj, Romania
e-mail: protaru@central.ucv.ro; petrerotaru@yahoo.com

## Introduction

The interest for using renewable energy resources increased more and more in the past decades. With exception of hydroelectricity and nuclear energy, the major part of all energy is produced from fossil resources such as coal, oil, natural gases and others [1]. Because the known fossil resources are considered almost exhausted and limited for the next centuries, the only chance of the society in developing (industrial, life style and number as well) for the near future remains the renewable resources. Bio-energy plays a vital role in the energy supply of many developing countries [2]; it provides roughly 35 % of energy demand in developing countries [3, 4], raising the world total to 13 % of energy demand [5]. Still, it is the main energy source in a number of countries and regions (e.g. Bhutan 86 %, Nepal 97 %, Asia 16 % and Africa 39 %). The main use of bio-energy in these countries is firewood for cooking and heating [6].

Co-firing of biomass and coal has been demonstrated to be successful in several coal-fired boilers in Europe and the United States. The results were promising—boiler efficiencies have not suffered considerably. However, when converting existing coal-fired boiler for biomass/coal co-firing, the save share of biomass depends on the biomass and coal properties, as well as on the boiler design and must be determined in each particular case.

Under the framework of the general tendencies related to generating clean energy, biogas industry has aroused a particular attention, gradually leaving his basic activities of waste cleanup and treatment and getting involved in energy production. Biogas can be used to generate electricity, heat and biofuels, while the secondary product, the fermentation residue (digestate) can be used as fertilizer. The largest biogas producing countries in the EU are Germany and

UK. These countries produce around 2/3 of EU biogas utilized as energy. In 2009, European primary energy production from biogas has increased with 4.3 % comparing to 2008 [7, 8]. Romania possesses a large potential of biomass, and is expected to make considerable efforts to make benefit of the European knowledge and dissemination of recent technologies in order to use the potential energy accumulated by the biomass [9].

Classic and novel exploitation in energy production of biomass is closely related with availability and existing quantities for the mentioned solid biofuels. Biogas production proves to have an increasing interest in regard to obtain clean energy through biochemical conversion, while co-firing can be applied, with minimum investments, in existing thermal power plants.

In this article, the thermal study of two types of Romanian coal (bituminous coal from Jiu Valley and lignite from Oltenia basin) and biomass (corn and beech sawdust) was performed in order to understand the characteristics and behaviour of the materials further used in the processes of co-firing and biogas production, which were also investigated here.

## Experimental

### Fuels used

The co-utilization of coal and biomass for energy production results in reducing the pollution. Most notably is the impact on the emission of $NO_x$, $SO_x$, volatile organic compounds and polyaromatic hydrocarbons [10].

Fuels investigated in this article by thermal analysis, co-firing tests, and anaerobic fermentation process, were biomass (corn and beech sawdust) and coal (bituminous coal from the Jiu Valley and lignite from Oltenia basin). Related to anaerobic fermentation process, one of the main indicators for the potential of the used substrates is the C/N ratio. This indicator is connected with good characteristics involving the quality and quantity for the produced biogas. Due to the mineral characteristics of the coal substrate, only the biomass material could be tested in fermentation process.

The experiments using different sorts of waste biomass were repeated several times during past 3 years, in order to obtain information related to the influences for using different combinations of materials. Corn is referring to a homogeneous mixture of degraded corn grains and corn cob; the used sawdust is resulted from beech wood processing.

Sawdust and degraded corn were obtained from local sources located near Timisoara city. Before grinding, the materials, biomass and coal, were stored in raffia bags for several months in a semi-controlled environment; room temperature (RT) was between 20 and 25 °C. After the grinding process, all the materials were spread on a plane surface, in thin layer, for drying purposes.

Table 1 gives the elemental analysis for the used coal and biomass. Notable is the S content, as well the reduced humidity of the bituminous coal in comparison to the used biomass. Also the N content in biomass is sensible reduced in comparison to the used coal.

The thermal analysis measurements (TG, DTG and DSC) of the fuels were carried out on a horizontal Diamond TG/DSC analyzer from PerkinElmer instruments, in dynamic air atmosphere (150 mL min$^{-1}$), in alumina crucibles, using as reference similar amounts of inert α-$Al_2O_3$ powder. For equipment calibration were applied standard procedures with tin, indium, aluminum and gold. The enthalpy calculation was performed with the specialized software Pyris. Samples from 0.75 to 9.0 mg, contained in alumina crucibles, were heated from RT to 800 °C for bituminous coal and lignite and RT to 600 °C for corn and sawdust, under non-isothermal linear regime, with the heating rate of 10 K min$^{-1}$.

### Co-firing pilot plant

The co-firing pilot plant, presented in Fig. 1, comprises several main parts and is based on an original design [11]:

– Main burning subassembly comprising the furnace, the air distributor, divided with grates for injection of the fluidisation air and main combustion air, the fuel bunkers (biomass and coal), the starting combustion burner working with natural gas, an appropriate air feeding system including all necessary adaptors and diverse measuring instruments and observation gaps.
– Heat transfer subassembly components are mainly formed by the convective case and one heat exchanger. The heat exchanger is made from 8 cold-drawn steel pipes, 4 in each side, connected to inlet and outlet manifolds.
– Flue gases de-dusting system components are formed by a cyclone dust separator, a convective connection, flow measuring sockets, extracting tubes for flue gas analysis and powder/dust sampling.

**Table 1** Elemental analysis for the used fuels, reported to the wet material

| Characteristics | Symbol | Bituminous coal/% | Lignite/% | Corn/% | Sawdust/% |
|---|---|---|---|---|---|
| Carbon | C | 58.84 | 23.48 | 43.62 | 35.97 |
| Hydrogen | H | 2.24 | 2.24 | 4.64 | 4.60 |
| Oxygen | O | 10.64 | 11.35 | 21.11 | 28.96 |
| Nitrogen | N | 2.26 | 0.59 | 0.44 | 0.35 |
| Sulphur | S | 1.80 | 0.85 | 0.01 | 0.01 |
| Humidity | $W_t$ | 2.4 | 27.4 | 11.5 | 5.5 |

**Fig. 1** Design of the co-firing pilot plant in fluidised bed [12]. *1* Start-up burner, *2* fuel bunkers, *3* bubbling fluidised bed furnace (BFB), *4* ash cooler, *5* convective case, *6* dust separator-cyclone, *7* scrubbing tower, *8* neutralisation reactor, *9* demister, *10*, *13* reagents circulation pumps, *11*, *12*, *14* containers, *15* filter, *16* air feeding system, *17* air distributor, *C* chimney
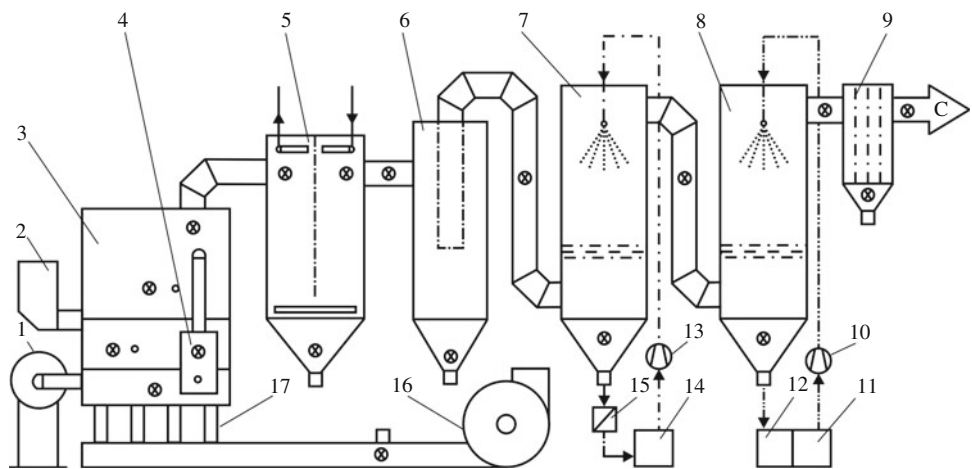
– Flue gases cleaning subassembly is formed by a scrubbing tower, a neutralisation reactor and the demister. Both scrubber and reactor are equipped with the necessary equipments for hydraulic circuit of washing liquids and a 100-mm layer of Raschig rings to increase the residence time and to provide a large surface area for interaction between washing liquid and flue gases.

In order to control the processes, the experimental facility is equipped with measuring instruments, devices for temperatures, pressures, water and gas flows and visors. All facility components are mounted on a steel frame with overall dimensions: $L = 6$ m, $W = 1.3$ m and $H = 2.6$ m. The main characteristics of the co-firing pilot plant are presented in Table 2.
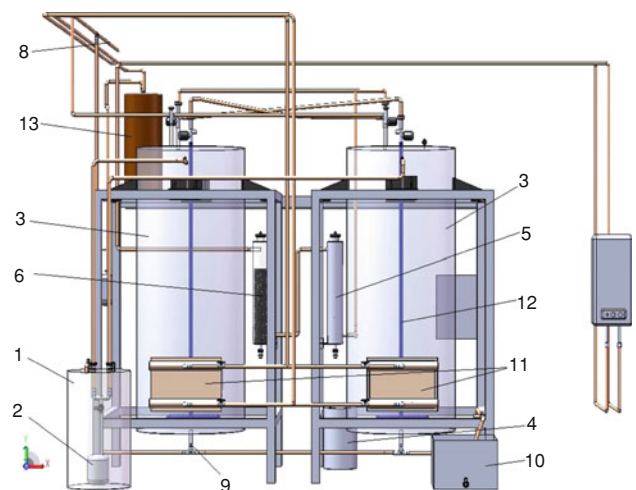
Biogas pilot plant

The pilot plant used for producing biogas from biomass through anaerobic digestion is presented in Fig. 2 and is based on an original design described elsewhere [13].

**Table 2** Main characteristics of the co-firing pilot plant

| Characteristics | Value |
| --- | --- |
| Thermal energy output | 45–90 kW$_{th}$ |
| Electrical power consumption | 2–4 kWh$_{el}$ |
| Water flow (in heat transfer system) | 2–4 m$^3$ h$^{-1}$ |
| Combustion/fluidization air flow | Max. 270 m$^3$ h$^{-1}$ |
| Compressed air flow (for washing pumps) | 0.5–1 m$^3$ h$^{-1}$ |
| Coal mass flow | 25–50 kg h$^{-1}$ |
| Biomass mass flow | 15–30 kg h$^{-1}$ |
| Washing liquid flow | 0.2–0.6 m$^3$ h$^{-1}$ |
| Resulted ash mass flow | 10–20 kg h$^{-1}$ |

From the biomass deposit, the used material is passed through a mill, and then it is sent to the tank where the preparation of the suspension of biomass is made (1). The biomass suspension is transported with the help of the pump (2) and introduced into the fermentation reactors (3). The correction agent tank for the pH assures, through the control system, the conditions for the process of anaerobic fermentation. The resulted biogas is passed through a filter for retaining the $H_2S$ (5) and after that, through a system used for retaining $CO_2$ (6), after which takes place the $CO_2$ desorption and the compression of the $CO_2$ in the adjacent system and the purified biogas is sent for being used (8). The used material is discharged through the means of a gravimetric system (9), and the solid material is retained for being dried using the natural drying, and after that is sent to a compost deposit for being used as a soil fertilizer.



**Fig. 2** Schematic configuration of pilot plant used to produce biogas from biomass [14]

A part of the resulting liquid is neutralised when the case, in the system (10) and sent to the sewerage network, or is transported by the recirculation pump (2) from the suspension preparation tank (1). The fermentation reactors are thermostat heated with the system (11). For the homogenisation of the suspension is used a bubbling system (12) made of polypropylene pipes to avoid the possible corrosion. Also, for depositing small quantities of biogas of the purpose of analysing, the installation is equipped with a small tank (13) positioned at the top of the reservoirs.

## Results and discussion

### Thermal analysis of fuels

The thermal analysis techniques are frequently used for the thermal characterization of fuels [15–20], for identifying combustion characteristics [21–25] and for creating more efficient design of combustion reactors [26–28]. For thermal analysis, fuel samples were prepared by grinding, followed by crushing for 10 min. The thermal stability of the bituminous coal, lignite, corn and beech sawdust

determined by thermal analysis measurements, as well as thermal effects, can be observed in the TG, DTG and DSC curves from Fig. 3 (bituminous coal), Fig. 4 (lignite), Fig. 5 (corn) and Fig. 6 (sawdust), respectively.

Drying and oxidative decomposition of the fuel occurs in three stages. The endothermic drying of coal occurs first, followed by coking and burning of coke (both exothermic processes). In the case of biomass, the drying occurs firstly also (endothermic process), followed by the oxidative elimination of volatile substances (exothermic process) and burning of formed charcoal (exothermic process). Table 3 contains the mass losses at all stages and total enthalpy variations ($\Delta H$) in exothermic processes.

Thermal analysis of the bituminous coal in dynamic air atmosphere has revealed also a distinctive process to those contained in Table 2; this is the loss of 2.4 % moisture up to 120 °C, followed by a plateau up to 200 °C. Between 200 and 260 °C it may be observed a gain in the mass of 0.8 % due to the oxygen chemisorption, accompanied by coal surface oxidation and formation of surface oxygen species—less or more stable—like: ethers, carbonyls, carboxyl, etc. [18, 22, 29]. Thermal analysis showed, for lignite, a relatively high water content (27.4 %). Coke
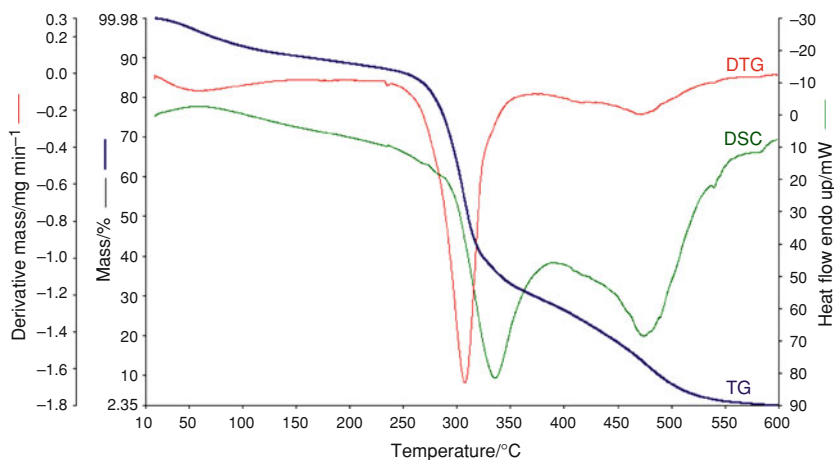


Fig. 3 Thermoanalytical curves (TG, DTG and DSC) of bituminous coal, at the heating rate of 10 K min$^{-1}$, in dynamic air atmosphere
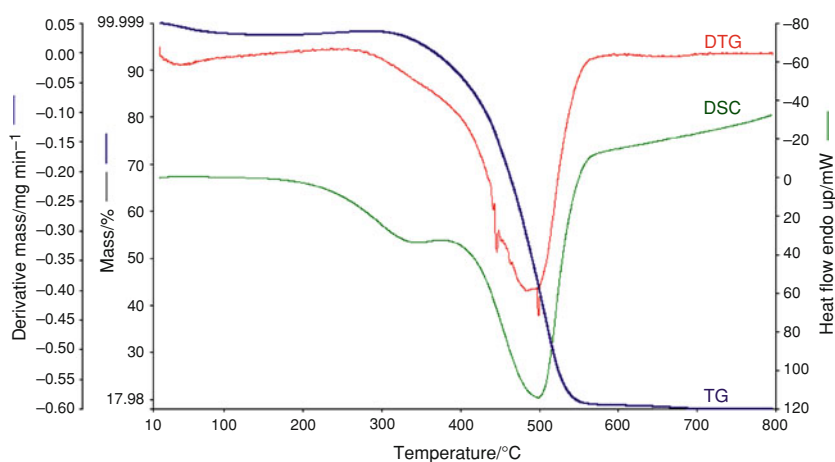


Fig. 4 Thermoanalytical curves (TG, DTG and DSC) of lignite, at the heating rate of 10 K min$^{-1}$, in dynamic air atmosphere
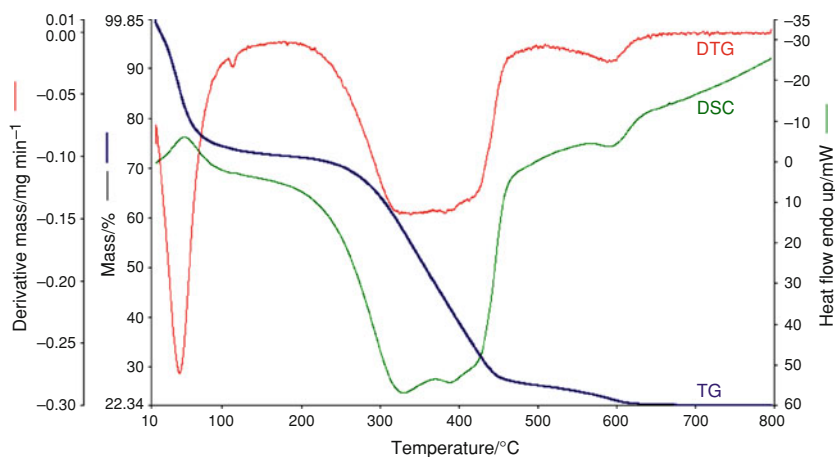
**Fig. 5** Thermoanalytical curves (TG, DTG and DSC) of corn, at the heating rate of 10 K min$^{-1}$, in dynamic air atmosphere



**Fig. 6** Thermoanalytical curves (TG, DTG and DSC) of sawdust, at the heating rate of 10 K min$^{-1}$, in dynamic air atmosphere
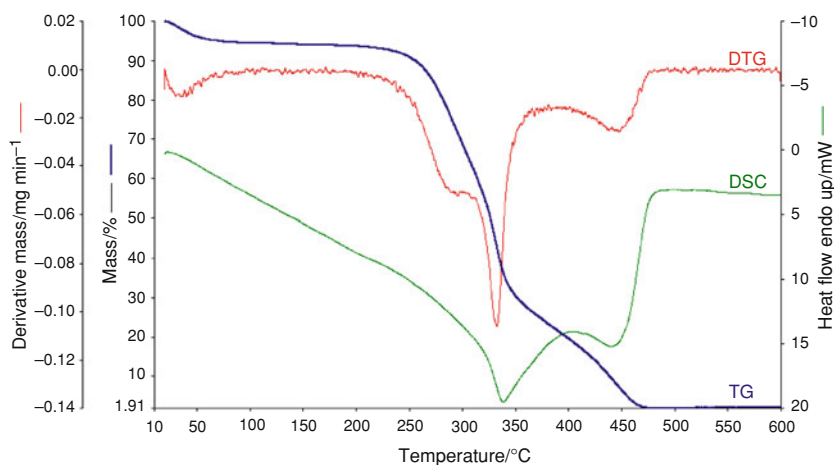


**Table 3** Thermoanalytical data of coal and biomass

| Fuel | Process | Maximum process temperature/°C | Temperature range/°C | Mass loss/% | Residual mass/% | $\Delta H$/kJ kg$^{-1}$ |
|---|---|---|---|---|---|---|
| Bituminous coal | Drying | 42.2 | 18–120 | 2.37 | 17.96 | $-16807 \pm 18$ |
| | Coker | 344.7 | 200–382 | 5.79 | | |
| | Burning | 483.8 | 382–700 | 73.75 | | |
| Lignite | Drying | 44.9 | 17–175 | 27.43 | 22.34 | $-10098 \pm 11$ |
| | Coker | 337.1 | 175–510 | 46.41 | | |
| | Burning | 589.6 | 510–690 | 3.68 | | |
| Corn | Drying | 55.6 | 19–200 | 11.48 | 2.35 | $-6569 \pm 7$ |
| | Oxidative elimination of volatiles | 306.8 | 200–375 | 58.92 | | |
| | Burning | 472.8 | 375–570 | 26.77 | | |
| Beech sawdust | Drying | 34.5 | 19–100 | 5.53 | 1.91 | $-6612 \pm 8$ |
| | Oxidative elimination of volatiles | 331.3 | 180–385 | 71.33 | | |
| | Burning | 444.6 | 385–490 | 20.54 | | |

burning ends at a temperature comparable to that of bituminous coal, as shown in Figs. 3 and 4. The exothermic effects of coking coals and coke combustion, are simultaneous with effects of mass loss. Major mass loss from corn, precedes exothermic effect (Fig. 5). For sawdust, thermogravimetric effect and exothermic effect are

simultaneous (Fig. 6). From co-firing biomass with coal, the major energy contribution will be due to coal (Table 3).

## Co-firing process

After drying and milling (granulation 1–4 mm), the biomass was mixed externally with the fossil fuel, before being fed to the combustion system. The co-firing tests have been achieved at a ratio of 15 % by mass biomass, the rest being coal. The temperatures and pressures have been recorded during tests with a data acquisition system, in situ, in several important points. All values were in the range of expected relevance: in the furnace 800–1,200 °C, in the convective part 300–1,200 °C, in the cyclone 150–300 °C, in the scrubber 90–150 °C and in the neutralisation reactor 70–90 °C. Flue gas composition was measured with Testo 350XL gas analysers mounted after the cyclone, equipped with $O_2$, CO, NO, $NO_2$, $SO_2$, HC sensors. The gas analyzer software calculates the $CO_2$ content and excess air ratio $\lambda$ and convert gaseous pollutant concentration from ppm (volume concentration) to $mg\ Nm^{-3}$ (mass concentration).

For dust concentration a Strohlein STE4 device was mounted before cyclone. Main results representing average values obtained after achieving a steady state, corrected according to reference oxygen content ($O_{2ref} = 11$ % for biomass and 6 % for coal), are given in Figs. 7, 8 and 9. For the basic comparison, the experiment with no biomass addition was used.

The results regarding $NO_x$ emissions from co-firing are comparable to those resulting from burning coal alone, as unique fuel. Nitrogen content of biomass is lower comparative to coal, fact that supposes to reduce the formation of $NO_x$. Nevertheless, the formation of thermal or proximate $NO_x$ is directly related to the operation techniques, as well, mainly the range of temperature levels covered and oxygen content in reaction zones. The thermal mechanism of $NO_x$ formation are not activated as expected, due to the
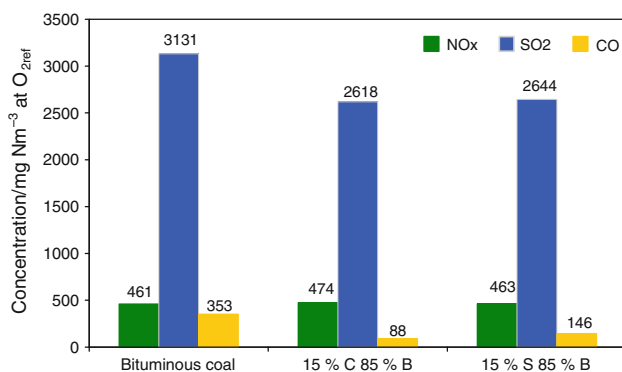
**Fig. 7** Mean values for $NO_x$, $SO_2$ and CO concentration in the case of biomass–bituminous coal co-firing, at 15 % mass participation of biomass in the mixture (*C* corn, *B* bituminous coal, *S* beech sawdust)
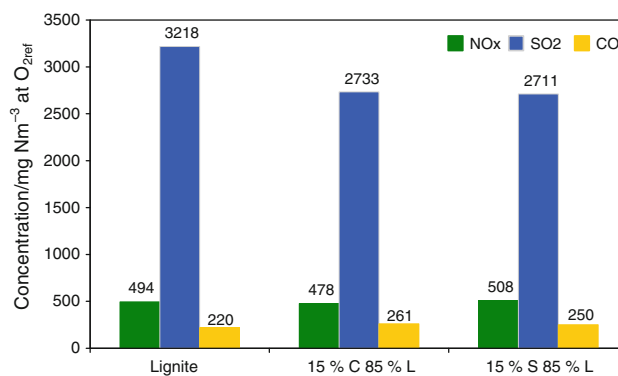
**Fig. 8** Mean values for $NO_x$, $SO_2$ and CO concentration in the case of biomass–lignite co-firing, at 15 % mass participation of biomass in the mixture (*C* corn, *L* lignite, *S* beech sawdust)
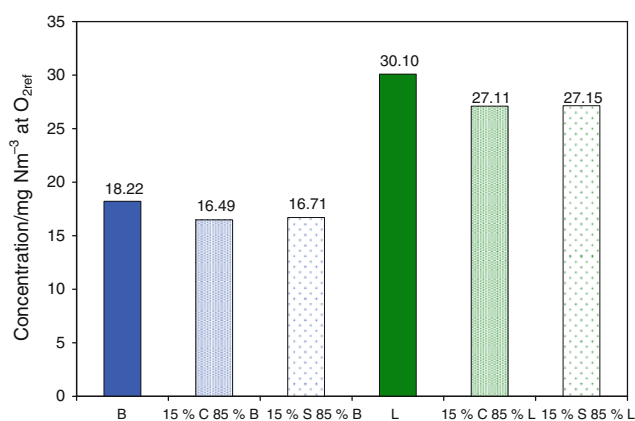
**Fig. 9** Mass concentration of fly ash resulted from co-firing 15 % by mass corn, respectively sawdust, with bituminous coal and lignite (*C* corn, *L* lignite, *S* beech sawdust, *B* bituminous coal)

fluidised system combustion that limits the temperature levels, and influences the residence time and the oxygen content, as well.

In the case of biomass-coal co-firing, the $SO_2$ concentration in the flue gases is lower. The explanation consists of the reduced S content of the used biomass sorts. The achieved desulphurisation efficiency accomplished only by the biomass addition (sawdust and corn) is around 15 %, compared to the reference, when no biomass was added.

An additional reduction beyond the amount anticipated on the basis of fuel sulphur content is sometimes observed; this is due to retention of sulphur in coal by alkali-based compounds in biomass ashes [30].

Analysing the fly ash concentration in the exhaust flue gases, one notes that co-firing determines a reduction of the particles amount, explicable by the lower ash content of the biomass and better combustion conditions, due to the higher volatile content of the biomass, which supports the stability of the ignition and combustion process.

Concerning the CO concentration, the amounts are considerable (between 220 and 270 mg $Nm^{-3}$ at $O_{2ref}$ for lignite) and thus, the efficiency due to un-burnt matter of the global co-firing process is reduced, in comparison to the basic case. This phenomenon suggests that the biomass addition can enhance the ignition of coal since volatile matter in biomass is easily evolved even at relatively low temperature, and because lack of oxygen, the CO is generated more intensively as if no biomass is added. For bituminous coal combustion the CO concentration was high ($\sim$350 mg $Nm^{-3}$ at $O_{2ref}$), which indicates a less efficient combustion; maintaining the temperature around preset value was not achievable due to impossibility to decrease fuel flow rate (dimmer position was at minimum) and to control the air–fuel mixture.

If the share of biomass is less than 5 % by mass, it was been demonstrated that there are no relevant CO increased values in the flue gases [24].

One of the co-firing advantages is the benefit concerning the $CO_2$ emission, knowing that the $CO_2$ exhaust from fossil fuel origin is reduced by the same amount as the biomass ratio. Despite the fact that normally not the total $CO_2$ resulted from the biomass share might be considered green, neutral, as according to the lack of relevant differences—in term of experimental results—concerning the two used biomass qualities attest the fact that fuel flexibility is possible.

Anaerobic fermentation process

The reactors were fed at the beginning of the experiment with $\sim$75 kg dry biomass and 2,000 L water. The gas composition was determined using a Delta 1600 IV gas analyser. The pressure difference was dropped with the help of a semi-automated system and afterwards the obtained biogas quantity was measured with the help of a gas counter. Temperature and pH were also continuously measured online. Figure 10 underlines the parameters evolution in time for the two batches. It can be observed a two-stage temperature regime (mesophilic and cryophilic) for the material batches, taking into consideration the possibilities of obtaining biogas using lower temperatures for the process. The two names describe the regimes of temperature used for biogas production using anaerobic fermentation—the first one is characteristic to mean values between 30 and 40 °C; the cryophilic temperature regime is characteristic to temperature values under 28–30 °C and the main property of this regime is that biogas is obtained after long periods of time (90–120 days).

Each fermentation tank is equipped with a heat exchanger used for heating up the suspension. The general constructive solution is identical for both reservoirs and the heating process is made periodically in order to adjust the
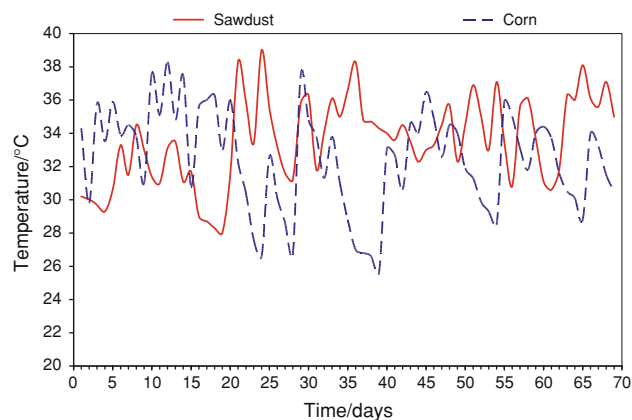


Fig. 10 Temperature variation for the two batches

fermentation process. In the first part (15 days) the temperature peaks were in the range of 34–38 °C, for start-up of the biogas production process. Because beech sawdust is difficult to degrade, for the next period of time (before 40th day of the process), the maximum temperature were around 38 °C and in the last part of the process (before 68th day) the maximum peak values were in the range of 36 °C, while for corn, which was more responsive to the heat input, the maximum values until the end of the process were maintained around 35 °C.

The pH correction is necessary in order to have a suitable environment to stimulate the anaerobe bacteria production and obtain good biogas quality. For low pH values, a lime-based suspension was used while for high pH values correction was made with small quantities of acetic acid. In the first part of the process, the general tendency for both batches was corresponding to values under the neutral domain (pH < 7–8). For corn material, the general tendency was specific to the first stage in biogas production—acidogenesis, while for beech sawdust the initial treatment was an acid hydrolysis to break the cellulose chains, which had as main result a pH value just under the neutral domain.

From Fig. 11 it can be observed that the pH varies differently in time for the two batches of material, presenting larger daily variations inside the first 15 days of anaerobic fermentation for the degraded corn, values corrected with the help of dosing pumps using low concentrations of acetic acid suspension for the correction. The beech saw dust batch presented a rather uniform behaviour, with values ranging from 6.7 to 7.5 during the entire process. After 15 days, the pH values for both batches entered in the optimum zone for biogas production (6.8–7.4).

The beech sawdust batch presented cumulative pressure values with maximum peaks of 1 bar and a reduced quantity of produced biogas (about 5.935 $m^3$) proving to be a material not suited for anaerobic fermentation processes (Fig. 12). The possibilities for using this type of material,
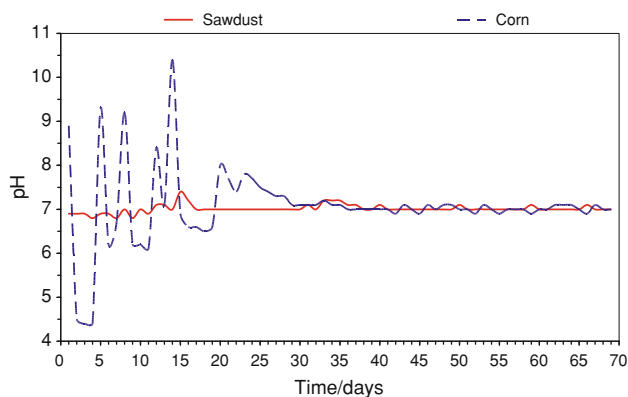
**Fig. 11** pH variation for the two batches
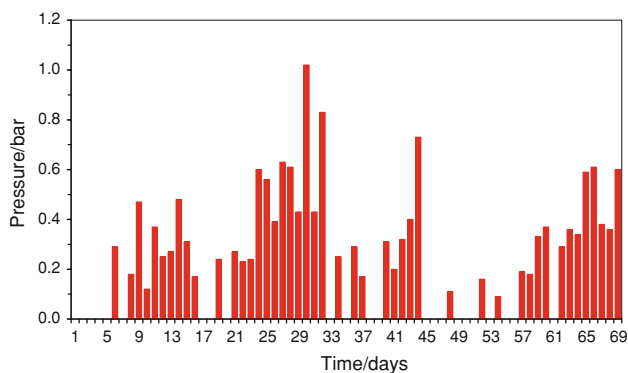


**Fig. 12** Pressure difference for beech sawdust batch
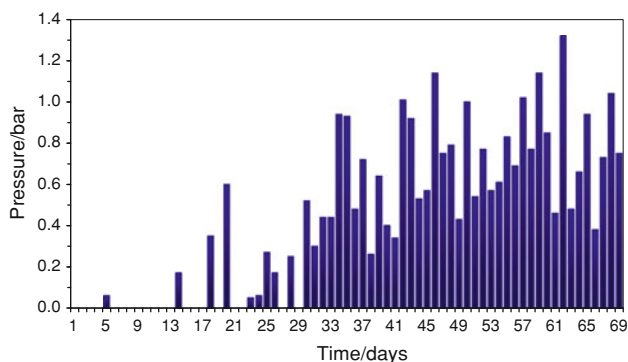


**Fig. 13** Pressure difference for degraded corn batch

connected with the large quantities of cellulose and lignocelluloses, are related with using different pre-treatments in order to break the cellular bonds between the composing elements before the process. The maximum concentration of methane inside the produced biogas was ∼ 50–55 % by volume.

The degraded corn batch presented a good time variation during the anaerobic fermentation with peeks of over

1.3 bar and a total produced biogas quantity of 51.389 m$^3$ (Fig. 13). The maximum concentration of methane inside the produced biogas was 67–68 % by volume.

## Conclusions

This article has pursued a goal immediately: energy from renewable sources, and use of non-renewable fuels together with the renewable fuels.

1. For experiments were used corn and beech sawdust obtained from local sources and two sorts of coal: bituminous coal from the Jiu Valley and lignite from Oltenia basin.
2. By thermal analysis have been determined the effects of oxidative degradation of fuel: $\Delta H_{\text{bituminos coal}} = -16807 \pm 18$ kJ kg$^{-1}$, $\Delta H_{\text{lignite}} = -10098 \pm 11$ kJ kg$^{-1}$, $\Delta H_{\text{corn}} = -6569 \pm 7$ kJ kg$^{-1}$ and $\Delta H_{\text{sawdust}} = -6612 \pm 8$ kJ kg$^{-1}$. In the co-firing, the major energetic contribution brings by the coals. When burning corn and sawdust, the amount of ash is negligible.
3. Co-firing 15 % by biomass with coal, the $SO_2$, $NO_x$, CO, $CO_2$ and fly ash concentrations in the flue gases is lower than at burning only of coals.
4. The anaerobic fermentation of corn and beech sawdust was obtained biogas with high methane content. The maximum concentration of methane in the produced biogas was 50–55 % in volume produced in sawdust beech, and 67–68 % in volume produced in corn.

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