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# COMPARISON OF INORGANIC CONSTITUENTS IN BOTTOM AND FLY RESIDUES FROM PELLETISED WOOD PYRO-GASIFICATION

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## **Abstract**

Wood biomass is a source of renewable energy and is now recognised as a potential alternative for sustainable energy production. During the pyro-gasification process, the mineral components of the biomass accumulate under the grate of the pyro-gasifier (bottom residue) or become volatile and are deposited as fly residue in the cyclone filters. This work analyses the constituents of the two residues produced by the pyro-gasification process of pellets in a pilot scale downdraft system. The residues are composed of char and ash. The ash makes up 7 % of the bottom residue and 38 % of the fly residue. The Ca, Mg, Na, S, P, Si and Cu contents in the two residues are almost comparable. Fe, Al, Cr, Zn, Ni, Pb, Cd, Mn and B are concentrated in the fly residue. Potassium is a particular

case and is present in low concentration in the fly residue. The mass balance has revealed that some elements can pass the first filtration phase (cyclones) and they are trapped in the gas which must be successively cleaned. Therefore, knowledge of the composition of the biomass (macro and microelements), and of the behaviour of their transformation products, is important for the plant design and functioning. It is also equally important for the disposal or the utilisation of the solid by-products.

Keywords: Pyro-gasification; Biomass pellets; Ash composition; Inorganic elements.

## 1. Introduction

An increase in global energy demand has exacerbated the problem of fossil fuel resource depletion. Wood biomass is a source of renewable energy and is seen as a potential feedstock for sustainable energy production. Gasification process is a form of thermo-chemical conversion that transforms solid biomass into gaseous fuel through a partial oxidation at high temperatures (900/1200 °C). The gas obtained from the gasification (syngas) (CO, H<sub>2</sub>, CH<sub>4</sub>, etc.) can be used for the generation of electricity and heat [1, 2]. However, this gas contains many impurities, such as particulates, ammonia, hydrogen sulphide, hydrogen chloride, alkali metals, metals, and organic compounds ranging from light hydrocarbons to tar.

With regard to the above, some studies have dedicated particular attention to investigate the main internal and external factors that affect gasification performance: the type of gasifier, the operating conditions and the biomass properties [3]. The main types of gasifier are fluidised bed, entrained flow bed and fixed bed. There are two types of fixed-bed gasifier, which are suitable for small scale applications: downdraft and updraft. The downdraft gasifier has the advantage of generating a low tar content syngas, thus

facilitating the gas cleaning phase for cogeneration [4, 5].

Studies related to downdraft gasification systems have generally focused on the aspects of main gas composition, heating values, gas yield and gasification efficiency [4-11]. However, few investigations have focused on the behaviour of the mineral part of biomass during the downdraft gasification process [12-14]. In fact, in suitable operating conditions of the reactor, some species of the mineral components become volatile, carrying chlorine, sulphur, alkali, alkali earth metals and other elements either in the gas phase or in the form of condensable species. They may damage or clog pipes and deactivate catalysts [15, 16]. Therefore, knowledge of the composition of the biomass (macro and microelements), and of the behaviour of their transformation products, is important for plant design and functioning, and also for the disposal or utilisation of process by-products.

The aim of this work is to identify the fraction of elements that deposit readily, and of those which follow the syngas stream, in relation to their content in the initial biomass. A pilot scale autothermal downdraft pyro-gasification plant has been used for this purpose. Preheated air at approximately 620 °C, together with wood pellets, is introduced from the top of the pyro-gasifier. The operating conditions of this plant ensure a fast heating of the biomass to generate a flash pyrolysis. After the gasification (1250 °C), the solid by-product that collects under the grate of the reactor is indicated in this work as bottom residue, and that which is trapped by the cyclones as fly residue.

## **2. Experimental**

### *2.1. Pilot scale pyro-gasification facility*

The diagram of the plant and related description is provided in Fig. 1. The configuration of the pyro-gasification plant is based on a continuous flow downdraft cycle in which a sub-stoichiometric quantity of air enters the top part of the pyro-gasifier together with the fuel.

The plant is fuelled with commercially available wood pellets. The biomass feedstock is preheated to approximately 85 °C in order to reduce moisture content, and exploits the residual heat of the engine exhaust fumes (path not shown in the diagram). The air introduced is preheated to approximately 620 °C by the heat of the syngas exiting the reactor (Fig. 1). The preheated air plays an important role in the flash pyrolysis process which precedes the gasification stage. The temperature profile inside the reactor rises to a maximum of approximately 1250 °C, whereas in the medium low zone of the reactor the outlet temperature of the syngas is approximately 900 °C. The produced gas exits from the lower part of the reactor which is equipped with a rotating grate under which the solid bottom residue collects (point 3 in the diagram). The fly residue entrained by the syngas is trapped by two cyclones operating in series with particle cut sizes,  $d_{p50}$ , of 4.5  $\mu\text{m}$ , and accumulates in a specific tank (point 4 in the diagram). After the cyclone filters the syngas is further purified, cooled, and sent to the engine, as shown in Fig. 1.

122.5 Kg/h of pellets produce 11.8 kg of bottom residue and 0.49 kg of fly residue (mean values in 5 hours of plant functioning). The gas produced is a mixture which consists of CO 17 %, CO<sub>2</sub> 15 %, CH<sub>4</sub> 16.5 %, H<sub>2</sub> 11 %, O<sub>2</sub> 0.5 % and N<sub>2</sub> 40 % with a lower calorific value of approximately 2200 kcal/Nm<sup>3</sup>. The hourly quantity of syngas produced is 300 Nm<sup>3</sup> and generates 250 kW<sub>el</sub>.

## *2.2. Characterisation of the pellets*

Moisture content, ash content, volatile matter and fixed carbon were determined. Moisture content was determined according to UNI EN 14774-2 standard (Solid biofuels - Determination of moisture content - Oven dry method - Part 2: Total moisture - Simplified method) and ash content was determined according to UNI EN 14775 standard (Solid biofuels - Determination of ash content). For the determination of volatile matter, the UNI

EN 15148 standard (Solid biofuels - Determination of the content of volatile matter) was followed.

Elemental analyses were carried out by inductive coupled plasma atomic emission spectrometry (ICP-AES) (Perkin Elmer Optima 7000) except for mercury and arsenic which were conducted by cold-vapor AAS and Hydride-generation AAS respectively (Perkin Elmer MHS-20). 5 g of pellets (dry weight) were dissolved with 25 mL of conc. HNO<sub>3</sub> followed by 20 mL of H<sub>2</sub>O<sub>2</sub> in a 250 mL flask and were maintained at boiling temperature until completely dissolved (except for insoluble silicate residues). The solution obtained, after filtering, was 50 mL. For the determination of total silicon, 5 g of pellets were incinerated at 550 °C and the resulting ash was melted with LiBO<sub>2</sub> at 900°C. The melt was dissolved in dil. HCl. The solution was made up to a final volume of 50 mL. For the determination of non-volatile sulphur, 5 g of pellets were subjected to dry distillation at 550°C and the distillation residue was incinerated at the same temperature. The resulting ash was dissolved in HCl 6 M, and the solution was made up to a volume of 50 mL. The solutions were then subjected to elemental analyses.

### *2.3. Characterisation of the residues*

5 kg of the bottom residue was sampled in subsequent periods during the operation of the plant and reduced to the amount appropriate for analysis through the coning and quartering method. It was ground into fine powder and homogenised in a mortar. The fly residue, present in a much lower amount than the bottom residue, was collected at the end of the period of experimentation and analysed immediately. This was already in fine powder form suitable for analysis.

Moisture content was determined according to the standard procedure indicated for the pellets. Ash content was determined at two different temperatures. At 550 °C, as described

in the standard procedure UNI EN 14775, and at 800 °C, according to the ISO 1171 (Solid mineral fuels - Determination of ash). The pH of both the residues and their ash, after combustion at 550 °C and 800 °C, was determined. The pH value was determined by suspending the sample in ultra-pure water with a solid/liquid ratio of 1:5 m/v (UNI EN 13037: Soil improvers and growing media - Determination of pH).

The elemental analysis was carried out by ICP-AES. The bottom and the fly residues (2 g each) were burnt at 550 °C and 800 °C for the purpose of eliminating the carbonaceous fraction (char). 0.1 g of ash from each residue was solubilised in 10 mL of HCl 6 M by heating. The determination of total silicon was carried out as previously described for the pellets.

XRPD analyses on the residues and their ashes (550 °C) were performed to identify the crystalline phases. X-ray diffractograms of powdered samples were obtained with a Siemens D 5000 diffractometer (Bragg - Brentano geometry, flat sample) using CuK $\alpha$  radiation. The scan interval ranges from 2.5 to 70° (2-theta scale) with increments of 0.02° per step and a counter time of 15 s per step. The operating conditions were 40 kV and 30 mA. The scanning and operating conditions were kept constant for all XRPD measurements in order to allow the immediate comparison between all the samples.

### **3. Results and Discussion**

Woody biomass consists primarily of cellulose, hemicelluloses, and lignin, along with small amounts of inorganic constituents [17, 18]. During wood biomass gasification undesired products such as tar, char and ash are produced. Therefore, they must be controlled to prevent damage to the environment and to the plant. This work has focused on the solid residues. These are made up of char and ash.

### *3.1. Characterisation of the pellets*

Classification of wood pellets can be made according to the UNI EN 14961-2 standard (Solid biofuels - Part 2: Fuel specification and classes - Wood pellets for non-industrial use). This standard classifies wood pellets for non-industrial use into three categories: A1, A2 and B, based on the ash content. Non-industrial use means that wood pellets are used for households, and small public or industrial buildings. The pellets considered in this work, based on the ash content, were classified in the category A2.

Analysis data of the pellets are shown in Table 1. Ash content is 1.0 %. Generally, ash content of vegetal biomasses is between 0.5-1.5 % [18]. Regarding the elements, some of them (Ca, K, Mg, S, P and Si) are present at high concentrations (> 200 mg/kg), Zn, B, Cu, Cr, Ni, Pb, Cd, Co, As and Hg at low concentrations (< 20 mg/kg). Fe, Mn, Al and Na are at concentrations between these two quantities. The major elements significantly affect the fusibility of ash and consequently on plant management. For instance, Si in combination with K may result in the formation of low melt silicates. K is relatively volatile, forming chlorides, hydroxides and sulphates which play an important role in corrosion mechanisms. Even Ca forms chlorides and sulphates but is less volatile than K and generally increases the melting point of the ashes. The behaviour of Mg is similar to Ca [19].

### *3.2. Characterisation of the residues*

The moisture and pH values of the two residues are given in Table 2. The ash contents at 550 °C and 800 °C are also indicated. For the ashes, the pH values and the concentration of the elements usually present in the biomass, at the two temperatures considered, are also reported. The two temperatures of incineration are the standards set for biofuels and mineral fuels. After the pyro-gasification the residues may be considered

to belong to either of these. Moreover, the two temperatures allow us to highlight the effect of heat treatment on the composition of the ashes.

The pH of the bottom and fly residues (9.8 vs. 12.4) is determined by the presence of alkaline species that form during thermo-chemical conversion of the biomass. The difference in pH between the bottom residue and fly residue is due to the different ash content that, for example at 800 °C, makes up 5.5 % of the bottom residue and 31.4 % of the fly residue. After the incineration of the bottom residue, the ash has a greater pH value than the residue. This is due to the increase of the inorganic fraction (ash) as a result of the combustion of the carbonaceous fraction (char). Regarding the fly residue and its ash, at the two temperatures considered, no variation in pH is observed.

The different ash content at the two different combustion temperatures of each residue reveals that the constituents (char and ash), at 550 °C, were still not completely transformed (7.0 % vs. 5.5 %). The incineration at high temperatures leads to a greater combustion of the char, to a transformation of the carbonates into oxides, and to the evaporation of volatile species present. These phenomena increase the concentration of each element in the inorganic fraction (ash) at 800 °C. The ratio between ash content at the two temperatures is equal to 1.27 for bottom residue and 1.20 for the fly residue. It can also be noted that incineration at 550 °C and 800 °C does not determine a variation in the pH of the resultant ashes (12.5). This result indicates that the constituents determining basicity are already formed at 550 °C, and that the change in concentration of these constituents involves a negligible increase in pH comprised within the uncertainty of the measurement.

The elemental analysis of the ashes (550 °C and 800 °C) shows an increase in concentration of the elements in the ashes at 800 °C, by a factor very close to that of the ash content. However, in the bottom ash at 800 °C, K and Zn show a reduction in

concentration of 57 % and 39 % respectively, due to their volatility [20]. In the fly ash, there is a decrease in concentration of potassium of 30 %, while there is no decrease in the concentration of Zn, probably due to the formation of ZnO stable up to 1000 °C [21, 22].

In the bottom residue, the concentration of soluble silicon in HCl 6 M shows an increase from 18167 mg/kg in the ash at 550 °C to 45549 mg/kg in the ash at 800 °C probably due to the formation of soluble potassium and sodium silicates [15, 23].

### *3.3. Distribution of inorganic elements between the two residues*

The assessment of the distribution of the elements in the two residues is based on the results of the analyses of their ashes at 550 °C. Despite the non-negligible carbonaceous content of the residues, the incineration temperature of 550 °C has been selected as a compromise between the need to burn the carbon and to limit volatilisation losses of more volatile species [18].

The results in the Table 2 show that ash content in the fly residue is higher than that of the bottom residue. This result is attributable to the greater amount of carbonaceous matrix (char) in the bottom residue. As can also be seen, Ca, Mg, Na, S, P, Si and Cu are present at almost the same concentration. Other elements such as Fe, Al, Cr, Zn, Ni, Pb, Cd, Mn and B are concentrated in the fly ash. Potassium is an exception, showing a concentration of approximately half in the fly ash respect with the bottom ash. This behaviour is due to the fact that, at the operating temperature of the pyro-gasifier (> 900 °C), potassium and its compounds (KCl, and KOH) are present in the gaseous phase and these species may give rise to other salts (for example  $K_2CO_3$ , and  $KBO_2$ ) that condense at slightly lower temperatures (at the bottom of the pyro-gasifier). Furthermore, the potassium can form the silicates that are stable at the temperatures of the pyro-gasifier and deposit as bottom ash.

Pb, Cd and Zn are the most environmentally toxic metals, and are also relatively volatile; they sublime or react forming gaseous compounds that accumulate in the fly ash upon cooling. Cr, Cu and Ni are considered the least volatile heavy metals. Vervaeke et al. [12] have found that Cr, Cu and Ni in a gasification system are distributed in a more or less equivalent amounts among all the ash fractions. In the case studied, Cr and Ni accumulate in the fly ash (Table 2). However, this data may be slightly affected by the fact that the rotating grate of pyro-gasifier is made of Ni-Cr stainless steel.

### 3.4. XRPD analysis

The results of XRPD analyses of the bottom residue show the presence of abundant amorphous fraction related to the carbonaceous residue (char) that generates a signal characteristic between 18 and 30° (2-theta scale). This indicates a very weak medium-range ordering. A similar signal is observed in the fly residue, although of lower intensity. At 550 °C, the ashes of the bottom and fly residues have similar composition in terms of crystalline phases (Fig. 2): in both samples Calcite ( $\text{CaCO}_3$ ) is the most abundant phase whereas Farringtonite ( $\text{Mg}_3(\text{PO}_4)_2$ ) and Ferrosilite ( $(\text{Fe, Mg})\text{SiO}_3$ ) are present as minor phases. In bottom ash Spurrite ( $\text{Ca}_5(\text{SiO}_4)_2(\text{CO}_3)$ ) and Quartz ( $\text{SiO}_2$ ) were also identified as additional.

### 3.5. Mass Balance

The mass balance was calculated to verify whether the elements of the initial biomass are found completely in the two residues. The mg content of the elements considered in the initial biomass ( $m_i$ ), in the bottom residue ( $m_B$ ), in the fly residue ( $m_F$ ), and the percentages of deviation ( $= [(m_B+m_F) - m_i] * 100/m_i$ ) are shown in Table 3. The concentrations of the elements (mg/kg) in the two residues are also indicated. The

amounts of the elements have been calculated considering that 122.5 kg of biomass produce 11.8 kg of bottom residue and 0.49 kg of fly residue.

Ca, Mg, Na, Mn, P and B show a deviation of around 10 %. Taking into account the difficulty of the analysis and the non-optimal homogeneity of the samples, these elements can be considered non-volatile. They do not exceed the barrier of the cyclones and remain distributed in the residues. The deviations of the other elements above 10 % may be due to various causes. Elements such as K, Cd, Cu, Pb, Zn and S show a negative deviation. These elements surpass the filtration stage and continue with the gas stream. The high value of the deviation of S, Pb, Zn and Cd is due to their volatility and to the high temperature of the syngas in the cyclones. The minor deviation of potassium, despite its volatility, is probably due to its tendency to accumulate in the bottom residue, as mentioned in subsection 3.3. Cu also presents a limited deviation in accordance with its restricted volatility in the operating conditions [16, 22]. The positive deviations of Al, Fe, Cr, Ni and Si may be affected by a contamination caused by the material of the rotating grate, and the refractory material of the pyro-gasifier.

With regard to the volatile elements, a particular attention must be paid to sulphur which, if present in the syngas, could create environmental criticalities. S may be present in plants as inorganic S and as organic S. The pellets used in the pilot plant have a total S content of 125 mg/kg, of which approximately 65 mg/kg is non-volatile sulphur. Taking into account that the hourly amount of syngas produced is 300 Nm<sup>3</sup> and the hourly consumption of biomass is 122.5 Kg, 1kg of biomass produces 2.45 Nm<sup>3</sup> of syngas. Therefore, the concentration of volatile S in the syngas is 24 mg/Nm<sup>3</sup> which, expressed as SO<sub>2</sub>, corresponds to 48 mg/Nm<sup>3</sup>. This data in part explains the SO<sub>2</sub> concentration in the exhaust fumes (78 mg/Nm<sup>3</sup>).

#### 4. Conclusions

The combustion of residues at two different temperatures (550 °C and 800 °C) has emphasised that 550 °C is a suitable temperature for elemental analysis. Assessing the distribution of the elements in the two residues, it has been found that some elements are present at almost the same concentration, while others are distributed in different amounts between the two residues. In particular, heavy metals such as Zn, Cd, Pb, Cr and Ni have been found to be concentrated in the fly residue. Therefore, a careful treatment of this solid by-product is necessary to avoid environmental pollution. The XRPD analysis has shown that the same crystalline phases, Calcite, Ferrosilite, and Farringtonite, are present both in the bottom and fly ashes. Quartz and Spurrite are only present in the bottom ash. The mass balance has shown that not all elements are completely present in the two residues. Further gas cleaning stages are necessary, such as scrubbers and filters, because of the elements carried away by syngas over the cyclones.

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## Captions

Fig. 1. Diagram of the plant: 1-silos, 2-reactor, 3-ash and char deposit, 4-cyclones, 5-catalyst, 6-heat exchanger, 7-scrubbers with nebulised water, 7a-water pump, 7b-washwater deposit, 8-gas cooler, 8a-cooling system, 9-electrostatic filter, 10-cartridge filter, 11-engine, 12-torch. The path of the air is indicated in red dashed line, the path of the syngas in black. The plant operates with a slight vacuum.

Fig.2. XRPD patterns of bottom ash (the upper part of the image) and fly ash (the lower part of the image) of the residues combusted at 550 °C. Both samples are strongly crystalline with the Calcite as a prevailing phase (Cc). Moreover, both samples exhibit Spurrite (Sp) and Farringtonite (Far) but in the fly ash their crystallinity is lower than that in the bottom ash. Quartz (Qz) and Ferrosilite (Fs) are present as crystallised phases only in the bottom ash.

Table 1. Proximate analysis and inorganic content of the biomass.

	%	SD
Moisture	6.1	
Volatile Matter	74.5	0.6
Ash Content	1.0	0.04
Fixed Carbon	24.4	0.5
Element	mg/kg	SD
Ca	2720	80
K	1064	49
Mg	272	10
Fe	105	3
Al	82	4
Na	52	4
Mn	35	3
P <sup>a</sup>	290	12
S <sup>a</sup>	378	21
Si <sup>b</sup>	481	65
Zn	11.59	0.27
B	3.31	0.24
Cu	1.84	0.07
Cr	0.55	0.07
Ni	0.46	0.04
Pb	0.34	0.02
Cd	0.17	0.01
Co	0.09	0.01
As	0.006	0.001
Hg	0.018	0.001

<sup>a</sup>S and P are expressed as Sulphate and Phosphate.

<sup>b</sup>Total silicon.

Table 2. Parameters of the residues and related ashes. The concentrations of the elements in the ash are expressed in mg/kg on the dry substance. The analyses were made in triplicate.

<i>Parameter</i>		<b>Bottom Residue</b>		<b>Fly Residue</b>	
		<i>550 °C</i>	<i>800 °C</i>	<i>550 °C</i>	<i>800 °C</i>
Moisture	%	3.2 ± 0.1		0.02	
	pH	9.8 ± 0.1		12.4 ± 0.1	
Ash Content	%	7.0 ± 0.2	5.5 ± 0.2	37.8 ± 0.8	31.4 ± 0.8
	pH	12.5 ± 0.1	12.5 ± 0.1	12.5 ± 0.1	12.4 ± 0.1
Ca		307975 ± 30408	365338 ± 2476	309219 ± 12331	354759 ± 12586
K		108521 ± 5298	47109 ± 5042	48258 ± 5612	33787 ± 6002
Mg		32575 ± 3747	37829 ± 823	34264 ± 2742	35364 ± 3006
Fe		17783 ± 2462	23111 ± 1240	33259 ± 3833	51398 ± 10376
Al		11722 ± 1898	19579 ± 986	16020 ± 1276	17465 ± 1865
Na		7159 ± 2248	8929 ± 1487	6212 ± 1114	5932 ± 408
Mn		3625 ± 542	4362 ± 63	4979 ± 673	5055 ± 643
P <sup>a</sup>		36717 ± 4956	44740 ± 647	41020 ± 4370	44347 ± 7774
S <sup>a</sup>		17143 ± 934	19903 ± 540	18487 ± 1445	21584 ± 2561
Si <sup>b</sup>		73684 ± 1585	n.d.	82897 ± 3695	n.d.
Zn		466 ± 65	283 ± 51	1416 ± 137	1700 ± 183
B		397 ± 35	464 ± 23	546 ± 25	538 ± 14
Cu		159 ± 22	353 ± 50	150 ± 10	178 ± 22
Cr		111 ± 22	234 ± 35	252 ± 21	455 ± 12
Ni		92 ± 11	104 ± 19	143 ± 23	165 ± 26
Pb		7 ± 1	8 ± 2	47 ± 3	53 ± 2
Cd		0.8 ± 0.1	1.1 ± 0.1	6.3 ± 0.9	6.3 ± 0.2
Co		9.0 ± 0.9	14.1 ± 1.9	n.d.	n.d.

<sup>a</sup>S and P are expressed as Sulphate and Phosphate.

<sup>b</sup>Total silicon.

n.d. – not determined.

Table 3. mg content of the elements in the various matrixes and concentrations in mg/kg in the residues.

Element	122.5 Kg		11.8 Kg		0.49 Kg		Total Sum Residues mg	Deviation %
	Pellet	Bottom Residue		Fly Residue				
	mg	mg	mg/kg	mg	mg/kg			
Ca	333166	254013	21526	57894	118150	311906	-6	
K	130399	89432	7579	9001	18370	98434	-25	
Mg	33355	26861	2276	6397	13056	33259	0	
Fe	12828	14668	1243	6240	12734	20908	63	
Al	10080	9670	820	2991	6105	12662	26	
Na	6405	5923	502	1157	2361	7080	11	
Mn	4343	2988	253	928	1894	3917	-10	
P <sup>a</sup>	35581	30291	2567	7653	15619	37945	7	
S <sup>a</sup>	46318	14167	1201	3459	7059	17625	-62	
Si <sup>b</sup>	58920	61004	5170	15913	32476	76918	31	
Zn	1419	384	33	265	542	649	-54	
B	405	328	28	102	208	430	6	
Cu	226	130	11	28	57	158	-30	
Cr	67	92	8	47	96	139	107	
Ni	56	76	6	27	54	103	83	
Pb	42	5	0.5	9	18	14	-66	
Cd	21	1	0.06	1	2	2	-91	

<sup>a</sup>S and P are expressed as Sulphate and Phosphate.

<sup>b</sup>Total silicon.

Figure 1

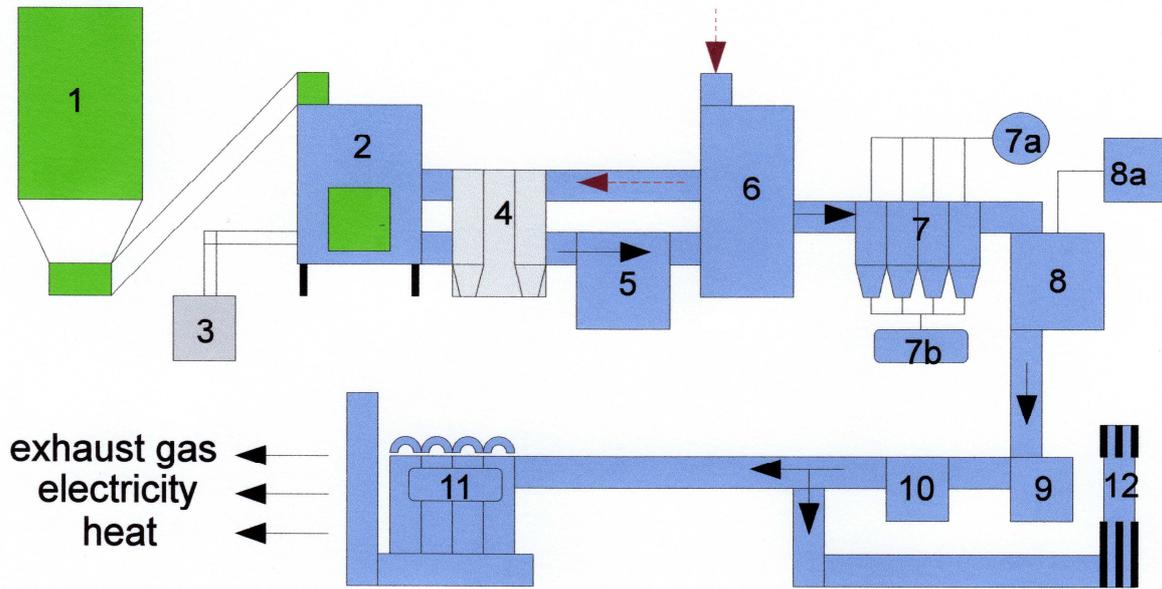


Figure 2

