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Fluidized Bed Combustion of a Lignin-based Slurry

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Unconverted lignin is available as residual sludge with water content in the range of 40-60% by mass from 2nd generation bio-ethanol production process. Fluidized bed combustion was studied as a possible method to valorize such a biomass material, upon mixing and homogenizing with rapeseed oil for producing a fuel slurry. Combustion tests were carried out at steady state in a pilot unit with submerged feeding of the fuel slurry. The operation with the slurry resulted reliable, after the adoption of measures for improving the slurry homogeneity and flowability. To this aim, particular care was dedicated to the production and characterization of the slurry, whose rheological properties are typical of a non-Newtonian (pseudo-plastic) fluid.
The combustion tests proved that C content in the ash samples at the cyclone was very low and the combustion efficiency was higher than 99.5%. A temperature increase was registered in the freeboard with respect to the bed as consequence of volatile matter combustion, typical of biomass fuels. The normalized NO emission was compliant with the Italian regulation for biogenic fuels. The bed material was enriched in K and Na from the ashes, although no bed agglomeration phenomena occurred.

1. Introduction

Ethanol is a well-known substitute of gasoline in Otto cycle endothermic engines. Its utilization allows to reduce in the short-to-medium term the greenhouse effect as well as the emission of pollutants into the atmosphere caused by vehicles. The 2nd generation bio-ethanol production process is carried out upon hydrolysis and fermentation of ligno-cellulosic feedstock (Lennartsson et al., 2014). Among the by-products of such process, the unconverted lignin is available as a residual sludge with water content in the range of 40-60% by mass. Such a lignin sludge undergoes degradation with release of odors and volatiles if simply stocked and not processed; alternatively, it might become a valuable energy source from wastes, if properly processed. Among possible routes for lignin-sludge conversion, e.g. pyrolysis, combustion, hydrogenation, hydrolysis, partial oxidation, the direct combustion would be the simplest and most effective one for producing heat, steam and power at the same site of the bio-ethanol plant. In this concern, the combustion of dried lignin residue was successfully proved in a conventional boiler by Eriksson et al. (2004). Fluidized bed (FB) technology is suitable for burning either coal or biomass, thanks to its flexibility toward particle size, ash content as well as moisture content (Basu, 2006). In particular, the large thermal inertia provided by the dense bed, e.g., of sand, makes the steady operation possible with fuels having high water content. The FB combustion of biomass-based slurries with water content in excess of 50% has already been investigated in the last decades: Ogada and Werther (1996) performed tests with wet sewage sludge and reported that the fluidized bed was mainly affected by diffusive combustion of the volatiles; co-combustion of a mixture of a distillation sludge and coal (Miccio and Miccio, 1997) was instead dominated by the coal presence and feeding conditions; Miranda et al. (2007) reported on co-combustion of olive mill wastewater and proved that olive wastes originated in a local plant could be totally eliminated; the combustion of wet olive pomace (Miccio et al., 2014) was smoothly carried at significant scale (550 kW_{th}) proving the need of a minimum plant size for such kind of applications; Solimene et al. (2010) and Urciuolo et al. (2012) characterized the devolatilization and the combustion pattern of wet sewage sludge, as well as the effective lateral spreading of the volatile matter and the comminution phenomena.

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The lignin sludge has a rather high N content (>1% on dry basis), therefore the chemical conversion of fuel-N to nitrogen oxides (i.e., NO, NO_2 and N_2O) and the resulting emissions may be enhanced. Also the presence of alkalis in the fuel ash may lead to the formation of amorphous phases with the silica that is usually the predominant material in the bed adopted for such combustion applications.
This work is aimed at the valorization of lignin as an energy source from wastes and the present paper reports an experimental research on combustion of a purposely prepared lignin slurry in fluidized bed. The addition of renewable oil was thought as a means to increase the heating value of the sludge in order to ensure efficient and reliable operation of the combustor. Specifically, rapeseed seed oil was taken as a model renewable oil in the present investigation. The experiments were carried out at steady state in an atmospheric pilot-scale unit, which is equipped with an under-bed feeding probe for the slurry and operated in bubbling bed regime.

2. Experimental

2.1 Combustion facility

A FB combustion facility with nominal thermal power of 80 kW was used for steady state tests with a lignin/rapeseed-oil slurry (Figure 1). The fluidization column with square section is made in stainless steel. It is composed by two trunks: the bottom one (290x290 mm) is 1350 mm high, whereas the upper trunk has a larger size (382x382 mm) and a height of 1012 mm, including a pyramidal element for the connection of the two pieces (Figure 1). The fluidization column is insulated with ceramic fiber boards, able to stand temperatures up to 1000 °C, enclosed in an aluminum shell. Compressed air is regulated by a valve and supplied to the plenum at the bottom of the combustion chamber (150 mm high) that is equipped with a perforated plate distributor, having 676 holes, 1 mm ID. This primary air is measured through a Brooks electronic flowmeter mod. SLA5800 (0-100 Nm^3/h). A secondary air stream is injected at a height of 210 mm above the distributor and also serves for pneumatic transport of the fuel slurry.
The fuel-slurry is supplied by means of a peristaltic pump (mod. Ragazzini PSF3S 3/8" size) that is driven by an inverter for fine regulation of the rotation speed. The slurry enters the combustion chamber through a 8 mm ID stainless steel probe located at the same port of the secondary air (i.e., 210 mm above the distributor).
A feeding system for solid fuel (granules and pellets) is also available. It is made of a sealed hopper (100 L), a 25 mm screw feeder, an electric actuator and an inclined discharging conduct for over-bed feeding (800 mm above the air distributor). An inverter allows the regulation of the screw rotation speed.
The primary abatement of dust is obtained by means of a cyclone (ID=98 mm) that allows the separation of entrained particles with a diameter up to 10 µm. A secondary fiber/ceramic filter can be installed in sequence.
The combustor is equipped with a 10 kW electric pre-heater system. Powder samples can be easily collected at the bottom of the cyclone and filter case.
Four type K thermocouples and two electronic pressure sensors are installed along the fluidization column. A gas analyzer for O_2, CO, CO_2 and NO (mod. ABB AO-URAS26) is connected to a gas sampling line for monitoring the composition of the flue gas at the exit of the experimental facility.

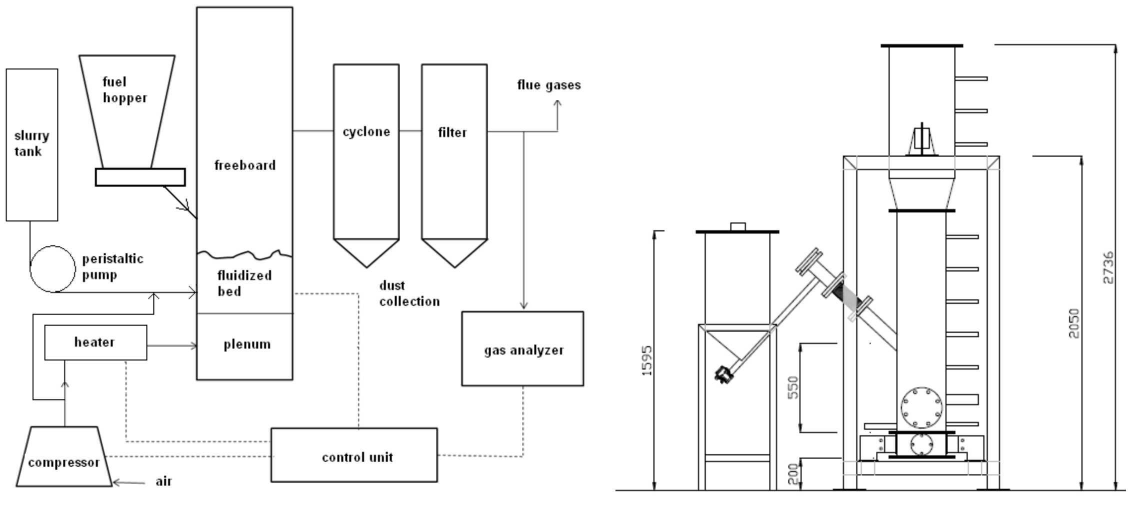


Figure 1: Schematics of the fluidized bed facility for pilot combustion tests.

2.2 Biomass-oil slurry fuels

Due to the high content of water and ash (Table 1), the lignin sludge cannot undergo as-it-is steady combustion in fluidized bed and the addition of an auxiliary fuel is needed for improving the heating value. Specifically, in the present investigation, a specific task was dedicated to the preparation of biomass-oil slurry fuels to be used for the experiments. Samples of slurry were firstly prepared in 250 ml beakers in order to detect the miscibility of the selected fuel components and the stability of the mixture. In accordance with Benter et al. (1997), biomass-oil slurry was termed unstable if i) coalescence led to the formation of an oil layer at the top of the slurry of more than 1 mm in depth; and ii) sedimentation led to a solids layer at the bottom of the vessel of more than about 1 mm. As a first attempt, the lignin sludge was mixed with wet olive pomace, i.e., a mix of fragments of stone, tegument and pulp of the olive having a moisture content of 62.71 % wt. (Brachi et al., 2015), and rapeseed oil (RS) in different proportion. After several trials, a stable biomass-oil slurry fuel was obtained, but its pumpability resulted very poor with frequent blocks occurring in the peristaltic pump due to the presence of coarse and hard stone fragments from olive pomace. Therefore, the wet olive pomace component was discarded and new additional samples of slurry were prepared by mixing the lignin sludge alone with rapeseed oil in different proportions. It was found that, irrespective of their particular composition, LS/RS slurry became unstable due to coalescence. Conversely, LS/RS/H_2O emulsions, having a water/oil mass ration larger than one, were found to be stable for more than 30 days without any additive. After several trials, the optimal mass ratio for the flowing property of the mixture was found in LS/RS/H_2O=59.5/16.1/24.4%, resulting into a total water content of around 60%.

For combustion experiments, the selected emulsion was prepared in a large batch that resulted stable for several days and required only mixing by a rotating anchor before utilization. In order to improve the reliability of the feeding system, the slurry was also passed through a 2.8 mm sieve for removing coarser particles. A photograph of a slurry sample is shown in Figure 2-A.

Table 1: Physical and chemical properties of the lignin sludge and lignin/rapeseed-oil slurry

	Lignin sludge (LS)	LS/RS/H_2O Slurry (LS/RS/H_2O)	Elements in the ash (LS/RS/H_2O)	
Proximate analysis (% on wet basis)			ppm	
Moisture	60.8	63.4	Si	9111
Volatiles	25.0	28.1	Ca	1579
Fixed carbon	8.1	4.8	Na	912
Ash	6.1	3.7	Fe	690
Ultimate analysis (% on dry basis)			Al	621
Carbon	47.1	59.0	K	505
Hydrogen	5.3	7.6	P	394
Nitrogen	1.3	1.1	Mg	162
Sulphur	0.2	0.2		
Oxygen (by diff.)	30.5	22.0		
Density, g/L	1250	1090		
Low heating value, MJ/kg (% on dry basis)	18.1	25.5		

The properties of the LS/RS/H_2O slurry are reported in the 2nd column of Table 1. The major elements detected by ICP analysis in the ash of LS/RS/H_2O slurry are listed in the 3rd column of Table 1, Si and Ca being the most abundant. The presence of alkali metals (i.e., Na and K) could be a possible cause of interaction with the bed material and formation of particle agglomerates.

A rheological characterization of the lignin/rapeseed-oil slurry was performed at 25°C by means of a rotational rheometer (CVOR 120, Bohlin Instruments, Malvern) with coaxial cylinder geometry and 4 rotor blades. The flow curve is displayed in Figure 2-B. The sample exhibited a pseudo-plastic behavior with viscosity values between approximately 10^5 Pa s (at low stress) and 0.3 Pa s (at high stress). The collapse of viscosity (of 6 orders of magnitude) occurs mainly in the range of shear stress between 50 and 100 Pa.

In comparison, the viscosity of rapeseed oil at 25°C is much lower and equal to 7.88 10^{-2} Pa s (Noureddini et al., 1992), indicating that the slurry viscosity approaches that of rapeseed oil at high shear stress (>100 Pa).

It is worth noting that under the conditions of present experiments, the slurry velocity in the pump tube and in the feeding probe was around 0.05 m/s and the maximum Reynolds number was $4 \cdot 10^{-3}$ for the lowest shear viscosity (0.1 Pa s). According to Eq (1), relating the shear τ to flow rate Q, tube radius R and viscosity μ,

$$\tau = 8\, Q\, \mu / (\Pi\, R^3) \quad (1)$$

the maximum shear stress in the tube was around 164 Pa, that is in the range of the transition to the low-viscosity rheological behavior.

A 

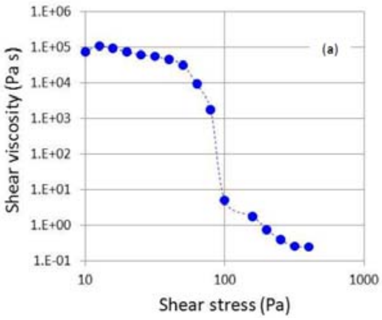
B 

Figure 2: photograph of LS/RS/H_2O slurry (A) and viscosity of the slurry versus shear rate at 25 °C (B).

2.3 Other Materials

Other materials used during the tests were silica sand (Ticino basin) as bed material and commercial wood pellets (spruce) as supplemental fuel for startup.

The silica sand was sieved in the size 0.3-0.8 mm with an average diameter of 0.50 mm. The particle density of the sand is 2600 kg/m^3. The minimum fluidization velocity is equal to 0.159 and 0.071 m/s at 25 and 800 °C, respectively. The concentration of the major elements present in the fresh sand is reported in Table 2 (upper section).

The spruce pellets have typical composition of wood and low ash content (0.3% by mass). Only a very limited amount of pellets (less than 5 kg) was used during start-up and, hence, it was not expected to affect the subsequent slurry combustion experiment.

Table 2: Major elements in the silica sand (Ticino basin)

Fresh sand															
Si	>10000	Fe	11790	Al	6114	Mg	5338	Ca	3530	K	656	Na	234		
Fatigued sand															
Si	>10000	Fe	10560	Al	9508	Mg	4310	Ca	6496	K	2468	Na	1488		

3. Results

The operating conditions and the main results of the tests carried out in the experimental FB facility are reported in Table 3.

The slurry flow rate was in the range 8-12 kg/h, corresponding to a nominal thermal power of 70-110 kW. The slurry was just pumped into the bed during the tests T1-3, T7 and T9; vice versa, dispersion air was adopted with velocity U_d (referred at ambient temperature) through the secondary air nozzle during the tests T4, T5 and T6. Each steady state run lasted for around 1 hour.

Table 3: Results of the tests carried out in the experimental FB facility

Test N.	Bed mass kg	U_d m/s	T_1	T_2	T_3	O_2 %	CO_2 %	CO ppm	NO ppm	NO* mg/Nm^3
T1	40	0	772	804		9.0	9.5	13	315	494
T2	40	0	785	840		4.7	12.8	12	298	342
T3	40	0	785	850		3.6	13.5	38	260	292
T4	50	1	810	810		6.0	12.0	20	270	338
T5	50	1	818	823	874	5.9	12.2	120	225	280
T6	50	2	822	828	878	6.3	11.8	125	218	278
T7	50	0	820	825	890	5.3	12.5	180	235	281
T8	50	0	830	835	918	3.6	13.8	290	205	221

* normalized to 11% vol. of O_2

The operation of the experimental plant with slurry resulted smooth and reliable, after the adoption of the cited measures for improving the slurry homogeneity and flowability (e.g. coarsely sieving, mixing, optimization of feeding line, etc.). At temperature higher than 700 °C, the dynamic response of the plant was very prompt indicating that no significant accumulation of carbonaceous materials occurred in the fluidized bed. Only the last thermocouple, installed at height of 2 m, was more slow in approaching a steady value of temperature, because of the decreased thermal transfer rate in the top section of the combustor. The concentration of CO ranged between 12 and 290 ppm, reflecting changes of the excess air ratio and maximum temperature in the combustion chamber.

An increase of temperature was registered between bed zone and freeboard. The increment of the temperature is due to the combustion of volatiles above the bed surface because of formation of fuel rich bubbles that bypass the in-bed combustion. This is a typical behavior of high-volatiles solid fuels as well as liquid fuels during FB combustion (Ferrante et al., 2008). The temperature increase in the freeboard (ΔT) is plotted against the O_2 concentration in the flue gas in Figure 3. The difference between the two series of data-points (square and diamonds) is not only due to the change of the bed inventory, but also to the position of the thermocouple in the freeboard (T_2 for 40 kg, T_3 for 50 kg). Overall, it appears a rather linear decrease of ΔT with O_2 concentration is obtained because of both effects of increased mixing in the bed and dilution of the gas. The adoption of dispersion air (solid symbols) seems to determine a decrease of ΔT, again as consequence of a better fuel-air mixing in the bed.

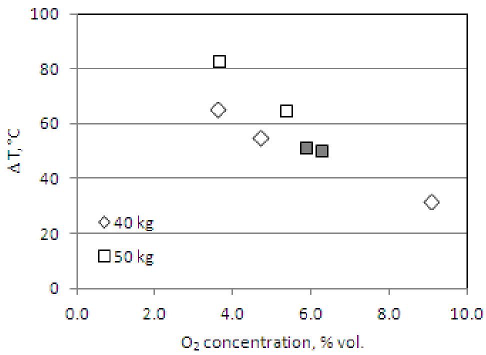


Figure 3: Temperature increase in the freeboard versus O_2 concentration in the flue gas for two different bed inventories.

The normalized NO emission (last column of Table 3) always resulted lower that Italian regulation limit (500 mg/Nm^3) for such kind of fuels. The concentration of NO in the flue gases is plotted against the CO concentration in Figure 4. The reducing effect of the carbon monoxide is evident as well as the beneficial effect of adopting fuel dispersion by the auxiliary air stream. The nitrogen oxide is mainly due to the N content of the fuel (LS), so the adoption of a staging, though to a limited extent, contributed to reduce the nitrogen oxide emission (Coda Zabetta et al., 2005).

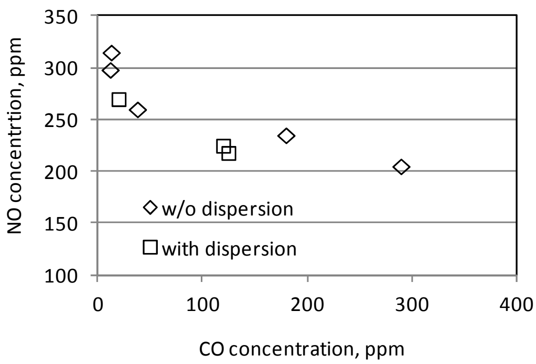


Figure 4: NO versus CO concentration in the flue gas.

The CO concentration turned out surprisingly high (>100 ppm) in the last four tests of Table 3; very likely, this may be attributed to an imperfect combustion of the rapeseed oil just in these tests, perhaps related to an uncomplete heat-up of the upper section of the combustor freeboard. The calculated combustion efficiency was always higher than 99.5 %.

The C content in the ash samples obtained at the cyclone during four tests was always less than 0.5 % by mass, indicating that the carbon conversion was very high thanks to the good reactivity of the lignin residue.

The lower section of Table 2 reports the concentration of the major elements detected in a sample of the fatigued sand, obtained after the experimental campaign. The enrichment can be noted in some elements that were present in the ash of the fuel. In particular, K and Na gave rise to the maximum relative enrichment because of their attitude to form chemical compounds and eutectics with SiO_2. However, no agglomeration of the bed materials was detected during the tests, thanks to the limited temperature of the bed zone (< 830 °C).

4. Conclusions

The goal of preparing a pumpable biomass-oil slurry fuel from residual lignin sludge was successfully achieved by adding rapeseed oil and water to it. The resulting slurry finally had a total water content of around 60%. The optimal mass ratio for the flowing property of the mixture was found in LS/RS/H2O=59.5/16.1/24.4%.

The subsequent goal of feeding and burning such slurry was successfully achieved by adopting a pilot-scale fluidized combustion plant with a bed of inert particles. The operation with slurry in several steady state tests resulted reliable, after the adoption of measures for improving the slurry homogeneity and flowability.

The C content in the ash samples obtained at the cyclone during four tests was always less than 0.5 % by mass and the combustion efficiency was always higher than 99.5%.

The post combustion in the freeboard was responsible of a temperature increase up to 80°C that is mitigated by adopting a higher excess air and dispersion air flow assisting the slurry injection.

The normalized NO emission resulted lower that Italian regulation limit (500 mg/Nm^3) for such kind of fuels.

The bed was enriched in some elements that are present in the ash of the fuel, in particular K and Na. However, no agglomeration of the bed materials was detected.

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