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## Research paper

# Co-gasification of wastewater sludge and different feedstock: Feasibility study



Salah Akkache<sup>a</sup>, Ana-Belén Hernández<sup>b</sup>, Gabriel Teixeira<sup>c</sup>, Franck Gelix<sup>c</sup>,  
Nicolas Roche<sup>a,\*</sup>, Jean Henry Ferrasse<sup>a</sup>

<sup>a</sup> Aix-Marseille University, CNRS, M2P2 UMR7340, Europôle de l'Arbois Bâtiment Laënnec, Hall C, 13454 Aix en Provence, France

<sup>b</sup> University of Johannesburg, Department of Civil Engineering Science, Kingsway Campus, PO Box 524, Auckland Park, 2006 Johannesburg, South Africa

<sup>c</sup> Veolia Recherche et Innovation, 78520 Limay France

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## ABSTRACT

Gasification experiments were performed for several feedstocks alone (wastewater sludge, waste wood, reeds, olive pomace, solid recovered fuel, paper labels and plastic labels) using a fixed bed reactor operating in semi-batch conditions. In order to combine them in an optimal gasifying blend, the gasification behavior of each feedstock was compared with that of wastewater sludge through the following criteria: the raw feedstock proximate and ultimate composition, the solid conversion, the gas heating value, the pollutants release and the ashes melting. Operated alone, the conversion rate of the feedstocks after 58 min of solid residence time was over 77% of initial mass. The Syngas low heating value produced at 1123 K was in the range of 9.0 to 11.9 MJ m<sup>-3</sup>. The major concerns regarding the wastewater sludge were the pollutants precursors' release (NH<sub>3</sub>, COS...) and the ash slagging and fouling. The calculated slagging and fouling indexes were high also for olive pomace and for waste wood. Finally, among the possible blends studied the paper labels and plastic labels can be co-gasified with secondary and digested wastewater sludge without any restriction, reeds and solid recovered fuel can be blended with secondary wastewater sludge without any restriction, a specific attention have to be taken to fouling when they are blended with digested wastewater sludge. The blend based on waste wood and olives pomace should be avoided for instance due to their ash slagging and fouling tendency.

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## 1. Introduction

The WasteWater Sludge (WWS) is a renewable energy source with a significant energy content, of about 24 MJ kg<sup>-1</sup> on dry ash free basis (daf) [1]. However, WWS may contain considerable amount of nitrogen, sulfur, as well as heavy metal, bacteria, virus, pharmaceutical and hormones. This particular composition leads to pollution release with the current disposal ways [2–6] (land farming, landfilling and incineration). Gasification is an alternative thermal process that allows for a solid mass reduction (approximately 70% of the solids initial dry mass (dm)) [7], the energy recovery and the removal of organic pollutants and pathogenic organisms. Unlike incineration, gasification may limit the presence of SO<sub>x</sub> and NO<sub>x</sub> precursors in the syngas [8] and reduce the leachability (or potential toxicity) of ash [5]. Co-gasification based

on multi materials can improve the quality of the raw fuel gasification [9–11]. The weakness of WWS are related to pollutants release and the presence of high moisture content. Coal – sludge co-gasification was investigated in literature [12–15]. The consensus is that adding WWS to coal increases the reactivity of coal with catalytic effect. This is probably due to the high mineral matter present in the WWS. However, the pollutants release (H<sub>2</sub>S, NH<sub>3</sub>, HCl) increases by adding WWS to coal.

There is a limited knowledge concerning WWS – biomass co-gasification in the literature. Van der drift et al. [16] carried out demolition wood – WWS co-gasification (at 20% mass fraction of WWS in the blend) in circling fluidized bed, they found that the NH<sub>3</sub> level in the syngas was the same level with the demolition wood alone, the H<sub>2</sub> and the syngas heating value were the same for both the blend and the demolition wood alone, the results suggest that blending WWS with biomass does not generate any operational problem at this concentration. Ong et al. [17] studied WWS – woody biomass air gasification in downdraft fixed bed reactor, they

\* Corresponding author.

E-mail address: [nicolas.roche@univ-amu.fr](mailto:nicolas.roche@univ-amu.fr) (N. Roche).

Abbreviation (Volumes are given in m <sup>3</sup> at standard conditions (273 K and 1.013 × 10 <sup>5</sup> N m <sup>-2</sup> ))			
WWS	wastewater sludge	Al	alkalin index
SWWS	secondary wastewater sludge	Rs	slagging index
DWWS	digested wastewater sludge	Fu	fouling index
WWTP	wastewater treatment plant	daf	dry ash free basis
OP	olives pomace	dm	dry basis
RE	reeds	$m_{gas}$	mass of the total gas collected along all experiment (calculated)
WW	waste wood	$m_{tar}$	mass of the total tar collected
SRF	solid recovered fuel	$m_{char}$	mass of the total char collected at the end of experiment
PA	paper labels	$m_0$	initial sample mass
PL	plastic labels	% <sub>daf</sub>	mass fraction of the dry ash free basis
LHV	low heating value	$y_i$	volume fraction of the specie CO, H <sub>2</sub> , CH <sub>4</sub> and C <sub>2</sub>
		$\eta_{conv}$	conversion rate

found that at 30% mass fraction of WWS in the blend caused the gasifier blockage due to the ash agglomeration. Seggiani et al. [18] studied the air co-gasification of WWS – wood pellets in updraft fixed bed. The authors found that adding wood pellets reduce the slagging behavior of sludge, increases the gas yield and the cold gas efficiency. André et al. [19] proved the technical feasibility of coal – olive bagasse co-gasification in fluidized bed reactor, however, the authors indicate that the bagasse should be taken below 40% mass fraction to maintain stable gasification. Pinto et al. [1,20] compared mixing coal and straw pellets to WWS in an air-steam fluidized bed gasifier. The authors showed that no significant changes are needed to carry out the gasification with the different blends and adding coal or straw pellets to WWS increases the conversion, CH<sub>4</sub>, C<sub>1</sub>H<sub>m</sub>, the gas low heating value (LHV) and reduce the pollutants release compared to WWS alone.

The biomass ash is known to cause several operational problems [21]. This is due to partial melting of ashes, leading to formation of melt slug on the reactor or deposition in the downstream equipment, especially heat exchanger [21,22]. The deposit formation involves a decrease in the heat exchanges as well as corrosion problems. The fluidized beds are sensible to bed material agglomeration, sintering and defluidisation, these problems may lead to total device failure [23]. A special care have to be taken when mixing WWS and waste, since their ash content can reach 30% mass fraction of dm to 40% mass fraction of dm [24,25]. The alkaline compounds are the most problematic species. The K<sub>2</sub>O can interact with SiO<sub>2</sub> generating low melting mineral phases and eutectic phases [26]. The ASTM Standard fusibility test can be used in order to predict the ash behavior. However, it has been reported as unrepresentative of real ash behavior [27–31]. Thereby, several empirical indexes based on the chemical ash composition were developed.

The Alkaline index “Al” (Eq. (1)) represents the alkaline content per heating value unit ratio

$$Al = \frac{(Na_2O + K_2O)}{HHV} \quad (1)$$

When the Al value is in range 170–340 g GJ<sup>-1</sup> fouling or slagging is probable, when it is greater than 340 g GJ<sup>-1</sup> slagging and fouling are virtually certain to occur [22].

The Slagging index “Rs” (Eq. (2)) represents the ratio of low melting temperature oxides per high melting temperature with taken into account sulfur effect. Sulfur may interact with alkaline and forming low melting temperature phases.

$$Rs = \frac{\%(K_2O + Na_2O + MgO + CaO + Fe_2O_3)}{\%(SiO_2 + TiO_2 + Al_2O_3)} \times \%S \quad (2)$$

When the Rs value is lesser than 0.6 there is a low slagging inclination, when it is in range 0.6–2.0 the slagging tendency is medium, high at 2.0–2.6 and sever at greater Rs values [32].

Fouling index “Fu” (Eq. (3)), represents the ratio of low melting temperature oxides per high melting temperature with alkaline effect emphasis.

$$Fu = \frac{\%(K_2O + Na_2O + MgO + CaO + Fe_2O_3)}{\%(SiO_2 + TiO_2 + Al_2O_3)} \times \%(K_2O + Na_2O) \quad (3)$$

When the Fu value is lesser than 0.6 there is a low fouling inclination, when it is in range 0.6–40 the fouling tendency is high, at greater Fu the fouling in severe [32].

The aims of this study are: 1 – to evaluate the behavior of the different feedstocks during their gasification in terms of gas quality, pollutant release and ash produced, and 2 – to analyze the co-gasification feasibility of WWS – biomass or synthetic feedstock blends by strengths and weaknesses identification for different feedstock. This comparison was carried out through pure steam gasification in semi-batch reactor. The criteria of comparison were conversion rate, gas composition, low heating value, ammonia release and ash composition and behavior.

## 2. Materials and method

### 2.1. Materials

Five different types of Feedstock illustrated in Fig. 1: B class waste wood (WW), reed (Re), olives pomace (OP), solid recovered fuel (SRF), paper labels (Pa) and Plastic labels (PL) were selected on technical-economic criteria such as cost, availability and seasonality. In addition, two different types of sludge were selected: 1 – a secondary wastewater sludge (SWWS) from wastewater treatment plant (WWTP) La Courtine (Avignon – France) which is only mechanically dewatered and 2 – a digested wastewater sludge (DWWS) from WWTP La Pioline (Aix en Provence – France) which is aerobically digested to reduce carbon continent and avoid its fermentation in end-use.

The raw materials were characterized in order to obtain their proximate and ultimate analysis (CHNS) composition and ash melting following standard methods. The results of characterization are given in Table 1.

### 2.2. Experimental setup

The experimental setup used in this study was developed by Hernandez et al. [8]. It has been established that this reactor is

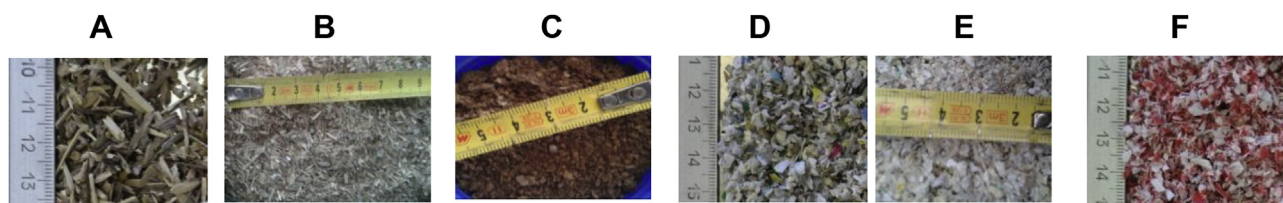


Fig. 1. Pictures of raw materials (A) Waste Wood (WW), (B) Reeds (RE), (C) Olives Pomace (OP), (D) Solid Recovered Fuel (SRF), (E) Paper Labels (PA), (F) Plastic Labels (PL).

Table 1  
Feedstock LHV, proximate and ultimate analysis.

	DWWS	SWWS	RE	WW	OP	SRF	PA	PL
Collected from	WWTP Aix en Provence – France	WWTP Avignon – France	Non-hazardous waste unit collection, Veolia Propreté Souilly – France)	WWTP Jonquiére – France	Olives oil mill Velaux – France	High efficiency waste sorting center Veolia Propreté Ludre – France	Labels manufacture Techmay Etiquetage (Millau – France)	
<b>Proximate analysis, mass fraction (%)</b>								
Raw material moisture	81.3	81.8	7.6	7.3	29.6	14.0	4.4	2
Dried material moisture	2.4	0.5	1.9	0.5	1.1	5.8	2.8	0.9
Mineral matter (dry basis)	26.9	19.6	10.7	8.5	1.5	11.7	9.1	3.8
<b>CHNS (mass fraction on dry ash free basis)</b>								
C	52.6	54.9	48.7	49.8	59.5	63.8	48.4	70.6
H	7.2	7.3	5.9	6.3	7.3	8.6	6.3	10.8
N	9.8	9.3	0.9	2.8	1.8	0.5	0.1	0.1
S	1.2	0.8	0.2	0.2	0.1	0.1	0.1	0.0
O	21.3	22.2	39.5	37.2	29.8	23.8	41	17.8
H/C (atom ratio)	1.6	1.6	1.5	1.5	1.5	1.6	1.6	1.8
LHV(Mj kg <sup>-1</sup> ) on dry basis	14.6	17.6	16.4	17.3	23.6	23.1	17.0	32.9
<b>ASTM fusibility tests, temperature K</b>								
Initial deformation	1547	1398	1536	1626	1723	1472	1728	1667
Softening	1644	1523	1557	>1773	>1773	1486	1757	>1773
Hemispherical	1650	1533	1542	>1773	>1773	1489	1759	>1773
Fluid	1655	1538	1580	>1773	>1773	1502	1761	>1773

consistent to study the pollutants and fuel gas release during pure steam gasification [5,8]. The equipment consists on a laboratory scale semi-batch gasifier. The apparatus set-up is given in Fig. 2. It is a vertical cylindrical (10 cm ID and 1 m high) surrounded by an electrical heated furnace (Carbolite®). The sample (about 6 g) is introduced in thin layer in the reactor from the bottom in a ceramic support. The support is placed above heat shield. The steam is generated in a heating mantle at 2.22 mg s<sup>-1</sup>. The steam is introduced in the furnace near the sample support. The produced gas leaves the reactor from the top and it is sent to analysis. The condensable fraction is trapped at ambient temperature before an inline Infra-red analyzer in order to protect it. A second trap at 268 K is used in order to measure the dry syngas flow rate. The syngas is caught in Kevlar bags in order to carry out a gas chromatography out line.

### 2.3. Procedure

The experimental procedure described below aims to compare different wastes in the same operating conditions. WWS or other samples were first dried at 353 K for 24 h in order to remove most of the moisture without impacting volatilization of organics. The sample was then introduced in the reactor and maintained at 343 K. The reactor was hermetically closed and Argon was introduced to inert the device. Once the inerting achieved and checked by gas chromatography, a heating rate was applied on the furnace simultaneously with the steam injection at 2.22 mg s<sup>-1</sup>. The heating rate consists in a 18 K min<sup>-1</sup> ramp from 343 K to 1123 K. The temperature is then kept constant at 1123 K for 15 min.

An inline Fourier Transform Infrared (FTIR) Perkin Elmer spectrum 65®, previously calibrated, allows the volumetric concentrations measurement of CO, CH<sub>4</sub>, and NH<sub>3</sub> in the produced gas. Other compounds, such as COS, C<sub>2</sub>H<sub>6</sub>, and H<sub>2</sub>O, were detected by FTIR, and their evolution was followed during the experiments. Given the complexity of spectral data, due to mixture, spectra matrix was analyzed with the SIMPLISMA algorithm [5,33].

A Gas Chromatograph Varian® 3800 series equipped with a back flush system (a 6-way valve Valco®, a Haysep P and a molecular sieve SA Agilent®) is used outline to measure the H<sub>2</sub>; CO; CO<sub>2</sub>; CH<sub>4</sub>; C<sub>2</sub> and C<sub>3</sub> content.

A thermo finnigan EA equipment is used in order to obtain the ultimate composition (CHNS) of ashes. A complementary Semi quantitative chemical composition is determinate through μ-XRF on X ray microscope XGT7000 Horiba-Jobin Yvon®.

## 3. Results

### 3.1. Feedstock thermochemical properties

Proximate and ultimate analyses are given in Table 1. It can be observed that both WWS present a moisture of 81% mass, mineral matter is present at 26.9% mass fraction of dm for digested one and at 19.6% mass fraction of dm for secondary one, which constitute weaknesses. Other wastes contain less moisture 2–22% mass fraction and mineral matter ranging 3.8–11.7% mass fraction of dm, lowest mineral matter content is noted to OP at 1.4% mass fraction of dm. After drying at 253 K for 24 h, all feedstock present the same

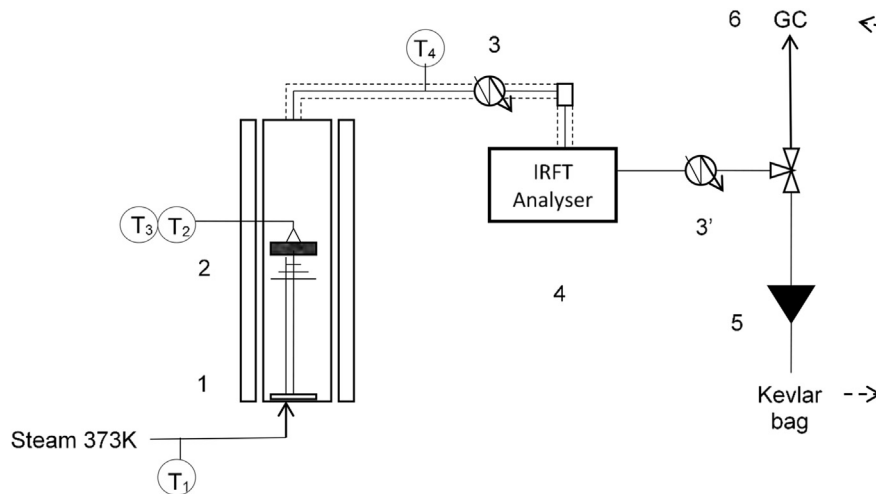


Fig. 2. Experimental device set-up: (1) electrical heated furnace, (2) ceramic support, (3) ambient temperature tar trap, (3') cold tar trap, (4) Infra-red analyzer, (5) flow meter, (6) GC analyzer.

range of moisture 0.5–5.8% mass fraction. This residual moisture is related to the low temperature of drying (<378 K) chosen in order to limit ammonia and volatile organic compounds release from the sample.

The ultimate analysis on dry ash free (daf) basis and the LHV on dry basis (Table 1) indicate that all feedstock are appropriate to thermochemical conversion process especially PL, OP, SRF where the LHV are respectively 32.9 MJ kg<sup>-1</sup> dm, 23.6 MJ kg<sup>-1</sup> dm, 23.1 MJ kg<sup>-1</sup> dm. These LHV are comparable or higher than some lignite and bituminous coal (LHV ranging from 9 MJ kg<sup>-1</sup> dm to 20 MJ kg<sup>-1</sup> dm) [34]. The feedstock H/C atom ratio is ranging from 1.5 to 1.6 except PL at 1.8, this is due to hydrocarbon polymer composition of this feedstock.

WWSs contains about 9.5% mass fraction on dry ash free basis (daf) of N and about 1% daf of S. The other wastes are composed of less than 0.2% daf of S element and 0.5% daf of N element, except WW, OP and Re where the N element content is about 2.8% daf, 1.8% daf and 0.9% daf respectively due to the vegetal nature of those biomasses.

Result of Standard ASTM ash fusibility tests are given in Table 1, the results show that the temperature at which the first deformation occurs is between 1398 K (DWWS) and 1728 K (PA), which is over expected temperature for feedstock gasification (1123 K). Softening, hemispherical and fluid temperature are undetectable (over the measuring limit of the equipment (>773 K)) for WW, OP, and PL. The lowest softening, hemispherical and fluid temperature are 1486 K, 1489 K and 1502 K respectively obtained For SRF, the others feedstock present higher value. The ASTM ash fusibility tests do not detect any problematic behavior for the tested feedstock.

### 3.2. Gas composition and solid conversion rate

The measurement of syngas flows rate, syngas composition, total tar released and char recovered at the end of the experiment allowed to calculate 1 – the mass balance 2 – the conversion rate and 3 – the syngas LHV, according to Eqs. (4)–(6) respectively. The results are given in Table 2.

$$\text{mass balance} = \frac{m_{\text{gas}} + m_{\text{tar}} + m_{\text{char}}}{m_0 + m_{\text{steam}}} \quad (4)$$

$$\text{LHV}_{\text{syngas}} = y_{\text{H}_2} \text{LHV}_{\text{H}_2} + y_{\text{CO}} \text{LHV}_{\text{CO}} + y_{\text{CH}_4} \text{LHV}_{\text{CH}_4} + y_{\text{C}_2} \text{LHV}_{\text{C}_2} \quad (5)$$

$$\eta_{\text{conv}} = \frac{m_0 - m_{\text{char}}}{m_0 \times \%_{\text{daf}}} \quad (6)$$

The mass balance (Table 2) were above 70%, the losses are due probably to the syngas volume estimation (calculated by instantaneous flow rate integration depending on time). The conversion rate ranged from 77 to 89%, except for OP at 48%.

The OP low conversion cannot be explained by losses (mass balance at 88%). In addition this biomass had the lowest mineral matter fraction (1.4% mass fraction of dm), in other words, its low conversion involved carbon accumulation in the char which is confirmed by char CHNS analysis where the carbon content is at 73% mass fraction of dm. This particular behavior can be explained by the low reactivity of this biomass compared other feedstock.

Limited carbon conversion rate is observed for the biomasses (only 55%, 55% and 27% of carbon was converted respectively for WW, RE and OP). The conversion rate obtained in the conditions of the study indicate the presence of a trend between conversion and the mineral matter fraction present in the feedstock (Fig. 3). The conversion seemed to increase with mineral matter increase. This might be due to the possible catalytic effect of mineral matter on gasification and char reactivity, indeed, the mineral matter is reported to have a catalytic effect on gasification [33,35–37]. An exception was observed for PL, even at low mineral matter fraction, this feedstock presents a conversion comparable to DWWS (87% and 89% at mineral matter fraction of 3.8% mass fraction of dm and 26.2% mass fraction of dm respectively). This behavior is probably due to the PL composition, with high content of hydrocarbon polymers easily converted by thermal cracking during devolatilisation.

The average syngas composition (calculated along all the experiments time) is given in Fig. 4. A high amount of CH<sub>4</sub> 15–25% volume fraction and C<sub>2</sub> (C<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>H<sub>4</sub> and C<sub>2</sub>H<sub>6</sub>) 2–10% volume fraction were collected along the experiment, which indicates that the reforming was limited in the device. This might be due to the fact that the volatiles released during devolatilisation leave the reactor at the same temperature than the one they are produced. In order to compare the different feedstock behavior, WWSs are used as references. It can be observed that there are no significant differences between DWWS and SWWS. The syngas obtained from



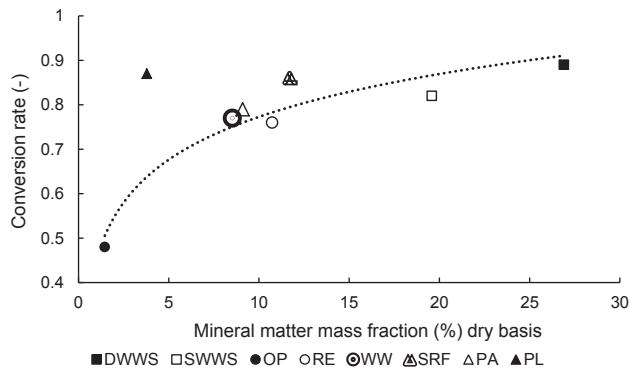
**Table 2**

Mass balance and feedstock conversion (in bold weak carbon conversion).

	DWWS	SWWS	RE	WW	OP	SRF	PA	PL
Mass balance (%)	70	71	85	71	88	74	76	88
Conversion rate %mass daf	89	82	86	77	48	86	79	87
Carbone conversion %	78	75	<b>55</b>	<b>55</b>	<b>27</b>	84	82	81
Gas LHV <sup>a</sup> (MJ m <sup>-3</sup> )	11.5	11.7	5.8	10.1	16.0	12.5	10.1	20.4
Gas LHV <sup>b</sup> (MJ m <sup>-3</sup> )	10.1	10.1	12.0	10.2	11.2	11.1	9.0	11.9

<sup>a</sup> LHV corresponding to average syngas composition obtained during whole experiment (53 min: devolatilisation + gasification).

<sup>b</sup> LHV corresponding to average syngas composition during gasification plateau (15 min at 1123 °C).



**Fig. 3.** Conversion rate of the different feedstock depending on the initial mineral matter mass fraction in dry basis.

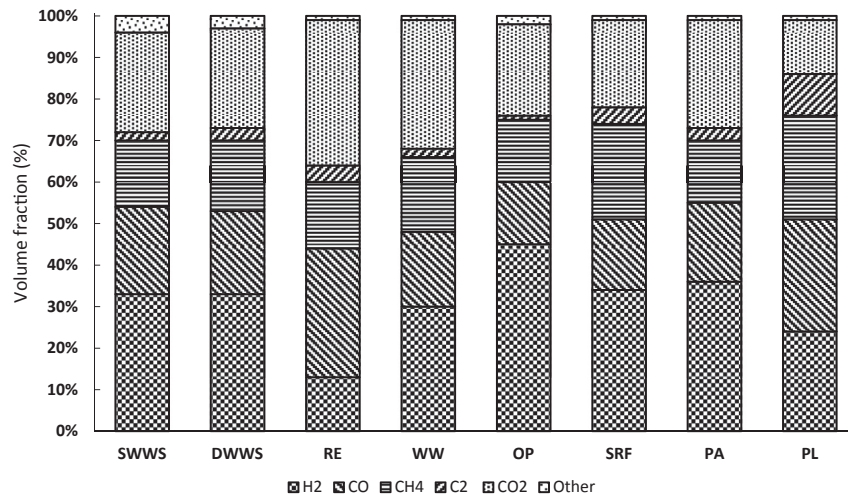
both WWSs are rich in fuel gas (total fuel gas volume fraction at 72% with CO at about 20% and H<sub>2</sub> at 33% volume fraction). The OP produced the highest amount of H<sub>2</sub> (45% volume fraction), followed by PA, SRF and WW (36, 34 and 30% volume fraction, respectively). Lower H<sub>2</sub> production than WWSs is noted to LP at 24% volume fraction and RE at 13% volume fraction. As it can be observed in Fig. 4 WW, SRF and PA produced a similar amount of CO compared to WWS (17%, 18% and 19% volume fraction respectively compared to 21% and 20% volume fraction for S & D WWS respectively). LP and RE produced the highest amounts of CO (27% and 31% volume fraction respectively) and lowest value of CO was obtained for OP at 15% volume fraction.

Table 2 gives the syngas LHV obtained according to Eq. (1) through average produced gas composition calculated for all experiment (53 min) given in Fig. 4 and average syngas composition calculated for 1123 K during 15 min given in Appendix A

respectively. The LHV obtained for all feedstock during whole experiment, except RE and PL, are typical for steam gasification [38]. The highest LHV was obtained for PL followed by OP and SRF (20.4, 16.0 and 12.5 MJ m<sup>-3</sup>). The high LHV noted to PL and SRF are due to CH<sub>4</sub> and C<sub>2</sub> in that syngas mostly released during devolatilisation (See Appendix B.2 and B.3). D & S WWS, presented LHV at 11.5 MJ m<sup>-3</sup> and 11.7 MJ m<sup>-3</sup>, PA and WW presented similar LHV at 10.1 MJ m<sup>-3</sup>. The RE had the lowest LHV value 5.8 MJ m<sup>-3</sup>, due to the low H<sub>2</sub> and high CO<sub>2</sub> production (13 and 34% volume fraction respectively). The high amount of CO<sub>2</sub> can be explained by the release of the initial oxygen present in the feedstock during devolatilisation. This CO<sub>2</sub> did not participate to Boudouard reaction and dry reforming reactions because it left the reactor in less than half a second after production and did not remain in contact with the char. Indeed, if we consider the syngas composition obtained at 1123 K during the plateau of 15 min interval it is found that the CO<sub>2</sub> level decreased (between 13 to 24% volume fraction) and LHV became more typical of steam gasification especially to PL at 11.9 MJ m<sup>-3</sup> and RE at 10.2 MJ m<sup>-3</sup> (Table 2) compared to syngas obtained during the whole experiment.

### 3.3. Ammonia and CO release

A problematic issue in WWS gasification is the ammonia release, because it is a NO<sub>x</sub> precursor. Kinetic of pollutants (NH<sub>3</sub>) release can be different from fuel gas (CO, H<sub>2</sub>, CH<sub>4</sub>...) release. Indeed Hernandez et al. [8] compared the NH<sub>3</sub> release to fuel gas release such as CO under pure steam gasification conditions for WWS, they found that the most part of ammonia is released below 773 K and fuel gas over 773 K. Thereby, in this work the NH<sub>3</sub> and CO kinetic release were selected as a comparison of parameters. The release of NH<sub>3</sub> and CO was followed by FTIR depending on time and temperature according to the protocol developed previously by Hernandez et al. [8].



**Fig. 4.** Composition (in %vol) of the syngas produced during the gasification of different feedstock.

The ammonia released (Fig. 5(C) and (D)) was similar for DWWS and SWWS. The ammonia production followed the raw fuel nitrogen amount (excepted OP) (Table 1). This fact is established in literature, similar observation is described by Van der drift et al. [16]. It was more important for OP, WW and RE compared to SRF, PA and PL. Moreover, it can be observed that the ammonia released have the same kinetics trend for all feedstocks: production begins at  $573 \text{ K} \pm 20 \text{ K}$ , the maximum production was reached at about 823 K (SWWS 7% volume fraction, DWWS 6% volume fraction and WW 3% volume fraction). The same trend of ammonia release for WWS was described in earlier work by Hernandez et al. [8]. WWS (S and D) are the most syngas pollutant release feedstock. Co-gasifying WWSs with other feedstock may tend to reduce the pollutant concentration in the syngas.

The carbon monoxide production kinetics depends on the raw feedstock composition unlike ammonia production. It can be observed in Fig. 5(E) and (F) that the WWSs started to produce CO at about 573 K. SWWS reach rapidly a plateau at about 7% volume fraction then a linear increase was observed from 1053 K to reach 15% volume fraction at 1123 K. DWWS was observed to produce a small amount of CO at 573 K then a linear increase from 773 K until it reached 14% volume fraction at 573 K. As a result for SWWS and DWWS the most part of CO was produced at temperature  $>773 \text{ K}$ . The SRF had the same CO kinetics trend compared to WWSs, where the max production took place at

1123 K (13% volume fraction). Until 898 K WW reached a plateau where the production became quasi constant at 7% volume fraction. RE started to produce CO at low temperature  $<523 \text{ K}$ , maximum production was reached at 723 K (14% volume fraction), and decreased over 773 K. PA and PL exhibited the same trend compared to RE, where the maximum CO production took place at 823 K (16%vol PL and 14% Pa) then the production decreased over  $600 \text{ }^\circ\text{C}$ . Therefore RE, PA and PL produced the main part of CO at temperature  $<823 \text{ K}$ . Results presented in Fig. 5 indicate that the release of the major N-pollutants (mainly ammonia) happened at low temperature, before 823 K. If this temperature is taken as reference for the different feedstock, it can be observed that OP, WW, SRF had same CO production with WWS. As result the staged gasification as proposed for WWS in Ref. [8] can be extended from WWS to that feedstock. A specific attention needs to be taken with extending staging for Pa, PL and RE, where a significant part of CO was produced simultaneously with  $\text{NH}_3$  release which represented 72%, 83% and 78% mass fraction of total CO produced during whole experiment.

### 3.4. Ash composition and melting

As mentioned in 3.1, the ASTM ash fusibility tests (Table 1) indicate that the ash melting problems can occur over the expected temperature of gasification (1123 K). Fusibility tests give an indication on ash behavior, however, these tests should be handle

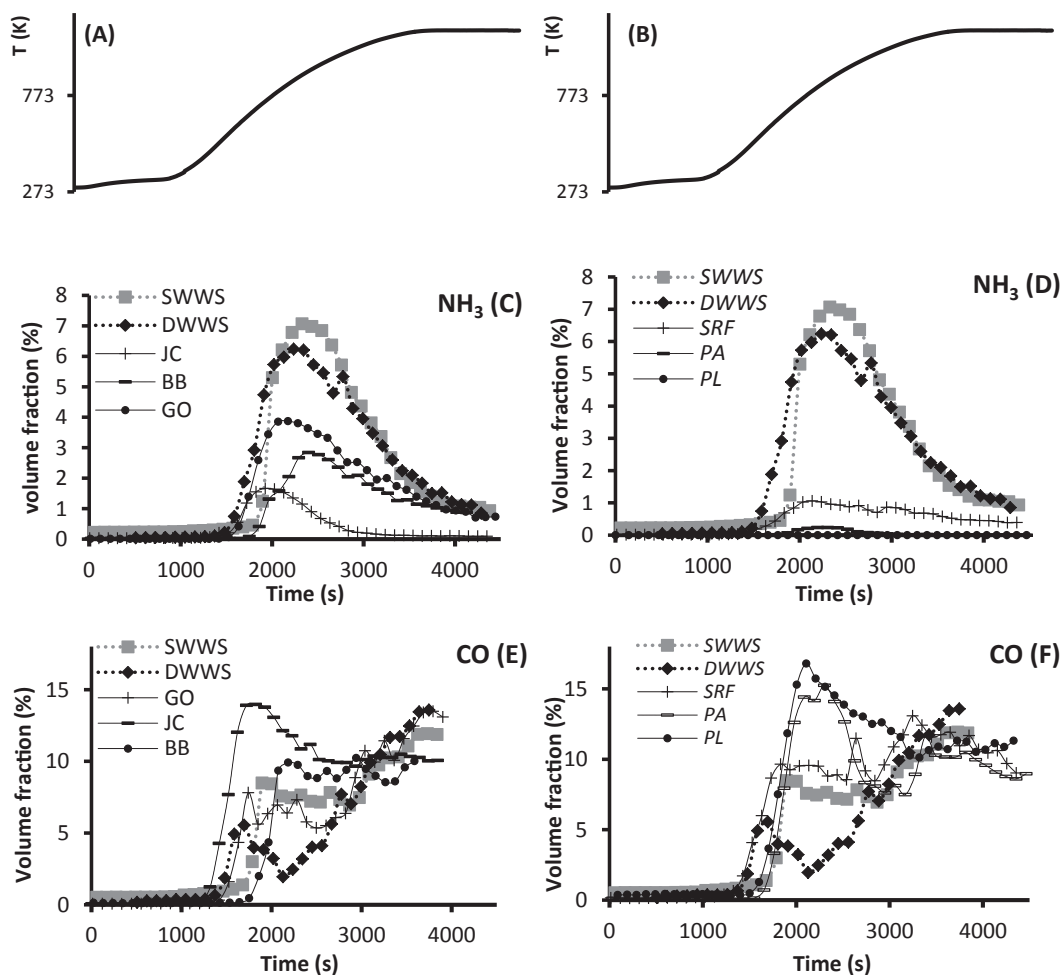


Fig. 5. Temperature profile applied during the experiment depending on time (A and B).  $\text{NH}_3$  release expressed in volume fraction depending on time for SWWS, DWWS, RE, OP and WW (C);  $\text{NH}_3$  release expressed in volume fraction depending on time for SWWS, DWWS, SRF, PA and PL (D); CO release expressed in volume fraction depending on time for SWWS, DWWS, RE, OP and WW (E); CO release expressed in volume fraction depending on time for SWWS, DWWS, SRF, PA and PL (F).

carefully as they are not always representative of real behavior of ashes [27–30].

The concentration of elements involved in slagging and fouling were expressed as oxides compounds and given in Fig. 6. Those compositions in oxides are typical from  $\mu$ -XRF data. In the following, oxide compositions are used for the discussion.

A significant amount of Na detected for all feedstock except PL. K amount was important for OP, SWWS, Re and PA (at 30%, 5%, 3% and 4% mass fraction of ash expressed as oxides respectively). The alkali elements (Na + K) are normally related to low melting temperature systems formation such as the mixture of  $\text{Na}_2\text{O} - \text{SiO}_2$  or  $\text{K}_2\text{O} - \text{SiO}_2$  which can lead to eutectic apparition (at about 22% mass and 25% mass respectively of  $\text{SiO}_2$ ). Melting point is mentioned to be close to 1063 K and 1053 K respectively [39]. Moreover alkali coupled with chlorine and sulfur can induce the formation of low temperature melting salts such as  $(\text{K,Na})\text{Cl}$ – $(\text{K,Na})_2\text{CO}_3$ – $(\text{K,Na})_2\text{SO}_4$  and create deposits downstream the reactor and generate corrosion [40].

It can be observed (Fig. 6) that both WWS had a similar composition, being Ca the major element (expressed as CaO 30% mass and 18% mass for SWWS and DWWS one respectively), this is probably due to the use of lime as stabilization agent for WWS in WWTP. Ca was also the main compound for PA, WW and SRF (expressed as CaO in mass fraction of ash 60.5%, 20.7% and 35.7% respectively). The Si was the main compound for Re and PL (expressed as  $\text{SiO}_2$  in mass fraction of ash 23% and 21%). Ti and Al (expressed as  $\text{TiO}_2$  and  $\text{Al}_2\text{O}_3$  in mass fraction of ash) were important for WW at 5% and for 14% respectively.

The K, Na, Ca, Mg elements in addition to Fe are involved on slagging and fouling indexes and are taken into account for the calculation of alkali index (Eq. (1)) slagging index (Eq. (2)) and fouling index (Eq. (3)). Results are given in Table 3.

In Table 3, the alkali index “al” indicates that, except PA and PL, fouling is virtually certain to occur for the different feedstocks according to Jenkins et al. [41] especially for OP. Regarding to other indexes: Rs, Fu and chlorine (Table 3), it can be observed that PA and PL do not cause slagging or fouling. SWWS and DWWS indexes indicate that Slagging and fouling are virtually certain to occur specially for DWWS. The same trend was observed for OP, WW and SRF. In addition the presence of chlorine in SRF and DWWS can increase the fouling tendency. Slagging and fouling tendency were less important for RE.

In order to co-gasify WWS – co-feedstock, a specific attention has to be taken on blends based on DWWS mixed with SRF or WW, where the interaction of ashes may complicate the gasification

process due to slagging and fouling phenomenon (high presence of chlorine and sulfur). On the other hand WWS – PL or PA may reduce slagging and fouling tendency of the WWSs.

### 3.5. Co-gasification feasibility

The co-gasification feasibility was evaluated regarding the characterization criteria based on thermochemical composition and gasification behavior. A particular attention was given to pollutant release kinetic and ash behavior which are critical for the possible implementation of co-gasifier especially fluidized beds ones.

The different characterizations indicated that all feedstock are recoverable by gasification. The characterizations indicated that the SWWS and DWWS presented similar thermochemical composition and gasification behavior. The most important difference was noticed to the ash composition and the predicted fouling and slagging tendencies. The Ash characterization indicated that the slugging, fouling and chlorine presence in DWWS induce high virtual slagging and fouling occurrence, when the fouling and slagging are virtually limited and lower for SWWS. For these reasons the blends should be based on SWWS.

PL and PA are low nitrogen amount fuels, the  $\text{NH}_3$  release for these fuel was very low and undetectable respectively. They presented low moisture, mineral matter and do not present virtually any slagging and fouling problems. As a result, these feedstock can be used in co-gasification with SWWS and even with DWWS without any restriction according to the study criteria.

Biomasses RE, WW and OP presented some weaknesses according to the study criteria. The feedstocks presented lower carbon conversion compared to other feedstock especially OP.

The OP presented a significant  $\text{NH}_3$  release, but it was lower compared to WWS. It presented high alkaline amount and low acid element content (Fe, Al, Ti) inducing high slagging and fouling tendency. Blending OP with DWWS should be avoided, especially for ash problems, however, the OP presented low mineral matter content (1.4% mass fraction of dm), blending with SWWS can bring acidic elements that can reduce the slagging tendency. For this reason the WWS – OP co-gasification needs additional experiments to state on this mixture.

WW was virtually more problematic than SWWS regarding slagging and fouling, it presented higher slagging and fouling indexes, for this reason blending with WWS should be avoided for instance. Complementary tests have to be carried out to confirm the prediction.

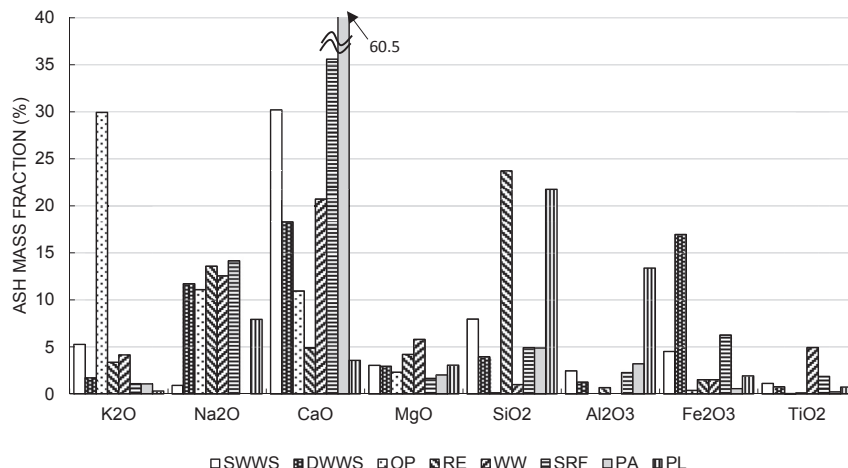


Fig. 6.  $\mu$ -XRF results on feedstock ash expressed as oxides.



**Table 3**  
Slagging and fouling index calculated according to  $\mu$ -XRF ash composition.

	SWWS	DWWS	RE	WW	OP	SRF	PA	PL
slagging index, Rs	2.1	5.7	0.1	1.0	50.41	0.6	0.5	0.0
fouling index, Fu	0.19	0.85	0.12	0.92	172.27	0.71	0.06	0.03
alkali index, Al (kg MJ <sup>-1</sup> )	0.47	1.46	0.03	0.88	0.38	0.64	0.05	0.08
chlorine index, Cl (mg kg <sup>-1</sup> )	640	2400	1200	770	620	4600	780	600

RE can be blinded with SWWS without any restriction regarding the criteria of the study. A specific attention should be taken at the solid residence time to obtain a target conversion. A specific care should be taken to Cl content in RE (1200 mg kg<sup>-1</sup> dm) it may virtually worsen fouling behavior of DWWS.

SRF presented similar carbon conversion compared to PA and PL, the NH<sub>3</sub> release is lower than the WWs. This feedstock presented a slagging and fouling tendency between SWWS and DWWS. In addition, this feedstock presents the highest chlorine concentration (4600 mg kg<sup>-1</sup>). For these reasons the blends based on DWWS – SRF should be avoided, because the Cl may contribute to worsen the fouling tendency. A specific attention have to be taken to fouling when SWWS is blended with SRF.

#### 4. Conclusion

In this study the thermal behavior of different feedstock was tested in order to evaluate the feasibility of their co-gasification. The test concerned the thermochemical properties, the NH<sub>3</sub> and fuel gas kinetic release and ash behavior.

The experimental results indicate that all feedstock can be recoverable by gasification. The Waste Water Sludge exhibit syngas composition with a Low Heating Value of 10.1 MJ m<sup>-3</sup>, other feedstock exhibit closer Low Heating Value between 9.0 and 11.9 MJ m<sup>-3</sup>. It was observed that staging gasification is possible to feedstock other than waste water sludge and should still be possible if Wastewater Sludge is combined with Olives Pomace, Reeds, Waste Wood and Solid Recovered Fuel.

Regarding the ash behavior through slagging and fouling prediction, Digested Wastewater Sludge is virtually more problematic than Secondary Wastewater Sludge. In order to limit possible ash problem the use of Secondary Wastewater Sludge is preferable. Olives Pomace exhibited an extreme virtual tendency of slagging and fouling the tendency was lower for Solid Recovered Fuel then Waste Wood, Reeds. Paper Labels and Plastic Labels do not present any considerable slagging or fouling tendency.

According to the different evaluation criteria the Paper Labels and Plastic Labels can be valorized by through co-gasification with Secondary and even Digested Wastewater Sludge without any restriction. Reeds and Solid Recovered Fuel can be blinded with Secondary Wastewater Sludge without any restriction. However their blend with Digested Wastewater Sludge may increase fouling problems. The blends based on Waste Wood and Olives Pomace should be avoided due to their ash slagging and fouling tendency. To conclude, this work proves that the concerns related with Wastewater sludge gasification (pollutant release and ash fusibility) can be overcome using the appropriate technology and blending it with other wastes improving its quality. Particularly, the blend of Plastic Labels with Secondary Wastewater sludge has been proven to limit ammonia release, maximize the heating value and limit the ashes problems.

#### Acknowledgments

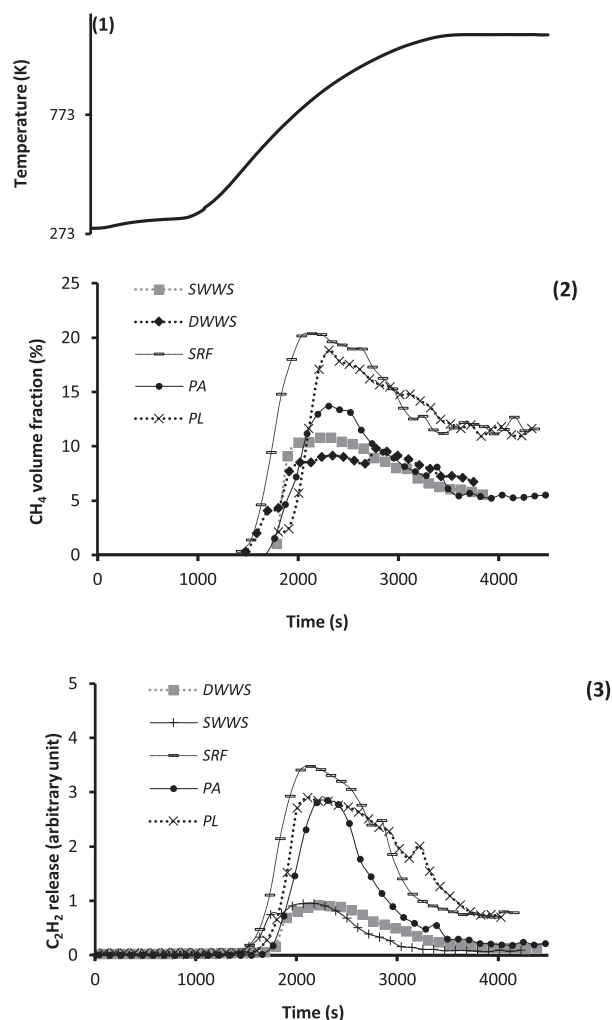
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#### Appendix A

Table A.1. Composition of the syngas during the gasification of different feedstock at 1123 K (average of 3 chromatograms)

Product	SWWS	DWWS	GO	JC	BB	CSR	PA	PL
<i>Product Gas (% vol)</i>								
H <sub>2</sub>	50	49	42	43	45	58	54	44
CO	19	19	22	19	20	9	15	19
CH <sub>4</sub>	10	9	14	7	16	10	9	20
C <sub>2</sub>	0	0	2	7	0	6	0	2
CO <sub>2</sub>	17	19	19	24	18	16	22	13
N <sub>2</sub>	4	4	1	0	1	0	0	1

#### Appendix B



**Fig. B.** (1) Temperature profile applied during the experiment depending on time. (2) CH<sub>4</sub> release expressed in volume fraction depending on time for SWWS, DWWS, SRF, PA and PL; (3) C<sub>2</sub>H<sub>4</sub> release expressed in arbitrary unit (from FT-IR measurement) depending on time for SWWS, DWWS, SRF, PA and PL.

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