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

Salah Akkache, Ana-Belén Hernández, Gabriel Teixeira, Franck Gelix, Nicolas Roche, Jean Henry Ferrasse

Aix-Marseille University, CNRS, M2P2 UMR7340, Europole de l’Arbois Bâtiment Laennec, Hall C, 13454 Aix en Provence, France
University of Johannesburg, Department of Civil Engineering Science, Kingsway Campus, PO Box 524, Auckland Park, 2006 Johannesburg, South Africa
Aix-Marseille University, CNRS, M2P2 UMR7340, Europole de l’Arbois Bâtiment Laennec, Hall C, 13454 Aix en Provence, France
Veolia Recherche et Innovation, 78520 Limay France

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$^{-3}$. The major concerns regarding the wastewater sludge were the pollutants precursors’ release (NH$_3$, 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 blinded 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$^{-1}$ 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$_x$ and NO$_x$ 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 mater present in the WWS. However, the pollutants release (H$_2$S, NH$_3$, 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$_3$ level in the syngas was the same level with the demolition wood alone, the H$_2$ 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
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-steamed 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, CH4, CnHm, 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 K2O can interact with SiO2 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−1 fouling or slagging is probable, when it is greater than 340 g GJ−1 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.

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

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 (DVWS) 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

<table>
<thead>
<tr>
<th>Abbreviation (Volumes are given in m³ at standard conditions (273 K and 1.013 × 10⁵ N m⁻²)</th>
<th>Al</th>
<th>alkalin index</th>
</tr>
</thead>
<tbody>
<tr>
<td>WWS wastewater sludge</td>
<td>Rs</td>
<td>slagging index</td>
</tr>
<tr>
<td>SWWS secondary wastewater sludge</td>
<td>Fu</td>
<td>fouling index</td>
</tr>
<tr>
<td>DWWS digested wastewater sludge</td>
<td>daf</td>
<td>dry ash free basis</td>
</tr>
<tr>
<td>WWTP wastewater treatment plant</td>
<td>dm</td>
<td>dry basis</td>
</tr>
<tr>
<td>OP olives pomace</td>
<td>mgas</td>
<td>mass of the total gas collected along all experiment (calculated)</td>
</tr>
<tr>
<td>RE reeds</td>
<td>mchar</td>
<td>mass of the total char collected at the end of experiment</td>
</tr>
<tr>
<td>WW waste wood</td>
<td>m0</td>
<td>initial sample mass</td>
</tr>
<tr>
<td>SRF solid recovered fuel</td>
<td>%daf</td>
<td>mass fraction of the dry ash free basis</td>
</tr>
<tr>
<td>PA paper labels</td>
<td>yi</td>
<td>volume fraction of the specie CO, H₂, CH₄ and C₂</td>
</tr>
<tr>
<td>PL plastic labels</td>
<td>ηconv</td>
<td>conversion rate</td>
</tr>
</tbody>
</table>
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 introduced in a heating mantle at 2.22 mg s\(^{-1}\). The steam gasification out line is used in order to obtain the H\(_2\); CO; CO\(_2\); CH\(_4\); N\(_2\) concentrations measurement of CO, CH\(_4\), and NH\(_3\) in the produced gas. Other compounds, such as COS, C\(_2\)H\(_6\), and H\(_2\)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 Hayesep P and a molecular sieve SA Agilent®) is used outline to measure the H\(_2\); CO; CO\(_2\); CH\(_4\); C\(_2\) and C\(_3\) 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 \(\mu\)-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 LHV (Mj kg\(^{-1}\)) and proximate and ultimate analysis.

### Table 1

Feedstock LHV, proximate and ultimate analysis.

<table>
<thead>
<tr>
<th></th>
<th>DWWS</th>
<th>SWWS</th>
<th>RE</th>
<th>WW</th>
<th>OP</th>
<th>SRF</th>
<th>PA</th>
<th>PL</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Proximate analysis, mass fraction (%)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Raw material moisture</td>
<td>81.3</td>
<td>81.8</td>
<td>7.6</td>
<td>7.3</td>
<td>29.6</td>
<td>14.0</td>
<td>4.4</td>
<td>2</td>
</tr>
<tr>
<td>Dried material moisture</td>
<td>2.4</td>
<td>0.5</td>
<td>1.9</td>
<td>0.5</td>
<td>1.1</td>
<td>5.8</td>
<td>2.8</td>
<td>0.9</td>
</tr>
<tr>
<td>Mineral matter (dry basis)</td>
<td>26.9</td>
<td>19.6</td>
<td>10.7</td>
<td>8.5</td>
<td>1.5</td>
<td>11.7</td>
<td>9.1</td>
<td>3.8</td>
</tr>
<tr>
<td><strong>CHNS (mass fraction on dry ash free basis)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>52.6</td>
<td>54.9</td>
<td>48.7</td>
<td>49.8</td>
<td>59.5</td>
<td>63.8</td>
<td>48.4</td>
<td>70.6</td>
</tr>
<tr>
<td>H</td>
<td>7.2</td>
<td>7.3</td>
<td>5.9</td>
<td>6.3</td>
<td>7.3</td>
<td>8.6</td>
<td>6.3</td>
<td>10.8</td>
</tr>
<tr>
<td>N</td>
<td>9.8</td>
<td>9.3</td>
<td>0.9</td>
<td>2.8</td>
<td>1.8</td>
<td>0.5</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>S</td>
<td>1.2</td>
<td>0.8</td>
<td>0.2</td>
<td>0.2</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>0.0</td>
</tr>
<tr>
<td>O</td>
<td>21.3</td>
<td>22.2</td>
<td>39.5</td>
<td>37.2</td>
<td>29.8</td>
<td>23.8</td>
<td>41</td>
<td>17.8</td>
</tr>
<tr>
<td>H/(\text{C}) (atom ratio)</td>
<td>1.6</td>
<td>1.6</td>
<td>1.5</td>
<td>1.5</td>
<td>1.5</td>
<td>1.6</td>
<td>1.6</td>
<td>1.8</td>
</tr>
<tr>
<td>LHV(Mj kg(^{-1})) on dry basis</td>
<td>14.6</td>
<td>17.6</td>
<td>16.4</td>
<td>17.3</td>
<td>23.6</td>
<td>23.1</td>
<td>17.0</td>
<td>32.9</td>
</tr>
<tr>
<td><strong>ASTM fusibility tests, temperature K</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Initial deformation</td>
<td>1547</td>
<td>1398</td>
<td>1536</td>
<td>1626</td>
<td>1723</td>
<td>1472</td>
<td>1728</td>
<td>1667</td>
</tr>
<tr>
<td>Softening</td>
<td>1644</td>
<td>1523</td>
<td>1557</td>
<td>&gt;1773</td>
<td>&gt;1773</td>
<td>1486</td>
<td>1757</td>
<td>&gt;1773</td>
</tr>
<tr>
<td>Hemispherical</td>
<td>1650</td>
<td>1533</td>
<td>1542</td>
<td>&gt;1773</td>
<td>&gt;1773</td>
<td>1489</td>
<td>1759</td>
<td>&gt;1773</td>
</tr>
<tr>
<td>Fluid</td>
<td>1655</td>
<td>1538</td>
<td>1580</td>
<td>&gt;1773</td>
<td>&gt;1773</td>
<td>1502</td>
<td>1761</td>
<td>&gt;1773</td>
</tr>
</tbody>
</table>

An inline Fourier Transform Infrared (FTIR) Perkin Elmer spectrum 65® , previously calibrated, allows the volumetric concentrations measurement of CO, CH\(_4\), and NH\(_3\) in the produced gas. Other compounds, such as COS, C\(_2\)H\(_6\), and H\(_2\)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].

### 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).
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⁻¹ dm, 23.6 MJ kg⁻¹ dm, 23.1 MJ kg⁻¹ dm. These LHV are comparable or higher than some lignite and bituminous coal (LHV ranging from 9 MJ kg⁻¹ dm to 20 MJ kg⁻¹ 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 results are given in Table 2.

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].

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 CH₄ (15–25% volume fraction and C₂ (C₂H₂, C₂H₄ and C₂H₆) 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

\[
LHV_{\text{syngas}} = y_{\text{H}_2}LHV_{\text{H}_2} + y_{\text{CO}}LHV_{\text{CO}} + y_{\text{CH}_4}LHV_{\text{CH}_4} + y_{\text{C}_2}LHV_{\text{C}_2}
\]

\[
\eta_{\text{conv}} = \frac{m_0 - m_{\text{char}}}{m_0 \times \delta_{\text{daf}}}
\]
both WWSs are rich in fuel gas (total fuel gas volume fraction at 72% with CO at about 20% and H₂ at 33% volume fraction). The OP produced the highest amount of H₂ (45% volume fraction), followed by PA, SRF and WW (36, 34 and 30% volume fraction, respectively). Lower H₂ 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, 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 time, 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⁻³). The high LHV noted to PL and SRF are due to CH₄ and C₂ in that syngas mostly released during devolatilisation (See Appendix B.2 and B.3). D & S WWS, presented LHV at 11.5 MJ m⁻³ and 11.7 MJ m⁻³, PA and WW presented similar LHV at 10.1 MJ m⁻³. The RE had the lowest LHV value 5.8 MJ m⁻³, due to the low H₂ and high CO₂ production (13 and 34% volume fraction respectively). The high amount of CO₂ can be explained by the release of the initial oxygen present in the feedstock during devolatilisation. This CO₂ 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 CO₂ level decreased (between 13 to 24% volume fraction) and LHV became more typical of steam gasification especially to PL at 11.9 MJ m⁻³ and RE at 10.2 MJ m⁻³ (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 NOₓ precursor. Kinetic of pollutants (NH₃) release can be different from fuel gas (CO, H₂, CH₄….) release. Indeed Hernandez et al. [8] compared the NH₃ 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 NH₃ and CO kinetic release were selected as a comparison of parameters. The release of NH₃ and CO was followed by FTIR depending on time and temperature according to the protocol developed previously by Hernandez et al. [8].
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 in 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 K ± 20 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 K. The SRF had the same CO kinetics trend compared to WWSs, where the max production taked 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 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 taked place at 823 K (16%vol PL and 14% Pa) then the production decreased over 600 °C. Therefore Re, PA and PL produced the main part of CO at temperature <823 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 NH₃ 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
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 μ-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 Na2O – SiO2 or K2O – SiO2 which can lead to eutectic apparition (at about 22% mass and 25% mass respectively of SiO2). 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 (K,Na)Cl-(K,Na)2CO3-(K,Na)2SO4 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 SiO2 in mass fraction of ash 23% and 21%). Ti and Al (expressed as TiO2 and Al2O3 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.

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 WWWS – 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 NH3 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 NH3 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 WW should be avoided for instance. Complementary tests have to be carried out to confirm the prediction.

![Fig. 6. μ-XRF results on feedstock ash expressed as oxides.](image-url)
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⁻¹ dm⁻¹) it may virtually worsen fouling behavior of DWWS.

SRF presented similar carbon conversion compared to PA and PL, the NH₃ release is lower than the WWSs. This feedstock presented a slagging and fouling tendency between SWWS and DWWS. In addition, this feedstock presents the highest chlorine concentration (4600 mg kg⁻¹). 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 NH₃ 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⁻³, other feedstock exhibit closer Low Heating Value between 9.0 and 11.9 MJ m⁻³. 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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### Table 3
Slagging and fouling index calculated according to μ-XRF ash composition.

<table>
<thead>
<tr>
<th></th>
<th>SWWS</th>
<th>DWWS</th>
<th>RE</th>
<th>WW</th>
<th>OP</th>
<th>SRF</th>
<th>PA</th>
<th>PL</th>
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<tr>
<td>slagging index, Rs</td>
<td>2.1</td>
<td>5.7</td>
<td>0.1</td>
<td>1.0</td>
<td>50.41</td>
<td>0.6</td>
<td>0.5</td>
<td>0.0</td>
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<td>fouling index, Fu</td>
<td>0.19</td>
<td>0.85</td>
<td>0.12</td>
<td>0.92</td>
<td>172.27</td>
<td>0.71</td>
<td>0.06</td>
<td>0.03</td>
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<td>alkali index, Al (kg MJ⁻¹)</td>
<td>0.47</td>
<td>1.46</td>
<td>0.03</td>
<td>0.88</td>
<td>0.38</td>
<td>0.64</td>
<td>0.05</td>
<td>0.08</td>
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<tr>
<td>chlorine index, Cl (mg kg⁻¹)</td>
<td>640</td>
<td>2400</td>
<td>1200</td>
<td>770</td>
<td>520</td>
<td>4600</td>
<td>780</td>
<td>600</td>
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</table>

### Appendix A

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

<table>
<thead>
<tr>
<th>Product</th>
<th>SWWS</th>
<th>DWWS</th>
<th>GO</th>
<th>JC</th>
<th>BB</th>
<th>CSR</th>
<th>PA</th>
<th>PL</th>
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<tr>
<td>H₂</td>
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<td>49</td>
<td>42</td>
<td>43</td>
<td>45</td>
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<td>54</td>
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<td>19</td>
<td>20</td>
<td>9</td>
<td>15</td>
<td>19</td>
</tr>
<tr>
<td>CH₄</td>
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<td>14</td>
<td>7</td>
<td>16</td>
<td>10</td>
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<tr>
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<td>0</td>
<td>0</td>
<td>2</td>
<td>7</td>
<td>0</td>
<td>6</td>
<td>0</td>
<td>2</td>
</tr>
<tr>
<td>CO₂</td>
<td>17</td>
<td>19</td>
<td>19</td>
<td>24</td>
<td>18</td>
<td>16</td>
<td>22</td>
<td>13</td>
</tr>
<tr>
<td>N₂</td>
<td>4</td>
<td>4</td>
<td>1</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>1</td>
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</table>

### Appendix B
Fig. B. (1) Temperature profile applied during the experiment depending on time. (2) CH$_4$ release expressed in volume fraction depending on time for SWWS, DWWS, SRF, PA and PL. (3) CO$_2$ release expressed in arbitrary unit (from FT-IR measurement) depending on time for SWWS, DWWS, SRF, PA and PL.

References


