# Thermochemical Decomposition of Sewage Sludge – An Eco-Friendly Solution for a Sustainable Energy Future by Using Wastes

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*Abstract: The study aims to promote clean energy technologies that ensure the recycling and recovery of waste, namely the sewage sludge (SS), by converting it into products (e.g. oil, gas) with added value, contributing thus to reducing the negative impact on environment and health. An experimental setup was proposed in order to achieve the pyrolysis process, by varying the heating rate, (5°C/min, 10°C/min and 50°C/min). The resulted products, namely i) char - $SS_{PyChar}$, ii) oil - $SS_{PyOil}$ and iii) gas - $SS_{PyGas}$, were investigated in terms of elemental content, high heat value (HHV), low heat value (LHV) and emission factor (EF). The pyrolysis oils obtained with lower heating rate, 5°C/min and 10 °C/min, presented higher HHV, in comparison with the oils obtained at 50 °C/min, which were rich in water. These oils can have a negative impact on the environment, through their combustion due to their high content of N (6 wt%) and S (1.2 wt%), responsible for the formation of NOx and SOx. Pyrolysis gas revealed in its composition high contents of hydrocarbons ($C_1$-$C_6$), carbon dioxide ($CO_2$) and hydrogen ($H_2$). The highest HHV was obtained by using 5°C/min increment, namely 33.81 MJ/$m^3$. Also, the pyrolysis gases had comparable energy values with natural gas, biogas or gases resulted from the plastic pyrolysis.*

*Keywords: gas, heat value, oil, pyrolysis, sewage sludge*

## 1.Introduction

**1.** The economic growth generated by rising living standards and technological levels, along with climate changes, due to greenhouse gas emissions and the acute shortage of resources are among the major challenges for a sustainable development. Therefore, the modern society is looking for new sources of raw materials that can be exploited over a longer sustainable time, but with energy values similar to fossil resources and without affecting the quality of the environment and life [1]. In the last decade, the industry development and the rapid urbanization led to the waste increase, as well as of the sewage sludge (SS), produced in the biological wastewater treatment plants (WWTP), through the anaerobic fermentation of organic particles.

The municipal and industrial water is treated before being discharged into rivers in order to remove the pollutants. Wastewater contains a number of organic, inorganic, toxic and pathogenic components [2-5]. Pollutants form a semi-solid residue in wastewaters, namely sewage sludge, which require sterilization, stabilization and disposal treatments [6, 7]

Sewage sludge (SS) is rich in nitrogen, phosphorus and potassium, being used worldwide in agricultural-forestry area, as an "ideal fertilizer", due to its low cost and abundance.

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In 2014, all European Union (EU) member countries used the SS for agriculture purposes, generating undesirable emissions for both soil and water. For example, the highest percentage of SS used in agriculture was in Ireland, ~ 70 %, followed by Bulgaria and France with ~ 50 % and ~ 45 %, respectively [8]. At the opposite were Malta, Netherlands, Slovakia and Slovenia with less than 1%.

However, due to the presence of potential toxic compounds (e.g. polycyclic aromatic hydrocarbon, heavy metals, dioxins, furans or drugs) the EU restricted the utilisation of SS in agriculture for soil fertilization [9-12].

The pollutants, mainly the heavy metal accumulations in water and in soil, along with the carbon dioxide ($CO_2$), have a hazardous impact on the environment [13]. Therefore, it is important to develop environmentally friendly methods to recycle the waste and to reduce the hazards caused by sludge. One of these methods can be the pyrolysis process, due to the thermal decomposition of organic substances of the sewage sludge, in the absence of oxygen, which generates products, such as bio-char, liquid bio-oil and non-condensable gas [14-16]. Also, this method can be a solution for sewage sludge volume reduction [17].

The char resulted as by-product from the sewage sludge pyrolysis (SS) can be used to improve the soil fertility and to increase the cationic capacity, *p*H value and soil ability to retain water [18-20]. Also, the sludge mixed with coffee ground residues, resulted from instant coffee processing, conducted to the obtaining of solid biofuels [21]. The thermogravimetric analysis of raw materials and blends, in air ($O_2/N_2$, 21/79) and oxy-fuel ($O_2/CO_2$, 21/79) atmospheres, revealed that the replacement of $N_2$ with $CO_2$ decreases the burnout performance. The resulted NO emissions, after the char combustions, were lower for blends than for sewage sludge [21].

Food production derived waste by mixing with sewage sludge, under subcritical hydrothermal conditions, conducted to the production of gas, oil and solid fuels [22]. Also, the obtained solids biochar and the effluent water can be used as agricultural biochar and liquid fertilizer, respectively, due to the organic carbon content and the small concentration of nitrogen [22].

The main objective of this study was to assess the feasibility of eliminating SS along with exploiting its valorisation for energy purposes. Therefore, it was investigated the pyrolysis process, at different pyrolysis heating rates, by using the sewage sludge as raw materials in order to obtain products with added value. The pyrolysis products (oil, char and gas) and the waste were characterized by different techniques, to better understand the properties of the obtained alternative fuels and the influence of heating rate.

## 2. Materials and methods
### 2.1. Sewage sludge samples
The SS samples were collected during February - April 2019, from the wastewater treatment plants in Ramnicu Valcea city, Romania, after the anaerobic digestion [23]. Regarding the textural characteristic, the SS was similar to a clay, with high humidity, over 80%.

### 2.2. Analytical investigations
The SS samples were firstly characterized in term of their organic content. In this respect, the SS was subjected to an investigation of the $^{13}C$ content by using an elemental analyzer (Flash EA1112 HT, Thermo Scientific, Italy).

The liquids obtained from the pyrolysis process were separated through centrifugation – (Hettich® EBA 20, Sigma Aldrich, Germany).

The analysis of elements, such as carbon (C), hydrogen (H) and oxygen (O) in SS samples and derived products (char and oil), was performed with an elemental analyzer (EA2000, Thermo Scientific, UK). Elements with negative impact, such as nitrogen (N), sulfur (S) and carbon (C) were investigated by combustion and pyrolysis, in interval 850-1060 ºC [24-26]. The obtained gases, after the pyrolysis, were separated through capillary columns packed with molecular sieve - SM 5A for carbon monoxide (CO) and polymer - Porapak Q for nitrogen dioxide ($NO_2$), carbon dioxide ($CO_2$), water ($H_2O$) and sulfur dioxide ($SO_2$) and analysed by TCD detector. Methionine (Thermo Fisher Scientific, Cambridge, UK) was used

as reference material, containing: 40.26 wt% C, 7.37 wt% H, 21.46 wt% S, 21.55 wt% O and 9.35 wt% N. Further, the measurements were validated by using cysteine (Thermo Fisher Scientific, Cambridge, UK), which has in composition: 29.95 wt% C, 5.09 wt% H, 26.67 wt%S, 26.67 wt% O and 11.59 wt% N.

The heating values (higher heating value - HHV and lower heating value - LHV) of the SS and pyrolysis products were determined with a calorimeter (C5000, IKA, Germany), via combustion method [27].

The composition of the pyrolysis gases was established by using the gas chromatography (CP 3800 Varian Inc., USA) and the applied method was also used in previous studies for natural gas and biogas evaluation [28-30].

The oils, resulted from pyrolysis process, were analysed by using Fourier transform infrared spectroscopy (Perkin Elmer, Massachusetts, USA) in transmission, in the range 400-4000 cm$^{-1}$ and with a resolution of 4 cm$^{-1}$. Thus, the samples were deposited on thallium-indium bromide (KRS-5), a material that does not absorb in the selected infrared domain. Also, the organic compounds were confirmed through gas chromatography coupled with mass spectrometry (Varian 450 GC-Varian 240 MS, California, USA).

In order to analyze the silica from oils it was used a high-resolution continuous source atomic absorption spectrometer (ContrAA 700, Analytik Jena AG, Jena, Germany), equipped with a standard burner head for the $N_2O$-$C_2H_2$ flame. Further, there were analyzed the elements content, such as Cr, Mn, Co, Ni, As, Sr, Cd, Hg, and Pb, in oils by using inductively coupled plasma mass spectrometer (Varian 820, Varian, Australia), equipped with a micro mist ultrasonic nebulizer.

## 2.3. Experimental set-up
### 2.3.1. Humidity extraction
The moisture extraction from the SS samples was achieved in a solar drying equipped with humidity extractor [31]. For sample drying it was required a time of 48 h, until the moisture decreased below 5 %. After this step, the resulted products were ground and sieved in order to obtain particles with size below 200 μm.

### 2.3.2. Pyrolysis process
The pyrolysis process was performed by using a lab-designed installation that is illustrated in Figure 1.
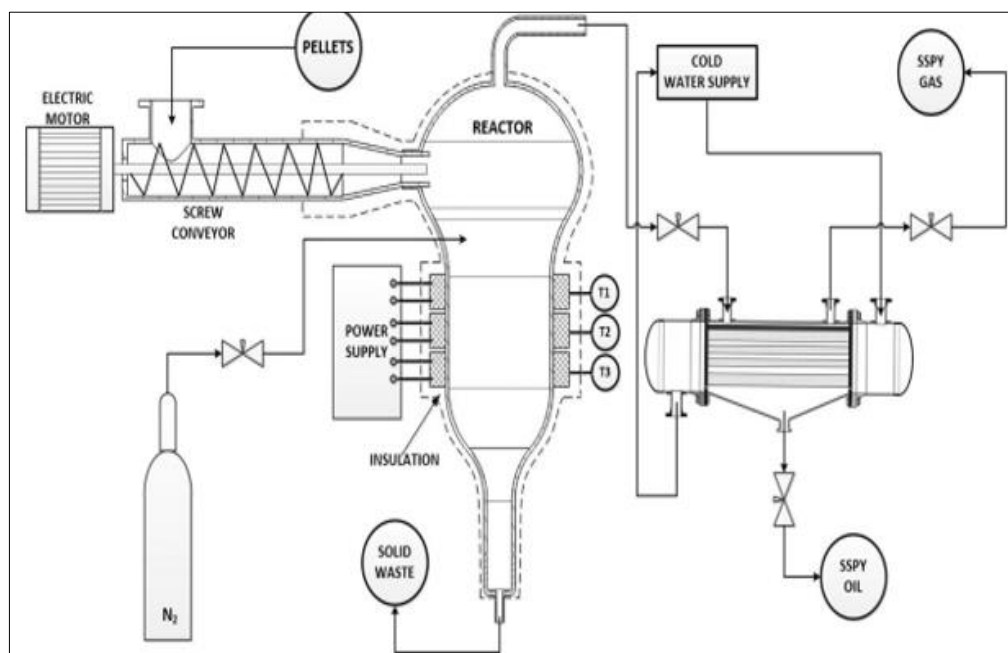


**Figure 1**. Experimental setup for sewage sludge pyrolysis

The main components of the experimental setup used in this study are: the sample feeder, the pyrolysis reactor and the condenser. The pyrolysis experiments were performed by using a SS quantity of 25 g. Thus, the SS was pushed into the reactor by the screw conveyor and then was heated until the temperature of 450°C was achieved. To reduce the oxygen level and to avoid the formation of environmentally harmful oxide compounds, it was assured a flow rate of 100 mL/min of high purity $N_2$ (99.999 vol%, Linde Gas, Germany), during the pyrolysis process. Prior to the experiments, it was calculated the required time for the total inertization, this being directly proportional with the inert gas flow and with the installation volume.

The unique design of the reactor, made from refractory steel, allows the continuous feeding process with SS and the superior spherical shape permits a longer contact between the raw material and the vapours, conducting to a better "extraction" of elements with high energy values, such as $H_2$, HCs, and $O_2$. To avoid the heat loss, the reactor was isolated with quartz and basalt wool (1:1), with a thickness of 5 mm.

The pyrolysis vapors pass quickly through the condenser, in about 20 s. The collected reaction products, during the pyrolysis process (at 450°C), were: (*i*) the liquid ($SS_{PyOil}$) - a semi-viscous mixture of black tar, water and oils; (*ii*) the non-condensable gases ($SS_{PyGas}$) - $H_2$, $O_2$, HCs, $H_2S$, CO, $CO_2$ and (*iii*) the solid char ($SS_{PyChar}$). Further, the pyrolysis products quantities (wt%) were calculated by using the equation (1):

$$SS_{PyGas} = 100 - \left( SS_{PyChar} + SS_{PyOil} \right) \qquad (1)$$

The reactor design permits to perform the pyrolysis tests by using dried SS samples and by varying the heating rate, namely 5°C/min, 10°C/min or 50°C/min, in order to observe the changes in resulted products ($SS_{PyChar}$, $SS_{PyOil}$ and $SS_{PyGas}$).

## 3. Results and discussions

In figure 2 are presented the ratios of liquid, gas and char (solid residue) obtained at different heating rates (5°C/min, 10°C/min or 50°C/min) of pyrolysis process.
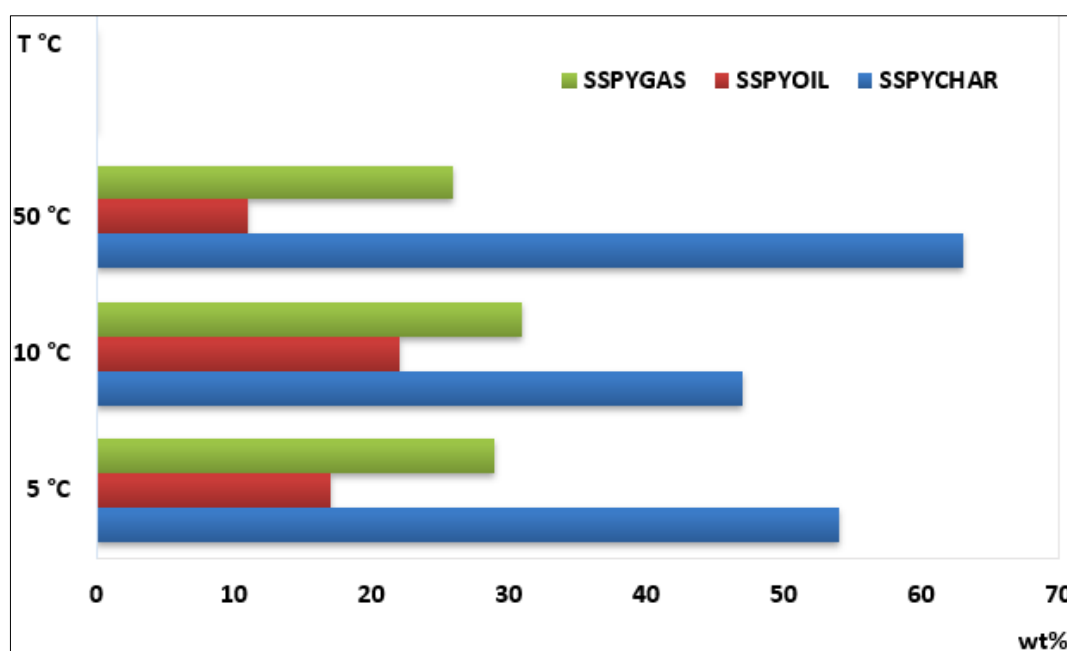


**Figure 2.** Variation of the yields of SSPyChar, SSPyOil and SSPyGas with the pyrolysis heating rate

Each series represents an average of 2 independent experiments in the same technical conditions, with a relative standard deviation below 5%. It can be observed that the highest content of char was obtained when the pyrolysis process was carried out with the heating rate of 50°C/min. The highest contents of gas and oil were obtained at the same heating rate, namely 10°C/min.

### 3.1. SS and SS$_{PyChar}$ properties

The ^{13}C investigation of the collected SS samples revealed a content over 95% of organic matter. Also, it was achieved a specific activity of 197 +/- 0.015 Bq/kg C, thus the fossil carbon intake being in interval 10.9 - 23 %.

The properties of both, SS and derived residue (SS$_{PyChar}$), resulted at different heating rate of pyrolysis process, are highlighted in Table 1. There were achieved HHVs around 2600 kcal/kg, in all cases, being between the values recorded in literature [32] and higher than the lignite HHV (~ 2100 kcal/kg) [23].

**Table 1**. SS and SS$_{PyChar}$ properties

| Parameter | SS | SS$_{PyChar}$ Heatig rate | | |
|---|---|---|---|---|
| | | 5 °C/min | 10 °C/min | 50 °C/min |
| W (wt%) | 82.37 | 1.09 | 0.79 | 1.25 |
| A (wt%) | 33.88 | 63.30 | 68.33 | 60.99 |
| V (wt%) | 55.71 | 10.96 | 8.67 | 6.53 |
| C (wt%) | 34.51 | 29.46 | 29.00 | 28.98 |
| H (wt%) | 5.01 | 1.17 | 1.04 | 1.33 |
| N (wt%) | 6.26 | 4.13 | 4.88 | 4.19 |
| S (wt%) | 0.86 | 0.47 | 0.46 | 0.56 |
| O (wt%) | 17.11 | 0.38 | 0.67 | 1.08 |
| C$^{fix}$ (wt%) | 8.04 | 24.65 | 25.77 | 24.65 |
| HHV (kcal/kg) | 3456 | 2633 | 2559 | 2539 |
| LHV (kcal/kg) | 3000 | 2209 | 2179 | 2007 |
| EF (t/TJ) | 92.05 | 103.14 | 104.04 | 106.98 |

W – humidity, V – volatiles, A – ash after combustion,
EF – emission factor, C$^{fix}$ – fixed carbon

Taking into account the high level of ash (> 60 wt%), caused by combustion of SSPyChar, due to inorganic phase, and to its content of nitrogen (> 4 wt%), this solid could not be an attractive fuel.

Also, the metals associated with the inorganic content of the SS remained in the SS$_{PyChar}$, being a distinct characteristic of the solid residue derived from the SS compared to those from lignocellulosic origin [12].

The different heating rates, used during experiments, did not influence the elemental composition of the obtained SS$_{PyChar}$. The typical contents of elements in SS and SSPyChar (at 10°C/min) are presented in Table 2.

**Table 2.** Elements level in SS$_{PyChar}$ compared to SS

| Material | Element concentration (mg/g) | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Cr | Fe | Mn | Ni | Cu | Zn | K | Na | Pb | Si |
| SS | 0.19 | 28.95 | 0.14 | 0.02 | 0.36 | 0.11 | - | - | 0.02 | 144.75 |
| SS$_{PyChar}$ | 0.45 | 0.09 | 0.26 | 0.23 | 1.64 | 1.52 | 4.70 | 2.65 | 0.06 | 323.32 |

Despite its high energy content, due to the presence of elements, such as H, C and O (Table 1), the SSPyChar has also high concentration of metals (Table 2).

### 3.2. SS$_{PyOil}$ properties

The condensed vapor resulted in this process represents the liquid fraction between the reaction products. Thus, the obtained products were introduced in polypropylene capsules and centrifuged at 5000 rpm/min, the solutions being separated into three fractions, namely ~ 15 wt% aqueous, ~ 83 wt% viscous

and ~ 2 wt% solid particles (tar). Tables 3 and 4 summarize the elemental compositions and the energy values of the oils resulted in this study against the values of various oils from different studies [1, 11, 12, 33-35].

**Table 3.** $SS_{PyOil}$ properties

| Parameter | $SS_{PyOil}$ 5 °C/min | $SS_{PyOil}$ 10 °C/min | $SS_{PyOil}$ 50 °C/min | $SS_{PyOil}$ [1] | $SS_{PyOil}$ [11] | $SS_{PyOil}$ [12] | $SS_{PyOil}$ [34] | $SS_{PyOil}$ [33] |
|---|---|---|---|---|---|---|---|---|
| W (wt%) | < 1 | < 1 | 66–70±7.75 | < 1 | < 1 | 10.90 | - | - |
| C (wt%) | 64.45±1.81 | 72.52±2.05 | 23.09±0.65 | - | - | - | 49.10-62.70 | 29.60-36.0 |
| H (wt%) | 8.97±0.23 | 9.09±0.23 | 4.14±0.10 | - | - | - | 9.80-11.5 | 0.70-5.20 |
| N (wt%) | 6.30±0.30 | 5.84±0.27 | 7.19±0.34 | - | - | - | 5.20-5.75 | 1.40-3.80 |
| S (wt%) | 1.12±0.05 | 1.27±0.06 | 2.03±0.10 | - | - | - | 0.43-0.56 | 0.52-0.72 |
| O (wt%) | 19.16±0.59 | 11.98±0.37 | - | - | - | 28.6 | 20.40-34.80 | 1.50-25.40 |
| HHV (kcal/kg) | 7230±90 | 8126±100 | 1230±15 | 6000 | 7729 | 5804-8980 | 4922-5193 | 2613-3955 |
| LHV (kcal/kg) | 6760±84 | 7650±95 | 769±9.54 | 5700 | 7215 | 5300-8122 | 4417-4609 | 2100-3421 |
| EF (t/TJ) | 82.18 | 82.27 | - | - | - | - | - | - |
| ρ 25 °C (g/cm³) | 1.06 | 1.21 | - | - | - | - | - | - |
| Colour/viscosity | black/ viscous | black/ viscous | black/ aqueous | - | - | - | - | - |

Higher HHVs were obtained for the oils resulted from pyrolysis processes which were performed at heating rates of 5°C/min and 10°C/min. Opposite, the oil obtained with the heating rate of 50°C/min, was rich in water (> 80 wt%) and had a low organic fraction (< 16 wt%).

**Table 4.** Properties and specifications of oils derived from different raw materials (reported in literature)

| Parameter | $PY_{OIL\ rice\ hull}$ [11] | $PY_{OIL\ biomass}$ [11] | $PY_{OIL\ sugar\ cane\ residue}$ [11] | $PPO_{HDPE\ 450}$ [35] |
|---|---|---|---|---|
| W wt% | - | - | - | < 1 |
| C wt% | - | - | - | 80.71 |
| H wt% | - | - | - | 13.24 |
| N wt% | - | - | - | 0.34 |
| S wt% | - | - | - | 0.005 |
| O wt% | - | - | - | 5.71 |
| HHV kcal/kg | 3941 | 4538 | 4872 | 11000 |
| LHV kcal/kg | 3442 | 4012 | 4336 | 9756 |
| EF t/TJ | - | - | - | 67.25 |
| ρ 25 °C g/cm³ | - | - | - | 0.76 |
| Colour/viscosity | black/aqueous | - | - | yellow |

The energy values for the pyrolysis oils obtained by using 5 and 10 °C heating rates were higher than the values of different oils obtained through the pyrolysis of various raw materials (Table 3 and Table 4). Thus, the use of these pyrolysis oils for energy purposes, either in their natural form or transformed by fractional distillation into fuels, cannot be ignored. The HHV recorded for the $SS_{PyOil}$, obtained with a heating rate of 10°C/min, namely 8126 kcal/kg, was similar to the values presented in literature [1, 11, 12, 35, 36] and in some cases being even double [11, 33]. In contrast, the concentration of N and S, two elements with high potential for negative environmental impact, through the formation of gaseous oxides, such as $SO_x$ and $NO_x$, after the oils combustion, were higher than the data reported in literature, namely, for N it was obtained 6.00 wt% in this study in comparison with 1.50 - 5.60 wt% [33, 37] and for S it was obtained 1.20 wt% in this study in comparison with 0.43 - 0.50 wt% [33, 34]. The high N content could be due to intensive utilisation of soil fertilizer for long period of time. The highest content of H, about 9 wt%, was obtained for $SS_{PyOil}$ with 10°C/min heating rate, while in the literature the values were between 0.70 and 11.50 wt% [33, 34].

Oxygen content is very important for the pyrolysis oil due to its caloric contribution and the values obtained in this study were in interval 12.00-19.00 wt%, comparable with oxygen values reported in

literature, namely in interval 1.50-28.60 wt% [12, 33, 34].

Comparing the HHV of oils obtained in this work with the data reported in literature of conventional liquid fuels [35], such as gasoline, kerosene, diesel and heavy fuel oil (Table 5), it can be observed that are similar.

**Table 5.** Conventional liquid fuels properties

| Parameter | Gasoline [35] | Kerosene/LFO [35] | Diesel [35] | Heavy Fuel Oil/HFO [35] |
|---|---|---|---|---|
| W (wt%) | < 1 | < 1 | < 1 | < 1 |
| C (wt%) | 85.16 | 84.00 | 83.46 | 86.93 |
| H (wt%) | 11.09 | 10.33 | 12.13 | 8.61 |
| N (wt%) | 0.31 | 0.59 | 0.75 | 0.64 |
| S (wt%) | 0.01 | 0.01 | 0.01 | 0.77 |
| O (wt%) | 3.43 | 5.07 | 3.65 | 3.05 |
| HHV (kcal/kg) | 10451 | 9782 | 11002 | 11355 |
| LHV (kcal/kg) | 9566 | 9200 | 9968 | 10471 |
| EF (t/TJ) | - | - | - | 88.16 |
| $\rho$ 25$^0$C (g/cm$^3$) | 0.81 | 0.84 | 0.78 | 0.80 |
| Colour | yellow-green | yellow | yellow-green | black |

The investigation of metals content in SS is very important, therefore Table 6 reveals the metal concentrations found in pyrolysis oils, but also in different types of liquid fuels from various studies [35, 38].

**Table 6.** Metal concentrations in $SS_{PyOil}$ in comparison with
data reported in literature for pyrolysis oils [35] and conventional liquid fuels [38]

| Metal | $SS_{PyOil}$ | Pyrolysis oil | | | | Conventional fuel | | |
|---|---|---|---|---|---|---|---|---|
| | | $PPO_{PP}$ [35] | $PPO_{HDPE}$ [35] | $PPO_{LDPE}$ [35] | $PPO_{PS}$ [35] | Kerosene [38] | Gasoline [38] | Diesel [38] |
| Cr ($\mu$g/g) | 1.79 | 19.27 | 91.49 | 35.11 | 106.03 | 3.30 | 5.40 | 8.60 |
| Mn ($\mu$g/g) | 0.29 | 0.29 | 8.11 | 0.01 | 0.37 | - | - | - |
| Co ($\mu$g/g) | 0.01 | 0.21 | 1.39 | 0.07 | 0.16 | - | - | - |
| Ni ($\mu$g/g) | 9.30 | 0.56 | 53.83 | 4.56 | 0.02 | - | - | - |
| As ($\mu$g/g) | 1.86 | 0.37 | 0.17 | 0.35 | 0.30 | - | - | - |
| Sr ($\mu$g/g) | 0.10 | 0.06 | 0.72 | 0.05 | 0.15 | - | - | - |
| Cd ($\mu$g/g) | 0.02 | 0.12 | 0.34 | 0.05 | 0.07 | 13.30 | 16.80 | 15.00 |
| Hg ($\mu$g/g) | 0.06 | 0.00 | 0.00 | 0.00 | 0.00 | - | 0.77 | - |
| Pb ($\mu$g/g) | 0.20 | 0.09 | 0.53 | 0.06 | 0.07 | 4.10 | 2.40 | 10.10 |

From Table 6, it can be notice higher contents for As and Hg in $SS_{PyOil}$ than in oils obtained from *i)* pyrolysis of polypropylene ($PPO_{PP}$), *ii)* high density polyethylene ($PPO_{HDPE}$), *iii)* low density polyethylene ($PPO_{LDPE}$) and *iv)* polystyrene ($PPO_{PS}$) [35]. Also, the Hg and Ni contents were higher than in gasoline [38] and in pyrolysis oils obtained from different polymers [35], respectively.

The FTIR spectrum of the $SS_{PyOil}$ illustrated in Figure 2, presents several vibrational bands, associated to bonds that are found in specific compounds (Table 7).
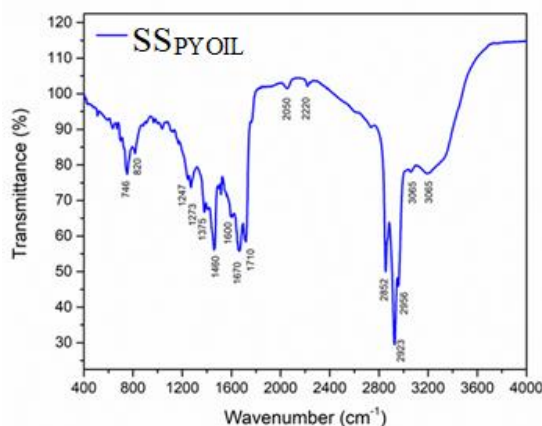
**Figure 2.** FTIR spectrum of $SS_{PyOil}$

**Table 7.** FTIR results for $SS_{PyOil}$

| Position of the band (cm$^{-1}$) | Bond | Compound |
|---|---|---|
| 746, 820 | C-H | Aromatic |
| 1247, 1273, 1375, 1460 | C-H | Alcan |
| 1600, 1670, 1710 | C=C | Aromatic |
| 2050, 2220 | C≡C | Terminal alkynes |
| 2852, 2923, 2956, 3065 | C-H | Aromatic |
| 3200 | O-H | Aromatic (phenols or alcohols) |

Thus, the organic compounds confirmed in $SS_{PyOil}$, through chromatography coupled with mass spectrometry, were fatty acids, alcohols, amine and hydrocarbons (aromatic > 45 %, aliphatic, cyclic).

### 3.3. SSPyGas properties

The compositional analysis of the obtained pyrolysis gas revealed that $CH_4$, $CO_2$, and $H_2$ are the dominant gases (Table 8). The gas composition and the energetic characteristics are presented in Table 8, compared to data found in literature [1, 12, 28, 30, 35].

The highest value for HHV (33.81 MJ/m$^3$) was obtained when the heating rate of 5°C/min was applied during the pyrolysis process.

**Table 8.** SSPyGas properties in comparison with conventional and alternative fuel gases

| Gas composition/ Energetic characteristics | SS$_{PyGas}$ (this work) | | | Geo-gas [28] | Natural Gas [28] | Sewage Sludge/ Biogas [28] | Pyrolysis plastic gas [35] | Biogas garbage [30] | SS$_{PyGas}$ [1] | SS$_{PyGas}$ [12] |
|---|---|---|---|---|---|---|---|---|---|---|
| | 5 °C/min | 10 °C/min | 50 °C/min | | | | | | | |
| C1 (vol %) | 33.41 | 13.75 | 7.58 | 80.79 | 91.85 | 64.22 | 3.93 | 29.12 | 8.00-26.00 | 32.97 |
| C2 (vol %) | 9.28 | 6.05 | 1.93 | 0.77 | 2.96 | 0.03 | 8.83 | 0.002 | 0.10-4.50 | 8.72 |
| Ethylene (vol %) | 5.74 | 5.58 | 2.31 | 0.00 | 0.00 | 0.00 | 5.17 | 0.00 | 0.01-3.00 | 2.83 |
| C3 (vol %) | 3.35 | 3.26 | 1.47 | 0.14 | 0.80 | 0.01 | 19.54 | 0.01 | 0.006-0.01 | 2.96 |
| Propylene (vol %) | 4.84 | 3.86 | 1.91 | 0.00 | 0.00 | 0.00 | 20.03 | 0.00 | 0.00 | 4.64 |
| i-C4 (vol %) | 0.32 | 0.30 | 0.22 | 0.02 | 0.25 | 0.01 | 0.15 | 0.01 | 0.01-0.05 | 0.41 |
| n-C4 (vol %) | 0.41 | 0.45 | 0.18 | 0.02 | 0.25 | 0.01 | 12.17 | 0.01 | 0.01-0.05 | 0.52 |
| neo-C5 (vol %) | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 10.94 | 0.01 | 0.00 | 0.01 |
| i-C5 (vol %) | 0.20 | 0.06 | 0.02 | 0.01 | 0.13 | 0.01 | 0.24 | 0.01 | 0.00 | 0.25 |
| n-C5 (vol %) | 0.30 | 0.08 | 0.02 | 0.01 | 0.06 | 0.01 | 3.74 | 0.01 | 0.00 | 0.38 |
| C6 + (vol %) | 0.30 | 0.52 | 0.21 | 0.01 | 0.06 | 0.01 | 1.42 | 0.01 | 0.00 | 0.37 |
| O2 (vol %) | 0.18 | 0.01 | 0.04 | 0.61 | 0.62 | 0.04 | 0.00 | 11.16 | 0.50-3.00 | 5.91 |
| H2 (vol %) | 21.06 | 3.03 | 2.06 | 15.66 | 0.00 | 0.26 | 2.19 | 0.00 | 8.00-36.20 | 32.51 |
| CO (vol %) | 9.36 | 6.20 | 16.64 | 0.00 | 0.00 | 0.00 | 0.65 | 0.00 | 6.50-25.00 | 0.15 |
| CO2 (vol %) | 11.03 | 22.45 | 65.03 | 0.34 | 0.27 | 35.4 | 1.25 | 11.32 | 0.50-20.00 | 7.09 |
| H2S (vol %) | 0.22 | 0.31 | 0.23 | 0.02 | 0.00 | 0.01 | 0.00 | 0.09 | 0.01-0.03 | 0.35 |
| H2O (vol %) | 0.01 | 0.01 | 0.01 | 0.04 | 0.00 | 0.05 | < 0.005 | 0.00 | - | - |
| HHV (MJ/m$^3$) 0 °C | 33.81 | 16.05 | 9.28 | 33.55 | 40.39 | 25.72 | 99.83 | 11.00 | 13.74-16.53 | 27.26 |
| NHV (MJ/m$^3$) 0 °C | 30.85 | 14.92 | 8.70 | 30.17 | 36.39 | 23.12 | 94.99 | 9.09 | 11.82-14.02 | 24.64 |

| d (kg/m³) 0 °C | 0.91 | 0.87 | 0.85 | - | - | - | - | - | - | - |
|---|---|---|---|---|---|---|---|---|---|---|
| ρ (kg/m³) 0 °C | 0.88 | 0.74 | 1.01 | - | - | - | - | - | - | - |
| Wobbe No. (MJ/m³) 0 °C | 35.45 | 18.67 | 10.08 | - | - | - | - | - | - | - |

From Table 8 it can be notice that the heating rate influences the HHV, thus the energy values increase up to ~34 MJ/m³ with the decrease of heating rate, this value being three times higher than the value obtained at 50°C/min. Also, the hydrocarbons content was significantly higher in the gas obtained in this study with 5°C/min, as well as the hydrogen and oxygen. The presence of hydrogen can be explained by the transition of the intramolecular content of the water contained by the SS into the gas phase. Also, the intramolecular hydrogen reacts with the organic carbon resulting hydrocarbons. During the pyrolysis several compounds are resulting (e.g. ethylene, propylene) due to cracking and dehydrogenation reactions. Thus, carbon dioxide and carbon monoxide began to form at 100 and 230°C, respectively. A higher heating rate conducted to the carbon monoxide and carbon dioxide content increase, up to 16.64 vol% and 65.03 vol%, respectively. The resulted energy values can be comparable with the values reported in literature [1, 12, 28, 30, 35] for different gases, such as i) geo-gas and natural gas, ii) obtained from sewage sludge and iii) from pyrolysis of various type of raw materials (plastic and garbage). It was reported the HHV [35], for pyrolysis plastic gas, three times higher than the value obtained in this study with a heating rate of 5°C/min. Also, the HHV of the obtained $SS_{PyGas}$ (at 5 °C/min) was lower than the HHV reported for natural gas [28] and higher than HHV of the pyrolysis gases obtained in other studies [1, 12], showing a high degree of feasibility compared to the gas mixtures obtained at higher pyrolysis temperature, namely in interval 425-850°C [39, 40].

## 4. Conclusions

The pyrolysis of sewage sludge, at 450 °C and different heating rates (5, 10 and 50°C/min), conducted to the obtaining of three phases, namely, gas - $SS_{PyGas}$, liquid - $SS_{PyOil}$, and solid - $SS_{PyChar}$. These were characterized in terms of energy value and elemental composition. It was demonstrated that the different heating rates have direct influence on the yields of final products. Thus, the highest content of char was obtained when a heating rate of 50°C/min was applied. Even if the obtained HHV for $SS_{PyChar}$ was 2600 kcal/kg, in accordance with literature, this could not be an attractive source of energy, due to its high derived ash level and to its nitrogen and metals content. Also, the 50°C/min heating rate had a negative influence on the pyrolysis process by the obtaining of pyrolysis oil and gas with the lowest HHV. Furthermore, the oil had the highest content of N and S.

The HHV of $SS_{PyOil}$ resulted with 10ºC/min heating rate, was similar to the values for conventional liquid fuels and higher than the HHV for pyrolysis oil derived from various raw materials, such as rice hull, biomass and sugar cane residue. Also, the HHV of $SS_{PyGas}$ resulted by using a heating rate of 5ºC/min was similar to the geo-gas and natural gas HHVs.

The sewage sludge pyrolysis can be an alternative solution for sludge use in agriculture, through unconventional fuels delivering, as in case of other wastes (raw materials).

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