An evaluation of renewable fuels microstructure after the combustion process

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Abstract

The aim of the presented study is to investigate the morphological characteristics of biomass and sewage sludge ash and raw samples by FTIR and SEM methods. Biomass and sewage sludge are adequate renewable fuels, but require further investigation focusing on the evaluation and degradation of organic and inorganic compounds in renewable fuels. In this study, biomass and sewage sludge and its ash were examined in terms of physical and chemical properties to gain an understanding of their compositional and structural characteristics through analytical approaches such as CHNS, ash composition, HHV, FTIR and SEM. The FTIR was recorded using the Bruker Alpha FT-IR Spectrometer. FTIR spectra reflects the complex and different compositions of studied fuels and the influence of the combustion process. The presented spectra evidently depict changes in the bond structure of the studied materials under the combustion process. Degradation of the morphology structure is also confirmed by SEM.

Keywords: Renewable fuel, Biomass, Sewage sludge, Ash, FTIR, SEM

1. Introduction

Biomass is well known for being a clean, abundant renewable fuel. During the last decade, the use of biomass as a fuel has been increasing steadily. Polish environmental policy has focused particularly on renewable fuels since Poland joined the EU. The main renewable source in Poland is biomass, a CO\textsubscript{2}-neutral energy resource which is widely available and increasingly used as an alternative to fossil fuel for energy supply [1]. Biomass is a photosynthesized product formed when chemical energy is stored in carbohydrate molecules, such as sugars, which are synthesized from carbon dioxide and water. Carbohydrates form part of the more complex organic compounds which build tissue biomass. Biomass is organic matter, often plants, agricultural and animal residue (e.g. wood, dung and liquid manure) as well as waste material produced by domestic, agricultural and industrial processes [2] (1).

The main components of lignocellulosic biomass are cellulose, hemicellulose, lignin, lipids, simple sugars, and hydrocarbons, respectively. The concentration of particular components is varied and depends on the origin of the biomass, the stage of development and the conditions for growth. According to [3] lignocellulosic biomass is composed of 35–55 % cellulose, 20–40 % hemicellulose, and 10–25 % lignin. Hemicellulose is a heterogeneous group of polysaccharides and its half products, linked by $\beta$-glycosidic bonds, forming branched chains. Cellulose is a polysaccharide composed of glucose molecules linked by an $\beta$-1,4-glycosidic bond. Lignin is a polymer of which the monomers are organic compounds which come from phenolic alcohol. Lignin plays the role of a binder which affects the compact structure of the cell for wood compressive strength and maintains rigidity. Wood as a source of energy has many advantages: a relatively high calorific value, relatively low mineral content, low sulfur content and a high melting point for the ash produced during combustion. Unfortunately, wood biomass combustion is a rather difficult process, not only because of moisture and volatile contents in biomass, but also because of corrosion and slugging problems which can occur [4]. The biological destruction of wet wood biomass and its hydrophilic properties may also cause severe problems during transport, storage and the milling process. Straw is the second relevant substrate for energy production. In Poland, the potential for its use as an energy source is enormous. For energy purposes around 9 million tons of straw
can be used, with an average calorific value of 16 MJ/kg [1]. The calorific value of straw depends on the type of grain (oat, wheat, barley, maize, or rapeseed) and its moisture content. Therefore, only straw which is not stored and exposed too long to atmospheric conditions retains its value as a fuel. For energy production, biomass is often pre-treated to improve its character by processes such as dewatering, drying, briquetting, pelletization and granulation. Nevertheless, these processes are not without difficulties in terms of raw biomass properties. For example, the pelletization process does not eliminate the main weak point of raw biomass: its hydrophilic character and easy biological degradation. Promising options include torrefaction, hydrothermal carbonization and slow pyrolysis processes, which are effective ways to densify the energy content of renewable fuels [5, 6].

According to Directive 2009/28/EC of the European Parliament and of the Council of 23 April 2009 on the promotion of the use of energy from renewable sources, biomass is defined as "the biodegradable fraction of products, waste and residue of biological origin from agriculture (including vegetal and animal substances), forestry and related industries, including fisheries and aquaculture as well as the biodegradable fraction of industrial and municipal waste" [7]. In addition to biomass, sewage sludge too is a very interesting source of energy. Sewage sludge is the major waste generated in the urban wastewater treatment process and has a high organic matter content as well as heavy metals and organic contaminants. Despite this, it can be treated as a potential energy resource. Sewage sludge generated in wastewater treatment plants requires processing for use in agriculture or thermal utilization (waste-to-energy). The basic processes pertaining to sewage sludge include: thickening, stabilization, dewatering and drying. These processes change the physical and chemical properties of sewage sludge. The chemical composition of sewage sludge is incredibly variable and depends on many factors, including the type of treated sludge and the processes applied. In recent years, rapid population growth, urbanization and industrialization have caused a significant increase in the amount of sewage sludge produced. At the same time, European and Polish legislation concerning sewage sludge treatment has become very restrictive, enforcing the prohibition of sewage sludge storage as of January 1, 2016 (according to the Minister of Economy - 8 January 2013) [8]. Unfortunately, even now, the most common forms of disposal of sewage sludge in Poland are: landfill, farming applications, and thermal utilization [1]. Therefore, the development of new utilization methods of sewage sludge presents an urgent challenge [9–11]. The thermal conversion techniques of renewable fuels are varied and include combustion, co-combustion, gasification and pyrolysis.

Combustion and co-combustion are applied to pulverized coal boilers, fluidized bed boilers, and grate furnaces, and more technologies are still being developed. Combustion is a complex phenomenon, involving simultaneous heat and mass transfer with chemical reaction and fluid flow [13, 14]. The wood biomass combustion process usually runs in three stages [15, 16]. The first stage is preheating and drying, when biomass is preheated. This process is mainly focused on the evaporation of moisture content in wood biomass. Combustion is an exothermic reaction and the evaporation of water is a strong endothermic process, and that is why moisture content in renewable fuels is a factor which limits combustion. Moisture content in biomass can vary from a few percent to up to approx. 80 % in sewage sludge. High moisture content affects combustion and lowers the combustion temperature, which affects the reaction products and, consequently, the quality of the combustion process. The next stage concerns the devolatilization of volatile matter combusted directly. Biomass has a very high content of volatile matter (up to 88 %). These compounds include volatile gases such as hydrocarbons, carbon monoxide, carbon dioxide, hydrogen and water. The third stage is final combustion. The biomass combustion process generates gaseous and solid products. Pollutant emissions generated by combustion include particular matter (PM), CO, HC, oxides of nitrogen (NOx), and oxides of sulfur (SOx). During combustion some specific pollutants such as Cl2, HCl, salts, dioxins and furances can also be found. Although complex in nature, biomass contains a small amount of sulfur, nitrogen and ash. Therefore, during biomass combustion lower harmful gas emissions such as nitrogen oxides, sulfur dioxide and soot compared to conventional fossil fuel combustion, are present. In addition, zero or negative carbon dioxide (CO2) emission is possible from biomass fuel combustion, because the CO2 released from the combustion of bio-oil can be recycled into the plant by photosynthesis. The emission of exhaust gases is a significant problem in the combustion of fuels [17, 18]. Wood biomass combustion is a rather difficult process, not only because of moisture and volatile contents in the biomass, but also because of the corrosion and slagging problems which can occur. The co-combustion of coal and biomass is reported as being a very
positive solution, in terms of technology, ecology and economics. However, it is known that this technology has disadvantages in the form of operating problems and storing large volumes of wet biomass [19]. The ash from biomass and sewage sludge can cause many problems during its thermal utilization due to mineral matter, heavy metals, and ash particles emission. The ash content in biomass varies depending on biomass origin: dry wood biomass might be less than 1 %, while sewage sludge may be up to 30%. Biomass ash—a combustion residue—is an inorganic, non-combustible material. The chemical composition of ash differs widely. The main elements are Si, Al, Fe, Ca, Mg, Na, K, S, and P, respectively [20]. The inorganic elements content has an impact on the melting point of the ash and the transformation of mineral matter. In consequence, slagging and fouling problems related to ash deposits on the heat transfer equipment of boilers can arise [21]. The Tanner diagram can be used to evaluate the possibility of sewage sludge thermal conversion [12]. This is a graph which depicts the correlation between moisture content, ash, and combustible organic matter. As can be seen, autothermic combustion has limitation values for an organic matter content of > 25 %, ash content of < 60 % and moisture content of < 50 % [2]. It can be concluded that for sewage sludge combustion, the sewage sludge has to be correctly dewatered. The content and chemical nature of the mineral matter in sewage sludge plays a significant role in the combustion process.

Although biomass and sewage sludge are good renewable fuels, some important problems relating to ash present during biomass combustion. Knowledge concerning the formation and transformation of the mineral part of biomass ash is needed to control problems associated with fouling and slagging in boilers during biomass combustion. Therefore, various experimental methods are involved to determine the physical and chemical characterization of biomass and sewage sludge and its ashes.

In order to provide a more in-depth description of the thermal behavior of biomass and sewage sludge ash, it is essential to investigate the morphological characteristics of lignocellulosic biomass and sewage sludge ash and raw samples. Accordingly, experimental methods such as FTIR and SEM can be used to understand their compositional and structural characteristics.

2. Experimental

In this study biomass and sewage sludge and its ash were examined in terms of physical and chemical properties to gain an understanding of their compositional and structural characteristics through analytical approaches such as CHNS (carbon–hydrogen–nitrogen–sulfur), ash composition, HHV, FTIR (Fourier Transform Infrared Spectroscopy) and SEM (Scanning Electron Microscopy).

2.1. Materials

Three different types of biomass, from different origins (straw and two wood samples) were used in this study. The biomass materials are typical renewable fuels used in energy units in the combustion process. The biomass samples were denoted as: B1 – oat straw (agriculture biomass), B2 – oak sawdust, and B3 – a mixture of different kinds of wood biomass, respectively. The ash samples reflected biomass ash in general and were referred to as A_B1, A_B2, and A_B3. Sewage sludge samples, S1 and S2, were collected from two different municipal wastewater treatment plants using mechanical and biological treatment. The sewage sludge ashes were named A_S1 and A_S2.

The results and knowledge obtained in this study can provide a better understanding of biomass and sewage sludge morphology transformation to ash during the combustion process.

2.2. Methods

Proximate analysis (moisture, ash, volatile matter, and fixed carbon) of the studied samples was carried out according to European Standards. The moisture content was determined by maintaining 1 g of the samples in the drying system at 105 °C to a constant mass according to EN 15934:2012. The ash content was determined by burning a 1 g sample of all studied solid recovered fuels in a muffle furnace at 600 ± 10 °C for 6 h according to PN-EN 14775:2010. The volatile matter was determined by maintaining 1 g of mass samples at 900 ± 10 °C for 7 min using the EN 15402:2011 method. The fixed carbon content was determined by the difference. The ultimate analysis (carbon, hydrogen and nitrogen content) was performed by Elemental Analyser Truespec CHN Leco. The Leco CHN628 is a combustion elemental C, H, and N instrument that utilizes only pure oxygen in a furnace, ensuring complete combustion and superior recovery of the elements of interest. An Analyzer Leco SC632 was used to determine the sulfur content at 1350 °C. The analyzer performs direct combustion and infrared detection for sulfur and carbon in various organic and inorganic materials. The higher heating value of the samples was calculated using the Dulong equation [2, 22]. The most important parameter in determining the character of ash is the chemical composition having highly crystalline materials and a high content of alkalai metals. The main chemical composition of biomass and sewage sludge ashes was determined by an X-ray fluorescence spectrometer (XRF) (Advanced Microanalysis Centre, Saskatchewan Research Council, Canada). Bruker S8 TIGER XRF spectrometers equipped with TouchControl and SampleCare provided repeatable and accurate results.

The FTIR (Fourier Transform Infrared Spectroscopy) was recorded using the Bruker Alpha FT-IR Spectrometer. It is a quick and useful method. The spectral region from 4000 to 400 cm⁻¹ was investigated. An infrared spectrum presents absorption peaks which correspond to the frequencies of vibrations between the bonds of the atoms making up the material. The size of the peaks in the spectrum can be used as a direct indication of the amount of material present.

The structure of biomass and sewage sludge and their ashes were characterized using scanning electron mi-
croscopy (FEI Inspect S50). Particles of the studied biomass, sewage sludge, and ashes were mounted on metal stubs using double sided carbon adhesive discs. The samples were observed in high vacuum mode by secondary electrons using an accelerating voltage - 1 kV.

3. Results and discussion

Table 1: Physical and chemical properties of biomass and sewage sludge

<table>
<thead>
<tr>
<th>Properties</th>
<th>B1</th>
<th>B2</th>
<th>B3</th>
<th>SS1</th>
<th>SS2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Proximate analysis, wt. %</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Moisture</td>
<td>7.15</td>
<td>24.0</td>
<td>4.3</td>
<td>18.2</td>
<td>5.30</td>
</tr>
<tr>
<td>Ash</td>
<td>4.76</td>
<td>1.05</td>
<td>0.9</td>
<td>13.5</td>
<td>37.9</td>
</tr>
<tr>
<td>Volatile Matter</td>
<td>77.8</td>
<td>88.1</td>
<td>86.9</td>
<td>64.3</td>
<td>60.5</td>
</tr>
<tr>
<td>Ultimate analysis, wt. %</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>43.5</td>
<td>38.6</td>
<td>48.6</td>
<td>30.2</td>
<td>34.6</td>
</tr>
<tr>
<td>H</td>
<td>5.87</td>
<td>6.84</td>
<td>6.19</td>
<td>6.08</td>
<td>5.47</td>
</tr>
<tr>
<td>N</td>
<td>0.48</td>
<td>0.15</td>
<td>0.18</td>
<td>4.75</td>
<td>5.50</td>
</tr>
<tr>
<td>S</td>
<td>0.09</td>
<td>0.01</td>
<td>0.00</td>
<td>1.39</td>
<td>2.01</td>
</tr>
<tr>
<td>Cl</td>
<td>0.06</td>
<td>0.01</td>
<td>0.01</td>
<td>0.07</td>
<td>0.08</td>
</tr>
<tr>
<td>O *</td>
<td>42.9</td>
<td>30.4</td>
<td>40.7</td>
<td>39.3</td>
<td>47.1</td>
</tr>
<tr>
<td>HHV, MJ</td>
<td>16.3</td>
<td>18.0</td>
<td>18.8</td>
<td>12.7</td>
<td>12.1</td>
</tr>
</tbody>
</table>

* calculated by difference

Table 2: Chemical analysis of ash

<table>
<thead>
<tr>
<th>wt. %</th>
<th>B1</th>
<th>B2</th>
<th>B3</th>
<th>SS1</th>
<th>SS2</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>18.80</td>
<td>9.16</td>
<td>9.80</td>
<td>17.80</td>
<td>15.50</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>1.13</td>
<td>1.62</td>
<td>2.51</td>
<td>7.11</td>
<td>7.67</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>0.38</td>
<td>1.34</td>
<td>15.60</td>
<td>9.94</td>
<td></td>
</tr>
<tr>
<td>TiO₂</td>
<td>-</td>
<td>0.08</td>
<td>-</td>
<td>0.87</td>
<td></td>
</tr>
<tr>
<td>CaO</td>
<td>10.20</td>
<td>35.10</td>
<td>45.90</td>
<td>20.40</td>
<td>33.60</td>
</tr>
<tr>
<td>MgO</td>
<td>2.73</td>
<td>7.86</td>
<td>10.70</td>
<td>4.50</td>
<td>3.48</td>
</tr>
<tr>
<td>K₂O</td>
<td>46.90</td>
<td>36.60</td>
<td>13.00</td>
<td>2.84</td>
<td>1.17</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.97</td>
<td>0.75</td>
<td>0.71</td>
<td>1.99</td>
<td>1.19</td>
</tr>
<tr>
<td>MnO</td>
<td>-</td>
<td>3.18</td>
<td>0.16</td>
<td>0.39</td>
<td></td>
</tr>
<tr>
<td>P₂O₅</td>
<td>14.50</td>
<td>3.62</td>
<td>10.00</td>
<td>26.80</td>
<td>19.50</td>
</tr>
<tr>
<td>SO₃</td>
<td>3.43</td>
<td>3.56</td>
<td>2.79</td>
<td>2.76</td>
<td>6.57</td>
</tr>
<tr>
<td>Cl</td>
<td>0.89</td>
<td>0.03</td>
<td>-</td>
<td>0.02</td>
<td>0.19</td>
</tr>
</tbody>
</table>

In this study biomass and sewage sludge were examined in terms of physical and chemical properties. The authors focused on the comparison between the wood biomass and sewage sludge, and its ash from the combustion process. The results of the proximate and ultimate analysis, high heating value, and chemical composition of ash from the studied samples are given in 1 and 2. The chemical properties of biomass and sewage sludge show that the main combustible component in the tested raw samples is carbon, up to 48.6 % for biomass, and up to 34.6 %for sewage sludge. The hydrogen content for biomass and sewage sludge has a typical amount of c.a. 6 %. The nitrogen content for biomass is low, which is an advantage during thermal processes, but in the case of sewage sludge it has a significant amount c.a. 5 %. Unfortunately, in the case of sewage sludge the sulfur content which appears can generate harmful exhaust gases.

As regards calorific values, the energy content for biomass ranges from 16 to c.a. 19 MJ/kg of the HHV and for sewage sludge it is c.a. 12.7 MJ/kg.

The concentration of the main oxides in the studied biomass and sewage sludge ashes was different because of the different origins, but the main ash elements were K₂O, SiO₂, CaO, Fe₂O₃, Al₂O₃, as well as significant amounts of MgO and P₂O₅. The SiO₂ and Al₂O₃ content varied widely and the oat straw ash (A_B1, agriculture biomass) had the highest alkali oxide content. Besides potassium and sodium, the presence of phosphorus can reduce the melting points of ash. The presence of CaO, MgO and Al₂O₃ may increase the ash melting points. High amounts of K₂O and CaO were identified for A_B2, whereas Ash A_B3 is typically a Ca-rich wood biomass ash, suggesting its usefulness for SO₂ capture. The sodium, aluminum and sulfur contents are low. However, the high concentrations of silicon, potassium and calcium may form low-melting-point eutectics, which can cause slagging. It should be emphasized that potassium and calcium are important in the formation of surface deposits on boiler surfaces. The ashes obtained from sewage sludge have different chemical compositions, compared to biomass origin ashes. The sewage sludge ashes contain mainly phosphorus, calcium and silicon, but A_SS2 is a Ca-rich ash.

FTIR spectra of the samples are presented in 4 and 6, and they reflect the complex and different compositions of the studied fuels. The interpretation of FTIR spectra was
based on a literature review (3) [23–26]. The most important peaks for raw material, B1, B2, B3, SS_1, and SS_2, respectively, exist between 400 and 3000 cm\(^{-1}\), whereas for the ashes the peaks are between 400 to 2500 cm\(^{-1}\). The FTIR spectra of biomass ash (A_B1, A_B2, A_B3) feature four main peaks. Carbonate (CO\(_3^{2-}\)) absorption bands are detected at around 880 cm\(^{-1}\) (C–O in plane bending) and 1028 cm\(^{-1}\) (P–O stretching and Si–O vibration). The characteristic peaks decrease after the ash is heated at 500 and 600°C. The broad band at 1431 cm\(^{-1}\) is due to C–O stretching. Additionally, a phosphate band is observed at 552 cm\(^{-1}\).

The FTIR spectra of sewage sludge ash (A_SS1, A_SS2) feature three main peaks. The most intensive changes in the absorption bands are observed at the range of 400 to 1100 cm\(^{-1}\). Two main peaks are assigned to S–O bending or Al-O bending vibration (466 cm\(^{-1}\)) and (560 cm\(^{-1}\)), but the
most intensive broad absorption band appears in the characteristic silica region with a maximum at S–O stretching (1028 cm\(^{-1}\)). After incineration at 600 °C, the absorption bands of organic matter disappear while that of carbonate appears due to carbonation of some calcium compounds by CO\(_2\), produced from incomplete combustion of organic matter. The FTIR spectra of sewage sludge differ from those of biomass (organic material). The protein (amide) appears at 1634 cm\(^{-1}\). Above 2350 cm\(^{-1}\) C–H stretching and deformation vibration from alkanes is observed.

4. Conclusions

The main conclusions of this study are the FTIR spectra and SEM analysis reflecting the complex behavior of biomass and sewage sludge ashes generated during the combustion process. Although the FTIR spectra and SEM images of the studied materials are strongly determined by the quantitative composition of the input material, they track the degradation of the material. Both techniques are comparatively simple, quick, and environmentally friendly compared to chemical methods, but unfortunately more advanced instrumental methods are needed to obtain a knowledgeable description of biomass and sewage sludge thermal conversion.

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