PROPORTION OF VOLATILE MATTER IN SELECTED BIOFUELS

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Abstract: Biomass provides a great diversity of input materials and universal use, not only for heat production but also for electricity production in modern combustion devices. The quality of biofuels depends on the total content of combustibles. Course of combustion is affected by the levels of volatile and solid combustibles. The aim of this research was to determine the amount and release course of combustibles in selected biofuels depending on temperature by the means of gravimetric method. For this purpose, we used a gravimetric furnace Nabertherm L9/11/SW/P330. The results are processed in tabular and graphic form and enable to characterize the release course of combustibles in the tested fuels. The highest content of combustibles was observed in samples of softwood pellets, in the amount of 99.64%. The highest proportion of volatile matter from the total amount of combustibles was present in cherry wood, in the amount of 74.4%.

Key Words: gravimetry, ash, biomass, combustible, dry matter

INTRODUCTION

Renewable energy has become more important globally especially with the current fuel and economic crisis (Bernama 2008). Solid biofuels in particular will be increasingly used as a source of thermal energy. Biomass refers to all organic matter that arose through photosynthesis, or to the material of animal origin. This term often represents plant biomass usable for energy purposes as a renewable energy source (Maga et al. 2010). Biomass provides a basis for renewable energy sources, without any doubts. It accounts for 75% of renewable energy sources such as wind, water, sun etc. Biofuel is the fuel derived from biomass. According to the chemical composition, the biofuels can be divided into solid, liquid and gas. Quality of solid biofuels as an energy source depends on the content of moisture, ash and combustibles (Vitazek et al. 2014). Chemical energy is released mainly from biofuel combustion process. The combustion process is considered as oxidation process, where the combustible components of the fuel are oxidized by atmospheric oxygen, while the energy content of the fuel is transformed into heat (Jandacka et al. 2011, Pitel et al. 2013).

Biofuels as an energy source depend on the quality of combustibles and the content of ballast - moisture and ash. Compared to solid fossil fuels, biomass has significantly higher proportion of volatile matter, which is essentially due to its origin. Biomass combustion does not pollute the environment by excessive production of CO₂ (Holubcik and Jandacka 2016). Another advantage of the biomass combustion is that the ash as a by-product of combustion can be used as a high-quality fertilizer. Biomass offers a great variety of raw materials and becomes universally used in the energetics. It is used for production of heat, as well as electricity in modern combustion plants (Misakova 2014, Trenciansky et al. 2007). Original composition of solid biofuels (wood, straw, corn) in terms of combustion is as follows (Piszczalka 2010): volatile matter (wood gas) 60–70%; non-volatile solid combustible (wood charcoal in the case of wood) up to 20%; ballast - water (up to cca. 14%), and ash from the burning of charcoal 0.5–4%.

This paper presents a method of determining the proportion of the biofuel components by gravimetric method. The release course of combustibles at a selected time interval and determined proportion of volatile matter is shown.
MATERIAL AND METHODS
In terms of the combustion of biofuels, the release course of combustibles and proportions of volatile and solid matter is important. The residue after combustion is ash. Tested sample consisted of pellets from spruce wood, spruce and fir wood (90% and 10%), unspecified softwood (labelled as Baumax), sunflower pressing and waste from post-harvest processing of grain. In addition, the wood chips from cherry wood with bark and charcoal sample were included in the experiment. To measure the proportion of components in solid biofuels, gravimetric method was used. For this purpose, a furnace Nabertherm L9/11/SW/P330 was used. Input power of the heater is 3.0 kW. The control unit P330 enables to program selected courses of the heating and endurance using the computer. Heating of tested samples is possible up to 1 100 °C, while our experiments were terminated at 815 °C. Digital scales Kern are also a part of the equipment. The device is connected to a computer and records the temperature and weight courses at the selected time intervals. Such device enables to determine the proportion of moisture, combustibles and ash in the tested solid biofuels. From the change in weight of the sample after the removal of moisture it is possible to obtain the release profile of combustibles and determine its individual components.

Figure 1 Gravimetric furnace Nabertherm L9/11/SW/P330

Proportions of particular components are calculated according to the following relations
Moisture content wet basis w:

\[ w = \frac{m_1 - m_2}{m_1} \]  \hspace{1cm} (1)

Ash content
- in original sample \( A' \):

\[ A' = \frac{m_3}{m_1} \]

- in dry matter \( p_{ps} \):

\[ p_{ps} = \frac{m_2}{m_2} \]  \hspace{1cm} (2, 3)

Combustible content
- in original sample \( h' \):

\[ h' = \frac{m_4}{m_1} \]

- in dry matter \( p_{hs} \):

\[ p_{hs} = \frac{m_2}{m_2} \]  \hspace{1cm} (4, 5)

where:

- \( m_1 \) – original weight of sample, g
- \( m_2 \) – weight of dry matter, g
- \( m_3 \) – weight of ash, g
- \( m_4 \) – weight of combustible, g

The identification of the proportion of volatile matter follows the norm STN EN15148. Ash content is determined in accordance with the norm STN EN 14775. In accordance with the standards we have carried out experiments. Using a computer, we have programmed the required temperatures and impact periods. Table 1 shows the parameters of gravimetric measurements.

The analysed sample is first heated to 105 °C ± 2 °C and then dried for 120 minutes in accordance with
the norm STN EN 14774–2. Weight loss in the interval of 0–180 minutes is accounted for the removed moisture. Mass residue at the end of the experiment is made up of ash.

Table 1 Parameters for gravimetric measurement procedure

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Impact period in minute</th>
<th>Time interval</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>60</td>
<td>60</td>
</tr>
<tr>
<td>2</td>
<td>120</td>
<td>60</td>
</tr>
<tr>
<td>3</td>
<td>60</td>
<td>60</td>
</tr>
<tr>
<td>4</td>
<td>60</td>
<td>60</td>
</tr>
<tr>
<td>5</td>
<td>60</td>
<td>60</td>
</tr>
<tr>
<td>6</td>
<td>60</td>
<td>60</td>
</tr>
<tr>
<td>Temperature, °C</td>
<td>20–105</td>
<td>105</td>
</tr>
<tr>
<td></td>
<td></td>
<td>105–500</td>
</tr>
<tr>
<td></td>
<td></td>
<td>500</td>
</tr>
<tr>
<td></td>
<td></td>
<td>500–815</td>
</tr>
<tr>
<td></td>
<td></td>
<td>815</td>
</tr>
</tbody>
</table>

RESULTS AND DISCUSSION

Temperatures above 100 °C lead to the removal of moisture – drying of the fuel. At temperatures above 150 °C, volatile matter begins to release. After exceeding temperatures from 260 °C to 410 °C, the release of volatile matter is significantly accelerated. The solid portion of combustible begins to oxidise at a temperature of about 500 °C. Temperature 815 °C leads to a perfect oxidation of solid residue.

The results of gravimetric measurements of analysed samples are shown in Table 2. Proportions of moisture, ash and combustibles are calculated according to the relations 1 to 5. Heating with biomass is increasingly used as an alternative to natural gas. The manufacturers of boilers for biomass heating began to react to this trend. A high proportion of volatile matter affects the supply of the secondary or even tertiary air. The aim is to provide enough air supply for complete combustion of the fuel and reduce the production of solid and gaseous emissions. Even with the gradual arrival of new innovations of biomass boilers, high ash content and inadequate temperature can lead to ash sintering. This can cause temporary interruption of combustion and lead to partial or permanent damage to the boiler. This is one of the reasons why it is necessary to know the information about the following parameters: composition of fuel, proportions of different types of combustibles and their release course in solid biofuel.

Table 2 Processed results of gravimetric measurements of analysed samples

<table>
<thead>
<tr>
<th>BIOFUELS</th>
<th>PARAMETER, %</th>
<th>w</th>
<th>A'</th>
<th>h</th>
<th>pW</th>
<th>ps</th>
</tr>
</thead>
<tbody>
<tr>
<td>spruce wood pellets</td>
<td></td>
<td>7.0359</td>
<td>0.3434</td>
<td>92.6208</td>
<td>0.3639</td>
<td>99.6307</td>
</tr>
<tr>
<td>waste pellets</td>
<td></td>
<td>7.3492</td>
<td>5.1206</td>
<td>87.5302</td>
<td>5.5267</td>
<td>94.4733</td>
</tr>
<tr>
<td>spruce-fir pellets</td>
<td></td>
<td>10.3288</td>
<td>0.5485</td>
<td>89.1228</td>
<td>0.6116</td>
<td>99.3884</td>
</tr>
<tr>
<td>Baemax pellets</td>
<td></td>
<td>8.5671</td>
<td>0.3322</td>
<td>91.1007</td>
<td>0.3633</td>
<td>99.6367</td>
</tr>
<tr>
<td>sunflower pellets</td>
<td></td>
<td>9.8347</td>
<td>3.5885</td>
<td>86.5768</td>
<td>3.9799</td>
<td>96.0201</td>
</tr>
<tr>
<td>cherry wood with bark</td>
<td></td>
<td>13.5512</td>
<td>0.4254</td>
<td>86.0235</td>
<td>0.4920</td>
<td>99.5080</td>
</tr>
<tr>
<td>charcoal</td>
<td></td>
<td>4.4884</td>
<td>2.3522</td>
<td>72.7785</td>
<td>3.1309</td>
<td>96.8691</td>
</tr>
</tbody>
</table>

Figure 2 shows the course of the experiment of the selected fuels during the whole time interval. Figure 3 depicts course of the experiment from the 180. minute to 300. minute, when the release of volatile matter occurs. The graphic course shows the mass calculated to 1 gram of dry matter. From the obtained data were calculated proportions of volatile matter shown in Table 3. These are the proportions of the total combustibles \( p_{hs} \) (Table 2).

Figure 4 shows the course of the experiment with biofuel with the highest proportion of volatile matter (cherry wood). The course for charcoal is given for comparison.

The overall proportion of combustibles in the tested samples is presented in Table 2. Proportion of the amount of volatile matter in dry matter at the interval from 180. minute to 240. minute is shown in Table 3, column 2. Values are quite balanced again and indicate high proportions of volatile matter in solid biofuels. In addition, the proportions to the period of 300 minutes, i.e. to the end of heating endurance at 500 °C, are listed as well. It is no longer regarded as volatile matter, but as a proportion of total oxidized combustibles. Course of the experiment for charcoal, where the proportion of volatile matter is very low, provides evidence of this.
Table 3 Proportions of combustibles at given time intervals

<table>
<thead>
<tr>
<th>BIOFUELS</th>
<th>Volatile matter (180–240 min), %</th>
<th>Proportion of combustibles (180–300 min), %</th>
</tr>
</thead>
<tbody>
<tr>
<td>spruce wood pellets</td>
<td>71.18</td>
<td>86.21</td>
</tr>
<tr>
<td>waste pellets</td>
<td>74.23</td>
<td>88.09</td>
</tr>
<tr>
<td>spruce-fir pellets</td>
<td>73.08</td>
<td>86.78</td>
</tr>
<tr>
<td>Baumax pellets</td>
<td>70.70</td>
<td>83.37</td>
</tr>
<tr>
<td>sunflower pellets</td>
<td>70.11</td>
<td>83.14</td>
</tr>
<tr>
<td>cherry wood with bark</td>
<td>74.40</td>
<td>88.32</td>
</tr>
<tr>
<td>charcoal</td>
<td>57.6</td>
<td>90.40</td>
</tr>
</tbody>
</table>

The highest proportion of combustibles in dry matter was present in the sample of Baumax pellets (99.64%). On the other hand, the lowest was found in the waste pellets (94.47%), i.e. that they had the highest ash content (5.53%). The data in Table 3 shows that the highest proportion of volatile matter was present in the cherry wood with bark sample (74.4%). The case of waste sample is particularly interesting, because it indicated the highest ash content and the second highest proportion of volatile matter (74.23%).

Figure 2 Course of the experiment of selected biofuels during the whole time interval

Figure 3 Course of the experiment of selected biofuels in the interval from 180. to 300. minutes
Figure 4 Course of the experiment of biofuels with the highest and the lowest proportion of volatile matter

Since we dealt with the waste from post-harvest processing, dust particles significantly account for high ash content. At the same time, husk and straw particles contain a high proportion of combustibles.

At low moisture, the wood burns virtually without smoke, easily ignites and produces low ash content of about 1% to 1.5% of the original weight (Hutla et al. 2005). The paper (Kazimirova et al. 2013) shows the results of gravimetric measurements. The research has shown that dry matter of the seeds of oil-seed rape of Catania variety contains, compared to cereal grain, higher ash content - namely 4.73% (hence the content of combustibles was 95.27%). Further findings indicate that the average ash content in the dry matter of tested cereal straw was 6.14% (hence the average content of combustibles was 94.92%). The dry matter of oil-seed rape Catania straw, compared to cereal straw, contained higher ash content of 9.20% (hence the content of combustibles was 90.80%). Similar results were obtained and described also in the works (Chrastina et al. 2015, Branca and Di Blasi 2015) – distillery waste from corn distiller dried grain with solubles contains 4.64% of ash. The paper of (Vitazek and Vitazkova 2012) presents the processed gravimetric measurements of selected types of biofuels. The obtained values of the ash content are as follows: pellets from rapeseed waste plus cereals: 7.98%, corn stalks pellets: 5.19%, burnt corn pellets: 4.70%, corn spindle pellets: 4.37%, softwood pellets: 1.02% and softwood without bark pellets: 0.46%. The paper of (Mikulova et al. 2014) shows that the fastest decline in weight loss and thereby the fastest release of volatile matter is indicated in the pellets composed of 10% brown coal, 90% sawdust (hardwood), while the lowest decline in weight loss is present in crushed brown coal briquette. Briquette composed purely of brown coal has ash content of 3.77%. Pellets composed of 10% brown coal, 90% sawdust have a slightly lower ash content, namely 3.48%.

Results presented in the paper contribute to the previously obtained knowledge about the proportion of moisture, ash and combustibles in solid biofuels and broaden it by the new findings about the release course of combustibles at selected time intervals. The decrease in weight from 180. minute to 240. minute (interval 3 in Table 1) can be accounted for the volatile matter.

CONCLUSION

In the agricultural sector, various types of biomass are suitable as a secondary raw material for the combustion process. Tested samples were made from different materials. These materials have different physical properties which determine their further processing and the choice of combustion device. Gravimetric method described above is highly applicable for examination of release course of combustibles in selected solid biofuels. Graphical representation of the weight loss course in the selected interval of time or temperature enables to observe the rate of volatile matter release, or more precisely, the rate of its oxidation. It affects the speed of combustion, consequently the construction of the boiler. The suitability of the examined fuel (or suggestions for its replacement with other biofuel) can be assessed for a particular boiler. Pellets from the mixture of crushed brown coal and biofuel in various ratios are already available on the market. They were also included in the experiments. Even in the case of new boilers with innovative technology, ash sintering caused by the high content of combustibles in
solid biofuels and inadequate temperature in the combustion chamber may occur. It may lead to permanent damage of the combustion devices. This threat only underlines the importance of sufficient information about the proportion of combustibles in the used solid biofuel, their release course and other thermophysical properties.

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REFERENCES