Torrefied biofuels production using different biomasses

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Abstract

Torrefaction is a process, where biomass material is converted into solid fuel with higher heating value. Torrefactiobn is used mainly for the energetic exploitation, as the product can replace the fossil fuels. The experimental results of torrefaction for three materials, oak wood, mixed wood and municipal sewage sludge at different temperatures are presented. The materials were treated in Bosio electric resistance furnace. The container was field with the sample and covered with ceramic lid that the inert atmosphere conditions were reached. The process started with warm up stage, which took place for 30 minutes, after that stage sample was torrefied for 2 hours at constant temperature. The process continued with cool down stage. The energy demands were covered by electric power. The influence of the operating time was analysed in order to determine optimal operation parameters. Furthermore, the optimal operation time for each material is evaluated. The results of heating value, mass drop and chemical compositions are presented. The results show that from energy point of view the optimal operation time for oak and mixed wood is around 1.2 h at 260°C. The torrefaction of sewage sludge is energetically unjustified.

Key words: solid fuel, torrefaction, sewage sludge, oak and mixed wood

1. Introduction

Biomass is one of the more important sources to produce energy and synthetic fuels. Tenacity of raw biomass is especially challenging, which prevents efficient pulverisation of biomass to use it in higher temperature gasifiers or in boilers of thermal power plants and heating plants. The torrefaction process (mild pyrolysis) is coming to the fore as a possible thermochemical conversion route that enhances the biomass properties obtaining ecologically acceptable energy source, which has similar properties as coal [1, 2]. Torrefied biomass is hydrophobic, resistant to biodegradation and is suitable for storage. Furthermore, the homogeneity and heating value of torrefied biomass is greater. Important advantage of torrefied biomass is also its reduced tenacity. The grind ability of the product is higher and easier milling and application in industrial equipment is achieved [3, 4]

Sewage sludge is a good source of easily available plant nutrients such as N, P, K, Ca, Mg, etc. as well as other organic constituents which are beneficial to agriculture, forestry and landscaping. Land application and land filling are suggested to be the most economical and useful options of sewage sludge disposal. The fertilizer application to agricultural land results in improved physical, chemical and biological properties of soil [5]. However, the legislation regarding sludge management is very strict for the safe sludge use in agriculture. Other applications, such as torrefaction of sewage sludge for biofuel production, became promising method.

The comparison between three materials is performed to evaluate the influence of temperature on heating value of the torrefied biomass and to determine optimal operation time. The first material is oak wood, the second material is dehydrated sewage sludge from waste water treatment plant and the third material is mixed wood.

2. The sewage sludge characteristics

Activated sludge contain 5 heavy metals fraction in form of Weak acid soluble, Reducible, Oxidizable, Residual, Solid fraction and supernatant.[6] Main fractions are residual and oxidizable fractions, which were difficult to dissolve and remove from WAS. Solubilization efficiency may be enhanced by oxidation treatment processes using H_2O_2.

Two groups of heavy metals could be devided regarding the toxicity to plants and animals. First group comprise neurotoxins Hg, Pb and Cd, which are not so toxic to plants. The second group comprises toxic to plants and less to animals [7].

The bioleaching with recirculation of the liquid and solid phases of sewage sludge is of considerable interest for the development of the bioleaching method itself, and for deeper investigation of its influence on the sludge dewatering.[8] The treated sludge usually meets the agricultural use standards. A drawback of these approaches is low conversion of the added elemental sulfur and potential soil acidification from the residual sulfur in the decontaminated sludge. Further, heavy metal from sewage sludge deposited in soil showed a leaching through the soil down to 0.8 m.

Various industrial wastewater originated from battery manufacturing, electroplating, mining operations, tanneries, paint manufacturing as well as photography contains both Pb(II) and Cd(II). [9]

Table 1. Properties of activated sludge in Slovene WWTP and EU directive of heavy metals in sewage sludge intended for agricultural application [10]

Parameter	Activated sludge	EU Directive 86/278/EEC
Cd [mg/kg s.s.]	12	20-40
Zn [mg/kg s.s.]	481	2500-4000
Cu [mg/kg s.s.]	94	1000-1750
Cr [mg/kg s.s.]	51	-
Pb [mg/kg s.s.]	26	750-1200
Ni [mg/kg s.s.]	24	300-400

Most of the EU countries adopted stringent limits for heavy metals in comparison with EU directive. Extracellular polymeric substances (EPS) are the main organic matters in sludge, consisting of polysaccharides, proteins and humic substances, etc. [11] Zn can bind to EPS with high binding capacity.

Sewage sludge may also contain harmful persistent organic compounds, such as polycyclic aromatic hydrocarbons PAH, polychlorinated biphenils PCB, phthalates, detergent residues, pharmaceuticals, hormones and others [12]

3. Materials and methods

The ash content was determined following SIST EN ISO 18122:2016, total moisture SIST EN ISO 18134-3:2015, heating value SIST EN 14918:2010. The total carbon, hydrogen and nitrogen contents was performed following SIST EN ISO 16948:2015 and Sulphur content as per ASTM D4239-14e2 by burning in tube furnace.

Samples of biomass were weighed before torrefaction and the mass of torrefied product was calculated as a percentage by comparing the obtained mass loss with the original dry mass sample, according to eq. (1):

$$m_{\mathrm{i}}\ (\%) = \frac{m_{\mathrm{sur}} - m_{\mathrm{tor}}}{m_{\mathrm{sur}}} \cdot 100\ \% \tag{1}$$

where

m_{i} mass loss (%),

m_{sur} mass of the raw biomass (kg),

m_{tor} mass of torrefied product (kg).

4. Experiment

Torrefaction was carried out in lab-scale furnace Bosio type EUP-K 6/1200. It is made of heating and regulation part. The nominal power was 2.7 kW. Torrefaction was performed by weighing biomass into ceramic dish, cover with a lid for inert atmosphere. The lid was placed in the way that flue gasses and water vapour could be removed. Samples were placed into Bosio furnace and torrefied. In Table 2 the properties of raw material are gathered.

Table 2. Properties of raw materials

Parameter	Oak wood	Sewage sludge	Mixed wood
GVC/LHV [kJ/kg]	19,074/17,793	15,520/14,421	19,722/18,405
Analytical moisture [%]	10.45	8.5	8.78
Nitrogen [%]	0.34	5.87	0.22
Volatiles [%]	79.12	61.14	75.3
Carbon [%]	48.53	36.59	49.6
Ash [%]	3.24	32.58	1.05
Hydrogen [%]	5.89	5.09	6.05
Sulfur [%]	0.02	0,.8	0.02

4.1 The temperature influence on torrefaction

The process (Figure 1) started with warm up stage, which took place for 30 minutes, after that stage sample were torrefied for 2 hours at constant temperature. The process continued with cool down stage. The energy demands were covered by electric power, while the flue gasses were not integrated in the process. The experiments were done at 220°C, 240°C, 260°C, 280°C, 300°C, 320°C, 340°C and 400°C, according to previous research [13, 14]. The analyses of chemical composition and heating value were performed for each sample.

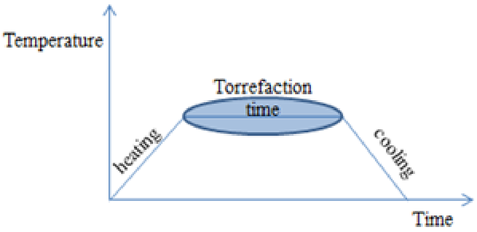

Figure 1: The torrefaction process

4.2 *The determination of optimum time*

Biomass was torrefied at 260°C and at 4 different time periods: 0.5 h, 1 h, 1.5 h and 2 h. Temperature was chosen on basis of preliminary results. It was shown that higher temperature does not affect the heating value. The temperatures of torrefaction as well as the time of heating and cooling were kept constant during the whole experiment.

5. Results and discussion

5.1 *Temperature influence*

Three different samples were torrefied, as shown from Figure 1. Torrefaction was performed at constant temperature for 2h. Torrefaction was performed at 8 different temperatures. The mass losses were measured. Chemical analyses of samples were performed and heating values were measured in dependence of temperature.

5.1.1 Mass loss

Results showed that mass losses increase with temperature with all 3 types of biomass samples. The most losses are due to moisture loss. Between wood samples the losses are comparable. Those are much higher compared with municipal sewage sludge, as seen from Figure 2.

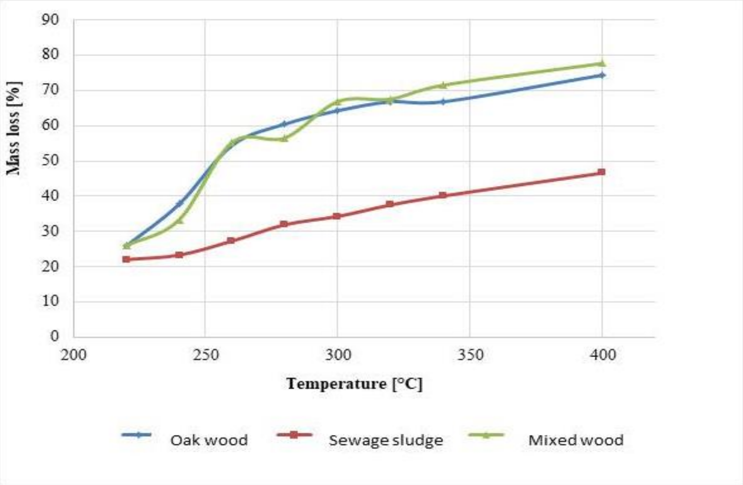

Figure 2: Mass loss of torrefied material in temperature dependence

An increase in mass loss under severe torrefaction conditions (i.e., 280 °C and 60 min) could be due to the loss of moisture and volatile organic matter and could also be due to the decomposition of cellulose and hemicellulose at severe torrefaction conditions. [15]

5.1.2 *Ash and volatile matter contents, elemental analysis*

Chemical analyses were performed for each torrefied sample. Results for oak wood are presented in Table 3. Results for municipal sewage sludge are presented in Table 4 and for mixed wood in Table 5.

The results showed that the most ash is present in torrefied municipal slaudge. Further, the content is increasing with increasing temperature. More volatile compounds are present in wooden material at lower temperatures, and above 280°C the content of volatile compounds is similar as in municipal sludge as well as they start to increase more in municipal sewage sludge. With increasing temperature the content of volatile compounds is decreasing. The share of carbon is the highest in mixed waste wooden material. In municipal sludge there was no effect of temperature on carbon share. In municipal sludge some nitrogen was detected, while it was very low in wooden samples. The share of hydrogen is similar in all samples, reaching 5 %. The share of sulphur is neglectable.

Table 3: The properties of torrefied oak wood in temperature dependence

Parameter	Temperature [°C]							
	220	**240**	**260**	**280**	**300**	**320**	**340**	**400**
Ash [%]	2.9	4.67	5.03	7.56	5.63	8.02	8.25	6.22
Moisture [%]	1.38	2.13	1.59	2.07	2.77	3.25	3.35	3.86
Volatile compounds [%]	73.59	64.44	47.94	42.96	40.23	39.38	35.96	34.1
Carbon [%]	52.27	56.56	65.01	65.93	68.35	67.13	68.75	72.43
Hydrogen [%]	5.58	5.1	4.24	3.87	3.75	3.72	3.34	2.77
Nitrogen [%]	0.34	0.39	0.42	0.54	0.53	0.55	0.6	0.71
Sulphur [%]	0.02	0.02	0.01	0.01	0.02	0.01	0.01	0.01

Table 4: The properties of torrefied municipal sewage sludge in temperature dependence

Parameter	Temperature [°C]							
	220	**240**	**260**	**280**	**300**	**320**	**340**	**400**
Ash [%]	37.9	37.5	39.61	42.85	43.99	45.89	48.58	55.32
Moisture [%]	1.16	0.58	0.61	0.66	1.24	0.6	1.12	0.9
Volatile compounds [%]	51.2	53.06	50.75	45.09	43.16	40.74	37.2	27.98
Carbon [%]	39.2	39.57	39.9	39.57	39.33	38.73	37.54	33.82
Hydrogen [%]	4.21	4.45	4.27	3.9	3.71	3.5	3.23	2.1
Nitrogen [%]	6.31	6.36	6.26	5.94	5.81	5.63	5.38	4.92
Sulphur [%]	0.87	0.88	0.79	0.7	0.66	0.61	0.55	0.46

Table 5: The properties of torrefied mixed wood material in temperature dependence

Parameter	Temperature [°C]							
	220	**240**	**260**	**280**	**300**	**320**	**340**	**400**
Ash [%]	1.17	1.38	1.7	1.77	2.18	2.63	3.28	4.65
Moisture [%]	2.32	2.59	4.72	4.11	6.2	5.71	6.45	9.25
Carbon [%]	53.79	56.91	66.66	68.35	71.61	72.26	73.61	72.4
Hydrogen [%]	5.58	5.43	4.45	4.63	3.58	3.66	3.27	2.47
Nitrogen [%]	0.22	0.29	0.32	0.34	0.43	0.42	0.54	0.64
Sulphur [%]	0.02	0.02	0.03	0.03	0.02	0.02	0.02	0.01

Cellulose partially decomposed at 275 °C and at 300 °C, and a rapid decomposition was recorded. This may be because cellulose is formed from a glucose polymer with no branches that provide thermal stability, resulting in its decomposition at a higher temperature.[15]

5.1.3 Heating value

The comparison of higher heating values (GVC) and low heating values (LHV) for torrefied oak wood, municipal sewage sludge and mixed wood at different temperatures are given on Figure 3 and Figure 4.

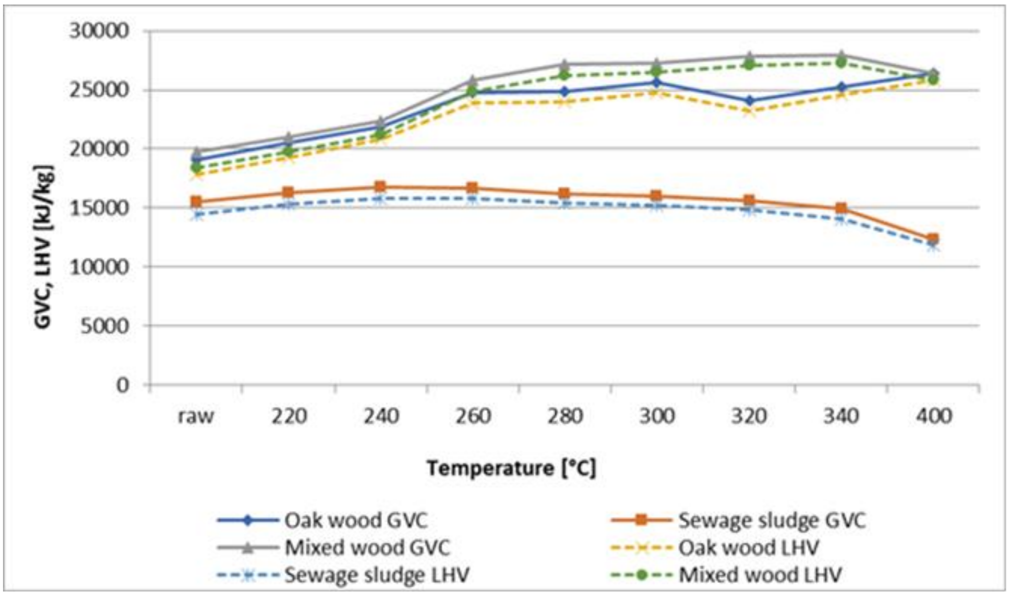

Figure 3: The GVC and LHV for torrefied materials depending on temperature

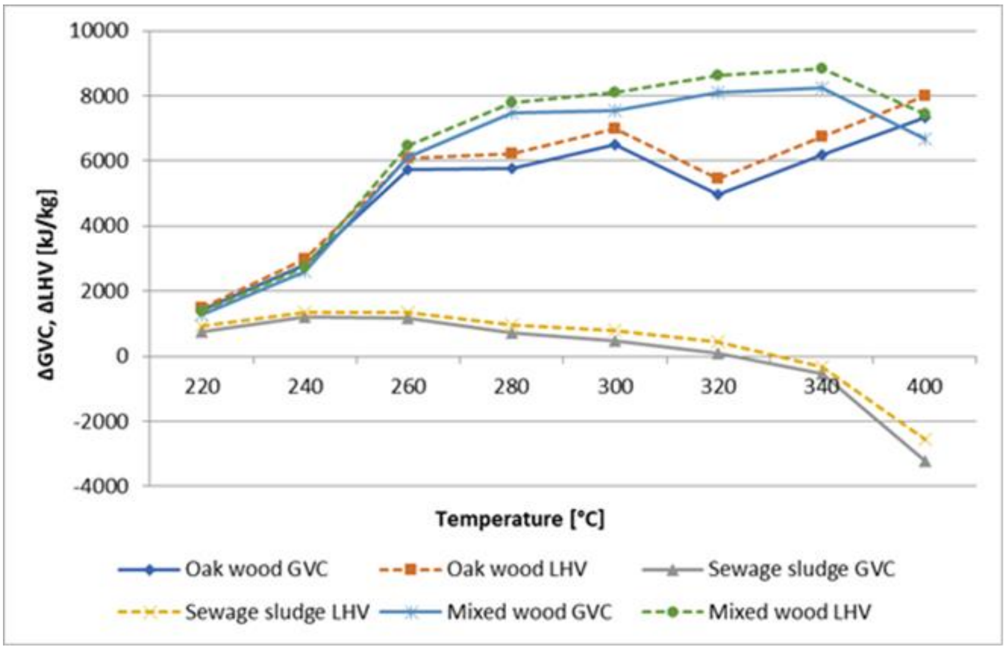

Figure 4: The difference in GVC and LHV depending on temperature

5.2 The influence of operating time

Experiments were performed at constant temperature at 260°C. Temperature was chosen upon results of the most increasing heating value between two temperature intervals. At higher temperature there was no effect on heating value. The chosen operating times were: 0.5 h, 1 h, 1.5 h and 2h, at constant temperature and inert atmosphere.

5.2.1 Mass loss

The results of mass loss at constant temperature and different operating time are presented on Figure 5. It could be seen that with the longer time the mass losses increased in all 3 tested materials. The highest mass loss was determined with mixed wood material, followed by oak wood and municipal sludge with the least mass loss. It could be due to a little lower volatile compound content before the process.

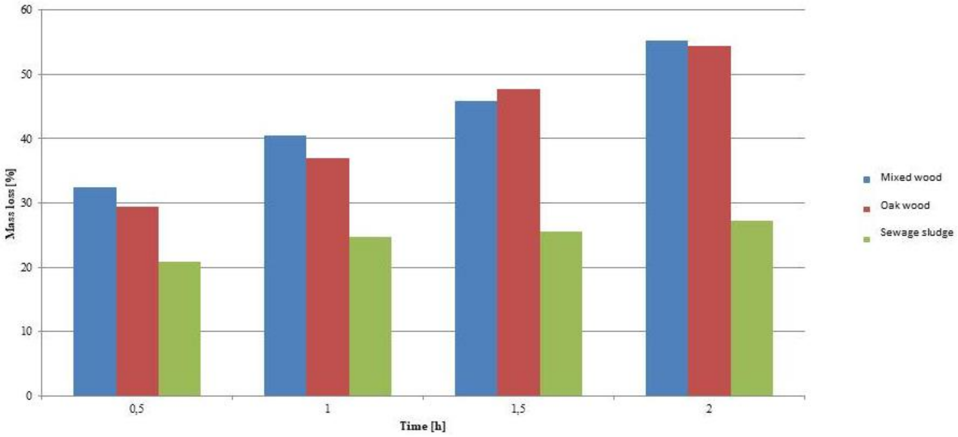

Figure 5: Mass loss of material upon operation times of torrefaction

5.2.2 Chemical analyses of biomaterial

The results of volatile compound content, moisture content, ash, as well as elemental analysis are presented in Tables 6, 7 and 8.

Table 6: The properties of torrefied oak wood at different operation times

	Time [h]			
Parameter	**0.5**	**1.0**	**1.5**	**2.0**
Moisture [%]	3.37	4.2	4.22	1.59
Nitrogen [%]	0.24	0.29	0.35	0.42
Carbon [%]	55.19	57.26	61.67	65.01
Ash[%]	2.31	3.34	3.96	5.03
Hydrogen [%]	5.39	5.03	4.53	4.24
Sulphur [%]	0.02	0.02	0.02	0.01

Table 7: The properties of torrefied municipal sewage sludge at different operation times

	Time [h]			
Parameter	**0.5**	**1.0**	**1.5**	**2.0**
Moisture [%]	2.68	1.81	2.35	0.61
Nitrogen [%]	6.17	6.24	6.22	6.26
Carbon [%]	38.73	39.29	39.29	39.9
Ash [%]	35.83	38.24	38.47	39.61
Hydrogen [%]	4.39	4.15	4.14	4.27
Sulphur [%]	0.83	0.8	0.76	0.79

Table 8: The properties of torrefied mixed wood material at different operation times.

	Time [h]			
Parameter	**0.5**	**1.0**	**1.5**	**2.0**
Moisture [%]	4.21	3.98	3.77	4.72
Nitrogen [%]	0.21	0.27	0.27	0.32
Carbon [%]	56.36	59.51	61.48	66.66
Ash [%]	1.06	1.36	1.26	1.7
Hydrogen [%]	5.57	5.3	5.1	4.45
Sulphur [%]	0.02	0.02	0.02	0.03

From the Tables 6 – 8 it is seen that the ash content is increasing with operating time. The most ash was found in samples of municipal sludge, from 35 % to 39 %, and the least in mixed wood samples from 1 % to 1.7 %. The sample of oak wood has low ash content, up to 5 %. The total carbon content is increasing with increasing operating time. The wooden samples showed more emphasized increase, while 10 % increase was found after 1.5 h. In municipal sludge only 1 % increase was determined. The hydrogen content is decreasing with the operational time. In municipal sludge no influence was detected. The hydrogen content was between 4 % and 6

% in wooden samples. In wooden samples was the low nitrogen and sulphur content. Nitrogen share was below 0.5 %, while sulphur content remained below 0.03 %. In municipal sludge the content of nitrogen is a little higher determined at 6 %, Sulphur content was below 1 %.

5.2.3 Heating value

The samples were torrefied for 0.5 h, 1 h, 1.5 h and 2 h at constant conditions. Figure 6 presents GVC and LHV for torrefied materials depending on operation time.

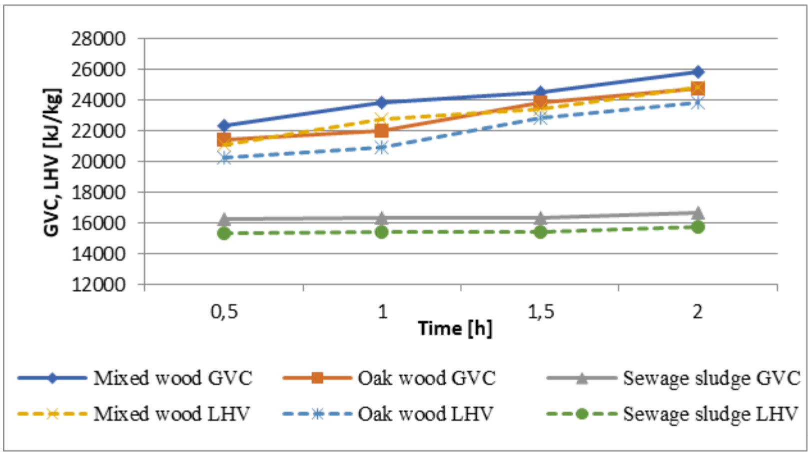

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Figure 6. The GVC and LHV for torrefied materials depending on operation time

The LHV and GVC are increasing with time for oak wood and mixed wood (Figure 6), while the GVC and LHV for sewage sludge is almost the same for different operation time. Figure 7 presents the difference in calorific value between torrefied material and raw material.

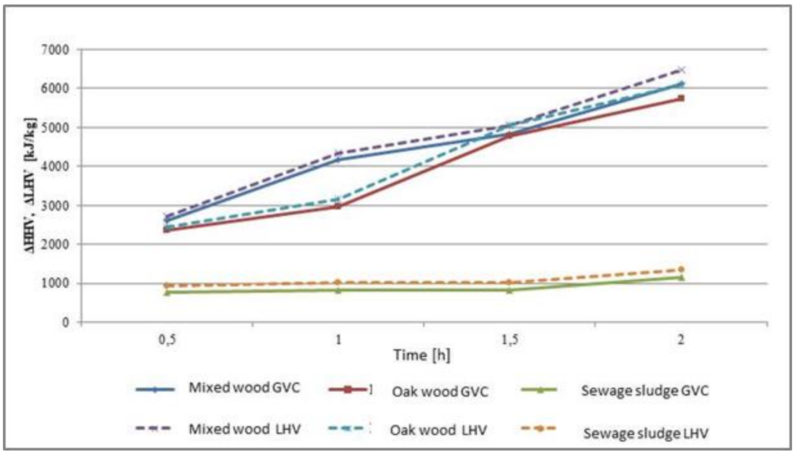

Figure 7. The difference in calorific value between torrefied material and raw material depending on operation time

6. Conclusion

The torrefaction of different biomasses was researched and optimal conditions were experimentally determined. Oak wood, dehydrated sewage sludge and mixed wood where processed at different temperatures, but for the same time (2 h) according to torrefaction conditions. The heating value of all materials increases with the temperature. The mass loss was higher for oak and mixed wood, mainly due to the higher moisture content of wood samples than sewage sludge According to the experimental results it was found out that for this material optimal operation temperature is at around 260°C, where the higher increase of heating values is achieved. Similar results are presented in various literatures [16, 17].

The materials became more hydrophobic after torrefaction, and the fragility of wood samples was also visibly improved.

Furthermore, at optimum temperature (260 ° C), the optimum time of the toreffaction process was determined. The optimum process time is about 1.2 hours, because till this time the increase in heating value is the largest. It can be concluded that solid biofuels with similar properties to coal can be produced through the process of torrefaction.

Presented work will be upgraded by determining the energy efficiency and the process improvement factor, also the degree of decarbonisation and dehydrogenation will be evaluated.

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