Thermal cracking in charcoal and ceramics of pyrolysis liquid from sewage sludge

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Abstract. The three products are formed as result of sewage sludge pyrolysis: solid residue, liquid fraction and non-condensable gases. The major product is the pyrolysis liquid (53 wt%). Pyrolysis liquid produced from sewage sludge is studied in present time yet. It has a relatively high calorific value, but it is stratified into fractions, contains a large amount of water and has an acid reaction of the medium, which complicates the process of its energy use. Therefore many researches of pyrolysis process is conducted to avoid producing of liquid fraction and obtain more gas fraction. This paper falls into this studies. To avoid pyrolysis liquid thermal cracking of it is used. The temperature in cracking zone is 1000 °C. The medium for cracking is charcoal and ceramics. In this paper it is presented the mass balances of pyrolysis and pyrolysis with cracking of sewage sludge, comparison of specific volume, degree of energy conversion, composition of gases mixtures obtained.

1. Introduction
Pyrolysis is the thermal decomposition of materials in an inert atmosphere producing vapors, which are formed by condensable and non-condensable gases, and a solid product. The major product obtained in this process is the pyrolysis liquid, which can be applied as a fuel and also as a source of valuable chemical products. In the case of lignocellulosic biomass pyrolysis, the yields achieved are 60–75 wt% for the liquid, 15–25 wt% for the solid residue and 10–20 wt% for the gas [1].

Pyrolysis liquid from lignocellulosic biomass has already been successfully tested as a direct fuel in engines, turbines and boilers [2,3]. However, the potential direct substitution of pyrolysis liquid for conventional petroleum-based fuels in transport applications requires upgrading processes which are currently being investigated [4].

The pyrolysis liquid consists of organic compounds and water. The main organic compounds are sugars carboxylic acids and phenolic compounds [5]. Two of the main chemical differences between biomass pyrolysis liquid and hydrocarbons fuels are water and oxygen. The water content in pyrolysis liquid varies a wide range (15–30 wt%) depending on the feedstock and the process conditions [3]. The oxygen content in pyrolysis liquid is usually 45–50 wt% depending on the liquid water content [6]. The oxygen is present in most of the more than 300 compounds that could be identified in the tar [3].

Since 1986, several authors have studied sewage sludge pyrolysis as a potential method for obtaining a liquid fuel and chemicals [5]. The differences in chemical composition between sewage sludge and lignocellulosic biomass involve important changes in the chemical and physical
Table 1. Properties of initial raw material and solid residue after pyrolysis.

| Raw material          | Sewage sludge | Solid residue |
|-----------------------|---------------|---------------|
| Elemental composition | C 42.78       | 38.23         |
|                       | H 5.67        | 0.58          |
| on daf basis (wt%)    | N 5.08        | 2.48          |
|                       | O 19.86       | 0             |
|                       | S 0.82        | 0.50          |
| Moisture content (wt%)| W 3.07        | 0             |
| Ash content (wt%)     | A 22.73       | 58.22         |
| Lower calorific value (MJ/kg) | $Q_L$ 18.19 | 13.61         |

properties of the pyrolysis liquids obtained with each feedstock [7]. Pyrolysis liquids produced from sewage sludge with energy point of view is studied in present time yet. Therefore many researches of pyrolysis process is conducted to avoid producing of liquid fraction and obtain more gas fraction. This paper falls into this studies.

2. Properties of initial raw material
The sewage sludge from Podol’sk waste treatment facilities were used as initial raw material for experiments. The relative moisture of sewage sludge was 3.07 wt%. To reach this moisture sewage sludge were dried by thermal methods. The common moisture of sewage sludge in waste treatment facilities after mechanical dehumidification is 75–80 wt%.

The properties of initial raw material before experiments is presented in table 1. The elementary composition of sewage sludge was measured with CHNS-analyzer Elementar Vario MACRO cube. The relative moisture and ash content were measured with SDT Q600 thermal analyzer. The lower calorific value was calculated on the basis of data on the elemental composition of sewage sludge with Mendeleev’s formula.

From table 1 it is seen that sewage sludge have a large for biomass ash content (22.73 wt%) and the lower calorific value [8]. Sewage sludge contain a significant amount of sulfur—0.82 wt%.

3. Experimental setup and researches
The experimental setup presented on figure 1 was made for experimental studies of pyrolysis and pyrolysis with cracking processes of sewage sludge.

The initial raw material (40 g) was lied in pyrolysis reactor 1. It was heated up to $T_1 = 800 \, ^\circ C$. The temperature was controlled with thermal couples T1 and T2. A gas and vapour of the thermal decomposition of feedstock, formed in the pyrolysis reactor were going through gas pipe 2 the temperature of whose was constant during experiments ($T_1 = 300 \, ^\circ C$) in the cracking reactor 3 that was filled with medium for cracking when the process of pyrolysis with cracking was studied. The charcoal and ceramics were used as medium for cracking. The temperature of cracking reactor $T_3$ was fixed during experiments ($T_3 = 1000 \, ^\circ C$). The liquid fraction of pyrolysis was destructed in cracking reactor. The non-condensable gases were formed. Heat exchanger 4...
was used for control of liquid fraction destruction degree in cracking reactor. Heat exchanger was cooled by water.

When process of pyrolysis was studied the cracking reactor was empty. The temperature $T_4$ was 15 °C. The liquid fraction formed during pyrolysis process was collected in cracking reactor. Only non-condensable gases were going in the heat exchanger.

The volume of product gas was measured with the gas flowmeter 5. Gas sampling for chromatographic analysis was made in point A. A chromatographic analysis allows to determine the current composition of the gas mixture at the exit of experimental setup (H$_2$, CO, CO$_2$, N$_2$ and C$_n$H$_m$). On the base of the obtained experimental data, the final composition of the gas mixture formed during the pyrolysis of initial raw material was calculated. An elementary composition of sewage sludge, charcoal and carbon layer from ceramics was measured before and after experiments. The experimental setup was purged by argon before experiments.

4. Mass balances of pyrolysis and pyrolysis with a cracking of sewage sludge

4.1. Pyrolysis

The mass balance of sewage sludge pyrolysis is presented on figure 2.

From figure 2 it is seen that three products are formed as result of sewage sludge pyrolysis: solid residue that is 37 wt% from feedstock, liquid fraction that is 53 wt% from feedstock and non-condensable gases. The volume of non-condensable gases produced from 1 kg of initial
sewage sludge, is 0.14 Nm$^3$. The composition of gases is heterogeneous. The CO$_2$ and CH$_4$ are contained in significant quantity. The calorific value of gas mixture is 11.03 MJ/Nm$^3$ because of content of methane. The divergence of mass balance is 7 wt%.

The liquid fraction formed as result of pyrolysis is unfavorable product. The mass of pyrolysis liquid is more than half of initial raw material mass. From energy point of view using of liquid fraction is difficult because of carbon dioxide content and small specific volume. Thus to increase energy efficiency of pyrolysis it was solved to use thermal cracking for liquid and gaseous products. The charcoal and ceramics were used as medium for cracking. The idea to use ceramics was took from paper [9]. The temperature in cracking zone was 1000 °C.

4.2. Pyrolysis with cracking (charcoal)
The mass balance of sewage sludge pyrolysis with cracking is presented on figure 3. The charcoal is used as medium for cracking.

From figure 3 it is seen that two products are produced as result of sewage sludge pyrolysis with cracking where charcoal is used as medium for cracking: solid residue that is 37 wt% from feedstock and non-condensable gases. The specific volume of gas is 1.07 Nm$^3$/kg. The main share of gas mixture is hydrogen and carbon monoxide (92 wt%). The carbon dioxide is almost absent (more than 1 wt%). The calorific value of gas is 11.4 MJ/Nm$^3$. It is necessary to turn attention to the ratio of H$_2$:CO in the gas mixture. It is 1.72. The ratio of H$_2$:CO in syngas obtained from other types of biomass is significantly less. For example, for wood or sawdust it stand at 1 [8]. The H$_2$:CO ratio close to 2 empowers to use syngas as feedstock in the process.
Figure 3. Mass balance of sewage sludge pyrolysis with cracking (charcoal).

of catalytic synthesis of methanol and dimethyl ether with producing of the base component of aviation fuel.

The change of charcoal mass is one of the characteristics of pyrolysis product cracking process. The additional consumption of carbon from charcoal happens according to Buduar’s reaction at decomposition of liquid fraction and carbon dioxide at temperature more than 1000 °C [10]. According to mass balance the mass of charcoal decreases on 0.035 kg at pyrolysis treatment of 1 kg of sewage sludge.

From the CHNS analyze of charcoal samples after the studies it was obtained that value of sulfur is increased. The maximum concentration of sulfur was observed on the upper layer of charcoal in cracking reactor. It was 0.53 wt%. The minimum concentration of sulfur was observed in the lower layer of charcoal in cracking reactor—0.04 wt%. The divergence of mass balance is 8.5 wt%.

4.3. Pyrolysis with cracking (ceramics)
The mass balance of sewage sludge pyrolysis with cracking is presented on figure 4. The ceramics is used as medium for cracking.

From figure 4 it is seen that two products are also produced as result of sewage sludge pyrolysis with cracking where ceramics is used as medium for cracking: solid residue that is
38 wt% from feedstock and non-condensable gases. The specific volume of non-condensable gases is 0.70 Nm$^3$/kg. The main share are H$_2$, CO and CH$_4$ in the composition of gas mixture. The calorific value of gas mixture is 13.04 MJ/Nm$^3$. The H$_2$ : CO ratio in the gas mixture is saved close to 2 at even using of indifferent medium for cracking. It is 1.93.

In result of experimental studies of decomposition process of gaseous and liquid fraction it was observed that some quantity of carbon going out from sewage sludge at pyrolysis sedimented on ceramics. Therefore the characteristic of the process is changing of ceramics mass. At pyrolysis processing of 1 kg of sewage sludge 0.07 kg of carbon layer consisting of carbon on 97 wt% sediments on ceramics. From the CHNS analyze of sample of this carbon layer it was obtained that it contains 0.66 wt% of sulfur. The divergence of mass balance is 13 wt%.

5. Result and discussion
The comparison of mass balance obtained after pyrolysis and pyrolysis with cracking is shown on figure 5. The mass balances are recalculated for the case of divergence absence.

From figure 5 it is seen that the absolute absence of liquid fraction is observed as result of thermal cracking using for products of pyrolysis treatment. Two products (solid residue and non-condensable gases) are obtained.
5.1. Solid residue after pyrolysis

The composition of solid residue after pyrolysis of sewage sludge is presented in table 1. From table 1 it is seen that oxygen went out fully from sewage sludge at pyrolysis. The content of carbon is decreased on 4.5 wt%. The content of sulfur is decreased: before pyrolysis sewage sludge contained 0.82 wt%, after pyrolysis—0.50 wt%.

If it is performed that 100 wt% is mass of sewage sludge before pyrolysis treatment distribution of sulfur in the products of pyrolysis is such as it is shown on figure 6.

From figure 6 it is seen that more than 79 wt% of sulfur containing in initial raw material goes out from sewage sludge. The 54 wt% of sulfur sediments on charcoal, 23 wt% of sulfur is took away by gases. On ceramics only 5 wt% of sulfur sediments. The 74 wt% of sulfur is took away by gases. From this data it is clean that charcoal at the temperature of 1000 °C is the
Table 2. Characteristics of gases obtained during pyrolysis without and with cracking of sewage sludge.

| Type of thermal conversion | Pyrolysis | Pyrolysis with cracking |
|---------------------------|-----------|-------------------------|
|                           | (charcoal)| (ceramics)              |
| Composition (vol%)        |           |                         |
| H₂                        | 11.29     | 58.27                   |
| CO                        | 10.79     | 33.83                   |
| CO₂                       | 54.31     | 0.21                    |
| CH₄                       | 23.61     | 2.40                    |
| N₂                        | 0         | 2.71                    |
| Calorific value (MJ/Nm³)  | Q_L       |                         |
|                           | 11.03     | 11.40                   |
| Specific volume (Nm³/kg)  | V         |                         |
|                           | 0.12      | 1.07                    |
| Degree of energy conversion | η       |                         |
|                           | 0.085     | 0.61                    |

Figure 7. Dependence of specific volume of non-condensable gases upon the temperature of initial raw material heating.

better filter for cleaning of gases from sulfur than ceramics at the same conditions. The presence of sulfur in the composition of syngas is one of the limitation conditions of this gas application for methanol producing.

5.2. Non-condensable pyrolysis gases
The characteristics of gas mixtures obtained during pyrolysis and pyrolysis with cracking of sewage sludge are shown in table 2.

From table 2 it is seen that gas mixture obtained at pyrolysis of sewage sludge has the lower degree of energy conversion of raw material into gas and specific volume. This gas mixture
consists of more than 50 wt% from carbon dioxide. In spite of the high calorific value this gas mixture would not find energy application.

In result of thermal cracking using for pyrolysis products gas mixtures with the specific volume in the range of 0.7–1.07 Nm\(^3\)/kg and the calorific value of 11.4–13.04 MJ/Nm\(^3\) are obtained. These gas mixtures consist of H\(_2\) CO mainly. The degree of energy conversion of raw material into gas for gas mixtures produced at pyrolysis with cracking is in 5–7 times more than for gas mixtures produced at pyrolysis.

The depending on specific volume of non-condensable gases from temperature of initial raw material is presented on figure 7.

From this data it is seen that gas yield is almost evenly changed at pyrolysis. The gas yield increases intensity from 210 \(^\circ\)C at pyrolysis with cracking. The intensive gas yield is finished at 450–500 \(^\circ\)C. The specific volume is increased only on 0.07 Nm\(^3\)/kg in the range of temperatures 500–800 \(^\circ\)C in the case of charcoal using, on 0.1 Nm\(^3\)/kg in the case of ceramics using. Therefore the temperature of feedstock heating can be decreased to 500 \(^\circ\)C for charcoal and to 600–700 \(^\circ\)C for ceramics.

6. Conclusion

As a result of the studies, it was found that when thermal cracking is used, irrespective of the medium in which it is proceed, only two products are formed after pyrolysis processing of sewage sludge: a solid residue that is less than 40 wt% of the initial mass of sewage sludge and non-condensable gases that have the H\(_2\) : CO ratio is close to 2. In the case of using charcoal as a cracking medium the gases produced have a calorific value and the H\(_2\) : CO ratio the lower than when ceramics is used. But in this case the resulting gases contain less sulfur. Charcoal works as a filter, on which sulfur leaving the initial sewage sludge during pyrolysis sediments. The liquid fraction is completely absent.

The resulting gas mixtures have several applications. As a consequence of the high for the gas obtained from biomass calorific value and the content of only H\(_2\), CO (and CH\(_4\) in the case of ceramics) the gas mixtures can be used in gas piston machines for the production of electric energy. As a consequence of the H\(_2\) : CO ratio close to 2, the obtained gases can be used to produce the basic component of aviation fuel. The obtained gases, despite some purification as a result of thermal cracking, still contain sulfur. Before using such a gases need to be cleaned.

Acknowledgments

The work was financially supported by the Ministry of the Russian Federation for Education and Science (project No. 14.607.21.0134, unique identifier RFMEFI60715X0134).

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