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PYROLYSIS OF SLUDGE FROM MUNICIPAL WASTEWATER TREATMENT PLANTS

PYROLÝZA KALŮ Z KOMUNÁLNÍCH ČISTÍREN ODPADNÍCH VOD

Abstract

The contribution deals with the pyrolysis of three samples of sludge obtained from municipal wastewater treatment plants under the same process conditions: 0.2 g samples of material were pyrolysed in the nitrogen atmosphere; the final temperature of pyrolysis process was set at 850 °C, and after reaching this value it was kept for the next two hours. The carbon enrichment of pyrolytic coke was the highest in the case of non-limed sludge from the Ostrava Central Wastewater Treatment Plant (CWTP), namely 67.47%, in the case of sludge from the Sviadnov WTP it was 45.99% and in the case of limed sludge from the Ostrava CWTP it was 44.54%; carbon contents in these samples did not differ too much. Pyrolytic gases from the non-limed sludge from the Ostrava CWTP and from the sludge of Sviadnov WTP show similar compositions (H2 forms about 70% and CO2 30% of detected gases). By pyrolysis of limed sludge from the Ostrava CWTP, a gas containing, in addition to hydrogen and carbon dioxide, also carbon monoxide (7% of detected gases) and methane (2.5% of detected gases) was produced. From experiments it is evident that above all the content of volatile organic compounds in sludge and the presence of monoxide calcium, which acts as catalyst in the pyrolysis reaction, in sludge influence the production of gases.

Abstrakt

Příspěvek se zabývá pyrolýzou tří různých kalů z komunálních čistíren odpadních vod za stejných procesních podmínek: vzorky materiálu o hmotnosti 0,2 g byly pyrolyzovány v atmosféře dusíku, konečná teplota pyrolýzního procesu byla nastavena na 850 °C a byla udržována ještě dvě hodiny po dosažení této hodnoty. Nabohacení pyrolytického koksu uhlíkem bylo nejvyšší pro nevápněný kal ÚČOV Ostrava 67,47 %, pro kal ČOV Sviadnov bylo 45,99 % a pro vápněný kal ÚČOV Ostrava bylo 44,54 %, přitom obsah uhlíku v původních kalech se příliš nelišil. Podobné složení (cca 70 % detekovaných plynů tvoří H2 a 30 % CO2) vykazovaly pyrolytické plyny z nevápněného kalu ÚČOV Ostrava a z kalu ČOV Sviadnov. Pyrolýzou vápněného kalu ÚČOV Ostrava vznikl plyn obsahující kromě vodíku a oxidu uhličitého také oxid uhelnatý (7 % detekovaných plynů) a methan (2,5 % detekovaných plynů). Základní charakteristika pyrolytického koksu z kalů ÚČOV Ostrava byla obdobná, pyrolytický koks z kalu ČOV Sviadnov obsahoval subjektivně méně fosforečnanů železa a více částic na bázi Fe-S. Z experimentů je zřejmé, že vliv má především obsah těkavé organické složky v kalu a přítomnost oxidu vápenatého v kalu, která působí na průběh pyrolýzní reakce katalyticky.

1 INTRODUCTION

Pyrolysis is a process of organic material decomposition at high temperatures in an inert atmosphere; it represents environmentally-friendly waste treatment. Pyrolysis products are a pyrolytic gas, pyrolytic liquid and pyrolytic coke [1, 2, 3, 4]. Gas and liquid products of pyrolysis of sludge

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from wastewater treatment plants can be utilized as source of energy or chemicals; pyrolytic coke can be used as carbon-based absorbent especially for the absorption of acid compounds formed in the course of wastewater treatment [1, 2, 3, 4, 5, 6]. Pyrolysis also represents a way of concentrating heavy metals in a final pyrolytic residue as well as of avoiding the formation of toxic compounds produced during sludge combustion [3, 4, 7].

Sludge from wastewater treatment plants is a complex heterogeneous mixture of inorganic and organic components. It contains undigested organics, such as cellulose, lipids and dead bacteria and microbes [1, 8]. The composition of sludge produced as waste in wastewater treatment can change depending upon the feedstock and the technological conditions of the treatment plant [1, 9]. The content of organic and also inorganic component in sludge influence considerably the distribution of pyrolysis products and their composition and properties [1, 2, 4, 10]. By the pyrolysis of sludge having a rather high content of inorganic compounds, the higher amount of pyrolytic gas and the smaller amount of liquid component are formed. [1, 10, 11]. According to Fonts et all [1], this can be caused by the fact that a rather high content of inorganic compounds in sludge (also of metals) supports the contact with the organic component, and thus volatile components may evaporate also at a rather low temperature range. On the other hand, Mendéz et all [12], who investigated the influence of the properties of sludge on the course of pyrolysis, state that the presence of metals in organic material may negatively affect the release of volatile matters during the pyrolysis. The content of inorganic component in sludge influences considerably the viscosity and the chemical composition of pyrolysis oil [1]. According to Raveedran et all [10], the content of minerals of e.g. silicon in biomass has a considerable influence on the course and the results of pyrolysis. Silicon binds carbon particles that are then unavailable for thermal transformation. Inorganic salts in sludge support the secondary pyrolysis reactions of coke formation; simultaneously the formation of liquid is suppressed [10].

The yield of individual fractions produced by the pyrolysis of sludge from CWTP is, in addition to the composition of them, also influenced by process parameters of pyrolysis, above all the final temperature of pyrolysis and the rate of heating. [3, 4, 5, 9]. An increase in final pyrolysis temperature supports the formation of gas products, whereas the amount of pyrolytic coke produced decreases and the amount of liquid fraction moderately grows with the increasing temperature from 450 to 600 °C; at temperatures above 650 °C it remains almost constant. The influence of rate of heating on the yield of individual fractions is marked merely at low pyrolysis temperatures. [5] At lower temperatures of around 450 °C, an increase in the rate of heating leads to enhanced thermal degradation, and thus to the formation of the greater amount of pyrolytic oil and gas at the expense of pyrolytic coke [3, 4, 5, 7]. By an increase in rate of heating, the natural moisture of the material changes more quickly to water vapour, and thus gasification processes take place [7]. At temperatures above 650 °C, the influence of rate of heating is negligible. [5] At lower temperatures, lighter compounds are formed by cracking reactions which can be supported by increasing the rate of heating; at temperatures above 650 °C, carbonization of oxygenous hydrocarbons and hydrogenation prevail over cracking reactions, which leads to polymerisation and polycondensation [5].

2 METHODS AND MATERIAL

For the experiment, three samples of sludge from two municipal wastewater treatment plants were selected: non-limed sludge from the Ostrava-Přívoz Central Wastewater Treatment Plant (henceforth referred to as sludge CWTP A) and limed sludge from the same treatment plant (sludge CWTP B). Here sludge is produced as waste from the mechanical biological treatment of wastewater on the principle of low-load activation with nitrification, primary denitrification and dewatering of anaerobically stabilized sludge in centrifuges. The third sample was sludge from the Sviadnov wastewater treatment plant for Frýdek-Místek (sludge WTP C). This plant utilizes the treatment technology based on the principle of low-load activation with nitrification, preliminary denitrification and sludge dewatering by belt presses.

For analytical determination and also pyrolysis tests themselves, the sludge samples were dried; the sludge contained about 28% of dry matter. Both the feedstock and the pyrolysis products were analysed according to the standards ČSN ISO 1171, ČSN ISO 441375 and ČSN P CEN/TS 15104

The pyrolytic gas was analysed by means of gas chromatography using an analyzer Agilent 3000 Micro Gas Chromatograph with a thermal conductivity detector. The following chromatographic columns were used: Plot U preliminary column having the diameter of 0.32 mm and the length of 3 m, Mol-sieve column having the diameter of 0.32 mm and the length of 10 m, as carrier gas argon was used, Plot Q column having the diameter of 0.32 mm and the length of 8 m; as carrier gas helium was used.

Analyses of pyrolytic coke were made in the metallurgical and chemical laboratory of ArcelorMittal Ostrava, JSC. The inorganic component in pyrolytic coke was analysed using the energy dispersive microanalysis. In all the samples, preliminary ED analyses were done on three various areas of about 3.3 x 3.3 mm size. At about 200x to 300x microscope magnification, particles of interest were sought in reflected electron mode. By individual microscopic fields, the whole area of the sample was examined and those particles in which a rather heavy element was expected were analysed.

3 LABORATORY PYROLYSIS TESTS

Experiments were carried out on a laboratory pyrolysis apparatus from the company Parr. The main part of this apparatus is a steel reactor from the company Parr; heating to the temperature of up to 900 °C is ensured by an electric heater and a temperature controller of type 4836 with a J type thermocouple from the company Parr. A temperature sensor is placed in the central part of the reactor. The pyrolysis takes place under a nitrogen atmosphere. Before the entry of inert gas into the reactor, a flow meter was placed into the reactor. The sample was put between two layers of quartz wool in the central part of reactor in the vicinity of thermocouple sensor. A schematic diagram of the pyrolysis apparatus is illustrated in Fig. No. 1.
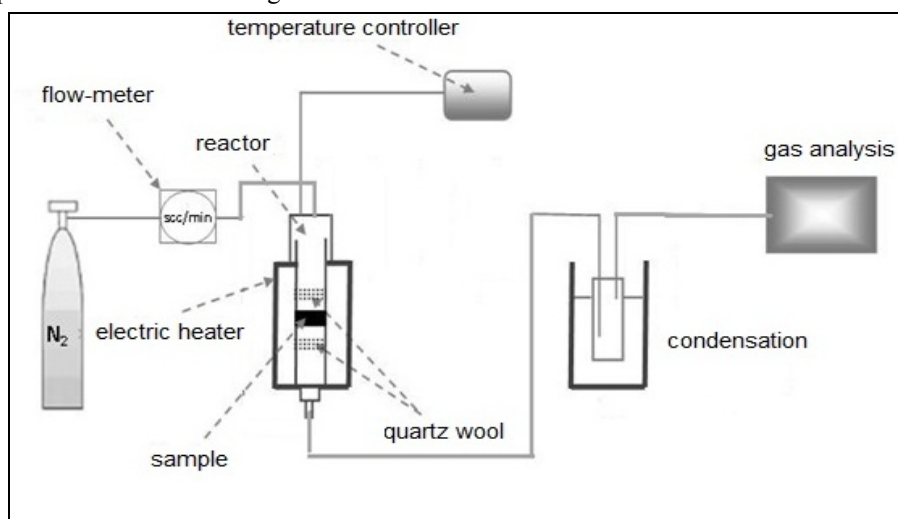
Fig. 1 Schematic diagram of pyrolysis apparatus

In this apparatus, 0.2 g samples of material were pyrolysed. The flow rate of nitrogen was set at 25 ml/min. The final temperature of pyrolysis process was 850 °C and was maintained for other two hours after reaching this value.

4 RESULTS

The analysis of gases was done continuously for the whole duration of the pyrolysis process. The amount of produced pyrolysis liquid was too small to enable sampling for the analysis. In Table 1 there is the elemental composition of elements in dry matter, ash content, heat of combustion, calorific value and moisture in the original sludge sample. The volatile matter was determined according to the standard ČSN ISO 562 (Solid fuels – Determination of volatile matter) at the laboratory of Karviná Mine, Lazy plant (OKD, JSC).

Tab. 1 Energy parameters of sludge for pyrolysis (in dry matter)

Sample	C	H	N	S	O	Com-busti-bles	Volatile Combustible	Heat of combustion	Mois-ture
	(%)							kJ/kg	(%)
Sludge CWTP A	21,73	3,76	2,92	<0,1	21,58	49,90	41,50	8449	62,63
Sludge CWRP B	22,62	5,07	2,78	<0,1	19,52	48,75	42,40	8651	58,54
Sludge WTP C	19,26	4,03	2,49	<0,1	24,21	41,15	30,20		

In Table No. 2 there are results of determination of elemental composition of pyrolysis coke, amounts of hydrogen, nitrogen and carbon given in percentage that released during the pyrolysis from the material and were transformed to components of pyrolysis gas and/or liquid. It is evident from Table No. 1 that the sludge from WTP Sviadnov contains a lower amount of organic component and an amount of volatile matter almost by 1/3 lower than the sludge from CWTP Ostrava.

Tab. 2 Calculation of amounts of majority elements released during pyrolysis

Material	After pyrolysis				Released		
	C	H	N	S	H	N	C
Sludge CWRP A	14,66	0,287	0,396	<0,1	92,36	86,45	32,53
Sludge CWRP B	10,074	0,184	0.203	<0,1	96,37	92,71	55,46
Sludge WRP C	8,857	0,157	0,351	<0,1	96,10	85,92	54,01

Lin et all [13] state that the contents of carbon, nitrogen and hydrogen in pyrolytic coke from sludge from wastewater treatment decrease with an increase in pyrolysis temperature, because these elements are desorbed during the process; on the other hand, the content of sulphur in the solid pyrolytic residue grows with temperature. This is probably caused by the strength of bonds between elements in the feedstock [13]. An indicator of different courses of pyrolysis of different sludge samples under the same process conditions can be semicoke enrichment in carbon [14]. The enrichment in carbon was calculated as follows:

$$N\,[\%] = \frac{TC_1}{TC_2} \times 100 \tag{1}$$

Where:
N – enrichment in carbon [%],
TC_1 - the content of carbon in the feedstock [-],
TC_2 - the content of carbon in pyrolytic coke [-].

The enrichment in carbon was the highest in the case of sludge CWTP A, namely 67.47%; in the cases of sludge WTP C and sludge CWTP B, the enrichments were 45.99% and 44.54%, respectively. The content of carbon in original sludge was very similar (see Tab. 1). The enrichment of pyrolytic coke with carbon increases with the content of fulvic acids in the original sludge [14, 15]. More functional groups in fulvic acids make this fraction of material more reactive during the pyrolysis, which leads to a rather high content of carbon in pyrolytic coke [15]. The course of pyrolysis, the yield and the composition of individual fractions are not always proportional to the content of carbon in pyrolysed sludge, but they can be influenced by different abundances of individual components (humic acids/fulvic acids).

4.1 Analysis of Gases

Major components of pyrolytic gas from sludge are CO_2, CO, H_2 and hydrocarbons CH_4, C_2H_4 and C_2H_6. [1] The pyrolytic gas was analysed by means of a gas chromatograph GC with a thermal conductivity detector. The analysis of gases took place continuously and the concentrations of hydrogen, nitrogen, carbon dioxide, carbon monoxide and methane were determined every 5 minutes. In Table No. 3 the total volumes of gases produced from a 0.2 g sample during the whole individual experiments under the above-mentioned conditions and the percentages of these volumes in the mixture composed of the gases analyzed are presented.

Tab. 3 Volumes of measured gases, obtained during pyrolysis

Material		H_2	CO	CO_2	CH_4
sludge CWTP A	ml	16.75178	0	5.997791	0
	% v/v	73.63558	0	26.36442	0
sludge CWTP B	ml	17.04427	1.932286	8.024297	0.688268
	% v/v	61.55583	6.978502	28.97997	2.485698
sludge WTP C	ml	11.68894	0	5.187004	0
	% v/v	69.26392	0	30.73608	0

A similar composition (about 70% of detected gases are formed by H_2 and 30% by CO_2) was exhibited by pyrolytic gases from the sludge CWTP A and the sludge WTP C. In the following graphs the courses of release of gases during the pyrolysis of individual samples are illustrated.
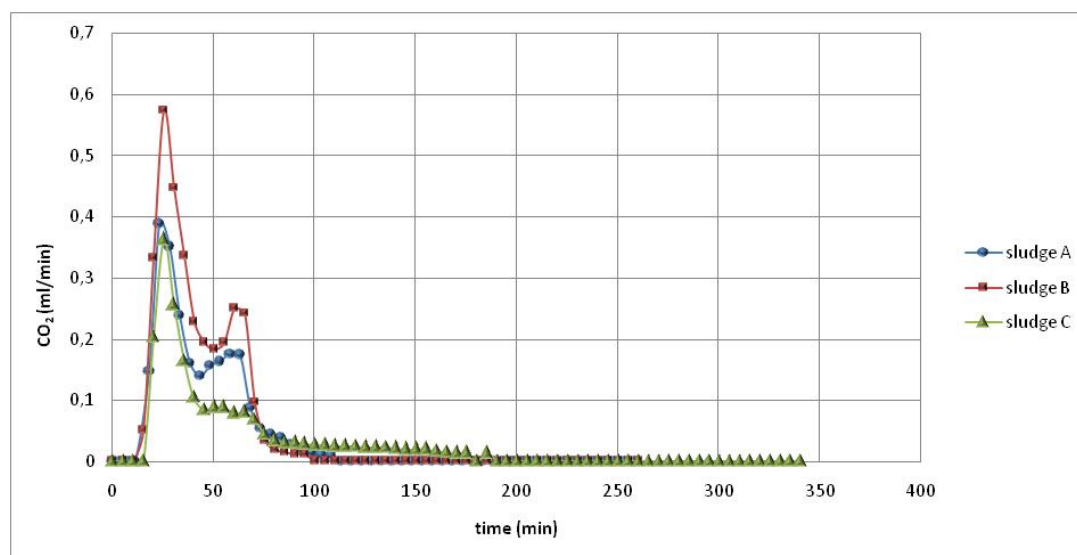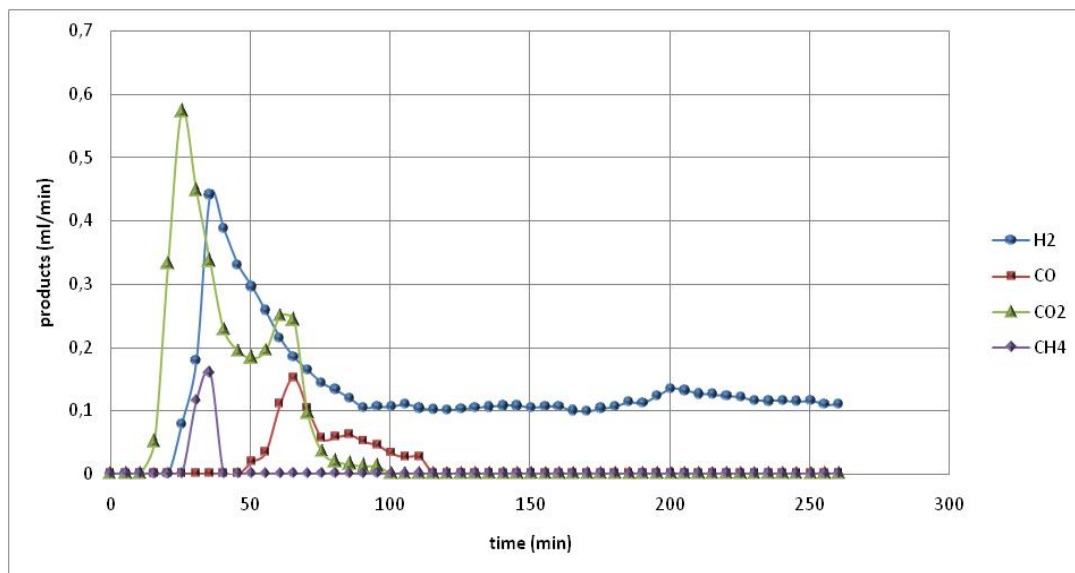

Fig. 2 The course of release of carbon dioxide during pyrolysis
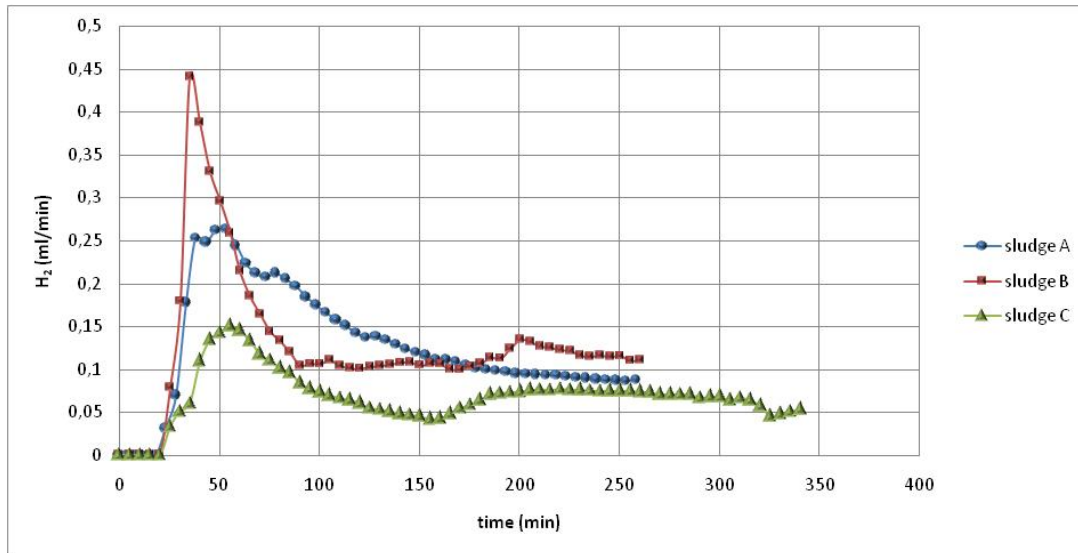
Fig. 3 The course of release of hydrogen during pyrolysis

According to Fonts et all [1], the concentration of hydrogen in the pyrolytic gas grows with the content of inorganic component in the feedstock, which can be caused by the catalytic effect of inorganic compounds in the course of dehydrogenation reactions. This statement is contrary to the results of these pyrolysis tests. The highest amount of inorganic component was contained in the sludge WTP C; the concentration of hydrogen in the pyrolytic gas of this sludge being the lowest in comparison with two other test samples. From this it follows that if the content of inorganic component has a positive influence on hydrogen concentration in the pyrolytic gas, under the set process conditions it is not sufficient and insignificant in comparison with the other influences. Further, Fonts el all [1] state that sludge containing a rather high content of aromatic and cycloaliphatic structures, when hydrogen is formed in the course of secondary aromatization, also shows a rather high amount of hydrogen in the pyrolytic gas. The result of these reactions is also a rather high amount of aromatic and polyaromatic hydrocarbons in the pyrolytic liquid [1]. From the results of the analyses it is evident that what has the greatest influence on the course and the products of pyrolysis is sludge liming. As can be seen in Figures 2 and 3, it is the course of gasification reactions during the pyrolysis of limed sludge CWTP B that differs most. By the pyrolysis of limed sludge CWTP B, a gas containing, in addition to hydrogen and carbon dioxide, also carbon monoxide (7% of detected gases) and methane (2.5% of detected gases) was formed; the course of release of gases during the pyrolysis is shown in Figure 4.

Fig. 4 The course of release of gases during the pyrolysis of sludge CWTP B

The content of CaO in the pyrolysed material increases its reactivity; it is active especially in the decomposition of functional groups producing carbon monoxide[16, 17]. Catalytic reactions caused by the presence of CaO can also support the formation of hydrogen in pyrolysis [6].

5 CONCLUSION

From the results of experiments it follows that the course of pyrolysis, the yield and the composition of individual fractions are not always proportional to the content of carbon in pyrolysed sludge due to different compositions of organic material. It has turned out that the content of inorganic component in sludge has not any positive influence on the formation of pyrolytic gas. The content of inorganic component has rather a negative influence on the production of gases or is, in comparison with the other influences under given conditions of experiments, insignificant. At the same volatile matter content in the sludge from Ostrava CWTP, it has been proved that it is the liming of sludge that has a considerable influence on the course and the products of pyrolysis; the content of CaO in the pyrolysed material increases its reactivity. This catalytic reactions influence the composition of pyrolytic gas as well as the enrichment of pyrolytic coke with carbon.

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