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## PHYSICOCHEMICAL, THERMAL AND KINETIC ANALYSIS OF SEWAGE SLUDGE

### FIZYKOCHEMICZNA, TERMICZNA I KINETYCZNA ANALIZA OSADÓW ŚCIEKOWYCH

**Abstract:** Sewage sludge (SS) is the residual matter generated from waste water treatment. Current treatment methods consist of mechanical dewatering and thermochemical treatment, which have become expensive, inefficient and energy consuming. Furthermore, European Union (EU) laws prohibit landfilling, agricultural and storage utilization of sewage sludge (SS). Consequently, innovative and sustainable treatment, management and utilization technologies for SS are urgently required. The pyrolysis of sewage sludge can be potentially address the outlined challenges. Therefore, the main aim of this investigation was to examine the physicochemical, thermal and kinetic properties of selected sewage sludge samples (SS1 and SS2). Thermogravimetric analysis was examined to provide comprehensive description of the decomposition behaviour and kinetic characteristics of SS1 and SS2 under pyrolysis conditions at heating rates: 5, 10, 20 and 40°C/min from 30-800°C. The kinetic parameters such activation energy  $E_a$  and pre-exponential factor,  $A$  were calculated using the Kissinger model. The  $E_a$  and  $A$  values for SS1 are 205.87 kJ/mol and  $9.68 \cdot 10^{14}$  whereas SS2 are 320.40 kJ/mol and  $7.44 \cdot 10^{24}$ . The general conclusion based on experimental studies is that the physicochemical and thermal kinetic properties of SS1 and SS2 are comparable with other pyrolysis feedstock and suitable for pyrolysis conversion.

**Keywords:** physical and chemical properties of sewage sludge, thermal analysis, kinetics

### Introduction

Sewage sludge (SS) is the residual matter generated from the treatment of waste water plants. Currently, SS treatment methods are mechanical dewatering, biological and chemical treatment techniques [1] aimed at reducing moisture content, microbial load, hazardous substances and volume density [2]. However, the high cost, low efficiency and energy consumption of current treatment processes present significant challenges to sewage sludge management. Furthermore, European Union (EU) Sewage Sludge Directive 86/278/EEC as well as regulations on health, safety and environmental (HSE) seeks to limit landfilling, agriculture utilization and long term storage of sewage sludge [3].

Consequently, there is an urgent need to explore low cost, energy efficient and sustainable solutions for the treatment, management and future utilization of sewage sludge. There are several thermal technologies for utilizing renewable fuels to obtain useful forms of energy through the correct pre-treatment (torrefaction, slow pyrolysis, and hydrothermal carbonization processes) [4-9]. The valorisation of sewage sludge through pyrolysis can potentially address the challenges related to sewage sludge treatment and management. Pyrolysis is considered as the most practical, efficient and sustainable technology for the synthesis of liquid, solid and gaseous fuels from various feedstock [6]. However, pyrolysis

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requires comprehensive knowledge of the physicochemical, thermal and kinetic decomposition characteristics of the feedstock [10]. This is an essential requirement for assessing the feasibility of implementing thermal conversion as well as process design, engineering economics and materials considerations. In addition, feedstock properties can be used to optimize operating conditions and improve selectivity of thermal conversion products during conversion [11].

Thermal techniques, in particular thermogravimetric analysis (TG, DTG) provide information about the thermal behaviour, reactivity and kinetics of sewage sludge in a simple and straightforward way [12]. The most important applications of thermal analysis is for evaluating kinetic parameters such as activation energy  $E_a$  and pre-exponential factor  $A$  through non-isothermal solid-state kinetics [13-15]. Numerous researchers have successfully investigated the non-isothermal thermogravimetry (TG, DTG) [16, 17] and kinetic analysis of various feedstock under pyrolysis conditions. Furthermore, the characterization of the physicochemical properties, and thermal behaviour of mechanical-biologically treated SS through gasification, pyrolysis and combustion has been investigated. However, this is lack of comprehensive understanding of the properties of mechanical-biological-chemically treated SS samples. The scientific data of SS fuel properties will potentially improve the efficiency of conversion technologies [18] products optimization [19] and reduce pollutant emissions [20].

Consequently, this study aims to investigate: (a) the physicochemical properties of two types of sewage sludge (b) the thermal behaviour of the selected SS using non-isothermal thermogravimetric (TG, DTG) analysis (c) the kinetic parameters; activation energy ( $E_a$ ) and pre-exponential factor ( $A$ ) according to conversion degree ( $\alpha$ ) using the Kissinger method under pyrolysis conditions.

## Experimental

### Materials

The sewage sludge samples investigated in this study were acquired from wastewater treatment plants (WWTP) in Poland.

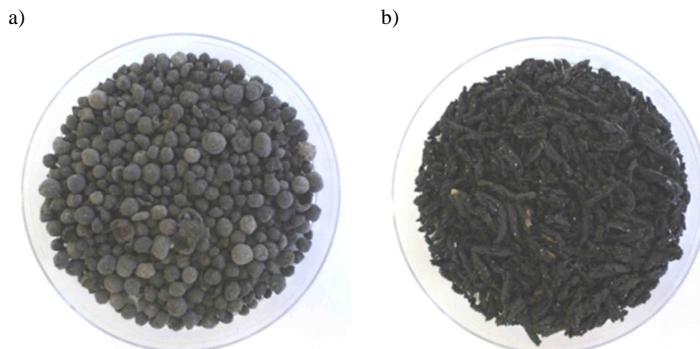


Fig. 1. Sewage sludge samples: a) Sewage sludge 1 - from mechanical and biological wastewater treatment plants (WWTP); b) Sewage sludge 2 - mechanical, biological and chemical WWTP with simultaneous phosphorus precipitation

Sewage sludge 1 (SS1) was obtained from mechanical-biological treatment while Sewage sludge 2 (SS2) was collected after mechanical-biological-chemical treatment with simultaneous phosphorus precipitation. Subsequently, the sludge was subjected to fermentation, dewatering, and drying. SS1 was dried in a cylindrical drier on shelves heated up to 260°C while SS2 was dried using hot air at 150°C in a belt drier. Therefore, SS1 appear as granules whereas SS2 as irregular thin “pasta” shaped crumbs (Fig. 1).

### Methods

The chemical qualitative analysis of the dried sewage sludge samples SS1 and SS2 was examined using an automatic IR (Infra-Red) analyser to determine the concentrations of major elements: carbon, hydrogen, nitrogen, chlorine, fluorine, sulphur and oxygen. Next, physicochemical analysis was conducted to determine moisture, volatile fractions and ash content using the gravimetric standards [21-23], respectively. The higher heating value was determined by the calorimetric method while the lower heating value was calculated using the mass fractions of the major elements in the SS samples.

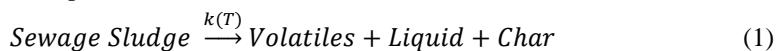
The thermogravimetric analyses were conducted using a Mettler Toledo TGA/SDTA 851 apparatus with accuracy  $10^{-6}$  g. The instrument was calibrated using indium, zinc and aluminium. For each TG run, 15 mg of sample was placed in an alumina crucible and heated from ambient temperature to 800°C at constant heating rates,  $\beta = 5, 10, 20$  and 40°C/min under argon atmosphere at the flow rate of 40 cm<sup>3</sup>/min. Each sample was measured under exactly the same conditions, including temperature range, atmosphere, and heating rate, to determine the correct conditions. The TG/DTG curve for each sample was obtained as the outputs for pyrolysis processes.

The derivative thermogravimetric (DTG) is based on the rate of mass loss as deduced from the mathematical transformation ( $da/dt = f(t)$ , where  $a$  - mass of sample,  $t$  - time). DTG profiles present vital information such as the mass loss taking place at a given temperature during thermal conversion. Consequently, the resulting weight loss [%] and corresponding temperature was analysed and numerically computed for kinetic analyses of the SS samples using the Kissinger kinetic model.

### Kissinger kinetic theory

The most important applications of thermal analysis is kinetic calculations. The kinetic parameters could be obtained by methods for analysing non-isothermal solid-state kinetics. Solid-state kinetic data are the major interest in thermal processes. In non-isothermal kinetics, the Friedman (F), Flynn-Wall-Ozawa (FWO) and Kissinger-Akahira-Sunose (KAS) methods are the most often used isoconversional methods [14, 24-26].

The kinetics of SS1 and SS2 decomposition under pyrolysis conditions was evaluated using the *Kissinger* model. The kinetic parameters, activation energy  $E_a$  and frequency factor  $A$  can be determine using the model. The decomposition of sewage sludge (SS) during pyrolysis can be represented as:



Consequently, the rate of sewage sludge decomposition under pyrolysis conditions can be expressed as:

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \quad (2)$$

Where the term  $f(\alpha)$  is the reaction model for SS pyrolysis (decomposition), and  $k(T)$  is the temperature dependent rate constant defined by the Arrhenius law in Eq. (3):

$$k(T) = A \exp\left(-\frac{E_a}{RT}\right) \quad (3)$$

The terms  $E_a$ ,  $A$ ,  $R$  and  $T$  denote activation energy [kJ/mol], frequency factor [ $\text{min}^{-1}$ ], universal gas constant [J/mol K] and temperature [K], respectively. Consequently, by substituting Eq. (3) into Eq. (2), an empirical model describing SS pyrolysis can be propounded Eq. (4):

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \quad (4)$$

Subsequently, Eq. (4) can be rewritten to account for Eqs. (2-4):

$$\frac{d\alpha}{dt} = A \exp\left(-\frac{E_a}{RT}\right) f(\alpha) \quad (5)$$

For SS pyrolysis at multi-heating rate, the term  $\beta = dT/dt$  must be introduced after separation of variables, therefore Eq. (5) can be rewritten as:

$$\frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} \exp\left(-\frac{E_a}{RT}\right) dT \quad (6)$$

By integrating Eq. (6) the function  $g(\alpha)$  describing the SS pyrolysis at a given heating rate can be deduced:

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} \int_0^T \exp\left(-\frac{E_a}{RT}\right) dT \quad (7)$$

The solution to the Eq. (7) for the pyrolysis of SS at temperature,  $T_m$  yields the expression for the *Kissinger* model in Eq. (8):

$$\ln\left(\frac{\beta}{T_m^2}\right) = \ln\left(\frac{AR}{E_a}\right) - \left(\frac{E_a}{RT_m}\right) \quad (8)$$

The term  $T_m$  is the peak decomposition temperature obtained from the DTG curve. Consequently, the kinetic parameters;  $E_a$  and  $A$ , for SS pyrolysis can be obtained from the slope and intercept of the plot of  $\ln(\beta/T_m^2)$  against  $1/T_m$  at different heating rates.

## Results and discussion

### *Physicochemical properties*

Table 1 presents the chemical qualitative characteristics of two sewage sludge (SS1, SS2) samples examined by ultimate, proximate and calorific analyses.

Analysing presented data it can be concluded that the sludge collected after mechanical-biological-chemical treatment (SS1) is characterized by the lower content of carbon, hydrogen, nitrogen, oxygen and chlorine in comparison to sludge obtained from mechanical-biological treatment (SS2). The main reason for this, is a chemical reaction of precipitation realized during the chemical stage of wastewater treatment process.

In addition, the results indicate the lower suitability of the sludge SS2 as a fuel in comparison to sludge SS1, This is based on the comparative empirical evidence from the volatile matter (VM) and ash content. The higher VM content of SS1 indicates lower

ignition temperature and reactivity during pyrolysis compared to SS2. Similarly, lower ash content of SS1 points to low potent for agglomeration, and slagging during thermal conversion, Furthermore, the results submit that chemical precipitation process of wastewater treatment significantly affects on the calorific value and overall physicochemical of the properties treated SS.

Table 1

Proximate and ultimate analysis of studied sewage sludge samples

	Element/Parameter	Sewage sludge 1 (SS1)	Sewage sludge 2 (SS2)
Proximate analysis [%] (as received)	Moisture	5.30	5.30
	Volatile matter	51.00	49.00
	Ash	36.50	44.20
Ultimate analysis [%] (dry basis)	C	31.79	27.72
	H	4.36	3.81
	N	4.88	3.59
	O (by difference)	20.57	18.84
	S	1.67	1.81
	F	0.013	0.003
	Cl	0.22	0.03
Calorific value	HHV* [MJ/kg], dry basis	14.05	11.71
	LHV** [MJ/kg], dry basis	12.96	10.75

\*HHV - Higher Heating Value; \*\*LHV - Lower Heating Value

### Thermogravimetric analysis

Figure 2 a,b shows the derivative thermogravimetric (DTG) profiles for sewage sludge samples (SS1 and SS2) at heating rates  $\beta = 5, 10, 20$  and  $40^\circ\text{C}/\text{min}$ . The thermal conversion of sewage sludge under argon atmosphere takes place with mass loss. The impact of heating rate is evident for both samples, but for SS1 the differences of mass loss rate are more significant with wider endothermic peaks and higher rates of thermal decomposition.

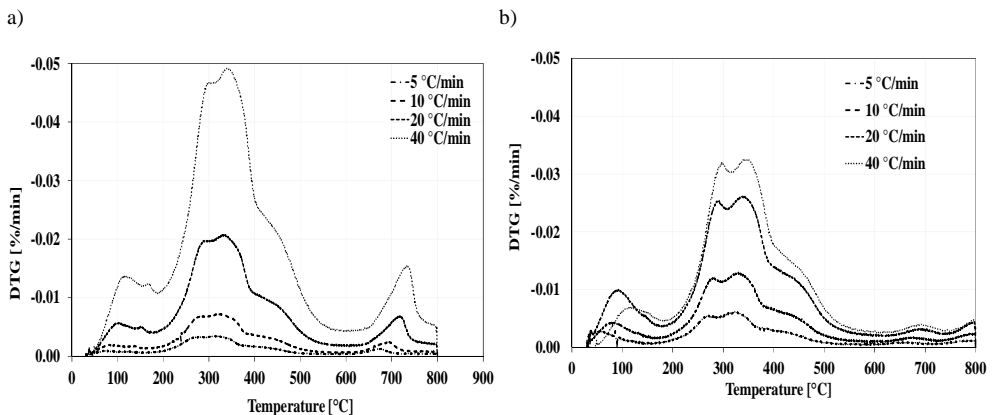


Fig. 2. DTG plots for SS1 from 5, 10, 20,  $40^\circ\text{C}/\text{min}$  under argon atmosphere (a) and DTG plots for SS2 from 5, 10, 20,  $40^\circ\text{C}/\text{min}$  under argon atmosphere (b)

The DTG curves indicate the pyrolysis of SS1 and SS2 occurred in three stages. The first stage ( $< 200^{\circ}\text{C}$ ) corresponds to drying and is typically attributed to the loss of moisture and devolatilization of low molecular weight compounds [27]. The moisture content of sewage sludge samples are similar which accounts for the similar mass loss, albeit at different rates. The main decomposition during the pyrolysis process is in the temperature range  $200\text{--}580^{\circ}\text{C}$ . This is mainly attributed to the decomposition of organic matter in sewage which comprises proteins, polysaccharides, cellulose and polymers that typically decompose below  $600^{\circ}\text{C}$ . The DTG curves also indicate the devolatilization peaks in Figure 2a,b. Two main peaks appear for SS1 and SS2, with the first at approximately  $290^{\circ}\text{C}$ , and the second is at approximately  $310^{\circ}\text{C}$  indicating the occurrence of two separate but simultaneous chemical reactions. During this stage, the pyrolysis of SS and breakdown of combustible volatiles (e.g.,  $\text{CH}_4$ ,  $\text{CO}$ ,  $\text{H}_2$ ) results in the release of non-condensable gases  $\text{H}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{CO}_2$  and  $\text{CH}_4$  [7]. The final decomposition takes place above  $580^{\circ}\text{C}$ , for sewage sludge SS2 is not significant and slight weight loss is observed. An increase in heating rate does not significantly influence the shape of DTG curves, but weight loss rate is increasing in higher temperatures.

### Kinetic analysis

The kinetic analysis of SS1 and SS2 was carried out using the Kissinger model from the plot of  $\ln(\beta/T_m^2)$  against  $1/T_m$  at different heating rates ( $\beta$ ). The term  $T_m$  is the peak decomposition temperature of the samples derived from the DTG curve.

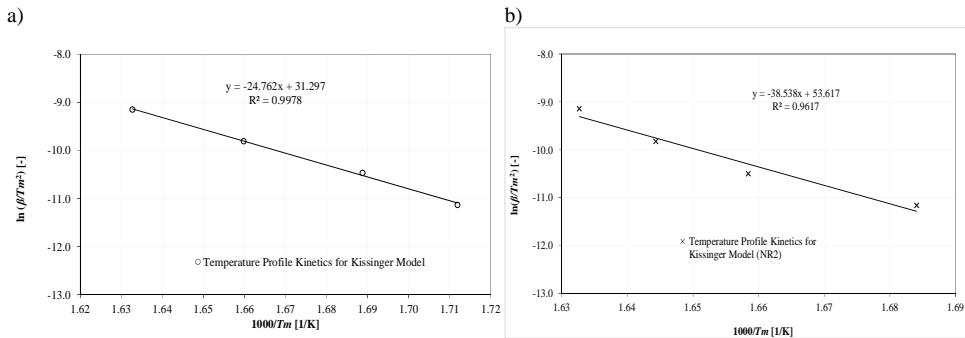


Fig. 3. Kissinger kinetic plots for: a) SS1, b) SS2

Consequently, the kinetic parameters;  $E_a$  and  $A$ , were deduced from the slope and intercept of the plots for SS1 and SS2 presented in Figures 3a,b. Table 2 presents the calculated kinetic parameters for the pyrolysis of the SS samples.

The results indicated the kinetic parameters of SS1 have lower values comparing to SS2 sample. The difference in the  $E_a$  and  $A$  values for the samples can be ascribed to the effect of chemical treatment on the SS2 sample. The chemical treatment of SS2 is clearly responsible for the loss of volatile organic matter and reactive components. Consequently, the SS1 higher proportions of reactive components aided rapid decomposition of the sample

compared to SS2. This is corroborated by the higher rate of devolatilization (higher mass loss) observed for the SS1 sample in Figure 2a. Hence, it can be inferred that chemical precipitation decreases the thermochemical fuel and kinetic properties of sewage sludge as feedstock for pyrolysis. This suggests that SS for prospective utilization in pyrolysis can only undergo mechanical-biological treatment.

Table 2

Kinetic parameters of sewage sludge samples SS1 and SS2

Sample	$E_a$ [kJ/mol]	A [ $\text{min}^{-1}$ ]	$R^2$
SS1	205.87	$9.68 \cdot 10^{14}$	0.9978
SS2	320.40	$7.44 \cdot 10^{24}$	0.9617

## Conclusions

The study was aimed investigating the physicochemical, thermal and kinetic properties of two types of sewage sludge SS treated via mechanical-biological and mechanical-biological-chemically methods. Thermal analysis of the sewage sludge SS was carried out under pyrolysis conditions to determine the kinetic parameters; activation energy ( $E_a$ ) and pre-exponential factor (A) using the *isoconversional* Kissinger method. The results showed the chemical precipitation treatment decreases the thermochemical fuel and kinetic properties of sewage sludge as feedstock for pyrolysis. Consequently, prospective pyrolysis of SS utilization requires mechanical-biological treated feedstock for efficient thermal conversion.

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## FIZYKOCHEMICZNA, TERMICZNA I KINETYCZNA ANALIZA OSADÓW ŚCIEKOWYCH

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**Abstrakt:** Osady ściekowe są stałym produktem procesu oczyszczania ścieków. Obecne metody zagospodarowania osadów obejmujące mechaniczne odwadnianie oraz termiczne wykorzystanie stają się drogie, nieefektywne i energochłonne. Co więcej, prawo Unii Europejskiej ogranicza składowanie oraz wykorzystanie rolnicze osadów ściekowych. W efekcie znalezienie innowacyjnych oraz zrównoważonych metod zagospodarowania i utylizacji osadów ściekowych jest niezwykle istotne. Proces pirolizy wydaje się odpowiedni, by sprostać tym wymaganiom. Celem pracy jest określenie fizykochemicznych, termicznych oraz kinetycznych właściwości wybranych próbek osadów ściekowych (SS1 i SS2). Zastosowano analizę termogravimetryczną w celu przeprowadzenia analizy porównawczej opisującej proces przemian termicznych oraz ich kinetyki w warunkach pirolizy dla stałych szybkości grzania wynoszących 5, 10, 20 i 40°C/min w zakresie temperatur od 30-800°C. Parametry kinetyczne: energia aktywacji  $E_a$  oraz czynnik przedeksponencjalny  $A$  zostały wyznaczone przy użyciu modelu Kissingera. Wartość  $E_a$  oraz  $A$  dla osadu ściekowego SS1 wynosi odpowiednio 205,87 kJ/mol i  $9,68 \cdot 10^{14}$ , podczas gdy dla osadu SS2 odpowiednio 320,40 kJ/mol i  $7,44 \cdot 10^{24}$ . Wyniki analiz zostały porównane z innymi materiałami poddawanymi pirolizie.

**Słowa kluczowe:** właściwości fizykochemiczne osadów ściekowych, analiza termiczna, kinetyka