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Kinetic Analysis of Pyrolysis of Sewage Sludge from Edible Oil Industry Wastewater Treatment Plant

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In this study, a thermogravimetric analysis of pyrolysis of sewage sludge (SS) obtained from physio-chemical wastewater treatment plant treating wastewater from the edible oil industry was performed. Thermogravimetric experiments were performed in a temperature range of 30–900 °C under inert atmosphere at three different heating rates: 10, 20 and 30 °C/min. Various parameters were analysed in the feedstock and in the produced biochar, including proximate and ultimate analysis. FTIR analysis was used to study the chemical changes in the materials before and after pyrolysis. Two different kinetic models were applied in the kinetic analysis, the Flynn–Wall–Ozawa model (FWO) and the Kissinger–Akahira–Sunose (KAS) model. In addition to the kinetic parameters, thermodynamic parameters were also calculated. Based on the experimental data and kinetic analysis, the potential of SS for use in the pyrolysis process was evaluated. The results of proximate and ultimate analysis of biochar showed an increase in ash and sulfur content and a decrease in volatile matter, carbon, nitrogen, hydrogen, oxygen content and calorific value. FTIR spectra showed significant changes in chemical bonds and functional groups in the pyrolyzed sample. The activation energy ranged from 49 to 352 kJ/mol for the KAS model and from 56 to 365 kJ/mol for the FWO model. The FWO and KAS kinetic models were found to be suitable for describing the pyrolysis of SS, as they exhibited high R^2 values. The correlation coefficients for the KAS model were > 0.88 and for FWO > 0.91. The relatively high calorific value of SS shows its promising potential for energy recovery by pyrolysis.

1. Introduction

In the edible oil industry, large amounts of wastewater are generated during the operation and washing of the equipment, which must be treated by physiochemical or biological methods to avoid environmental pollution, i.e. contamination of soil and water. The SS produced in such treatment plants contains a high content of lipids (fats, oils, and greases) and has a promising calorific value, so it could potentially be used for energy recovery in the form of biofuels (bio-oil, biochar and biogas). Thermal treatment processes, such as combustion (Urbancl et al., 2015) and pyrolysis are widely used for SS treatment; they also efficiently reduce its volume (Shao et al., 2021). Another advantage of thermal treatment of SS and by-products from edible oil production is that the recovered energy can be reused for their production, which saves costs and contributes to the circular economy. Several studies, including kinetic and thermogravimetric studies have been conducted on the combustion and pyrolysis of SS from municipal wastewater treatment plants (Jiang et al., 2015). Sewage sludge with high ash content was tested for biochar production (Fan et al., 2020). The effects of operating parameters on heavy metal speciation in SS char were investigated in another study (Jin et al., 2016). Co-pyrolysis of SS with other organic wastes (Naqvi et al., 2019) and polymer materials (Zaker et al., 2021) has also been studied extensively. The thermo-kinetic behaviour of SS with high-ash content during the pyrolysis process was studied by Naqvi et al. (2018), while the pyrolysis and combustion kinetics of oil sludge were investigated by Shao et al. (2021). The most commonly used kinetic models in these studies include FWO (Parthasarathy et al., 2021), KAS (Tibola et al., 2020), and the Friedman (Naqvi et al., 2018) model. Despite numerous studies performed with municipal SS, studies on SS from industrial wastewater treatment plants, which have more specific characteristics than municipal SS, are less common.

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The aim of this study was to characterise the sewage sludge from edible oil industry wastewater treatment plant and determine its added value based on thermal treatment by pyrolysis. The TGA experiments were performed in a temperature range of 30 – 900 °C at three different heating rates: 10, 20 and 30 °C/min. Various parameters were analysed in the feedstock and in the char. FTIR analysis was used to study the changes in the chemical composition of the material before and after pyrolysis. Two different kinetic models were used for the kinetic analysis, the FWO and the KAS models. In addition, the thermodynamic parameters were calculated. Based on the experimental data and the kinetic analysis, the potential of the tested SS for use in the pyrolysis process was evaluated. To the best of the authors' knowledge, no thermogravimetric study on such type of sludge has been carried out before, so this study provides valuable insight into its potential for energy recovery by pyrolysis.

2. Materials and methods

This section describes the material preparation and characterization methods. Besides, the procedure for TG analysis is presented and the kinetic models used in the kinetic study are described.

2.1 Characterization of samples and thermogravimetric analysis

The sewage sludge sample was obtained from physio-chemical wastewater treatment plant treating wastewater from the edible oil industry (production of edible oils and salad dressings). The sample was dried at 40 °C in a laboratory dryer to constant weight, ground, and stored in a desiccator until further use. The basic characteristics of the raw sample and biochar were determined, such as proximate and ultimate analysis. The analyses were performed in triplicate, and the average values are presented in the paper. The higher heating value (HHV) was determined by combustion the samples in a bomb calorimeter according to the standard method (SIST-TS CEN/TS 16023:2014, 2014). Fat content was determined according to the ISO standard 1443:1973 (ISO 1443:1973, 2016). Ash content was determined as the mass percentage of residues after combustion of samples at 815 °C (DIN 51719:1997-07, 1997). Volatile matter (VM) content was determined by measuring the weight loss after combustion of the samples at 900 °C (1 h). The Elemental Analyser PerkinElmer Series II 2400 was used to perform ultimate analysis, including the determination of C, H, N and S content (SIST EN ISO 21663:2021, 2021). The FTIR (Fourier-transform infrared spectroscopy) spectra were recorded using a Shimadzu IRAffinity FTIR spectrophotometer.
The TGA study was performed using a TGA/SDTA851e thermogravimetric analyzer (Mettler Toledo) in the temperature range of 30 to 900 °C in an inert atmosphere (N_2 flow rate of 100 mL/min). Samples weighing 15 ± 3 mg were exposed to slow pyrolysis (three replicates) at heating rates of $\beta =$ 10, 20 and 30 °C/min. TG curves (mass weights vs. temperatures) and derivative (DTG) curves were generated using the MS Excel software tool. For the characterization analyses and FTIR analysis, the biochar samples were obtained by pyrolysis of feedstocks at 800 °C in a tube furnace under an inert atmosphere at a heating rate of 20 °C/min. After achieving the desired temperature, the biochar were kept in a furnace for another 2 h under the same conditions. After cooling to room temperature, the biochar were stored in a desiccator until characterization.

2.2 Kinetic study

Based on the results of the TGA measurements, the kinetic study was performed using the Flynn-Wall-Ozawa (FWO) and Kissinger-Akahira-Sunose (KAS) kinetic models (Yao et al., 2020), presented in Table 1.

Table 1: The equations for the KAS and FWO kinetic models used in the kinetic study

Name of equation/parameter	Equation*	Eq. number
Flynn-Wall-Ozawa (FWO) equation	$ln[\beta] = ln\left[\frac{A \cdot E_\alpha}{R \cdot g(\alpha)}\right] - 5.331 - 1.052\frac{E_\alpha}{R \cdot T}$	(1)
Kissinger-Akahira-Sunose (KAS) equation	$ln\left[\frac{\beta}{T^2}\right] = ln\left[\frac{R \cdot A}{E_\alpha \cdot g(\alpha)}\right] - \frac{E_\alpha}{R \cdot T}$	(2)
Pre-exponential factor, A (1/s)	$A = [\beta \cdot E_\alpha \cdot exp\left(\frac{E_\alpha}{R \cdot T_p}\right)]/(R \cdot T_p^2)$	(3)
Enthalpy, ΔH (kJ/mol)	$\Delta H = E_\alpha - (R \cdot T)$	(4)
Gibbs free energy, ΔG(kJ/mol)	$\Delta G = E_\alpha + R \cdot T_p \cdot ln\left(\frac{K_B \cdot T_p}{h \cdot A}\right)$	(5)
Entropy, ΔS (kJ/(mol·K))	$\Delta S = \frac{\Delta H - \Delta G}{T_p}$	(6)

* K_B - Boltzmann constant ($1.381 \cdot 10^{-23}$ J/K), h - the Planck constant ($6.626 \cdot 10^{-34}$ J·s), T - absolute temperature (K), T_p - peak temperature of the DTG curve (K), and R - universal gas constant (8.314 J/(mol·K)).

KAS and FWO models were used since they are less susceptible to errors than differential iso-conversional methods, such as the Friedman method (Naqvi et al., 2018). The left sides of Eq(1) and Eq(2) were plotted on the y-axis against (-1/(R·T)) on the x-axis. The activation energies (E_α) for the selected conversion points (α), were then calculated from the slope of the linear fit plots of the KAS and FWO models. Eq(3) was used to determine the pre-exponential factor A (Zaker et al., 2021). Later, based on the calculated kinetic parameters, a thermodynamic analysis was performed to determine parameters such as enthalpy (ΔH), Gibbs free energy (ΔG), and entropy (ΔS) using Eqs(4-6) (Naqvi et al., 2019).

3. Results and discussion

3.1 Characteristics of material and thermogravimetric behaviour

The TG and DTG curves of SS, recorded under inert atmosphere at heating rates of 10, 20, and 30 °C/min, are presented in Figure 1a. Four main degradation steps can be observed from the curves. In the first step, which ranged from 30 to 275 °C, the average weight loss was ~15 wt.%. The peak values occurring in this range represent the peak temperatures at which the hydrolysis occurred. The second step was observed in the range between 275 and 390 °C, where the average weight loss was around 12 wt.%. The weight loss in this range was related to volatiles and oil degradation (Eliche-Quesada and Corpas-Iglesias, 2014). The third step occurred between 390 °C and 640 °C, where the highest weight loss was observed for all three heating rates (> 20 wt.%). The peaks appeared in this range could be due to the degradation of high-thermally stable components and waxes (Vamvuka et. al., 2014) The highest peak of the DTG curves was observed at around 465 °C. The fourth step occurred between 640 °C and 900 °C, with an average weight loss of ~5 %. The peaks appeared in the range between 670 °C and 700 °C are associated with the deep decomposition of sludge, such as refractory organic matter, inorganic matter and char residues (Li et al., 2017). Most of the SS sample was degraded in the temperature range of up to 550 °C. The average total weight loss for all three heating rates was 56 %. The impact of increasing the heating rate on the mass loss of the SS sample was negligible, as the difference in total mass loss was approximately 1 %. The peak temperature increased slightly with heating rate.

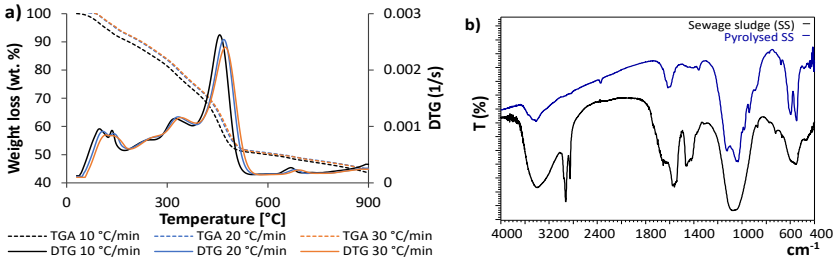

Figure 1: a) TG and DTG curves of SS recorded in the temperature range of 30 – 900 °C (under inert atmosphere) at three different heating rates: 10, 20, and 30 °C/min, b) FTIR spectra of raw and pyrolyzed SS.

The results of the characterization study of raw (SS) and pyrolyzed sludge (PSS) are presented in Table 2. Proximate analysis showed that the volatile matter and fixed carbon content (FC) decreased in the PSS. The fixed carbon content decreased from 3.01 to 0.62 %, while the ash content increased from 42.29 to 96.09 wt.%. SS contained a high content of fats (21.88 wt.%), while the value in the PSS sample was much lower (6.03 wt.%). The calorific value (HHV) of the raw sample was relatively high (14.66 MJ/kg) and comparable to calorific values reported in the literature for the municipal SS (15.52 MJ/kg) (Simonic et al., 2020) and other materials, for example miscanthus (16.41 MJ/kg) (Ivanovski et al., 2022) and hops (16.50 MJ/kg) (Ivanovski et al., 2021). After pyrolysis, the HHV value was below 6 MJ/kg, indicating a great potential of tested sample for energy recovery by pyrolysis. The ultimate analysis showed a decrease in carbon, nitrogen, hydrogen and oxygen content in the PSS. Carbon content decreased from 31.75 to 2.05 wt.%, nitrogen from 1.25 to 0.06 wt.%, hydrogen from 6.04 to 0.04 wt.% and oxygen from 17.27 to 0.18 wt.%. The content of sulphur in PSS increased from 1.40 to 1.58 wt.%. Both the H/C and O/C ratios decreased in PSS. The H/C atomic ratio dropped from 2.28 to 0.23 and atomic ratio O/C from 0.41 to 0.07. The H/C ratio is a carbonization degree parameter that can be used to characterize the degree of aromaticity. A low molar H/C ratio indicates a higher degree of aromatic condensation in the biochar (Jin et al., 2016).

Comparison of the FTIR spectra of raw and pyrolyzed SS (Figure 1b) shows significant changes in chemical functional groups caused by pyrolysis. After pyrolysis the peaks at 2850, 2890, 1560 and 1450 cm^{-1} representing organic components such as hydroxyl (-OH), amine (-NH) and aliphatic groups (-CH_x) almost disappeared, indicating that most of the organic compounds were transformed into bio-oil. This was also confirmed by

elemental analysis. On the other hand, the peaks between 500 - 600 cm^{-1} reflect the vibrations of different oxides and silicates, such as Fe-O, Mg-O, Si-O-Si and Si-O-Al vibrations, which become stronger and sharper. The peak at 1050 cm^{-1} besides Si-O-Si vibrations represents the vibrations of the P-O group (Jin et al., 2016). The absorption peak at 984 cm^{-1} could refer to Al-O bonds, while peaks between 600 and 800 cm^{-1} represent aromatic or hetero-aromatic compounds. The biochar obtained according to the results of FTIR analysis contains functional groups (different oxides, carboxyl and alkyl group) that could interact in the adsorption process, so biochar could potentially be used as adsorbent. Further chemical modification of the biochar could provide additional functional groups and increase the surface area. Similar observations and characteristics of the FTIR spectra of SS and PSS were also found in the study performed by Fan et al. (2020).

Table 2: Proximate and ultimate characteristics of raw (SS) and pyrolyzed sewage sludge (PSS)

Parameter	VM (wt.%)	Ash (wt.%)	FC[a] (%)	HHV (MJ/kg)	C (wt.%)	N (wt.%)	H (wt.%)	S (wt.%)	O[b] (wt.%)	H/C	O/C	Fats (wt. %)
SS	54.71	42.29	3.01	14.66	31.75	1.25	6.04	1.40	17.27	2.28	0.41	21.88
PSS	3.29	96.09	0.62	<6	2.05	0.06	0.04	1.58	0.18	0.23	0.07	6.03

[a]FC (wt.%) = 100 - VM - Ash
[b]O=100 - C - H - N - S - Ash (all in wt. %)

3.2 Kinetic and thermodynamic parameters

Kinetic analysis was performed using the KAS and FWO kinetic models. The linear fit plots for the conversion points between 0.1 and 0.8 constructed by using Eq(1) and Eq(2), are shown in Figure 2. The data above the conversion level of 0.8 were excluded due to the low correlation coefficient. The correlation coefficients for the KAS model were > 0.88 and for FWO > 0.91. Both models showed good agreement with the experimental data.

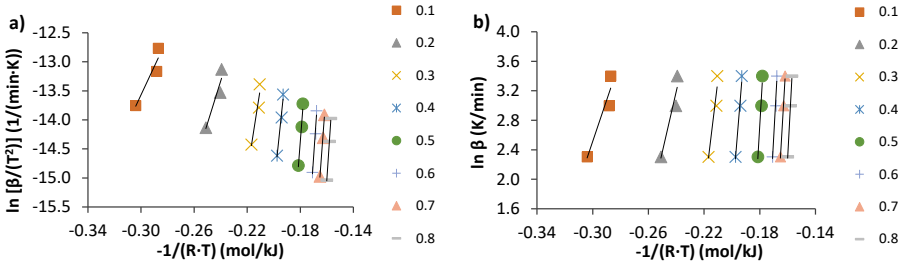

Figure 2: Linear fit plots constructed to determine the activation energy by: a.) KAS model, and b.) FWO model

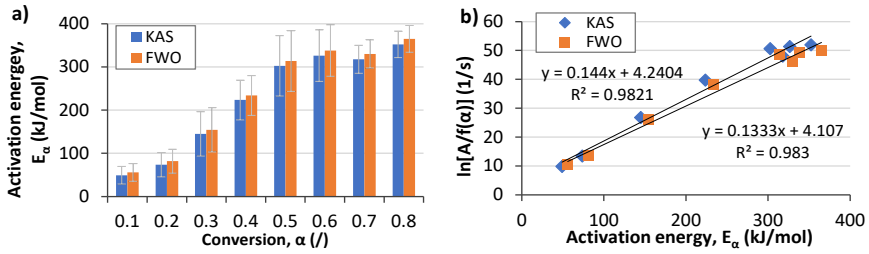

Figure 3: a) Activation energies (E_α) vs. conversion degree calculated by KAS and FWO kinetic models, b.) Linear fit plots for the compensation effects between the pre-exponential factor and the activation energy

The activation energies calculated with the KAS and FWO kinetic models, are shown in Figure 3a, while Figure 3b shows the linear fitting plots for the compensation effects between the pre-exponential factor and the activation energy. The pre-exponential factor describes the solid phase reaction dynamics and is directly related to the material structure (Naqvi et al., 2018). In general, the pre-exponential factors showed the same variability trend as the activation energy (Table 3). The activation energy indicates the barrier that must be overcome for a chemical reaction to occur, and it determines the reactivity of a material (Ivanovski et al., 2021). Activation energy values varied between 49 and 352 kJ/mol for the KAS model and from 56 to 365 kJ/mol for the FWO model. These values are comparable to those for municipal SS (63 - 323 kJ/mol) in the literature (Zaker et al., 2021). For SS with high ash content, values between 46 and 232 kJ/mol were reported (Naqvi et al., 2018),

while oil sludge exhibited lower values, 36 - 185 kJ/mol (Shao et al., 2021). Direct comparison of the results is not possible, due to significant differences in the type and chemical composition of the sludge. The linear relationship between Arrhenius parameters was observed for both kinetic models (Figure 3b). The R^2 value of the linear fit plot for the compensation effects was 0.9821 for the KAS model and 0.9830 for the FWO model. The results show that chosen kinetic models are suitable describing the experimental data.

The thermodynamic parameters, enthalpy, entropy, and Gibbs's free energy varied with the conversion degree, as shown in Table 3. Enthalpy followed a similar trend as activation energy. Enthalpy values for SS ranged from 49 to 352 kJ/mol in the KAS model and from 56 to 365 kJ/mol in the FWO model. The KAS model gave lower values in all cases. Thus, an endothermic process takes place, so it is necessary to provide an external energy source to convert the biomass to its transition state (Naqvi et al., 2019). Gibbs's free energy shows the bioenergetic potential of biomass by reflecting the total energy increase of the active complex formation system. The Gibbs's free energy ranged from 210 to 222 kJ/mol, with small variation of values with the degree of conversion. The values of both models were close to each other. Entropy values ranged from -241 to 184 kJ/mol for the KAS model and from -231 to 201 kJ/mol for the FWO model. Negative entropy values indicate a more organized structure of the product compared to the raw material, so the reactivity is low with a long reaction time. Positive entropy values indicate that the material is far from its thermodynamic equilibrium and the reactivity is high with a short reaction time (Naqvi et al., 2019).

Table 3: Kinetic and thermodynamic parameters calculated by KAS and FWO model

	KAS model					FWO model				
	A (1/s)	R^2	ΔH (kJ/mol)	ΔG (kJ/mol)	ΔS (J/mol·K)	A (1/s)	R^2	ΔH (kJ/mol)	ΔG (kJ/mol)	ΔS (J/mol·K)
0.1	$1.03 \cdot 10^{1}$	0.88	42.94	222.10	-241.46	$3.49 \cdot 10^{1}$	0.91	49.71	221.31	-231.27
0.2	$8.20 \cdot 10^{2}$	0.90	67.47	219.60	-205.03	$3.41 \cdot 10^{3}$	0.92	75.62	218.96	-193.17
0.3	$1.71 \cdot 10^{8}$	0.91	138.84	215.42	-103.21	$8.28 \cdot 10^{8}$	0.92	148.19	215.04	-90.08
0.4	$9.08 \cdot 10^{13}$	0.97	217.50	212.75	6.40	$4.99 \cdot 10^{14}$	0.97	227.73	212.47	20.57
0.5	$4.38 \cdot 10^{19}$	0.96	296.37	210.89	115.20	$2.75 \cdot 10^{20}$	0.96	307.48	210.66	130.48
0.6	$2.21 \cdot 10^{21}$	0.97	320.08	210.42	147.79	$1.55 \cdot 10^{22}$	0.98	331.89	210.20	164.00
0.7	$5.54 \cdot 10^{20}$	0.99	311.71	210.58	136.30	$4.17 \cdot 10^{21}$	0.99	323.94	210.35	153.09
0.8	$1.66 \cdot 10^{23}$	0.99	346.26	209.94	183.71	$1.33 \cdot 10^{24}$	0.99	358.87	209.73	201.00

4. Conclusions

The results of thermogravimetric and kinetic study of pyrolysis of SS from edible oil industry wastewater treatment plant are presented in this paper. The TGA analysis revealed four main degradation steps of the tested material. The highest weight loss (> 20 wt.%) was observed at about 465 °C, where the degradation of thermally stable components occurred. KAS and the FWO model fitted the experimental data very well, as the correlation coefficients were > 0.88. The activation energy ranged from 49 to 365 kJ/mol, which is comparable to values reported in the literature for similar types of SS. The thermodynamic parameters, enthalpy, entropy, and Gibbs's free energy varied strongly with the conversion degree. The results of the characterization study, the chemical composition of SS, and its relatively high calorific value (14.66 MJ/kg) indicate its great potential for use in energy recovery processes such as pyrolysis. FTIR analysis showed that the pyrolyzed SS contains functional groups that could cooperate in the adsorption process and could be potentially used as adsorbent. In the future, additional analyses should be conducted regarding the adsorption characteristics of the biochar, and germination tests should be performed with plants like cress or cabbage to investigate the potential of SS and its char for agricultural use.

Nomenclature

FTIR – Fourier-transform infrared spectroscopy
FWO – Flynn–Wall–Ozawa kinetic model
HHV – Higher heating value
KAS – Kissinger–Akahira–Sunose kinetic model
TGA – Thermogravimetric analysis

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