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Pyrolysis Behaviour and Kinetic Analysis of Food Waste Sludge Cake

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Concerns regarding energy security are raised due to the conventional fossil fuel depletion, which drives the need of diversifying fuel sources for power generation. Sewage sludge, which is a waste product from the wastewater treatment plant, contains energy that could be retrieved and reused. Typically, these sludge are treated as a form of schedule waste and disposed of in a landfill. In this work, the valorisation potential of sludge cake to produce higher-value products was studied through thermogravimetric analysis.The thermal degradation behavior of the sludge cake under inert atmosphere was observed to possess two distinct zones: 1) moisture removal (62.86-131.76 °C) and 2) devolatilization (155.96-517.2 °C). The highest mass loss at 66.78 % was recorded during devolatilization. Kinetic analysis through model-free methods (Flynn-Wall-Ozawa (FWO) and Kissinger) revealed that an average activation energy in the range of 286.59 to 287.98 kJ/mol is required during pyrolysis. Characterisation of the sludge cake also revealed the potential of yielding a significant amount of bio-oil and gaseous products due to its high volatile content (72.3 %). The volatiles evolved were then sent to an FTIR instrument for further analysis. A variety of bio-oil compounds (phenols, alkanes, aromatics, acids, aldehydes, ketones, and carbonyl compounds) and gaseous products (CO, CH_4, and CO_2) were detected. In addition to these, the low ash content (6.68 %) measured portrayed the possibility of transforming this sludge cake feedstock into biochar with solid fuel properties. It has been demonstrated through this study that the sludge cake from food processing industries is a promising feedstock pyrolysis to yield bio-products of higher values.

1. Introduction

With the growing demand for cleaner and sustainable fuel for energy production, biomass is a potential alternative to reduce the reliance on depleting fossil fuels. As a matter of fact, biomass contains energy that could be extracted in various forms (e.g., biochar, bio-oil or bio-syngas) with the potential to be utilised as an energy source. As an example, sewage sludge is a type of biomass-waste from the industrial wastewater treatment plant, which requires specific treatment before disposal. The conventional management of sludge includes landfilling and incineration (Peng et al., 2015). Landfilling requires large land area. However, the harmful pathogen, toxic chemicals and heavy metals within this waste might pollute nearby water source and land. On the other hand, incineration has been demonstrated to be able to eliminate the pathogen and significantly reduce sludge volume while generating heat and power. However, this approach has the potential to release toxic fumes. In addition to these, the unsystematic management and disposal of sewage sludge have also often caused irreversible environmental issues that pose a significant risk to human health. In view of this, an alternative processing route for sewage sludge is required.
One feasible method to transform the sewage sludge waste into biofuels is through thermochemical conversion methods. Pyrolysis is a promising method in processing biomass under elevated temperature in a non-oxidative

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environment to produce improved quality bio-products (Lestinsky et al., 2016). Pyrolysis of solid feedstock involves complex chemical reactions to break and to form new chemical bonds. Thermogravimetric analysis has been widely used to describe the solid-state reaction and analyse the pyrolysis kinetics (Mong et al., 2020). Model-free methods are then adopted to determine the activation energy and pre-exponential factor (Lin et al., 2016). The mass loss and kinetic mechanism on the thermal decomposition of sludge have been reported to vary with different sludge sources due to their different composition. For example, textile dyeing sludge experienced a 49.9 % of mass loss in the temperature between 197.9 to 856.8 °C (Peng et al., 2015) while municipal solid waste records a mass loss of 79.13 % between 264.1-883.12 °C.
Although many studies have been conducted on sludge pyrolysis, most of them tend to focus on sludge from municipal waste, textile dyeing and paper mill with limited literature being reported on industrial food sludge. Sewage sludge from food processing industries has been known to have a lower amount of heavy metals and toxic chemicals. Such a nature of this sludge increases its potential for soil amendment purposes as it consists of mostly bio-degradable compounds. However, it is also realised that a synthetic polymer tends to be added during wastewater treatment, which could pose a speculative effect on the environment. The main focus of this study is to investigate the possible alternative transformation of a food-based sludge into biofuels through pyrolysis using a thermogravimeter. The mass loss behaviour and kinetic mechanism of sludge cake pyrolysis were then analysed, and the potential of this sludge to be upgraded into higher-value end products were evaluated.

2. Material and methods

In the present study, fresh sludge cake was obtained from the wastewater treatment plant of QL Figo Sdn Bhd. The sample was dried in a conventional oven at 110 °C for 24 h before grinding into the size of 0.1-0.5 mm for subsequent analysis. The physical and chemical properties of sludge were analysed through elemental and proximate content analysis. The former method was conducted using an elemental analyser (Elementar Vario Micro Cube) an the latter was conducted using a thermogravimeter (TA Instrument Q500) to identify moisture, volatile matter, ash content and fixed carbon. Composition content of sludge was identified and quantified through Kjedahl method – AOAC 923.03 (protein), BS ISO 8262-3:2005 (fat), method analysis for nutrition labelling (carbohydrate) and AOAC 962.09 (crude fiber). Finally, the sludge calorific value is measured through bomb calorimeter (IKA C2000 basic).

2.1 Thermogravimetric analysis couple Fourier-transform infrared spectroscopy (TGA-FTiR)

Thermal degradation of sludge cake was investigated using a thermogravimeter (TA Instrument Q500), which provided real time data on the sample mass loss with temperature. A sample size of 10 mg was heated from 27 to 950 °C at a heating rate of 20 °C/min under an inert environment created by a constant flow of nitrogen at 0.02 l/min. The vapour evolved during pyrolysis was directed to a Fourier-transformed infrared spectroscopy (Thermo Fisher Scientific, Nicolet iS10) through a transfer line maintained at 210 °C. FTiR was set at 64 number of scans at a resolution of 8 cm^{-1} for a spectrum ranging from 800 to 4,000 cm^{-1}.

2.2 Kinetics analysis

The kinetic analysis of sludge cake was conducted through model-free method, where TGA was conducted with at least three different heating rate (Lin et al., 2016). The common expression used to correlate the conversion rate of a feedstock with the Arrhenius expansion rate constant can be written as Eq(1):

$$\frac{d\alpha}{dt} = Ae^{-\frac{E}{RT}}f(\alpha) \quad (1)$$

Where the kinetics triplets are: 1) pre-exponential factor (A), 2) activation energy (E) and 3) reaction model, f(α). The activation energy is defined as the minimum amount of energy needed to activate the molecules of a reactant to a certain condition where they can undergo chemical transformation. The energy needed is used for breaking and forming chemical bonds to create an active or transition-state complex. The pre-exponential factor is a measure of the number of collisions required to achieve the proper orientation for compounds to react. The reaction model is a mathematical representation of the reaction progressing mechanism, describing the quantitative relationship between the conversion rate and extend of conversion. In the model, the conversion rate, α can be describe as Eq(2),

$$\alpha = \frac{m_0 - m_i}{m_0 - m_f} \quad (2)$$

where m_0, m_i, and m_f represent the initial, instantaneous and final mass of feedstock.

The activation energy is then obtained through the Flynn-Wall-Ozawa (FWO) and Kissinger methods. The FWO method is an isoconversional integral method that does not require any form of pre-assumption on the reaction model (Lin et al., 2016). It measures the temperature corresponding to a fixed set of values of α obtained from TGA experiments at various heating rates, β. The FWO method is conceivably adaptable for a system with high reaction rate, especially when the activation energy varies with time. The relationship described by the FWO method is given as Eq(3):

$$\ln\beta = \ln\frac{AE_\alpha}{RG(\alpha)} - \frac{E_\alpha}{RT} \quad (3)$$

where G(α) is the integral form of kinetic model. The expression of FWO implies that for each value of α, a plot of ln β against 1/T from the mass loss curve at several heating rates would generate a straight line in which it can then be used to determine the activation energy. For the FWO method, Eq(4) was used to determine the pre-exponential factor (Kim et al., 2010).

$$A = \beta E_\alpha exp\left(\frac{E_\alpha}{RT_p}\right)/\left(RT_p^2\right) \quad (4)$$

On the other hand, Kissinger method is given in a differential form derived as a first-order reaction from Eq(1). It provides a simple and direct (model-free) way in estimating the overall activation energy in a single value for the entire process. Although this estimation does not directly represent the actual situation, it remains comparable to other isoconversional method. The expression given by the Kissinger method is:

$$ln\left(\frac{\beta}{T_p^2}\right) = \ln\frac{AR}{E_\alpha} - \frac{E_\alpha}{RT_p} \quad (5)$$

where T_p is the temperature at maximum DTG peak. The activation energy can then be measured from the gradient of the straight-line plot of $\ln(\beta/T_p^2)$ against $1/T_p$. The pre-exponential factor for the Kissinger method can be calculated from the y-intercept of Eq(3).

3. Result and discussion

3.1 Properties of sludge cake

Several analyses have been conducted on the dried sludge cake to identify its physical and chemical characteristics. The investigated sludge cake was found to contain a relatively high oxygen content of 40.52 % and is comparable to sewage sludge from different sources, such as urban wastewater treatment plant (32.3 %) (Dominguez et al., 2008) and paper mill sludge (43.4 %) (Lee et al., 2017). As the sludge cake is a product obtained after aerobic digestion, it is expected to also contain a large proportion of oxygen content. Carbon, hydrogen and nitrogen are recorded at 44.2 %, 6.6 % and 8.0 %. The sulphur content was found to be at trace amount of 0.69 %.

The sludge sample was also determined to contain a major portion of protein (46.0 %) followed by carbohydrate (28.0 %) while fat (6.5 %) and crude fibre (7.6 %) were at minor proportions. The high protein content is most likely due to the nature of processing plant, where food products are being processed. In addition to this, the presence of dead bacteria in the sludge from the aerobic digestion process could have also contributed to the protein proportion. The fat content was also found to be low, which is likely due to the wastewater being already passed through an oil and grease removal trap before biological digestion process.

Volatile content was reported to be the major composition, making up of 72.3 % of the sludge cake. This property indicates that such a sample could potentially yield significant bio-oil or gaseous product through thermal decomposition. Feedstock of high volatile content has been used to derived bio-oil (Park et al., 2010) or gaseous products (Lestinsky et al., 2016) through thermal decomposition processes, such as pyrolysis and gasification. The moisture and fixed carbon were detected at 8.0 % and 13.0 %. In comparison with common sewage sludge feedstock from waste treatment plant (ash-29.6 %)(Park et al., 2010) and textile-dyeing (ash-60.75 %) (Zhang et al., 2017), the ash content (6.7 %) of the tested sludge cake is considered to be relatively low, indicating the potential of this feedstock to be utilized for solid fuel production. This is because low ash content is one of the main requirements for solid fuel.

3.2 Mass loss analysis (TGA) and volatile analysis (FTiR)

The mass loss behavior of sludge cake during pyrolysis is shown in Figure 1a and the volatile compounds evolved is given in Figure 1b. The first mass loss falls in the temperature range of 62.86 °C to 131.76 °C owing to the removal of moisture at increased temperature. The second mass loss is reported to be in the range of 155.96 °C to 517.2 °C and accounts for a major portion of the feedstock. A total of 66.78 % in mass has been found to have decomposed in this region. Considering only the portion of volatile within the sludge cake, approximately 92.37 % of volatile was expected to have evolved. This can be attributed to the degradation of carbohydrates, protein and lipids. Protein typically decomposes within temperature region of 231-309 °C, carbohydrate in 185-467 °C and lipids in 200-635 °C (Chen et al. (2018). The third mass loss region from 517.2 °C to 950 °C records a minor loss of 4.62 %. This could be due to the ash decomposition and the secondary cracking of carbonaceous residue at high temperatures (Peng et al., 2015), leading to a final residue of 26.36 % in mass.

The volatiles evolved during TGA was then transferred to an FTiR instrument for analysis. It should be noted that a slight delay in detecting the volatile compounds was found when using TG/DTG curve when compared with the FTiR curve. This could be as a result of the volatile evolved being analysed ex-situ, requiring additional time for the volatiles to be transferred to the FTiR instrument from the TG reactor. The two points in the DTG graphs, labelled as ‘X’ and ‘Y’, were analysed as the DTG recorded the intensity of mass loss rate. At the highest DTG peak with mass loss rate of 1.976 %/min (point ‘X’), CO_2 was detected at 586-726 cm^{-1} and 2,250-2,400 cm^{-1}. Various bio-oil compounds, for example, phenol (1,200-1,300 cm^{-1}), alkanes (1,365-1,460 cm^{-1}), aromatics (1,450-1,690 cm^{-1}), acids, aldehydes, ketones (1,650-1,900 cm^{-1}) and carbonyl compounds (1,772 cm^{-1}) (Ma et al., 2015) were also detected. In addition to these, water (3,400-4,000 cm^{-1}) was also found to be present.

At point ‘Y’, the mass loss rate was at a minimum, indicating decomposition was almost completed. However, it is to also note that all the volatiles evolved were still being transported to the FTiR at which several other compounds were being detected with an increase in intensity for some of the previously detected compounds at point ‘X’. Larger molecular compounds, such as alcohol (1,000-1,200 cm^{-1}), ethers (1,060-1,275 cm^{-1}) and lipids (1,050-1,300 cm^{-1}) were found to be present along with smaller gaseous compounds, namely CO (2,000-2,250 cm^{-1}) and CH_4 (2,700-3,000 cm^{-1}). The volatiles detected could also indicate the possible bio-oil collection with various compounds along with valuable syngas as derived products.

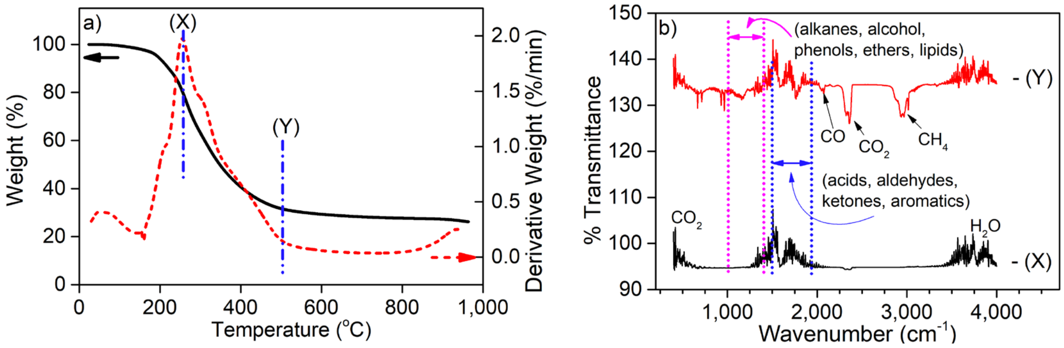

Figure 1: Thermal degradation of sludge cake at 20 °Cmin^{-1} in (a) mass loss and derivative mass loss curve along with (b) volatile evolved as detected by FTiR

3.3 Activation energy and pre-exponential factor using model-free method

The activation energy evaluation using model-free method requires TG and DTG data at a minimum of three different heating rates. The mass loss data of the investigated sludge cake at different heating rates is given in Table 1.

Table 1: Data extracted from DTG curve of sludge cake decomposition at heating rate of 5, 10 and 20 °Cmin^{-1}

β (°Cmin-1)	Ti *(°C)	Tm (°C)	DTG (%/min)
5	148.08	243.44	1.976
10	155.16	254.89	4.132
20	163.33	263.07	9.296

* T_i represent the intial temperature where decomposition occur and T_m represent the temperature where maximum mass loss is recorded.

The rate of mass loss is shown to be proportional with the imposed heating rate while the temperature at the initial degradation and the maximum degradation were shifted to higher values with an increase in heating rate. This is because of the heat transfer limitation or known as thermal lag at high heating rate. In other words, a higher heating rate would cause a higher thermal gradient between the outer surface (detected temperature) and inner core (actual temperature), which introduces a delay in the decomposition process. Feedstock is then forced to react at a higher rate to ensure the inner core of the feedstock have attained enough thermal energy while the outer surface could attain a much higher thermal energy (more chemical reactions can be performed in a shorter time). Similar findings on the heating rate effect on mass loss behavior has also been reported in pyrolysis of horse manure (Mong et al., 2019).

The conversion of the studied sludge cake was analysed from 15 % to 70 %. The initial and final decomposition stage were not included to eliminate the possible error induced at DTG tail. It is to note that such as assumption is commonly adopted in kinetic analysis studies (Ma et al., 2015). The linear graph at different conversional level was then plotted using FWO method in Eq(4) (Figure 2a) and Kissinger method in Eq(3) (Figure 2b). The linear regression, R^2 with a value close to unity indicates the accuracy of pyrolysis measurement. An average R^2 of 0.979 was recorded for FWO method while the Kissinger method gave an R^2 value of 0.8731. The linear curve was subsequently used to obtain the activation energy of sludge cake pyrolysis.

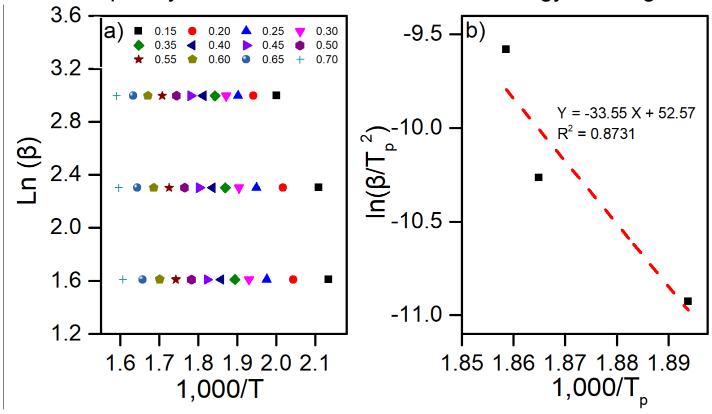

Figure 2: Linear plot for (a) FWO and (b) Kissinger methods

From Figure 3a, the activation energy of sludge cake obtained from FWO has a range of 76.9 to 693.1 kJ/mol and is found to vary with α. This indicates that the decomposition of sludge cake is a multi-step reaction mechanism that involves complex chemical reaction. The activation energy is low at the initial conversional level, which is probably due a simpler reaction, such as moisture removal and light volatile being released. The activation energy increased gradually from α=0.2 to α=0.6, owing to the decomposition of carbohydrate, protein and lipids composition. From α=0.6, a sudden spike in activation energy by a factor of 2 is observed (from 372.34 to 693.06 kJ/mol). This could be attributed to the degradation of polymer in the sludge cake, which was added during the dewatering process in wastewater treatment plant. It has been reported that polymer used in wastewater treatment for flocculation has been found to be difficult to decompose (Steudel et al., 2019). Similar high activation energy (up to 630.73 kJ/mol) has also been reported for the pyrolysis of sewage sludge containing polymer (Xu et al., 2017). The changes in pre-exponential factor with α is found to have a similar behavior as the activation energy, E (shown in Figure 3b). This is because both properties are related, where at high pre-exponential factor, a greater number of collisions is required for the molecules to attain the right configuration for a particular chemical reaction to occur. A lower number of collisions indicates the likelihood for a reaction to take place and directly leads to a lower activation energy.

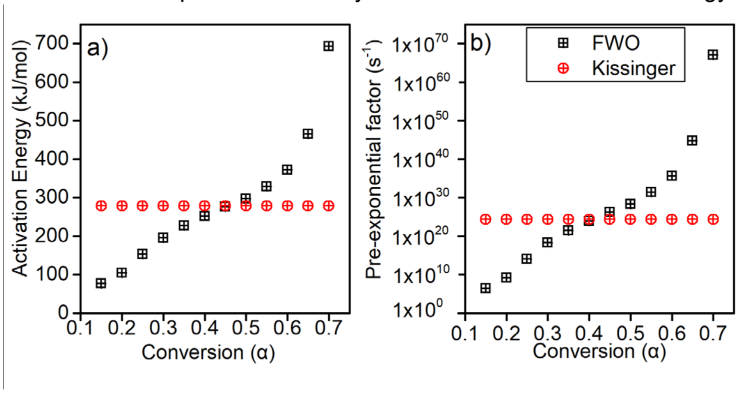

Figure 3: (a) Activation energy and (b) pre-exponential factor obtained using FWO and Kissinger methods in relation to the conversional level

In the present study, the activation energy obtained from Kissinger method is recorded at 287.98 kJ/mol with R^2 of 0.8731, which is comparable with the averaged activation energy from FWO (286.59 kJ/mol). The Kissinger method presents the kinetic parameters as an averaged value (constant for the entire pyrolysis process) and the FWO method gives the apparent values of kinetic parameters. The FWO method evaluates both physical changes (conversional level measured by mass loss) and chemical reactions (activation energy and pre-exponential factor) that occur simultaneously during the pyrolysis process. Even though both models have different approximations, they could still serve as a reliable comparison in describing the pyrolysis mechanism (Mong et al., 2020).

4. Conclusion

Mass loss behavior of sludge cake from food processing industry under pyrolysis was studied through TGA-FTiR. The sludge cake is composed of protein (46 %), carbohydrate (28 %) and minor portion of fats (6.5 %) and crude fiber (7.6 %), where the high protein content originates from food sources and dead bacteria. The high volatile (72.3 %) and low ash content (6.7 %) in sludge cake indicate the potential in yielding significant portion of bio-oil/gas and biochar of potentially good fuel quality. The sludge cake under pyrolysis was found to have experienced a maximum mass loss of 66.78 % within temperature range of 155.96 °C and 517.2 °C. The volatiles evolved contain various chemicals (ketones, aldehydes, etc) and gaseous composition (CH_4, CO and CO_2). The activation energy obtained from the FWO and the Kissinger method are in agreement with each other with an average value of 286.59 and 287.98 kJ/mol. In short, the pyrolysis of sludge cake from food industry could present itself to be a viable processing pathway to produce biochar, bio-oil and gaseous product of alternate uses.

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References

Chen W.H., Chu Y.S., Liu J.L., Chang J.S., 2018, Thermal degradation of carbohydrates, proteins and lipids in microalgae analyzed by evolutionary computation, Energy Conversion and Management, 160, 209-219.

Dominguez A., Fernandez Y., Fidalgo B., Pis J.J., Menendez J.A., 2008, Bio-syngas production with low concentrations of CO_2 and CH_4 from microwave-induced pyrolysis of wet and dried sewage sludge, Chemosphere, 70(3), 397-403.

Kim Y.S., Kim Y.S., Kim S.H., 2010, Investigation of thermodynamic parameters in the thermal decomposition of plastic waste-waste lube oil compounds, Environmental Science & Technology, 44, 5313–5317.

Lee J., Choi D., Ok Y.S., Lee S.R., Kwon E.E., 2017, Enhancement of energy recovery from chicken manure by pyrolysis in carbon dioxide, Journal of Cleaner Production, 164, 146-152.

Lestinsky P., Grycova B., Koutnik I., Pryszcz A., 2016, Microwave pyrolysis of the spruce sawdust for producing high quality syngas, Chemical Engineering Transactions, 52, 307-312.

Lin Y., Liao Y., Yu Z., Fang S., Lin Y., Fan Y., Peng X., Ma X., 2016, Co-pyrolysis kinetics of sewage sludge and oil shale thermal decomposition using tga–ftir analysis, Energy Conversion and Management, 118, 345-352.

Ma Z., Chen D., Gu J., Bao B., Zhang Q., 2015, Determination of pyrolysis characteristics and kinetics of palm kernel shell using tga–ftir and model-free integral methods, Energy Conversion and Management, 89, 251–259.

Mong G.R., Chong C.T., Ashokkumar V., Ng J.H., Chong W.W.F., 2020, Determination of the activation energy and kinetics properties of algae (sargassum polycystum) via thermogravimetric analysis, Chemical Engineering Transactions, 78, 133-138.

Mong G.R., Ng J.H., Chong W.W.F., Ani F.N., Lam S.S., Chong C.T., 2019, Kinetic study of horse manure through thermogravimetric analysis, Chemical Engineering Transactions, 72, 241-246.

Park H.J., Heo H.S., Park Y.K., Yim J.H., Jeon J.K., Park J., Ryu C., Kim S.S., 2010, Clean bio-oil production from fast pyrolysis of sewage sludge: Effects of reaction conditions and metal oxide catalysts, Bioresource Technology, 101, S83-85.

Peng X., Ma X., Lin Y., Guo Z., Hu S., Ning X., Cao Y., Zhang Y., 2015, Co-pyrolysis between microalgae and textile dyeing sludge by tg–ftir: Kinetics and products, Energy Conversion and Management, 100, 391-402.

Steudel A., Friedrich F., Lieske W., Baille W., Konig D., Schuhmann R., Emmerich K., 2019, Simultaneous thermal analysis of cationic, nonionic and anionic polyacrylamide, Heliyon, 5(12), e02973.

Xu X., Zhao B., Sun M., Chen X., Zhang M., Li H., Xu S., 2017, Co-pyrolysis characteristics of municipal sewage sludge and hazelnut shell by tg-dtg-ms and residue analysis, Waste Manag, 62, 91-100.

Zhang H., Gao Z., Ao W., Li J., Liu G., Fu J., Ran C., Liu Y., Kang Q., Mao X., Dai J., 2017, Microwave pyrolysis of textile dyeing sludge in a continuously operated auger reactor, Fuel Processing Technology, 166, 174-185.