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Akor, C., Osman Ahmed, A. O., Farrell, C., McCallum, C., Doran, W. J., Morgan, K., Harrison, J., Walsh, P., & Sheldrake, G. (2021). Thermokinetic study of residual solid digestate from anaerobic digestion. *Chemical Engineering Journal*, 406, [127039]. <https://doi.org/10.1016/j.cej.2020.127039>

Published in:
Chemical Engineering Journal

Document Version:
Peer reviewed version

Queen's University Belfast - Research Portal:
[Link to publication record in Queen's University Belfast Research Portal](#)

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Thermokinetic Study of Residual Solid Digestate from Anaerobic Digestion

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ABSTRACT: Anaerobic digestion (AD) has become an effective waste management method in the agri-food sector to dispose of livestock and food wastes. As AD becomes more widely used new challenges emerge, such as the disposal of digestate by-products. Currently, the principal method for handling solid digestate (SD) is direct application to land as an organic fertiliser. However, as the sector grows, this option is less viable due to nutrition loading on the land and increased eutrophication. This paper explores the potential of using SD, as a biofuel source. Additionally, the pyrolysis kinetic triplet of residual SD and thermal predictions was reported for the first time using Advanced Kinetics and Technology Solutions (AKTS) thermokinetics software to model and calculate the activation energy (E_a) and other kinetic parameters. ASTM-E698, Ozawa-Flynn-Wall and differential iso-conversional (model-free) methods were used and the E_a values calculated from each model were 169.8, 75 – 175.0, and 85 – 190.0 kJ mol⁻¹, respectively. The kinetic triplet can be used in the scale-up or designing of reactor systems considering SD as a feedstock. The kinetic prediction of isothermal pyrolysis of SD indicated that a temperature higher than 210 °C is required for onset of decomposition in the sample. Furthermore, SD has the potential to produce an additional ~27.9 MJ per day at a 500 kW standalone on-farm AD plant. This work has

highlighted the potential of waste solid digestate as a potential solid biofuel that could add an additional revenue stream to AD plants and make them more sustainable.

Keywords: Thermokinetics, Residual Digestate, Pyrolysis, Kinetic modelling, Sustainable Energy, Circular Economy

1.0 INTRODUCTION

The primary carbon feedstock for producing transportation fuels and a wide range of chemicals are fossil sources such as oil, coal and natural gas [1-3] and global energy demand continues to grow and is expected to increase to ~778 EJ by 2035 [4]. The burning of fossil fuels represents a significant and real worldwide environmental and health concern [5]. Recent research has presented clean renewable fuel options with proven technology that reduce emissions to the environment [6-8]. The United Nations sustainable development goal (UN SDGs) No.7 (Affordable and Clean Energy) mandates that sustainable modern clean energy is reliable, affordable and accessible for all, UN SDG no. 12 (Responsible Consumption and Production) also stipulates the reduction of waste through recycling and reuse [9-12]. Waste biomass has the potential to offer a sustainable resource for meeting future energy demands [13-16]. The term 'biomass' comprises organic plant matter; such as those derived from agricultural residues, food wastes, energy crops, grasses, algae, wastes from anaerobic digestion (AD) plants and sewage sludge [17]. Biomass energy, considered to be a form of solar energy trapped in plant matter, is environmentally benign because of its carbon neutrality and low sulphur content compared to fossil derived fuels; hence biomass can be a cleaner fuel for power generation [18-20]. Emissions from biomass fuels can be minimal, especially when CO₂ emissions from its usage are sequestered effectively. Also, the seasonal challenges/irregularity in energy supply witnessed with other forms of renewable energy such as solar and wind is avoidable with biomass [21]. Therefore, biomass has the potential of contributing to the future energy demand and meeting the UN SDGs. Various authors have reported different types of biomass such as cotton stalk, sugar cane bagasse, shea meal [22],

barley straw, miscanthus, waste wood, wheat straw, wood pellets and short rotation coppicing willow [18] for energy generation.

Thermochemical and biochemical processing are the two principal technologies employed for the depolymerisation and conversion of lignocellulosic biomass [23]. This is typically how residual SD has been treated and processed to date. Undertaking physical pretreatment such as milling, grinding, extrusion, ultrasonication etc prior to chemical processing is not inexpensive due to the energy consumption [24]. However, it is an important step to optimise bioconversion, the production of depolymerising enzymes, reduce particle size and increase particle distribution to facilitate the overall transformation of lignocellulosic materials (LM) into biofuels without producing toxic by-products [25]. One mode of mechanical reduction involves milling with a variety of mills to breakdown the lignocellulosic material, reducing the crystallinity of cellulose. A range of mills are frequently used for this purpose including: ball mills, centrifugal mills, colloid mills, hammer mills, extruders, knife mills, attrition mills and vibratory mills [26].

According to Osman *et al.*, [2] and Arenas *et al.*, [27] biochemical conversion of lignocellulosic biomass occurs through the process of fermentation or digestion, whilst the thermochemical route is via combustion, gasification, pyrolysis and liquefaction. As such, there is potential to apply established thermochemical, biochemical and mechanical processes for lignocellulosic biomass in the treatment of residual digestate materials. Thermochemical pyrolysis converts biomass in syngas, bio-oil and char [28]. The fixed carbon content, heating value and combustion processes of biomass can be improved via pyrolysis [18]. Biomass pyrolysis/combustion has been reported most often using thermogravimetric analysis (TGA). Different temperature zones of biomass devolatilisation associated with the individual polymeric fractions of the lignocellulosic biomass can also be determined with TGA. Sher *et al.*, [18] used non-isothermal TGA with different gas environments such as N₂, air, CO₂ and oxy-fuel to examine and report the thermal and kinetic analysis of six diverse biomass fuels.

AD is a promising treatment method for biomass, combining energy recovery and waste treatment to produce biogas [29]. Food waste (household and commercial) and livestock waste from the agricultural industry (e.g. poultry litter, cow slurry) are commonly used as feedstocks for AD to produce biogas [30]. The implementation of AD has been a major development in the treatment of waste biomass over the last decade [30]. AD of organic matter involves the chemical transformation of particulate and dissolved organic matter into biogas (approx. 65% CH₄, 35% CO₂ and trace gases including H₂S, H₂ and N₂) through a consortium of interrelated microbial metabolisms [31].

Energy can be recovered from biomass in the form of biogas/biomethane which is utilised in the combined heat and power (CHP) engines for electricity generation [3]. Miguel *et al.*, [32] reported that in 2014, approximately 2,503 million tonnes of waste was produced from domestic and commercial sources in the European Union (EU). The report further stated that ~ 45 – 55% was food waste (FW) [32], which can be converted to energy in an AD plant [33]. However, biogas/biomethane alone cannot guarantee a sustainable industry; as the market becomes saturated the cost of electricity will decrease and so other revenue streams are essential to ensure a viable and sustainable industry.

Currently, AD plants produce high volumes of waste digestate which are underutilised. AD in the UK generates a total 277, 000 tonnes of digestate per year, which is composed of solid and liquid fractions [34]. In Northern Ireland (NI) in 2017 there were 103 AD sites, either in construction or already approved [3]. It is reported that there will be capacity to treat 1.4 million tonnes of feedstock annually to generate bio-fuel once construction of NI AD plants is complete [3]. Thermal utilisation of waste and residual material through AD can reduce CO₂ emissions and help solve waste disposal problems [35]. AD facilitates the recovery of nutrients, lowers landfilling and generates renewable bioenergy [36, 37]. Over the last decade, there has been a doubling [38] in the output of municipal solid waste (MSW), biosolids from

municipal wastewater treatment plants (WWTP) and both solid and liquid digestate from AD plants. It is well recognised that traditional landfilling and incineration of MSW is fast becoming less viable due to landfill availability, cost and environmental constraints [39], making AD a more attractive and feasible option. AD of sewage sludge (SS) in WWTP can be used to produce electricity supply to the grid [40]. The use of activated sludge (AS) [41] as a biological treatment of MSW requires some modelling kinetics to mitigate the negative effect of heavy metals on the heterotrophic bacterial concentration. electricity generated from energy produced by anaerobic digestion of sewage sludge reduces the electrical power requirements from the main grid network to about 27% in the proposed wastewater treatment plant. Obernberger [42] reported that low SO_x emissions is an added advantage in the pyrolysis/combustion of MSW and agricultural residue. This is in part due to the SO_2 produced during combustion being captured by the 'alkaline ash' from the biomass, thus, co-firing with biomass can also lower overall SO_2 emissions [42].

The EU Wastes Framework Directive (2018) are currently investigating the feasibility of valorising solid digestate (SD) from AD plants into biofuels and other chemicals [43]. Monlau *et al.*, [39] and Moretti *et al.*, [44] reported the valorisation of SD from agricultural waste for energy use through pyrolysis. It was further reported that by-products from this process were not toxic, and that coupling pyrolysis to AD presented the best environmental performances as compared to combustion [39]. This was confirmed by the life cycle analysis of SD pyrolytic valorisation of swine and dairy manure feedstock carried out Fernandez-Lopez *et al.* [45]. According to Silva [46] and Zakzeski [47], residual SD is recognised as important for the production of renewable energy, chemicals and fuels. The new EU regulatory framework under the Renewable Energy Directive (RED-2) includes a combined renewable energy target for 2030 of 32%, with an upward revision clause by 2023 [48, 49]. In Europe, it is reported that a larger percentage (approximately 45.1%) of the renewable energy is currently generated from biomass [48], hence the need to further optimise valorising of solid residue from AD to increase energy efficiency of AD.

In order to make better use of SD waste streams and in the targets outlined above [39],[43-45] the kinetics of the pyrolysis process, especially the determination of the kinetic triplet (i.e. rate of reaction, activation energy and pre-exponential factor) is required. The kinetic parameters can be used in the scaling up and designing of reactor systems. Additionally, the parameters can be used in process models to describe how the pyrolysis of SD would behave at scale before being employed at an industrial level.

Arenas *et al.*, [27] reported that analysis of kinetic reactions of biomass feedstocks under pyrolysis provides valuable insight on the decomposition, aiding process optimisation and informing reactor design. Huang *et al.*, [50] reported that such analysis reveals key data regarding reaction mechanisms which can help establish mathematical models to describe processes. He *et al.*, [51], Vyazovkin *et al.*, [52], and Osman *et al.*, [4] described the kinetic modelling of biomass pyrolysis/combustion using model-free (iso-conversional) and model-fitting methods. Iso-conversional methods are suited to estimating complex reaction behaviour in a simple manner, such as those consisting of numerous steps, each with varying rates for which basic kinetic models are unsuitable and might lead to wrong kinetic parameters [51]. The differential iso-conversional method requires a number of heating rate curves to calculate the kinetic parameters with respect to the conversion (α), enabling E_a to be calculated for each conversion point [4]. Given that the thermal analysis mechanism is understood to be complex; having numerous steps and rates, the differential iso-conversional method is more suitable and frequently used in this setting. The Kissinger method is the only model-free method unable to identify the E_a as a function of progressive conversion (α), in this method activation energy (E_a) is assumed to be constant therefore it is not an iso-conversional method [4]. Scott *et al.*, [53] and Varhegyi *et al.*, [54] stated that the Distributed Activation Energy Method (DAEM), which is a model-fitting method was a precise, flexible and powerful methodology for the assessment of the devolatilisation of kinetic processes of complex feedstocks such as coal or sewage sludge. However, a major limitation of the DAEM is that it is difficult to estimate kinetic parameters due to complexity of the model. Also, it assumes that reaction proceeds through

infinite and irreversible number of independent parallel reactions [55, 56]. Kumar *et al.* [57] reported that the Starink model uses approximation and empirical relation between reaction rate and temperature, hence other iso-conversional models such as Flynn-Wall-Ozawa (FWO) are considered to be better [57]. The thermal pyrolysis/combustion of SD is considered an endothermic [39] and non-adiabatic process, as a result heat released can lead to a rapid rise in temperature alongside gas release [2]. Therefore, an understanding of the reaction kinetics and endothermicity of the thermal decomposition of SD is critical to clearly characterise the physiochemical pyrolytic attributes and the consequent limits of its application to energy production.

To date there have been very few kinetic modelling studies for the pyrolysis of digestate [55, 58], although these have only reported limited details of the feedstocks for the AD process. Furthermore, there was no clarity in the report of pre-exponential factor (k_0) and only a single kinetic model was utilised in these previous reports.

In this study, the pyrolysis of dry SD, which contains lignocellulosic material (40, 30 and 29% of cellulose, hemicellulose and lignin, respectively) [59, 60] was investigated using a thermogravimetric analysis/differential scanning calorimetry (TGA/DSC) technique operated in a N₂ environment. The original AD feedstocks include grass silage, chicken litter and cattle slurry, as is reported previously [61]. The differential iso-conversional method was used for the calculation of the kinetic parameters from the thermogravimetric (TG) curves and from the simulated differential reaction progress, which was validated using the non-isothermal iso-conversional model methods. As such it is anticipated that using this robust kinetic modelling approach (in conjunction with experimental thermal analysis) that the current study will provide more details on the potential to valorise AD waste streams (specifically SD) for energy, thereby supporting the circular economy.

To best report on the kinetic modelling for the pyrolysis of SD material, the methods and results/discussions sections are separated into both experimental and theoretical subsections as follows:

- Characterisation
- Thermal analysis experiments
- Kinetic modelling using AKTS Thermokinetics
- Thermal predictions based on the model

2.0 EXPERIMENTAL

2.1 Solid Digestate Preparation. Digestate samples were collected from AgriAD and AFBI AD plants located in Northern Ireland. The digestate sample (1L) was separated into liquid and solid fractions using a centrifuge B 4i model operated at 6000 rpm for 9 minutes. The liquid and solid were then stored in the fridge at 0 °C overnight before being freeze-dried (Lyotrap freeze dryer operated at -50 °C and 0.1 millibar vacuum pressure) to completely evaporate the moisture. The freeze-dried samples were ground to a 1 mm particle size using a polymix grinder (PX-MFC 90D) for the TGA analysis.

2.2 Heat Treatment of Solid Digestate SD (3 g) was heated in ceramic crucibles in a muffle oven (Carbolite ELF 11/6 laboratory chamber furnace, 6L capacity) to 700 °C at a constant heating rate of 5 °C min⁻¹ with a dwell time of 6h, then cooled to room temperature inside the furnace. The resultant biomass is referred to as the SD biochar.

2.3 Solid Digestate Characterisation

Powder X-ray diffraction (XRD) was performed on both the SD and SD biochar using a PANalytical X'pert Pro X-ray diffractometer. XRD was used to assess the change in mineral composition in the SD after heat treatment. The diffractometer was fitted with CuK_α X-ray source with a wavelength of 1.5405 Å. Diffractograms were collected from 5° to 90° with a step

size of 0.01°. The X-ray tube was operated at 40 kV and 40 mA. The phases were characterised by comparing with diffraction pattern using the automatic search function reference data base in the X'pert software library [62].

Elemental (C, H, N, and S) analysis was performed using a PerkinElmer PE2400 CHNS/O Elemental Analyser. From the C, H, N and S percentage composition data acquired, the balance is assumed to be oxygen (i.e. oxygen content was calculated by difference of known total amount of sample and the measured amounts of C, H, N and S). ASTM standards were used for the analysis, these include the % of moisture (ASTM D2867-95), volatile matter (ASTM D5832-95), ash content (ASTM D2866-94) and fixed carbon (by difference) was determined [62, 63].

TGA was performed using a simultaneous thermal analysis NETZSCH Jupiter STA 449C (TGA/DSC) thermogravimetric analyser. Samples were heated at a specific temperature range from 20 – 900 °C with different ramp rates of 0.5, 1.0, 4.0 and 8.0 °C min⁻¹, under a dry N₂ stream at a flow rate of 40 cm³ min⁻¹. The weights of the samples used for TGA analysis were in the range of 11 to 14.3 mg. For quantitative evaluation of weight loss, the TGA instrument was calibrated by running a blank prior to the samples. TGA analysis was run in duplicate.

2.4 Advanced Kinetics and Technology Solutions (AKTS) Study

Kinetic modelling is used for the description of kinetic parameters which can be used to help inform industry and the wider audience by providing insight into the reaction and as well explain the thermal behaviour of the material. The modelling in this study predicts the behaviour beyond the experimental TGA (which is considered analogous to pyrolysis) data by making an accurate prediction for an operation involving isothermal heating [64]. AKTS software from Setaram KEP Technologies has been reported in literature for kinetic modelling studies [65, 66]. The AKTS software follows the recommendation of international confederation

for thermal analysis and calorimetry (ICTAC) kinetics committee on fundamental principles that underpins the correct calculation of kinetic analysis data.[67]

Herein AKTS Thermokinetics was used in order to determine E_a and pre-exponential factor (k_0) using the ASTM E-698 method and non-isothermal iso-conversional methods (Ozawa-Flynn-Wall and differential iso-conversional) in the manner reported previously [4, 68]. The differential iso-conversional method is known to be more accurate as it avoids assumptions of the reaction formation, while it does not assume that the k_0 and E_a are constant as the reaction progresses [69], unlike the Ozawa-Flynn-Wall and ASTM-E698 methods. The non-isothermal iso-conversional methods, however, can still provide some useful insights and so were still utilised in this work for comparison and validation purposes. Simulations generated from the calculated kinetic parameters also allow for validation via comparison on a point by point basis with the experimental data.

Experimental data from TGA with the 4 different heating rates (0.5, 1.0, 2.0 and 4.0 °C min⁻¹) was imported (in ASCII file format) into the AKTS solid-state kinetic solver. The data was subsequently changed to DTG format, the first derivative of the TGA. Tangential sigmoid baselines were constructed on the DTG plots to integrate the curve and give the evaluation of the kinetic parameters such as rate of reaction, activation energy and pre-exponential constant [64]. This allows for the determination of a temperature dependence which can be used to predict behaviour of the reaction progress at other temperatures. As the digestate pyrolysis reaction progress, there is a change in the specific heat of the reactant-products mixture, thus changing the heat of reaction and as well the kinetic parameters. Specifically, using the AKTS package; the progress/extent of reaction (α) and the reaction rate can be predicted for a wide variety of temperature profiles (non-isothermal, isothermal, modulated or periodic temperature variations or step base heating). The software ultimately provides a robust and accurate result due to strict thermokinetics criteria of average correlation coefficient R having to be greater than 0.95 and the plotting of high-resolution data over 10,000 specific data points for the parameters and alpha values.

This allows for the determination of a temperature dependence which can be used to predict behaviour of the reaction progress at other temperatures. The calculated kinetic parameters are used to generate simulations for the reaction progress and reaction rate. These simulations can be compared with the corresponding experimental dataset in order to assess the accuracy of the calculated kinetic parameters at different ramp rates and at different stages of the reaction. The calculated results from the pyrolysis are affected by the heat of the reaction and by the change of the specific heat of the mixture reactant-products as the reaction progresses. The equation for the solver for the reaction progress $A(t)$ are included below in eqn.1 and 2

$$\frac{dA}{dt} = \frac{(S(t) - B(t))}{\int_{t_0}^{t_{end}} (S(t) - B(t)) dt} \quad (1)$$

$$A(t) = \frac{\int_{t_0}^t (S(t) - B(t)) dt}{\int_{t_0}^{t_{end}} (S(t) - B(t)) dt} \quad (2)$$

With $0 < A(t) < 1$ and $B(t) = (1 - A(t)) * (a_1 + b_1 * t) + A(t) * (a_2 + b_2 * t)$

Where $B(t)$ is the baseline, $S(t)$ is the differential signal, $\frac{dA}{dt}$ is the reaction rate, $a_1 + b_1 * t$ is the tangent at the beginning of the signal $S(t)$ and $a_2 + b_2 * t$ is the tangent at the end of the signal $S(t)$.

2.5 Kinetic Modelling Methods

2.5.1 Iso-conversional methods

Model generation (which is dependent on the best fitting of the TG data with the distinct models using a single TGA/DSC curve) and model-free (iso-conversional) are the two frequently used methods in the study of TGA/DSC solid-state kinetic data [19, 51]. This is due to the simplicity of the differential iso-conversional method and elimination of error associated with the model fitting method, as the former is advantageous over the latter. The higher accuracy of the differential iso-conversional is attributed to the avoidance of assumptions made of the reaction

formation, as well as considering that the k_0 and E_a vary as the reaction progresses. The solver evaluates the apparent activation energy and pre-exponential factor at numerous intervals across the entire data signal thereby determining the kinetic parameters as the reaction progresses. The equations in ESI (Eqn. S1 – S5) [4, 70] detailed the fundamental principles of the differential iso-conversional (model-free) method.

2.5.2 Non-isothermal Methods

2.5.2.1 Non-isothermal non- Iso-conversional Methods

ASTM-E698 Method [4]: This method is in-between the model fitting and model-free methods. The model-free approximation of the activation energy assessed from the Kissinger's plot is used for calculation [52]. In a single-step reaction, this method is more suitable and further details are given in the ESI.

2.5.2.2 Non-isothermal Iso-conversional Methods

Ozawa-Flynn-Wall Method [71]: This method suggests the calculations of the difference of the apparent activation energy with regards to various linear thermogravimetric curves using the integral iso-conversional analysis method [68, 71]; hence, it is considered suitable for multiple-step reactions like autocatalytic reactions. E_a is calculated as detailed in the ESI.

2.5.3 Model Fitting

The accuracy of the calculated kinetic parameters is validated by comparing the experimental data with the simulated reaction progress using an error analysis using a previously reported method [72]. Further details are provided in the ESI.

2.6 Experimental Overview

Fig. 1 is a schematic which presents a graphical overview of the experimental methods reported within this manuscript alongside some peripheral items to help to contextualise the current work. The process of energy production is depicted in the schematic occur in two

phases i.e., biogas production in AD from biomass feedstocks and post AD pyrolysis of SD. The SD was pyrolysed using a TGA and experimental data extracted as described in section 2.4 and modelled with AKTS software. Kinetic parameters were determined using the Ozawa-Flynn-Wall, differential iso-conversional and ASTM-E698 thermokinetics models. Furthermore, characterisation was conducted using CHNS elemental analysis for SD and XRD of SD and its biochar. Finally, the isothermal kinetic predictions for pyrolysis of SD at a range of temperatures was completed with the AKTS software.

Fig. 1. Flowchart of research methodology

3.0 RESULTS AND DISCUSSION

3.1 Biomass Ultimate and Proximate Analysis

Biofuels produced from biomass tend to be more reactive than conventional fuels from fossil sources and as well contain higher volatile yields and lower fixed carbon, hence the understanding of its elemental components is important for the analysis of the heating values [73, 74]. From the data reported in Table 1, both sewage sludge (SS) and bituminous coal

(BC) have a higher content of C, H, N and S. The oxygen in the solid digestate (57.5%) is higher than in sludge (32.1%) and coal (7.7%). Also, the moisture content of the solid digestate is higher (12.3%) than that of sludge and coal (6.9 and 4.9%, respectively) [63]. The lower oxygen content for sludge and coal could presumably give rise to a higher energy output per gram when combusted. This also correlates with the higher moisture content in the digestates. Fixed carbon (FC) represents the portion of the coal that must be burned in a solid state and its knowledge aids in equipment selection for combustion/pyrolysis. FC reveals the caking properties (e.g. moisture, ash) of coal and biomass as a fuel [75]. The FC content of the SD is lower (6.6%) compared to the sewage sludge and coal (7.0 and 48.1, respectively). In summary, these parameters would all indicate that combustion of SD may not be beneficial due to potentially lower calorific values while the higher oxygen content would create further issues with higher soot production than coal or sludge [76]. The volatile matter content of the SD is relatively high (62.0%) compared to sewage sludge and coal (44.6 and 32.3%, respectively). While the sewage sludge volatile content is still higher than that of coal, it has a higher N content compared to the SD (6.3% versus 2.3 %). This is expected due to the high ammonia content in the sludge [77]. This means that sewage sludge is not ideal for combustion (higher NO_x emissions) while the ammonia content may give rise to issues in other processes such as pyrolysis (e.g. corrosion) [78].

Furthermore, using the method by Channiwala [79], the gross energy (higher heating value, HHV) and net calorific value (lower heating value, LHV) of SD was calculated from the elemental analysis in Table 1 as 11.72 and 9.90 kJ kg⁻¹, respectively. As such, ultimate and proximate analysis indicates the potential use of SD as feedstock in pyrolysis processes for bio-oil production [27].

Table 1. Ultimate and Proximate analysis of sewage sludge [80], bituminous coal [73] and residual digestate

FUEL	ULTIMATE ANALYSIS (%)					PROXIMATE ANALYSIS (%)					Reference
	C	H	O	N	S	Moisture	Volatile	FC	Ash	HHV kJ kg ⁻¹	
Sewage Sludge	52	6.3	32.1	6.3	3.1	6.9	44.6	7	41.5	21.6	[80]
Bituminous Coal	65.7	5.6	7.7	1.2	0.5	4.9	32.3	48.1	14.7	28.5	[73]
Solid Digestate	34.9	5	57.5	2.3	0.3	12.3	62	6.6	19.1	11.7	This work

3.1.1 van Krevelen diagram

Solid fuels are characterised by their degree of carbonisation. The van Krevelen diagram of SS, BC and SD which helps to determine the degree of carbonisation of the reported fuels is shown in Fig. 2. This diagram also aids to better understand the development path of organic matter and the distinct regions of similarity of the solid fuels. As shown in Fig. 2, SD in this study is located in the region known for biomass [18]. SS has an O/C ratio of 0.62 and H/C of 0.12 placing, BC has an O/C ratio of 0.12 and H/C of 0.09. SD by comparison has an O/C of 1.42 and H/C of 0.14. As reported by Sher *et al.* [18], biofuels have a higher proportion of O/H and falls in the category limits of $0.7 \leq O/H \leq 1.3$ and $0.075 \leq H/C \leq 0.25$, whilst coal fuel ranges from $0 \leq H/C \leq 0.1$ and $0 \leq O/C \leq 0.3$. As defined by Sher the SD is located within the “biofuel” range and is at the upper limit of the O/C content. A possible reason for the higher oxygen content is within the AD process cellulose, and therefore glucose molecules, are consumed as part of the process. This results in lignin and hemicellulose remaining post AD. Lignin contains a higher ratio of oxygen to carbon in comparison to cellulose and therefore would lead to an increase in the O/C ratio remaining post AD.

Calculated HHV for SS, BC and SD were 21.60, 28.46 and 11.72 kJ kg⁻¹ respectively and LHV were 19.84, 27.09 and 9.90 kJ kg⁻¹, respectively. Biofuels with high H/C and O/C ratios have a low calorific values compared to fossil fuels like coal with lower H/C and O/C [25, 81]. This explains why BC with a lower H/C and O/C has a high heating values than SS and SD.

Fig. 2. van Krevelen showing solid fuels characterisation by H/C and O/C atomic ratios

3.2 Solid Digestate characterisation.

Fig. 3. XRD pattern of Solid digestate before heat treatment and after heat treatment (biochar)

The XRD results for the SD before and after heat treatment (biochar) are reported in Fig. 3. SD sample was heated at 700 °C and the purpose is to ensure all minerals and volatiles contained in the SD is burned off to obtain the biochar. Temperature ranging from 500 – 800 °C was used but 700 °C was the optimum and gave the desired result by the XRD characterisation indicating the peak assigned as graphite. The effect of heat treatment on the inorganic fraction of minerals found in the digestate (e.g. SiO_2 , KCl) was examined using XRD. For SD, prominent peaks were observed where 2θ equals 15.9, 21.5 and 29.8°, which were assigned to SiO_2 , (JCPDS No. 03-0226) [82], KHSi_2O_5 (JCPDS No. 19-968) [82] and KHCO_3 (JCPDS No. 03-0289) [83], respectively. Other less significant peaks were also observed at 2θ of 40.6 and 50.2° (JCPDS No: 01-073-0380) which were assigned to KCl [84, 85] and along with other phases including $\text{K}_4\text{H}_2(\text{CO}_3)_3 \cdot 1\frac{1}{2} \text{H}_2\text{O}$ ($2\theta = 30.8, 36.8$ and 45.03°) [83, 86]. Heating the SD at 700 °C removed these mineral fractions as can be observed in the diffractogram of biochar. After heat treatment one prominent amorphous peak formed at 22.1° which was assigned to graphite.

Fig. 4 reports the devolatilisation process starting at 110 - 120 °C, with water loss as the SD contains approximately 12.3% moisture content, and hydrolysis of certain extractives such as esters and fats [87] because of their instability and start to degrade at lower temperature as a result of how highly volatile they are; the devolatilisation of SD biomass commenced at 200 °C and achieves maximum weight lost in the range 200 – 290 °C. There was a sharp change in gradient with a point of inflection at 300 °C. Above 350 °C, a sudden change in the slope of the TGA curve occurs which leads to a moderate weight loss in the temperature range of 370 – 500 °C. At a higher temperature, decomposition of the strongest bonds in lignin take place up to 630 °C. This agrees with reports from other literature sources [27, 88, 89]. Generally, the pyrolysis of SD occurred in three stages/zones at varying temperatures were drying (water evaporation at 110 - 120 °C), devolatilisation of hemicellulose and cellulose at 200 – 350 °C, and Lignin decomposition/breakdown (combustion zone) at 350 – 650 °C [58, 90]. During the

devolatilisation zone (200 – 350 °C), ~ 40 % weight loss was observed. At the end, from 650 °C the slow decomposition over the remaining temperature down to 800 °C produced pyrolysis residue (ash) which is often referred to long tailing section [18, 21, 22].

Fig. 4. TGA curves of solid digestate at different heating rates: 0.5, 1.0, 2.0, and 4.0 °C min⁻¹ under a nitrogen atmosphere

3.3 Kinetic Models Discussion

The TGA under nitrogen flow is analogous to the pyrolysis of SD from which the activation energy and the kinetic parameters were calculated from the TGA curves at various heating rates (0.5, 1.0, 2.0 and 4.0 °C min⁻¹). The TGA experiments for each of the heating rates were repeated twice and the results were reproducible and within experimental error of $\pm 3\%$ (see Fig. S2 – S9 in ESI).

TGA detects the mass loss at numerous temperatures as the reaction progresses during the experiments [91]. TGA/DTG results for the mass loss during the pyrolysis of SD under a

nitrogen atmosphere with different heating rates are reported in Fig. S1. Table 2 reports further details of the pyrolysis. It was evident that as the heating rate increases from 0.5 °C min⁻¹ to 4.0 °C min⁻¹, the temperature range of the decomposition increased correspondingly. The time taken for the thermal decomposition decreased significantly with increasing heating rates from 20 h (0.5 °C min⁻¹) to 2.7 h (4.0 °C min⁻¹). This is expected because as the heating rate increases, the decomposition is faster and takes less time. Williams and Besler [92] stated that as heating rate becomes high, char formation reduces in yields, whilst gas and oil yield increases, and the aqueous phase is independent of the heating rate and remains constant. As the reaction is endothermic, there is a high rate of devolatilisation and reduced residence/retention time in the reactor; hence the reduction in char formation [93]. Also, the peak height increased to about eight times as the heating rate increases from 0.5 to 4.0 °C min⁻¹ whilst the peak maximum was shifted towards a higher decomposition temperature by 27.1 °C [92]. At a heating rate of 0.5 °C min⁻¹, peak maximum was 261.8 °C at 476.7 mins and as the heating rate increased to 4.0 °C min⁻¹, the peak maximum temperature also increased to 288.9 °C at 65.5 mins. This is reported in the thermal decomposition data in Table 2, which was derived from the DTG curves reported in the ESI (Fig. S1).

Table 2. Thermogravimetric analysis of solid digestate at heating rates in the range of 0.5 to 4 °C.min⁻¹

HEATING RATE (°C MIN ⁻¹)	TEMPERATURE RANGE (°C)	TIME RANGE (MIN)	PEAK MAXIMUM TEMPERATURE (°C)	PEAK MAXIMUM TIME (MINS)	PEAK HEIGHT (% MIN ⁻¹)	Mass Loss (%)
0.5	104 - 629	160 - 1200	261.8	477	-0.17	64.12
1	147 - 628	123 - 605	267.9	245	-0.34	63.54
2	156 - 676	67 - 327	279.1	128	-0.81	50.18
4	155 - 695	32 - 167	288.9	66	-1.42	57.96

Fig. 5. Experimental (solid lines) and simulated reaction progress (dashed lines) versus the temperature for the solid digestate at different heating rates

Fig. 6. Experimental (solid lines) and simulated (dashed lines) reaction rate versus the temperature for the solid digestate at different heating rates

The decompositions of hemicellulose and cellulose occur in the range of 200 – 350 °C, whereas lignin decomposes in the temperature range of 300 – 600 °C, dependent on the substrate [58]. This is the rate-determining step during the pyrolysis/combustion of the SD biomass [94]. As stated earlier, the reaction mechanism is complicated and difficult to describe using the model-fitting method, as the reactions overlap during the pyrolysis/combustion process. Hence, it is not practicable to detect the kinetic parameters of SD using model-fitting methods. The three stages of weight loss of biomass decomposition in TGA analysis are; dehydration, devolatilisation (active pyrolysis) and char oxidation (passive pyrolysis) [90]. In terms of validating the calculated kinetic parameters, there is an excellent correlation between the experimental data and the simulation based on calculated data for all the heating rates, except for 2 °C min⁻¹, where there is a slight variation in the temperature range 400 – 500 °C as reported in Fig. 5. The shapes of the reaction progress versus temperature curves of each of the heating rates are consistent with each other, with only a slight variation for the heating rate of 2 °C min⁻¹ (350 – 500 °C) and 4 °C min⁻¹ (550 – 600 °C). Furthermore, the critical error obtained from the reaction progress, a measure of the variation between experimental and simulation, for the heating rate of 2 °C min⁻¹ is 0.96%. This indicates that there is a high level of accuracy in the kinetic parameters calculated and in the subsequent prediction of the behaviour of the reaction progress.

From the comparison of simulation with experimental data in Fig. 5, the critical error for the heating rates for 0.5, 1.0, 2.0 and 4.0 °C min⁻¹ were 0.60, 0.52, 0.96 and 0.47%, respectively, which indicates a high-quality fit. The respective error analysis plots are reported in the ESI in Fig. S2 – S5. Overall, the excellent correlations between experimental and simulated data support the validity of the kinetic parameters calculated with the AKTS software. The slight variations between the experimental and simulations in Fig. 5 are also confirmed in Fig. 6, which reports the reaction rate versus the temperature curves. There was a slight overlap of

the peak at 290 °C, the inflection at 340 – 510 °C and 620 – 630 °C for the 2 °C min⁻¹ heating rate. Also, for 4 °C min⁻¹ there was an inflection and peak overlap at (350 – 450 °C, and 560 – 610 °C), respectively. The critical error obtained for the reaction rate (Fig. 6), which measures variation between experimental and simulation, for the heating rates for 0.5, 1.0, 2.0 and 4.0 °C min⁻¹, were 0.49, 3.16, 0.43 and 0.38%, respectively; indicating a high-quality fit. The corresponding error analysis plots are reported in the ESI in Fig. S6 – S9.

The kinetic parameters were calculated by the differential iso-conversional method and are reported in Fig. 7 and 8. The natural logarithm of the reaction rate in (s⁻¹) versus the temperature inverse (T⁻¹) for the different heating ramp rates is reported in Fig. 7. By interpreting this data, the differential iso-conversional method in AKTS determines the Arrhenius dependence, thereby giving details on the apparent E_a and the k_0 at each stage of the reaction progress.

In Fig. 8, initially the calculated E_a was ~ 85 kJ mol⁻¹ at which point the reaction progress was still zero ($\alpha = 0$), while the pre-exponential factor $\ln(A(\alpha) f(\alpha))$ is ~ 12 s⁻¹. The high activation energy at the beginning of the reaction is ascribed to the carbohydrate polymer (cellulose and hemicellulose) [95]. High energy is required during pyrolysis to break the strong bonds of the lignin, which enclose the cellulose within a lignin-hemicellulose matrix [96]. Activation energy continues to increase reaching an initial peak of ~140 kJ mol⁻¹ at $\alpha = 0.3$. As the lignin component breaks down at a temperature range of 300 – 600 °C, E_a decreases to ~ 60 kJ mol⁻¹ at $\alpha = 0.87$ before increasing again to ~190 kJ mol⁻¹ at $\alpha > 0.9$. The explanation for this increase can be attributed to the complexity in reaction mechanism of SD pyrolysis or autocatalytic reactions with the decomposition of lignin and formation of ash. This ash contains minerals with catalytic properties with the tendency to melt and sinter due to high reaction temperatures. The sintering can cause some fused deposits, hence the increase in E_a as the reaction comes to completion [4, 18, 97]. In general, the E_a calculated using the differential iso-conversional method was in the range of 85 – 190 kJ mol⁻¹.

The suggested mechanism equation [2] from previous studies will be:

- (a) Biomass.H₂O = Biomass + H₂O
- (b) Biomass = Y-Char + Pyrolysis Gas
- (c) Hemicellulose = Hpy-Char + Hpy-Gas
- (d) Cellulose = Cpy-Char + Cpy-Gas
- (e) Lignin = Lpy-Char + Lpy-Gas

Where Hpy-Char, Cpy-Char, and Lpy-Char and Hpy-Gas, Cpy-Gas, and Lpy-Gas are the chars and gas produced during the pyrolysis of hemicellulose, cellulose, and lignin, respectively.

However, a single value of E_a is not sufficient to robustly define the thermal decomposition of SD because of the complexity of the reaction. Therefore, other methods such as Ozawa-Flynn-Wall and ASTM-E698 have been used to validate the results [4, 27, 52]. The calculated E_a of SD using the ASTM-E698 is 169.8 kJ mol⁻¹ as reported in ESI, (Fig. S10). The ASTM method reports a single constant value as it assumes that the kinetic parameters, including the E_a , remains constant as the reaction progresses. Fig. 9a, 9b and 9c report the calculated Arrhenius plots, E_a , and correlation coefficient from the Ozawa-Flynn-Wall method, respectively. From this method, the variation in the E_a during the reaction progress was between 75 – 175 kJ mol⁻¹ as reported in Fig. 9b. This was observed as the reaction progressed and nears completion between 0.9 – 0.98. The Ozawa-Flynn-Wall method is more accurate than the ASTM-E698 method as it considers that the kinetic parameters, including the E_a , vary as the reaction progresses, though it is less accurate than the differential iso-conversional method due to systematic errors dependent on the small ranges of reaction progress that are integrated [64].

Fig. 7. Natural logarithm of the reaction rate (s⁻¹) versus the inverse temperature (T⁻¹) using the differential iso-conversional method

Fig. 8. The activation energy (blue) and pre-exponential factor (orange) calculated with the differential iso-conversional method

Fig. 9a. Arrhenius plots of SD using Ozawa-Flynn-Wall [4] method

Fig. 9b. The activation energy (E_a) calculated by the Ozawa-Flynn-Wall [4] method

Fig. 9c. The correlation coefficient of the activation energy determined by the Ozawa-Flynn-Wall [4] method

3.3.1 Comparison of Results with Literature

The activation energy reported in this work from ASTM-E698, Ozawa-Flynn-Wall and differential iso-conversional are 169.8, 75 – 175 and 85 – 190 kJ mol⁻¹, respectively. These values agree with reports from other authors, as compared in Table 3.

For instance, Alvarez *et al.* [98] reported that the differential iso-conversional method is a more appropriate method to determine the kinetic parameters as it observes differences in the trend of the E_a and k_0 as a function of the reaction. Cai *et al.* [99] and Navarro *et al.* [100] also explain the activation energy required for the pyrolysis of biomass. Bartocci *et al.* [58] reported activation energy of solid digestate from energy crop with values as 99 – 204.1 kJ mol⁻¹; Zhang *et al.* [55] reported activation energy of corn stover digestate with values as 99 – 331 kJ mol⁻¹; Osman *et al.* [4] examined activation energy for miscanthus and reported that it was between

40 – 165 kJ mol⁻¹; Jayaraman *et al.* [101] investigated activation energy for poplar wood, hazelnut shell, and wheat bran with values reported as 66.80 – 68.56, 83.73 – 93.25, and 162.17 – 167.4 kJ mol⁻¹ respectively. Munir *et al.* [22] stated that the activation energy of cotton stalk, shea meal, and sugar cane was between 108 – 116 kJ mol⁻¹, while Cortes and Bridgwater [102] reported activation energy for the same biomass in the range of 129 – 156 kJ mol⁻¹. Kok and Ozgur [103] used Ozawa-Flynn-Wall method for hazelnut shell and it was reported that the activation energy was 83.8 kJ mol⁻¹.

Table 3. Activation energy of different biomass feedstocks using different kinetic models

METHOD USED	FEEDSTOCK	ACTIVATION ENERGY (kJ mol ⁻¹)	Reference
Differential-Iso Conversional	Digestate	85 – 190.0	This Work
ASTM-E698	Digestate	169.8	This Work
Ozawa-Flynn-Wall	Digestate	75 -175.0	This Work
Isoconversional	Sawdust	170.1	[18]
Starink model-free	Digestate	99 - 204.1	[58]
Distributed activation energy model	Digestate	99 - 331.0	[55]
Ozawa-Flynn-Wall	Miscanthus	40 -165.0	[4]
Ozawa-Flynn-Wall	Popular Wood	66.8 - 68.6	[98]
Ozawa-Flynn-Wall	Hazelnut Shell	83.73 - 93.3	[98]
		83.8	[22]
Ozawa-Flynn-Wall	Wheat Bran	162.17-167.4	[98]
Non-isothermal and Ozawa-Flynn-Wall	Cotton Stalk	108 – 116.0	[22]
	Shea Meal	108 -116.0	[22]
	Sugar Cane	129 -156.0	[100]

3.4 Isothermal prediction of the SD pyrolysis

The kinetic prediction of SD isothermal pyrolysis reaction progress is possible by the AKTS software when the temperature dependence is derived from the different heating ramp rates. As can be seen in Fig. 10, the prediction suggests that decomposition of the sample requires a temperature greater than 210 °C to commence. It is also predicted that only 20 % ($\alpha = 0.2$) of the SD sample decomposes after a quarter of an hour at 435 °C. At an increased temperature of 615 °C, 70 % ($\alpha = 0.7$) decomposes within the same time period. It is predicted as indicated from the plot that at 660 °C, maximum conversion is eventually achieved, beginning at $\alpha = 0.8$ at ~30 s and approaching $\alpha = 1.0$ by ~15 min. Additionally, it is worth noting that at above 345 °C diminishing returns begin to arise in the pyrolysis of SD. For instance, a step change of 45 °C yields a higher rise in reaction progress at lower temperatures. However, above this temperature of 345 °C, there is a smaller change in reaction progress when considering higher temperatures. An example of this can be seen at 14 minutes, where below this temperature (300 °C), the reaction progress was seen to be 0.56. Whereas at 345 °C, it is measured at 0.69. This means that the alpha value changed by 0.13 over this 45 °C gap. However, the reaction progress at 390 °C was shown to be 0.76 and therefore the alpha value only varied by 0.07 in this 45 °C change. Ultimately the implications of this are that diminishing returns will exist in the pyrolysis of SD and it is, therefore, recommended that if isothermal pyrolysis was to occur, the reaction should be carried out in this range. As there is negligible difference in 615 °C and 660 °C, it is also recommended that the reaction should be conducted at 615 °C to yield positive benefits in terms of reaction time.

Fig. 10. Kinetic isothermal prediction of solid digestate pyrolysis using AKTS software

The calculated activation energy of SD is relatively high, hence the relatively high temperature of 210 °C required for the onset decomposition. Although hemicellulose is typically completely converted by 180 °C [104], the onset decomposition temperature of 210 °C is not unexpected since it is reported that decomposition of cellulose and lignin initiates at 210 °C [105] and ~200 °C [106], respectively. This also accounts for the HHV (11.72 kJ kg⁻¹) and LHV (9.90 kJ kg⁻¹) for SD being lower than that of other biomass; for instance the HHV for miscanthus (16.58 kJ kg⁻¹) and bagasse (17.30 kJ kg⁻¹) [62, 107]. Nevertheless, these values still show that SD is combustible and has a significant energy potential.

Blades *et al.* [61] investigated the potential of a circular economy at a 500 kW standalone on-farm AD plant. This AD plant produces 102429 MJ per day of biogas from a combination of three feedstocks (grass silage, chicken litter and cattle slurry at 20.5, 8.5 and 13.7 tonnes per day, respectively). This biogas production was found to generate ~ 66 kg of solid digestate per tonne of feedstock [108]. As such, based on the lower heating value, this would indicate

the potential of pyrolysis of SD to produce an additional 653.4 kJ per tonne of feedstock, meaning a potential increase of at least 27.9 MJ energy production per day. Furthermore, the post pyrolytic char will have become even more concentrated in metals, such as potassium, which means that this char can become a viable feedstock for the fertiliser industry, as has been previously suggested [4]. This understanding aids the concept of a circular economy for anaerobic digestion and the energy potential of SD, thereby making AD plants more profitable.

4.0 CONCLUSIONS

In this study the physiochemical pyrolysis properties of SD from AD were analysed and the resultant char to assess the potential valorisation of the residual SD. AKTS software was used to calculate the activation energy ($E_a = 85 - 190 \text{ kJ mol}^{-1}$) and pre-exponential factor ($k_0 = -4 - 23 \text{ s}^{-1}$) kinetic parameters for the pyrolysis of SD using the differential iso-conversional model. The calculated parameters were compared with results from alternative models (the Ozawa-Flynn-Wall and the ASTM-E698). Furthermore, the calculated kinetic parameters were used to generate simulations for the reaction progress and reaction rate. A high correlation was observed with the comparison between these simulations and the experimental data, highlighting the accuracy of the calculated kinetic parameters. The kinetic predictions from the AKTS software for the isothermal pyrolysis of SD indicated that a temperature higher than 210 °C is required for the onset of decomposition of the SD sample. From the prediction, it shows that at above 345 °C diminishing returns begin to arise in the pyrolysis of SD and implies that diminishing returns will exist in the pyrolysis of SD. It is, therefore, recommended that if isothermal pyrolysis was to occur, the reaction should be carried out in this range. As there is negligible difference in 615 °C and 660 °C, it is also recommended that the reaction should be conducted at maximum 615 °C to yield positive benefits in terms of reaction time. Importantly, calculations of the thermokinetics data have indicated the potential for an increase of 27.9 MJ per day for a 500 kW AD plant. This information demonstrates the energy potential of SD and

so will aid the concept of a circular economy for AD plants while also contributing to UN SDG no. 7 (clean and affordable energy) and no. 12 (responsible consumption and production). In consideration of future work, greater mechanistic insights for the pyrolysis of SD are still required while it is expected that the kinetics and reaction parameters recommendations from this work will aid the design of reactor systems for pyrolysis of biomass substrate at any scale.

ACKNOWLEDGMENTS

The authors would like to acknowledge The Bryden Centre and Renewable Engine for funding. The Bryden Centre (Project ID VA5048) and Renewable Engine (Project ID VA5033) projects are both supported by the European Union's INTERREG VA Programme, managed by the Special EU Programmes Body (SEUPB) with match funding provided by the Department for the Economy in Northern Ireland and the Department of Business, Enterprise and Innovation in the Republic of Ireland.

The authors would like to thank Dr Mark Russell of School of Natural and Built Environment at Queen's University Belfast for TGA experiments. The continued support of and supply of digestate material from Thomas Cromie (AgriAD) as well as Chris Johnston and Dr Gary Lyons (Agri-food and Biosciences Institute) are also greatly appreciated.

Disclaimer: The views and opinions expressed in this paper do not necessarily reflect those of the European Commission or the Special EU Programmes Body (SEUPB).

NOTATION

Notation		Abbreviations	
A(t)	Reaction Progress	AD	Anaerobic digestion
B(t)	Baseline	AKTS	Advanced kinetics technology solutions
$\frac{dA}{dt}$	Reaction rate (s^{-1})	ASTM	American society for testing materials
E_a	Activation energy ($kJ.mol^{-1}$)	BC	Bituminous coal
$g(\alpha)$	Conversion function	DAEM	Distributed activation energy method
k_o	Pre-exponential factor (s^{-1})	DSC	Differential scanning calorimetry
m_i	Initial weight (mg)	DTG	Derivative thermogravimetry
m_a	Actual weight (mg)	EU	European Union
m_f	Final weight (mg)	FWO	Flynn-Wall-Ozawa
R	Gas constant ($8.3145 J. K^{-1}.mol^{-1}$)	HHV	Higher heating value
S(t)	Differential signal	ICTAC	International confederation for thermal analysis & calorimetry
		JCPDS	Joint committee on powder diffraction standards
		LHV	Lower heating value
		MSW	Municipal solid waste
		NI	Northern Ireland
		RED	Renewable energy directives
		SD	Solid digestate

SS	Sewage sludge
TGA	Thermogravimetric analysis
UK	United Kingdom
UNSDGs	United Nations sustainable development goals
WWTP	Wastewater treatment plant

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