

DEVELOPMENT OF AN ANALYTICAL REACTION KINETICS MATHEMATICAL MODEL BASED ON THERMOGRAVIMETRIC DATA FOR RECLAIMED PLASTIC WASTE FROM ACTIVE LANDFILLS

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ABSTRACT

Landfill mining (i.e. waste reclamation) has been receiving renewed attention in research circles. This strategy provides a solution to the overgrowing problem of land use for the classical solution of landfilling. In addition, it provides added value for the materials recovered with a potential of boosting local economies, especially considering *circular economy* market development. In this work, the degradation kinetics were investigated for solid waste retrieved from three active landfill sites. The landfill sites operate unsanitary processing schemes for the management of the municipal solid waste they receive. Thermogravimetric analysis was used to study the micro-kinetics using standardized ICTAC methods, which yielded an apparent activation energy (E_a) for one of the sites in the range of 100 to 121 kJ mol⁻¹ using the Criado method. Another site showed a range between 87 to 107 kJ mol⁻¹ using the same method. The Avrami-Erofeev expression for degradation mechanism was identified as the prevailing one based on the analysis conducted. Furthermore, an analytical solution model based on reaction order and degradation curves' initial and final set-points was developed to yield the desired parameters in a more realistic manner. We conclude that the type of waste, period of burial and sensitivity of kinetic models used are the most prevailing parameters in determining reaction mechanisms and kinetics expressions, which effect the development of industrial units that use thermal kinetics data for their design of treating various waste components.

Keywords: *landfilling, thermogravimetry, landfill mining, kinetics, thermolysis.*

1 INTRODUCTION

Unsanitary landfilling that utilises open dump sites, is still practiced the world over as a waste management method to dispose of municipal solid waste (MSW). This practice is still undertaken in many developing world countries namely on the Asian continent [1]–[3]. This practice is also associated with various adverse environmental effects such as leachate infiltration to groundwater [4]–[5] and landfill occupation beyond operational lifespan [6]. Landfilling plastic solid waste (PSW) is also considered to be one of the main environmental threats that could compromise a site for future rehabilitation and causes various economical loss due to lack of proper management [7]–[11]. The majority of these plastics are thermoplastic in type and could be valorised in thermo-chemical treatment (TCT) units to produce various types of fuels and energy [12]–[14]. Prime examples of such plastics are low density (LDPE) and high-density polyethylene (HDPE), polypropylene (PP), and polyvinyl chloride and alcohol (PVC and PVA). Readers are referred to Al-Salem et al. [15]–[17] for a review on the state of art regarding TCT technologies. One of the main solutions that present itself as an advantageous option for land rehabilitation and reduction of environmental burdens, is landfill mining [18]–[21]. The reclamation of the MSW from the landfill site would reduce the occupied space and could potentially be used as a feedstock material for various fuel and energy production processes [22], [23]. Various research efforts the world over are reporting on PSW



reclamation processes and their potential use post mining of landfill sites [23], [24]. On the other hand, technical literature is quite lacking a major element that can determine the appropriateness of TCT application of such waste. The fact that basic material degradation kinetics are lacking for PSW reclaimed from landfill sites, is a major research gap that needs to be addressed.

In this work, thermogravimetric analysis (TGA) was used to study the micro-kinetics of PSW reclaimed from two active landfill sites by applying the standardized international confederation for thermal analysis and calorimetry (ICTAC) methods [25], [26]. The methods of Criado and the method of Al-Salem and Khan [27] which is based on an analytical degradation reaction kinetics model used for solving complex reaction systems, were used in this work. The results are considered to be the cornerstone for reactor design and simulation of such results for industrial scale-up in the future.

2 MATERIALS AND METHODS

The waste was mined from two active unsanitary landfill site, namely Mina Abdullah (MAB) (lat. 29° 19' 33.24" N; long. 47° 36' 41.04" E) and Al-Jahra (JAH) (lat. 28° 59' 54.564" N; long. 48° 6' 25.146" E) landfill sites within borders of the State of Kuwait. Readers are referred to Al-Salem et al. [24] for a detailed map location of the sites and to Al-Salem et al. [28] and Al-Jarallah and Aleisa [29] for more information on the daily activities and operation of the sites. The mining and reclamation of the buried SW was conducted following internationally recognised protocols previously published and applied in research and development works [11], [24], [30]. The SW was mined from a singular ditch where the MSW was buried for six months (under 1 meter of soil), and the sampling of the material was conducted after removing the topsoil (≈ 10 cm) [31]. Details on the landfill site and pollutants levels including soil characteristics are shown elsewhere [32]–[34]. Fig. 1 shows a pictorial depiction of the process giving an overall view and black matter was noticed of the reclamation/mining process. The reclaimed waste (30 kg) was air blown, washed and conditioned in accordance with previous waste mining protocols [24], [31]. All samples during this work were stored in laboratory conditions (22–23°C/50% relative humidity) and kept in sealed containers. The PSW was shredded using a Vema Company machine operated at 580 rpm speed (mesh size: 5–15 mm) [31]. The majority of the reclaimed waste was PSW ($> 20\%$) for both sites as reported in Al-Salem [35]. The materials were then subjected to cryogenic milling to a particle size using the protocol shown previously in Al-Salem et al. [24] to give particles of c. 50 μm in diameter which was verified using micrograph analysis [24], [31]. Table 1 shows an example of the mass of samples reclaimed (JAH site), and the percentile analysis of all waste categories in this work is shown in Table 2 for JAH site as an example. Elemental Analysis was conducted by dynamic flash combustion using a 2 ± 0.1 mg in a Thermo Flash 2000 analyser as per ASTM D5373 [36] and ASTM D5291 [37]. Ash Content was determined using gravimetric analysis with a muffle furnace as per ASTM D5630 [38] for plastics and ISO/DIS 1762 [39] for the adjusted temperature of $525 \pm 25^\circ\text{C}$ by testing 4 ± 0.1 g of the reclaimed PSW (Table 3).

Thermal degradation of the samples was investigated using a Mettler-Toledo TGA 3+ Model set to record the data every second under multiple heating rates (β) (i.e. 5, 10, 15, 20 and $25^\circ\text{C min}^{-1}$) conforming with the approved methods of the ICTAC [25], [26]. These were conducted to diminish sample size influences on the weight loss and kinetic analysis. A constant flow of nitrogen (N_2 , dry–99.99% purity) with a flow rate of 50 ml min^{-1} was maintained throughout the experiments. The measurements were conducted in triplicate using 1 ± 0.1 mg samples from room temperature (RT) to 600°C and showed high



repeatability. The crucibles used in all experimental runs were made of alumina with a 70 μl size. Mass loss (%) and first derivative (DTG, % $^{\circ}\text{C}^{-1}$) were recorded constantly to the properties of the thermogram. The TGA unit was externally calibrated and maintained regularly before each experimental batch using standard reference materials as per ISO 11358 [40].



Figure 1: Pictorial depiction of the landfill mining process showing (left) soil top view of JAH landfill site, (middle) ditch excavation process at MAB, and (right) spade tractor operation/excavation of waste at MAB.

Table 1: Weight measured (kg) during the shredding of waste samples (Al-Jahra landfill site).

Date of sampling	Site		Flake size	Shredding cycles
4 Nov. 2018	JAH landfill site		5–90 mm	3
	Initial weight	After washing	After drying	After shredding
Plastic	6	12.48	3.7	3.45
Metal	1.4	1.4	1.2	
Paper	1.4	/	1.2	
Wood	8.2	/	8.2	
Organic	0	/	0	
Others	5.1	/	5	

Table 2: Percentile analysis of waste reclaimed from Al-Jahra landfill site.

Waste type	Percentile before washing	Waste type	Percentile after drying
Plastic	27.1	Plastic	19.1
Metal	6.3	Metal	6.2
Paper	6.3	Paper	6.2
Wood	37.1	Wood	42.4
Organic	0.0	Organic	0.0
Others	23.0	Others	25.9

Table 3: Elemental analysis and physio-chemical properties conducted on reclaimed plastic solid waste.

Sample	Total nitrogen (TN) %	Total carbon (TC) %	Total hydrogen (TH) %	Moisture at 105°C
Al-Jahra	0.123 ± 0.02	75.137 ± 0.09	11.412 ± 0.35	0.155 ± 0.02
MAB	0.084 ± 0.00	77.902 ± 0.16	12.968 ± 0.15	0.005 ± 0.00
Sample	Moisture at 105°C	Organic matter at 550°C	Ash at 550°C	Oxygen (O) %
Al-Jahra	0.155 ± 0.02	93.795 ± 0.12	6.050 ± 0.10	8.85 ± 0.00
MAB	0.005 ± 0.00	95.180 ± 0.06	4.815 ± 0.06	6.27 ± 0.60

3 DEGRADATION REACTION KINETICS ANALYSIS

The plastic fraction under weight loss investigation is reported with respect to the conversion of the polymeric material (α) thus [41]–[43]

$$\alpha = \frac{m - m_o}{m_o - m_f}, \quad (1)$$

where m , m_o and m_f are the mass of polymeric material at a specific reaction time (t), initial and final mass of the polymer at the investigated temperature, respectively. The degradation rate was defined with respect to rate of reaction by incorporating a first order Arrhenius equation [27], [43]–[46]

$$\frac{d\alpha}{dt} = A_o \exp\left(\frac{-E_a}{RT}\right) f(\alpha), \quad (2)$$

where A_o stands for the frequency factor (min^{-1}), E_a is the apparent activation energy (kJ mol^{-1}), T is the reaction temperature at desired time (K) and $f(\alpha)$ is the reaction model that represents the degradation mechanism following reaction order (n). Multiple heating rate (β) values were used in this work as recommended by various authors for accuracy reasons [44]. ICTAC Kinetics Committee recommendations for the application of Criado's approach has identified that the Avrami-Erofeev expression for $f(\alpha)$ be applied for the estimation of Arrhenius parameters for polymer degradation kinetics from the following:

$$\frac{d\alpha}{dt \cdot f(\alpha)} = f(T), \quad \int \frac{d\alpha}{(2(1-\alpha))^n \sqrt{1-\alpha}} = \int A_o e^{\frac{E}{RT}} dt. \quad (3)$$

Apparent activation energy calculated by this method showed similar trends. The reader is referred to Al-Salem and Khan [27] for the full derivation of the model. The LHS of the eqn was plotted against the inverse of Temperature in K and the slope yielded the energy of activation and pre-exponential factor for each set of experiments. The whole exercise was repeated for the estimation of non-isothermal kinetics of all samples where n is not fixed but optimized

$$\frac{d\alpha}{dt} = -A_o e^{-\left(\frac{E}{RT}\right)} \cdot \alpha_n. \quad (4)$$

Eqn (4) is the rate expression for non-isothermal, if $n = 1$

$$\alpha = \exp\left(-A_o e^{-\left(\frac{E}{RT}\right)} t\right) \text{ and for } n \neq 1, \quad \alpha = \left((n-1) \cdot A_o e^{-\left(\frac{E}{RT}\right)} t + 1\right)^{-\frac{1}{(n-1)}}. \quad (5)$$

The experimental data were smoothed using mathematical function of first order kinetics presented previously and was normalized using initial and final weights of the experimental dataset (W_{i0} and W_{tfinal}) for 5°C/min as seen below. The reader is referred to Al-Salem and Khan [27] for the full derivation of the analytical solution model

$$W(t) = \exp\left(-A_0 \cdot \exp\left(-\frac{E}{RT}\right)t\right)(W_{i0} - W_{tfinal}) + W_{tfinal} \quad (6)$$

The smoothed data plots for three landfill sites presented in the next section were used for testing different reaction kinetics models. The exact reaction mechanism based on the best fit to the smoothed experimental data was selected and all the chemical kinetic parameters were evaluated.

4 RESULTS AND DISCUSSION

Thermal characterization of the reclaimed PSW was conducted using TGA describing the thermal decomposition of the material by measuring the weight loss as function of sample temperature or reaction time under isothermal conditions. It also determines the temperatures that depicts the steps (weight loss/change). The thermal behaviour of the material identified from the TGA thermogram and DTG (i.e. first derivative curve) are essential for evaluating the thermal stability of the material from which the thermal profile is also identified. The experimental campaign included samples of PSW from different landfills. The comparison with previous results from literature was made. Samples in this work have also been tested for pyrolytic properties and estimation of the kinetic parameters under five heating ramps. The resulting data helps in determining the influence of the effect of burying of plastics on the physio-chemical properties and thermally degradation characteristics. For further discussion on the aforementioned properties, the reader is referred to the cited references of our previous work [24], [31], [35].

TGA data of used plastic from three landfill sites were studied using smoothening techniques and were used for the evaluation of decomposition reaction parameters. Fig. 2 shows the raw experimental TGA data for PSW tested from the MAB and JAH sites. The result of MAB site shows that a one-step mass loss exists in the beginning due to volatilization in the temperature range from 230 to 350°C. A minor second degradation step was also detected within the temperature range of 370 to 450°C. JAH site samples showed a mass loss due to volatilization in the temperature range from 250 to 360°C (Fig. 2). In the work of Tuffi et al. [47] the thermal analysis of polymeric mixtures from waste packaging plastics was performed. The mixture mainly consists of waste polymers (PP, polyethylene film (PE), PET and PS). In addition, the thermal behaviour of three synthetic mixtures demonstrating commingled postconsumer plastics wastes (CPCPWs) from material recovery facilities, were considered. A 10 mg of powder samples in alumina crucibles was prepared and tested in their work. The thermal analysis experiments were carried out under a N₂ flow rate of 60 ml/min in the temperature range 25 to 600°C. The degradation temperatures of single polymers and their mixtures were determined at heating rate 10°C/min. The elemental and proximate analysis of the samples were performed and gave volatile matter of approximately 100% except for PET with a very low ash content is. The TG curves of the four polymers show that the degradation occurred in the temperature range 400 to 500°C) in a one-step mass loss. Furthermore, the onset temperatures for PE film, PP, PS and PET were (which are equivalent to 477, 456, 411, 434°C respectively). This is in-line with TGA analysis conducted in this work implying that the samples are of Polyolefin PE origin as supported by the thermal profile depicted in Table 4. The thermal behaviour of the synthetic mixtures, CPCW1, CPCW2 and CPCW3 were also determined.



The degradation occurred in two steps mass losses for CPCW2 and CPCW3 where in CPCW1 is one-step. The onset temperature for CPCW1 was 452.85°C. The first step of CPCW2 and CPCW3 in a similar range to the degradation temperature for PS and PET (418°C) where, the second step is close to PP and PE film (461–465°C). The experiments occurred at different heating rates (2, 5, 10 and 15°C/min).

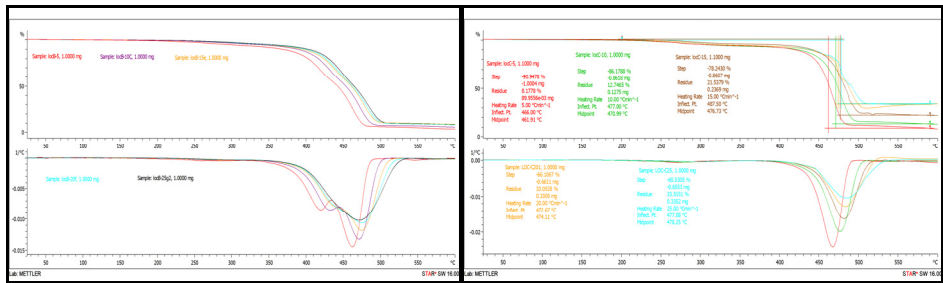


Figure 2: Experimental TGA results for MAB (left) and JAH (Right) landfill sites showing the thermogram and first derivative (DTG) curves.

Table 4: Thermal degradation and stability profile showing onset temperature (T_{os} , °C), inflection point (T_{if} , °C), midset temperature (T_{ms} , °C), and end of set temperature (T_{ed} , °C).

β (°C/min)	T_{os} °C	T_{if} °C	T_{ms} °C	T_{ed} °C	T_{os} °C	T_{if} °C	T_{ms} °C	T_{ed} °C
5	403.9	454.1	448.1	498.6	404.5	453.5	449.3	498.0
10	415.0	466.0	460.83	513.1	415.8	466.3	462.0	512.5
15	421.7	474.5	468.5	522.0	422.5	473.5	469.7	521.2
20	426.6	482.0	474.0	528.3	427.3	480.0	475.3	527.6
25	430.41	484.1	478.33	533.3	431.2	484.5	479.5	532.5

Blazevska-Gilev and Spaseska [48] studied the thermal degradation of polyvinyl chloride by dynamic thermogravimetry (TGA), up to around 450°C at heating rates between 4 and 10°C/min using 100 ml/min of argon gas. The first degradation step ended at around 300°C, with a weight loss of about 65%, while the second step ended with a 85% total weight loss. It has been reported that the degradation of PVC is a more complex than the other plastic [48]. Thermal analysis for the degradation of starch/poly (vinyl alcohol) (PVA) blends were carried out using TGA under atmospheric conditions by Taghi Taghizadeh and Abdollahi [49]. Their dynamic experiments were conducted at different heating rates (5, 10 and 15°C/min) from RT to 600°C. The pure starch and starch/PVA blend curves showed a three-step decomposition curve. The first step mass loss was around 260°C due to the loss of volatile matter and water. The second step mass loss occurred in the temperature range of 260°C to 360°C described the polymer decomposition and was attributed to deterioration of the polymer’s backbone. Another study in our earlier work investigated the TGA degradation of PVA [50]. The experiment was conducted between 40 to 700°C at a heating rate of 10°C/min under N₂ flow rate of 50 ml/min. The first step mass loss was due to the water content in the sample at temperature of 100°C. At a temperature around 300°C, the sample started to further degrade because of the acetate group with a third step between 350°C and 450°C, which related to the PVA degradation rate.

Furthermore, the onset temperature was evaluated to be $301 \pm 2^\circ\text{C}$ with a T_{peak} at 334 to 440°C [50]. Kuźnia and Magdziarz [51] studied three types of PSW based polyolefins as well using a combustion set-up. The beginning of the degradation process was around 250°C due to the combustion of the alkane groups; the temperature of spontaneous combustion is lower than 250°C for alkanes such as n-hexane and n-heptane, n-octane, n-nonane, n-decane and n-undecane. The end-set temperature of PE was estimated to be 550°C and approximately 400°C for PP [51]. Tables 5–8 and Fig. 3 show some of the results from the mathematical modelling exercise executed in this work. The average value of Activation Energy for the MAB samples based on n^{th} order kinetics model was 260 kJ mol^{-1} and 240 kJ mol^{-1} based on the 1^{st} order model, where the optimum value of n was equal to 1.1. The average value of Activation Energy using the Criado model for the MAB sample is $109.828 \text{ kJ mol}^{-1}$, while the average activation energy for the JAH sample is 240 kJ mol^{-1} using the first order reaction model. The average Activation Energy of the JAH samples based on n^{th} order kinetics model was 230 kJ mol^{-1} where the optimum value of n was equal to 1.1. The average value of Activation Energy using Criado model for JAH is $97.922 \text{ kJ mol}^{-1}$. MAB samples showed a single thermal degradation step that could be presented by a general pyrolytic reaction. The JAH samples clearly followed two stages of thermal degradation showing similar behaviour as past reports [52]. The data indicate that there are different mechanisms of degradation for plastics buried in sand in dry and arid climates. Al-Salem and Khan [27] have analysed the TGA data of polymeric blends of different plastics in various proportions. They reported two sets of Arrhenius coefficients of parallel reactions. Agrawal [53] has proposed simple reaction mechanisms for non-isothermal kinetics of thermal degradation which are strongly influenced by physical factors such as particle size, and geometry of the sample holder. These physical factors could be defined as diffusion-limited or by other mechanisms that strongly influence $f(\alpha)$, which are crucial for the evaluation of kinetic parameters for the reaction model. Zong et al. [52] have reported thermal degradation kinetics of polyethylene and silane-crosslinked polyethylene samples based on n^{th} order of reaction. The orders of reaction were lower than reported in the literature, ranging from 0.24 to 0.59 and the corresponding Activation Energy values were similar to those reported in the literature ranging between 226 to 294 kJ mol^{-1} . Further results extracted from similar modelling approach on polyolefin polymers are depicted elsewhere [41], [42].

Table 5: Summary of obtained kinetic parameters for MAB site using present mathematical model.

Ramp	Pre-exponential (s^{-1})	Activation energy (kJ mol^{-1})
5°C/min	2.17678×10^{16}	280
10°C/min	9.74489×10^{15}	275
15°C/min	4.42434×10^{15}	270
20°C/min	2.02573×10^{15}	265
25°C/min	9.32373×10^{14}	260



Table 6: Summary of obtained kinetic parameters for MAB site using present mathematical model with reaction order equal to 1.1 and Criado method results.

Ramp for $n = 1.1$ expression	Pre-exponential ($\alpha^{-0.1}\text{s}^{-1}$)	Activation energy (kJ mol^{-1})	Activation energy from Criado method kJ mol^{-1}
5°C/min	4.93×10^{15}	270	121.46
10°C/min	2.29×10^{15}	265	119.80
15°C/min	1.09×10^{15}	260	104.25
20°C/min	5.08×10^{14}	255	102.76
25°C/min	2.41×10^{14}	250	100.84

Table 7: Summary of obtained kinetic parameters for JAH site using present mathematical model.

Ramp	Pre-exponential (s^{-1})	Activation Energy (kJ mol^{-1})
5°C/min	8.82×10^{13}	250
10°C/min	4.00×10^{13}	245
15°C/min	1.84×10^{13}	240
20°C/min	8.57×10^{12}	235
25°C/min	4.01×10^{12}	230

Table 8: Summary of obtained kinetic parameters for JAH site using present mathematical model with reaction order equal to 1.1 and Criado method results.

Ramp for $n = 1.1$ expression	Pre-exponential ($\alpha^{-0.1}\text{s}^{-1}$)	Activation energy (kJ mol^{-1})	Activation energy from Criado method kJ mol^{-1}
5°C/min	1.99×10^{13}	240 kJ mol^{-1}	107.08
10°C/min	9.04×10^{12}	235 kJ mol^{-1}	106.50 kJ mol^{-1}
15°C/min	4.48×10^{12}	230 kJ mol^{-1}	99.60 kJ mol^{-1}
20°C/min	2.16×10^{12}	225 kJ mol^{-1}	89.04 kJ mol^{-1}
25°C/min	1.03×10^{12}	220 kJ mol^{-1}	87.38 kJ mol^{-1}

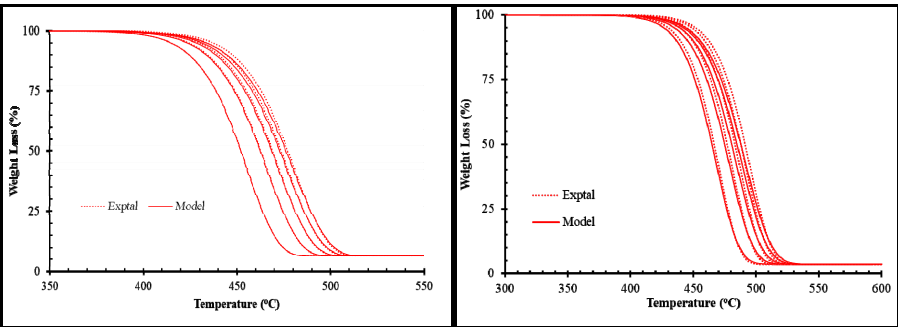


Figure 3: Chemical reaction model for 1st (eqn (5), left section) and nth (eqn (5), right section) order reaction model for all heating rates used (MAB site).

5 CONCLUSION

Two landfill sites that are characterised in being both unsanitary and in located in an arid-land, were mined and the solid waste from both sites was reclaimed. The plastic waste was conditioned and subjected to thermogravimetry to study its thermal stability and behaviour. The thermal properties detected were in-line with past efforts; and showed that the materials were of polyolefin polymer origin namely polyethylene. The degradation was modelled by two kinetic of reaction models were, using an analytical solution model that smoothened the thermograms and determined the properties based on optimising the weight loss steps; and a second solution based on the Criado approach. The analytical model showed more realistic results following the mass losses detected and based on the activation energy estimated. This is deduced based on the similarity of energies estimated and the estimation of the model for each thermal loss (step) on its own, accounting for each polymer's degradation as a single loss. Furthermore, the results of both kinetic approaches shows that the materials have similar properties to virgin polyolefin polymers, making it appropriate to further design and investigate the scale-up opportunities of the thermolysis design for mined waste to fuel and energy. This also paves the way for future plans in managing sold waste from various landfill sites to reduce the burdens on land and resources.

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