Ain Shams Engineering Journal xxx (xxxx) xxx

Contents lists available at ScienceDirect

Ain Shams Engineering Journal

journal homepage: www.sciencedirect.com

Engineering Physics and Mathematics

Thermal degradation kinetics of *real-life* reclaimed plastic solid waste (PSW) from an active landfill site: The mining of an unsanitary arid landfill

S.M. Al-Salem [a,*], H.J. Karam [a], M.H. Al-Wadi [a], S. Alsamaq [b], G. Jiang [c], J. Wang [b], G.A. Leeke [c]

[a] *Environment & Life Sciences Research Centre, Kuwait Institute for Scientific Research, P.O. Box: 24885, Safat 13109, Kuwait*
[b] *European Bioenergy Research Institute, Aston University, Aston St., Birmingham B4 7ET, UK*
[c] *School of Chemical Engineering, University of Birmingham, Edgbaston, Birmingham B15 2TT, UK*

ARTICLE INFO

Article history:
Received 4 March 2020
Revised 8 April 2020
Accepted 19 May 2020
Available online xxxx

Keywords:
Plastic
Degradation
Kinetics
Pyorlysis
Mining

ABSTRACT

Landfilling is viewed nowadays as a serious threat associated with various burdens and stressors on the urban environment. To date, there is little information available on actual value of landfilled waste namely plastic solid waste (PSW) resulting from mining operations. In this work, PSW reclaimed from an active unsanitary landfill site (MAB) has been studied with the aim of determining its thermal profile and degradation behaviour for future utilisation in thermo-chemical conversion (TCC) processes. The materials were characterised by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) in accordance with internationally approved test methods in a simulated pyrolytic environment. In addition, chemical analysis using Fourier Transform Infrared Spectroscopy (FTIR) was applied to study the nature of the materials reclaimed. The degradation kinetics of the reclaimed PSW were studied with the aim of determining the apparent activation energy (Ea) of the pyrolytic reactions. The Ea values determined ranged from 199 to 266 kJ mol^{-1} which is in-line with pyrolytic reactions applicable for future use in fuel recovery units. TGA showed a clear shift in thermograms indicating a clear change in the degradation mechanism. The physico-chemical studies conducted on the materials also favours TCC treatment over other conventional end of life options such as physical (mechanical) recycling or incineration. The degradation mechanism was also determined from the Criado method showing that *Avarami-Erofeve* was the model that best represents PSW degradation. Overall, this work points towards future intervention schemes for reclaimed municipal solid waste (MSW) and in particular PSW favouring TCC technologies.

1. Introduction

Municipal Solid Waste (MSW) landfilling is still considered to be one of the most popular waste management (WM) options the world over. However, reliance on this technique varies between regions of the world on the basis of energy demand, supporting networks availability, infrastructure and compliance to regional regulations. Within a European Union (EU) and UK context, the reliance has decreased on MSW landfilling to a great extent within the past five years. According to recently published reports [1,2], 46% of MSW in the EU is recycled and only 25% of different types of waste is directed to landfill sites. In addition, EU legislations have enforced the reduction on landfilling reliance across the continent in general by encouraging sustainable waste management through implementing various Directives [3,4]. On the

---

Abbreviations: A, Ash Content (%, dry basis); DSC, Differential Scanning Calorimetry; E_a, Apparent Activation Energy (kJ mol^{-1}); EU, European Union; f(α), Reaction Model Representing Degradation Mechanism; FC, Fixed Carbon Content (%, dry basis); HDPE, High Density Polyethylene; LDPE, Low Density Polyethylene; MSW, Municipal Solid Waste; PE, Polyethylene; PET, Polyethylene Terephthalate; PP, Polypropylene; PS, Polystyrene; PSW, Plastic Solid Waste; PVC, Polyvinyl Chloride; SW, Solid Waste; T, Reaction Temperature at Desired Time (K); TCC, Thermo-Chemical Conversion; TGA, Thermogravimetric Analysis; T_m, Melting Point (°C); VM, Volatile Matter (%, dry basis); WM, Waste Management; WtE, Waste to Energy; α, Conversion Rate.

[*] Corresponding author.

E-mail address: ssalem@kisr.edu.kw (S.M. Al-Salem).

Peer review under responsibility of Ain Shams University.

Production and hosting by Elsevier

https://doi.org/10.1016/j.asej.2020.05.011

Please cite this article as: S. M. Al-Salem, H. J. Karam, M. H. Al-Wadi et al., Thermal degradation kinetics of *real-life* reclaimed plastic solid waste (PSW) from an active landfill site: The mining of an unsanitary arid landfillreal-life reclaimed plastic solid waste (PSW) from an active landfill site –>, Ain Shams Engineering Journal, https://doi.org/10.1016/j.asej.2020.05.011

other hand, Asian countries differ in their level of sophistication when it comes to WM technologies. In Japan, 70% of solid waste (SW) is directed towards waste to energy (WtE) schemes which surpasses the US and Sweden by far where 13% and 50%, respectively, is directed to the same route [5]. However, some 1.2% of SW is landfilled in Japan which represents an extreme estimate of the scale when compared to other parts of the Asian continent such as Kuwait and Qatar where reliance on landfilling represents about 100% for their WM treatment [6,7].

Plastic solid waste (PSW) represents a hefty proportion of SW directed to landfill sites in many developing world countries representing 12% of total SW generated [8]. Discarding PSW without materials recovery or directing it to thermal or thermo-chemical conversion (TCC) without the aim of chemicals recovery, represents a major loss in economical terms and goes against the newly adapted concept of '*circular economy*'. A key issue remains as to how to valorise the waste in landfill sites and recover maximum value out of it whilst reducing land use, environmental stressors and lechate migration to groundwater aquifers. This results in the concept of excavating and mining landfill sites, in an attempt to treat landfill sites as a temporary storage location until the technology to valorise the waste is within reach [9–13].

The majority of plastics consumed on daily basis are of thermoplastic in origin which allow re-melting and processing them post-reclamation [14–16]. These thermoplastics include the following types of plastics: low density (LDPE) and high-density polyethylene (HDPE), polyethylene terephthalate (PET), polypropylene (PP), polystyrene (PS), and polyvinyl chloride (PVC). Readers are referred to Canopoli et al. [3] for a review on the fate of plastics in landfill sites. The recent work of He et al. [17] has also pointed towards PSW in landfill sites being a source of microplastics (<5 mm) after examining leachate of six Chinese sites. Canopoli et al. [18] analysed samples from MSW landfills in the UK to report the type and degree of degradation of the plastics. The dominant plastic types were polyethylene (PE) and polypropylene (PP) with samples analysed from sites >10 years having greater extent of degradation by carbonyl index (CI) evaluation. Kamura et al. [19] determined the contents from landfill sites. Their work showcased the fact that rare metals were present at higher rates in when compared to naturally occurring ones. Mönkäre et al. [20] recovered fine fractions (<10–24 mm) from landfill mining which represent 40–70 wt% of landfill contents. Their work has scaled-up anaerobic and aerobic treatment of such materials coupled with physical treatment to reduce associated harmful emissions. Quaghebeur et al. [21] mined Flemish-Belgian sites and have reported that PSW represented 25% of the total mined landfill waste. Plastics buried at landfills have been reported to undergo a twenty years' degradation process related to thermo-oxidative degradation and anaerobic conditions summarised in Appendix A of this manuscript.

Excavated PSW is expected to be of lower integrity when compared to virgin converted plastic products. Therefore, it is considered a good engineering practice to valorise this type of SW by TCC methods (e.g. pyrolysis) which require minimal pre-treatment to provide high-value products. Such methods are known to produce light gases that simulate refinery fuel gas, tars which comprise aliphatic and aromatic waxes and oil, and solid pyro-char equivalent to carbon black [22–24]. To date, only few studies have attempted to detail the characteristics of reclaimed PSW or investigated its potential for fuel recovery. In addition, to do so it is essential to investigate the thermal behaviour and profile of such materials to determine its fate when introduced to TCC processes and provide a detailed guidance for reactor design. The first step for such studies is the determination of the thermal profile and degradation kinetics of the reclaimed PSW. Bosmans et al. [24] have investigated the degradation kinetics of refuse derived fuel (RDF) processed from two types of plastics reclaimed from a mixture of municipal and industrial sources. The kinetics parameters were estimated using non-linear least squares algorithms. The apparent activation energy (E_a) of the kinetics model developed varied between 99 and 353 kJ mol^{-1}. Chabbra et al. [25] studied the thermal degradation behaviour and kinetics of collected PSW from a waste site that included a range of plastic materials (e.g. LDPE, HDPE and PP). The degradation kinetics were investigated by studying the fraction of plastic weight rate against degradation time. The determined E_a values for LDPE, HDPE and PP were 232.2, 313.6 and 227.3 kJ mol^{-1}, respectively. On the other hand, Gunasee et al. [26] observed a synergetic effect using thermogravimetric analysis (TGA) coupled with mass spectroscopy (MS) whilst investigating PSW components. Miteva et al. [27] investigated the degradation and kinetics of polyolefin PSW using two kinetic models, namely the Flynn–Wall–Ozawa and Kissinger–Akahira–Sunose methods. There were no observed changes in the results obtained by both methods. The current study aims to investigate the thermal profile and degradation kinetics of real-life reclaimed PSW by determining the degradation behaviour of materials excavated from an active landfill. The materials were characterized by TGA and differential scanning calorimetry (DSC) in accordance with internationally approved test methods in a simulated pyrolytic environment [28–31]. The apparent activation energy (E_a) of the degradation reaction was also determined by applying model free and model dependent analytical kinetic models, and were compared with each other and available technical literature. To the best of the authors knowledge, no such work of this nature has been attempted in the past. The work in this study also aids in future scale-up plans, in understanding the behaviour of reclaimed PSW in TCC units and how to best approach its treatment as a source of chemical products and fuels.

2. Materials and methods

2.1. Description of studied landfill

The materials were mined and reclaimed from the Mina Abdullah (MAB) landfill site within the southern boarders of the industrial estate in the State of Kuwait (*lat.* 29°19′ 33.24″N; *long.* 47°36′ 41.04″E) as depicted in Fig. S1 of the Supplementary Materials File. The landfill site operates an unsanitary landfill where commingled MSW collected from daily kerbside schemes are directed to the landfill site. The materials are landfilled after weighing on dedicated bridges with no separation for recylables. The MAB landfill was opened for operation in 1991 occupying 1.11 km^2 area and is still operational. It is considered the smallest landfill of Kuwait that deals with MSW management. It is located some 70 km from the city and serves the suburban areas of the country. Unsanitary landfilling is conducted in Kuwait utilizing disposal sites and ditches without lining or segregation. The landfills are currently dedicated for MSW generated within Kuwait which includes components reported previously by Al-Jarallah and Aleisa [32]. For more information on quantities and daily activities and operation for MAB, readers are referred to Al-Salem et al. [33] where quantities of waste and detailed operation of the landfill site are described.

2.2. Sampling protocol and materials acquirement

The overall sampling and analysis protocol is shown schematically in Fig. S2. The mining and reclamation of the buried SW was conducted following internationally recognised protocols previously published and applied in research and development works [21,34–36]. The sampling was conducted after the selection of an

Please cite this article as: S. M. Al-Salem, H. J. Karam, M. H. Al-Wadi et al., Thermal degradation kinetics of *real-life* reclaimed plastic solid waste (PSW) from an active landfill site: The mining of an unsanitary arid landfillreal-life reclaimed plastic solid waste (PSW) from an active landfill site –>, Ain Shams Engineering Journal, https://doi.org/10.1016/j.asej.2020.05.011

active landfill site within MAB and the mining process was executed with a cactus grab spade crane tractor vehicle [34]. The SW was mined from a singular ditch where the MSW was buried for six months (under 1 m of soil), and the sampling of the material was conducted after removing the top soil (≈10 cm) and black matter was noticed. The mining process was conducted on the 13th November 2018 and the granulometric distribution of the landfill sites in Kuwait has been reported in the past [34]. The landfill site was also noted to be of a sandy texture which confirms with previous analysis conducted on sand composition in Kuwait which also contains a subsurface horizon of *Gatch* which is a caliche layer [37,38]. Fig. 1 depicts various stage of the mining and sampling of the SW conducted in this work.

2.3. Waste samples assessment, segregation and conditioning

The reclaimed waste (30 kg) was initially air blown and washed using a Jet-X (JX 8070 model) high pressure washer under two bar of water stream to ensure all dust particles were removed from the surface of the materials. After which, the reclaimed materials were washed using regular tap water pre and post open air drying for three continuous days. All samples during this work were stored in laboratory controlled conditions (22–23 °C/50% relative humidity) and kept in sealed rigid plastic containers. Weighing scales were used to quantify the amount of the reclaimed waste. The waste samples were segregated and categorised into six types in accordance with accepted international waste segregation and handling protocols for waste management [39–41]. These categories were plastics, metal & white goods, paper & cardboard, wood, organics and miscellaneous (others). PSW composed some 20% of the total reclaimed SW and was later removed and shredded using a three V cutting knifes Vema Company shredding machine operated at 580 rpm speed, with a mesh size of 5–15 mm for an approximate time of 3 min. The waste samples were yielded as flakes with an approximate size of 4–90 mm (manually measured) after three shredding cycles. The PSW flakes were then cryogenically milled using a Retsch Co. Cryomill equipped with a 50 L liquid nitrogen tank (stainless steel grinding ball size = 25 mm) with a grinding and pre-set program as follows: Number of cycles (9), pre-cooling time and frequency (30 s and 5 Hz), cycle time (3 min and 25 Hz) and pre-set time (1 min and 5 Hz) [34]. The material produced was of an average size of 50 × 50 (±8) mm as verified by placing them under JEOL-JSM-6010 LA SEM using a voltage of 15 kV (to prevent damage of polymeric film) resulting in various micrographs taken with a 100–10,000- fold magnification. The sample surfaces were placed on a double sided carbon tape positioned on a metal holder then coated with a layer of platinum with a thickness of 8–10 nm by sputtering using a JEOL-JFC-1600 sputter coater for 30 s. Fig. S3 in the Supplementary Materials File shows the shredding unit assembly and Fig. S4 depicts the average size obtained for the PSW after cryogenic milling. In addition, Table S1 shows the mass of the samples reclaimed, and the percentile analysis of each waste category in this work is shown in Table S2.

2.4. Elemental analysis, physcio-chemical properties and calorimetry

Elemental Analysis was conducted by dynamic flash combustion using a 2 ± 0.1 mg in a Thermo Flash 2000 analyser as per ASTM D5373 [42] and ASTM D5291 [43]. Ash Content (A) was determined using gravimetric analysis with a muffle furnace as per ASTM D5630 [44] for plastics and ISO/DIS 1762 [45] for the adjusted temperature of 525 ± 25 °C by testing 4 ± 0.1 g of the reclaimed PSW. The fixed carbon (FC) content was estimated using Eq. (1) based on the dry weight basis [46].

$$FC(\%) = 100\% - VM(\%) - A(\%) \quad (1)$$

where VM (%) is the volatile material calculated as the difference between the raw material and the fixed carbon (FC) content. The ash (A) is experimentally determined from the averaged

Fig. 1. Pictorial Analysis of Sampling Procedure Followed For Waste Reclamation Using (a) Spade Tractor to Excavate The Landfill Ditch; (b) Obtaining Black Matter Where Waste is Buried; (c) Reclaiming The Waste, and (d) Segregating The Material Before Washing. Published with permission from. Source Al-Salem et al. [34] (Published with permission)

Please cite this article as: S. M. Al-Salem, H. J. Karam, M. H. Al-Wadi et al., Thermal degradation kinetics of *real-life* reclaimed plastic solid waste (PSW) from an active landfill site: The mining of an unsanitary arid landfillreal-life reclaimed plastic solid waste (PSW) from an active landfill site –>, Ain Shams Engineering Journal, https://doi.org/10.1016/j.asej.2020.05.011

components of the weight loss thermograms obtained from thermogravimetry conducted between room temperature (RT) to 850 °C using 1 mg of sample weight (Fig. S5). The higher heating value (HHV, MJ kg^{-1}) of the materials tested was also calculated using three distinct methods; namely the Dulong's, Boie and the Institute of Gas Technology (IGT) formulas as per the following [47]:

$$HHV\,(\mathrm{MJ\,kg^{-1}}) = 0.336\,C\ + 1.418\,H\ + 0.094\,S - 0.145\,O \tag{2}$$

$$HHV\,(\mathrm{MJ\,kg^{-1}}) = 0.3515\,C\ + 1.1617\,H\ + 0.1046\,S - 0.1109\,O \tag{3}$$

$$\begin{aligned} HHV\,(\mathrm{MJ\,kg^{-1}}) = {} & 0.3147\,C\ + 1.3221\,H\ + 0.1232\,S \\ & - 0.1198\,(O + N) - 0.153A \end{aligned} \tag{4}$$

where C, H, N, S, O and A; stand for the dry weight basis content of carbon, hydrogen, nitrogen, sulphur, oxygen and ash contents. The identification of the PSW was performed using chemical printing and calorimetric analysis by segregating the reclaimed waste into six categories by colour as depicted in Fig. S6 thus: White (61 wt %), black (11 wt%), blue (2 wt%), yellow (6 wt%), pink (2 wt%) and others (18 wt%). Fourier-transform infrared spectroscopy (FTIR) and differential scanning calorimetry (DSC) were used to identify the type of polymers constituting the PSW. The infrared spectra of different colour samples were measured using a PerkinElmer Frontier FTIR spectroscopy with an Attenuated Total Reflectance (ATR) attachment. All Spectra were taken with a resolution of 4 cm^{-1} and 32 scans (Fig. S7) which recorded a distinct PE band in the region of 3000–2750 cm^{-1}. DSC thermograms-heat flow were measured by heating samples ($\approx$1 mg) from −50 to 300 °C at a rate of 10 °C min^{-1} under a constant flow of N_2 (50 ml min^{-1}) using a Mettler-Toledo DSC 3 Calorimeter (Fig. S8).

2.5. Thermogravimetric analysis and stability

Thermal degradation of the samples was investigated using a Mettler-Toledo TGA 3+ Model coupled with StarE data acquisition/analysis software set to record the data every second under multiple heating rates (β) (i.e. 5, 10, 15, 20 and 25 °C min^{-1}) conforming with the protocols and approved methods of the International Confederation for Thermal Analysis and Calorimetry (ICTAC) previously published in Vyazovkin et al. [48,49] for non-isothermal (dynamic) thermogravimetry. These were conducted to diminish sample size influences on the weight loss and kinetic analysis. A constant flow of nitrogen (N_2, dry gas with 99.99% purity) with a flow rate of 50 ml min^{-1} was maintained throughout the experiments. The measurements were conducted using 1 ± 0.1 mg samples from RT to 600 °C made with at least triplicates showing high repeatability with standard deviation (std) not exceeding 1%. The crucibles used in all experimental runs were made of alumina with a 70 µL size. Weight loss (%) and first derivative (DTG, % $^{\circ}C^{-1}$) were recorded constantly to estimate the onset (T_{os}), midset (T_{ms}), inflection point (T_{if}) and maximum degradation temperatures ($T_{max.}$) of each obtained thermogram. The TGA unit was externally calibrated and maintained regularly before each experimental batch using standard reference materials as per ISO 11358 [50].

2.6. Kinetic analysis

A detailed kinetic investigation was performed in this work following the recommendations of the ICTAC aforementioned [48,49] and are shown in Appendix B of this manuscript.

3. Results and discussion

3.1. Identification of reclaimed PSW

The majority of the reclaimed PSW (>60%) were soft white plastics which are most likely to be packaging materials and carrier bags (Fig. S6). Among the others, there were some rigid plastic and polymeric articles as well. The absorption bands investigated in this work were characteristic of polymeric - commercial plastic articles with some pigments present as well (Fig. S7). PE has two absorption bands assigned to —CH_2— asymmetric and symmetric stretching vibrations, while polypropylene (PP) has four superimposed absorption bands corresponding to asymmetric and symmetric stretching vibrations of methylene and methyl groups. All samples in this work have typical PE doublets in the range of 1460 cm^{-1} and 780 cm^{-1} (Fig. S7). In the doublets, the absorption bands with lower wavenumbers could be attributed to the amorphous fraction in the sample. On the other hand, the ones with higher wavenumbers result from the crystalline fraction within the polymeric matrix. The other absorption bands in the spectra would be due to the dyes or other additives commonly present in plastics. Therefore, it can be deduced that the reclaimed materials in this study are all of PE origin.

Thermoplastic polymers, PO plastics such as PE and PP, constitute the majority of the consumers' demand around the world and major share of PSW found in municipal sources [2,15,51,52]. The recent work of Canopoli et al. [18] showed that PSW made up an average of 8% of mined SW from UK sites of less than ten years of disposal. In addition, PE made up over 55% of the total PSW reclaimed from landfill sites. He et al. [17] has also noted that PE made up over 34% of the PSW found in Chinese landfill lechate. In this work, the age of the landfill ditch and the disposed waste was of six months. No organics fraction was present within the reclaimed SW which can be attributed to the arid conditions of the state of Kuwait and the fact that the landfill site was unlined and directly buried in the ground. The past work of Al-Salem [52] showed that LDPE and HDPE polymers represent about 80 thousand tons per annum of the total plastic conversion capacity of Kuwait which was estimated at 350 thousand tons per annum. These two polymers were also amongst the highest value imports of the State. Therefore, the fact that all of the reclaimed PSW in this work was of PE nature, goes in-line with overall consumption and waste disposal trends in Kuwait and around the globe; does not represent a unique or a standalone case of recently mined MSW.

The DSC thermograms obtained in this work confirm the samples reclaimed were of PE origin (Fig. S8). All samples showed a melting point (T_m) around 126 °C with the exception of the blue sample which had a slightly higher melting temperature of around 133 °C. In the earlier work of Al-Salem et al. [53], it was noted that PSW of plastic film-type in Kuwait had the following composition (by polymer type): LLDPE (46%), LDPE (51%), HDPE (1%) and PP (2%). The fraction of PE was dominant and any other plastic materials can be considered negligible. The Tm obtained in this work also confirm with published MSDS of most commonly used PE resin in Kuwait [54], namely LLDPE which is also confirmed by the fact that the majority of the reclaimed waste was of film nature which LLDPE is used for its manufacture.

3.2. Physico-chemical characteristics and main properties

Table 1 shows the main characteristics of the reclaimed PSW in this study and the standard deviation reported is based on the experimental analysis conducted. The average moisture content obtained was 0.005% which represents a very dry sample in comparison to typical components of MSW or past studies conducted

Please cite this article as: S. M. Al-Salem, H. J. Karam, M. H. Al-Wadi et al., Thermal degradation kinetics of *real-life* reclaimed plastic solid waste (PSW) from an active landfill site: The mining of an unsanitary arid landfillreal-life reclaimed plastic solid waste (PSW) from an active landfill site –>, Ain Shams Engineering Journal, https://doi.org/10.1016/j.asej.2020.05.011

Table 1
Summary of Elemental Analysis and Physico-Chemical Properties Conducted on Reclaimed Plastic Solid Waste.

Moisture (%)	Volatiles (%)	Ash (%)	Total Carbon (%)	Total Nitrogen (%)	Total Hydrogen (%)	Oxygen (%)
0.005 ± 0.00	95.18 ± 0.1	4.81 ± 0.1	77.90 ± 0.2	0.084 ± 0	12.96 ± 0.1	6.27 ± 0.5

on mined PSW [54–58]. Moisture in PSW is typically associated with precipitation in landfill sites and the biological decomposition of the organic waste fraction [58]. In addition, with the exception of plastics encompassing a renewable-biodegradable fraction, plastics are hydrophobic materials that repel the majority of moisture from its surrounding environment. The low moisture content was expected in this work as the samples were attained from an unsanitary landfill site leading to the decomposition of organics very rapidly; and the arid climatic conditions of the site which allows summer ambient temperatures above 55 °C in a sandstone desert. Furthermore, the reclaimed PSW in this work represents a first layer mined SW which is also typically lower in moisture content if perpendicular water penetration is to be taken into account [58]. Adrados et al. [56] characterised real-life PSW samples reclaimed from a materials recovery facility in Spain. The ash content of the samples, which contained PE by 18.7%, was 28.2% in their work. The amount of ash represents the inorganic fraction of the samples which is complimented by the organic fraction (volatiles) in making up the total sum of the material. In this work, the ash content was estimated as 4.81 ± 0.064% and the total volatiles were 95.18 ± 0.05%. The PSW landfilled in this study was relatively fresh (six months old) when the mining process to reclaim it commenced. Therefore, the total decomposable fraction represented by the volatiles was higher than past work on reclaimed PSW from landfill sites with an age of ten years and more [58]. This could be attributed to the fact that fresh PSW is less prone to photo and anaerobic degradation stressors, which yield more crystalline zones within the polymeric matrix rendering it more hard to vaporise with temperature. This is also complimented by the high carbon content obtained (77.9%) which shows that the material has not lost the majority of the organic carbon fraction bound to its molecular structure. Readers are also referred to the raw experimental data obtained in this work depicted in Table S3. Past findings on PSW showed that carbon content could reach levels as low as 35.23% as reported by Hashem et al. [59] showing severe degradation and integrity loss of the material.

The characteristics of the materials tested in this work, also favours TCC treatment from a circular economy point of view over other conventional recycling option such as physical (mechanical) recycling or incineration. Mechanical recycling will require various segregation efforts and the determination of the feedstock integrity for it to be suitable and comparable to market standards. On the other hand, incineration can't be practical considering the feedstock preparation required to process PSW as a feedstock [18]. TCC technologies can be divided into three main categories depending on the treatment and operating conditions. These are pyrolysis, gasification and hydrogenation [16]. Out of the three technologies, pyrolysis has received renewed attention nowadays due to various reasons. These could be summarised as relatively ease in operation (in comparison to the other two), high value product yielded at relatively moderate conditions, and easily marketable products [60]. It was also recently estimated by Fox and Stacey [61] that the potential revenue of alkene products (potentially recovered from pyrolysis) is between $80 and $160 per tonne of processed feedstock material. Canopoli et al. [18] used these estimates in their work and determined that reclaimed PSW with high PO proportions can yield a rate of return on investment of about $805 million. Pyrolysis can also produce monomer feedstock and chemicals that feed into the petrochemicals production chain and close the loop when it comes to recycling and end of life treatments. This feeds also into the overall circular economy thought process that can stimulate investors in supporting such green technologies for future studies and establishing environmentally friendly projects.

3.3. Thermal stability of reclaimed waste

Thermogravimetry has been applied in the past to study the degradation behaviour of various types of organic materials [31,62–66]. It is also essential to understand the degradation mechanism and the thermal stability under the conditions that simulate the targeted process which can be done using TGA. Fig. 2 shows the raw experimental data obtained for the reclaimed PSW and subjected to pyrolysis. The temperature ranges between 350 and 500 °C demonstrated the major share of the decomposition stage for the five heating rates employed in this study. In addition, it was observed that a residual mass of 3–8 wt% was left by the material tested and the duplication of the experimental runs did not result in an equal amount of residue under specific β values. Nonetheless, this behaviour didn't affect estimations of neither the maximum degradation temperature (T_{max}) or the inflection point (T_{if}). Therefore, smoothing the experimental curves for further modelling exercises could be beneficial to the case at hand similar to past efforts by Al-Salem and Khan [67]. This behaviour was also observed previously by Bach et al. [62] on reclaimed polyvinyl chloride (PVC) industrial waste. Khedri and Elyasi [68] pyrolysed HDPE in a thermogravimetric set-up using a β value in the range between 40 and 55 °C min^{-1} and reported near zero residual mass in their work. A mixture of PSW containing 7.4 wt % of HDPE was also studied by Mumbach et al. [46] in TGA resulting in a range of residual mass between 1 and 5 wt% depending on the β value which was between 5 and 30 °C. Al-Salem et al. [63] reported some 1 wt% of residual mass post TGA experiments on virgin HDPE. The slight increased amounts of residual mass in this work compared to previous findings reported on virgin HDPE could be attributed to the level of degradation the waste material was subjected to. Photo-degradation will induce the cross-linking of the polymeric matrix and will result in a more rigid plastic material that can require higher amount of thermal energy to fully decompose. In addition, the majority of the materials analysed in this study where observed to be of commercial grades and product commonly found in the plastics waste stream. It has been previously reported that commercial grade polymers will result in high amounts of residual char post thermogravimetric studies [69]. This is due to the elevated level of commercial additives present in such plastic articles. The increase in the β values also led to a clear shift in the degradation curve (Fig. 2). This also confirms that a clear change in deterioration mechanism is attributed to the change in heating rate which results in a clear difference in the material response. The displacement of the TG curves could also be attributed to the thermal lag effect resulting from the increased β values [70]. This provides insights into the materials behaviour when simulating fast pyrolysis as it was previously described by Hato et al. [71].

Table 2 shows the temperature profile obtained for the materials tested in this work. PE typically degrades with an onset temperature in the range of 377–415 °C [63]. Virgin HDPE started to degrade at 425 °C in the work of Khedri and Elyasi [68]. On the

Please cite this article as: S. M. Al-Salem, H. J. Karam, M. H. Al-Wadi et al., Thermal degradation kinetics of *real-life* reclaimed plastic solid waste (PSW) from an active landfill site: The mining of an unsanitary arid landfillreal-life reclaimed plastic solid waste (PSW) from an active landfill site –>, Ain Shams Engineering Journal, https://doi.org/10.1016/j.asej.2020.05.011

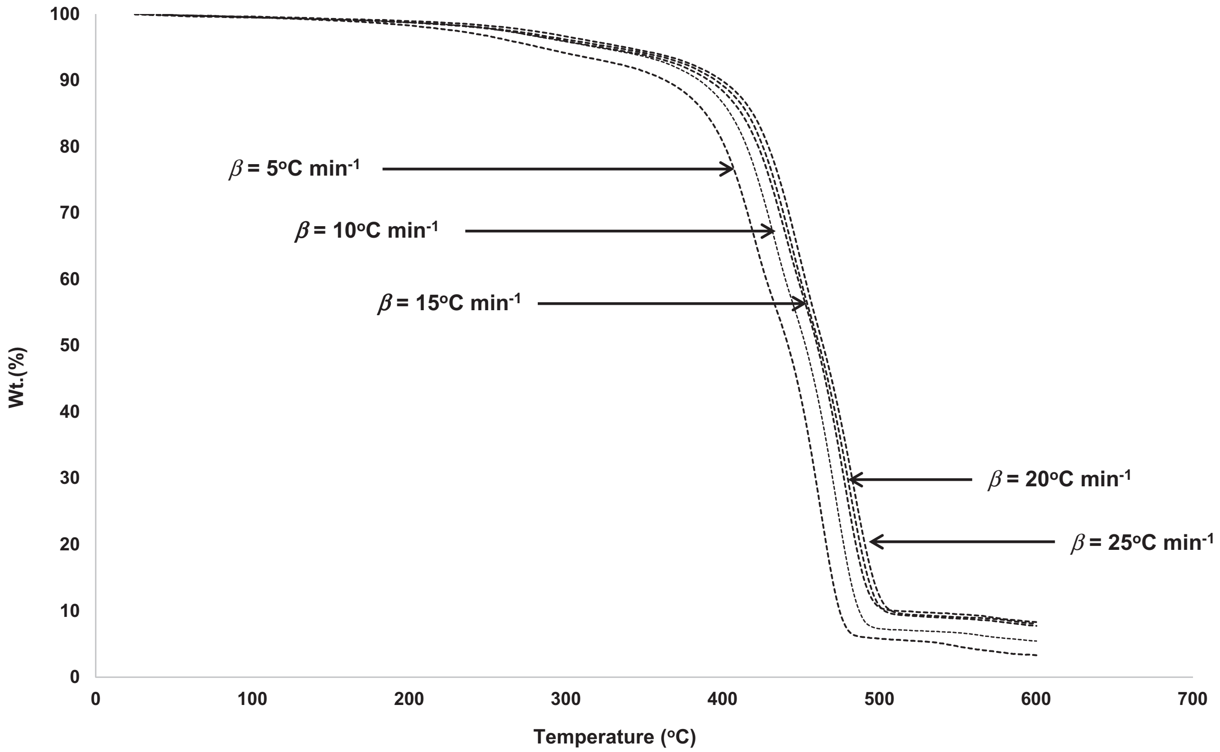


Fig. 2. Thermogravimetric Analysis (TGA) Thermograms Obtained For The Reclaimed PSW Samples.

Table 2
Temperature Degradation Profile of the Reclaimed PSW Material.

β (°C min^{-1})	T_{os} (°C)	T_{if} (°C)	T_{ms} (°C)	$T_{max.}$ (°C)
5	403.92	454.17	448.17	498.67
10	415.00	466.00	460.83	513.16
15	421.75	474.50	468.50	522.00
20	426.66	482.00	474.00	528.33
25	430.41	484.17	478.33	533.33

other hand, Mumbach et al. [46] showed that a mixture of plastic waste/refuse (containing minimal HDPE content of 7.41%) exhibits a T_{os} at around 250 °C. In this work, the T_{os} was determined using TGA in the range of 403.92–430.41 °C with respect to the varying β values. These findings also confirm and falls within past results on HDPE for the start of degradation temperatures reported by previous authors [62,72]. A singular T_{if} was prominent in the studied samples and showed an average value of 475 °C indicating the temperature of maximum change in weight loss (Table 2). The maximum degradation temperature estimated in this work also shows a range of values between 498 and 533 °C which is considerably lower with respect to β values than previous findings on virgin HDPE used in Kuwait (500–629 °C), [63] or elsewhere (535–565 °C), [68]; 560–600 °C, [62]. On the other hand, T_{max} reported in this work fell within the range of reclaimed PSW reported by Mumbach et al. [46] (490–540 °C).

3.4. Estimated kinetic parameters from model free methods

The obtained thermograms were used to estimate the E_a values from the model free methods previously described in Section 2. The isoconversional method of Friedman was firstly used to study the degradation reaction of the material. Isoconversional methods are known to be independent of the degradation mechanism and can estimate the E_a across the whole breadth of the degradation reaction using various β values. The Friedman plot is shown in Fig. 3 which shows high regression coefficient values (r^2) generally > 0.93 indicating linearity. The value of α was chosen as 5% to present a broader range of the dataset and extent of conversion which results in a more accurate estimate of E_a value which was determined to be as 261.88 ± 9 kJ mol^{-1} [48]. Guanasee et al. [26] estimated the E_a value of commingled SW containing a plastic fraction using Friedman's method to be 250 kJ mol^{-1}. Khedri and Elyasi [68] estimated the E_a values between 134 and 185 kJ mol^{-1} with respect to conversion rates between 0.90 and 0.05 for virgin HDPE. On the other hand, virgin HDPE were studied by Al-Salem et al. [63] and Aboulkas et al. [62]; and the E_a values were reported to be 184 kJ mol^{-1} and 247 kJ mol^{-1}, respectively.

The FWO method was also used in this work to estimate the E_a values of the PSW degradation reaction. The FWO is one of the most popular methods reported in literature and was previously used to estimate the kinetic parameters namely the E_a values for PP (127 kJ mol^{-1}), [22], HDPE (208 kJ mol^{-1}), [63], cattle manure (126–192 kJ mol^{-1}), [65] and egg shell waste biomass (221 kJ mol^{-1}), [30]. The FWO is also considered an isoconversional method of an integral form that produces a mechanism independent value of E_a [30]. The FWO plot depicted in Fig. 4 shows high linearity amongst the studied dataset population (>0.97) and the average E_a value was estimated to be 109.89 ± 6 kJ mol^{-1}. Fig. 5 shows the variation in the obtained E_a values using both isoconversional methods of Friedman and FWO. It is essential to consider more than one method for the kinetic parameters estimation, in order to, attain a good understanding of the true behaviour of the material under pyrolytic conditions. It was noted that a similar

Please cite this article as: S. M. Al-Salem, H. J. Karam, M. H. Al-Wadi et al., Thermal degradation kinetics of *real-life* reclaimed plastic solid waste (PSW) from an active landfill site: The mining of an unsanitary arid landfillreal-life reclaimed plastic solid waste (PSW) from an active landfill site –>, Ain Shams Engineering Journal, https://doi.org/10.1016/j.asej.2020.05.011

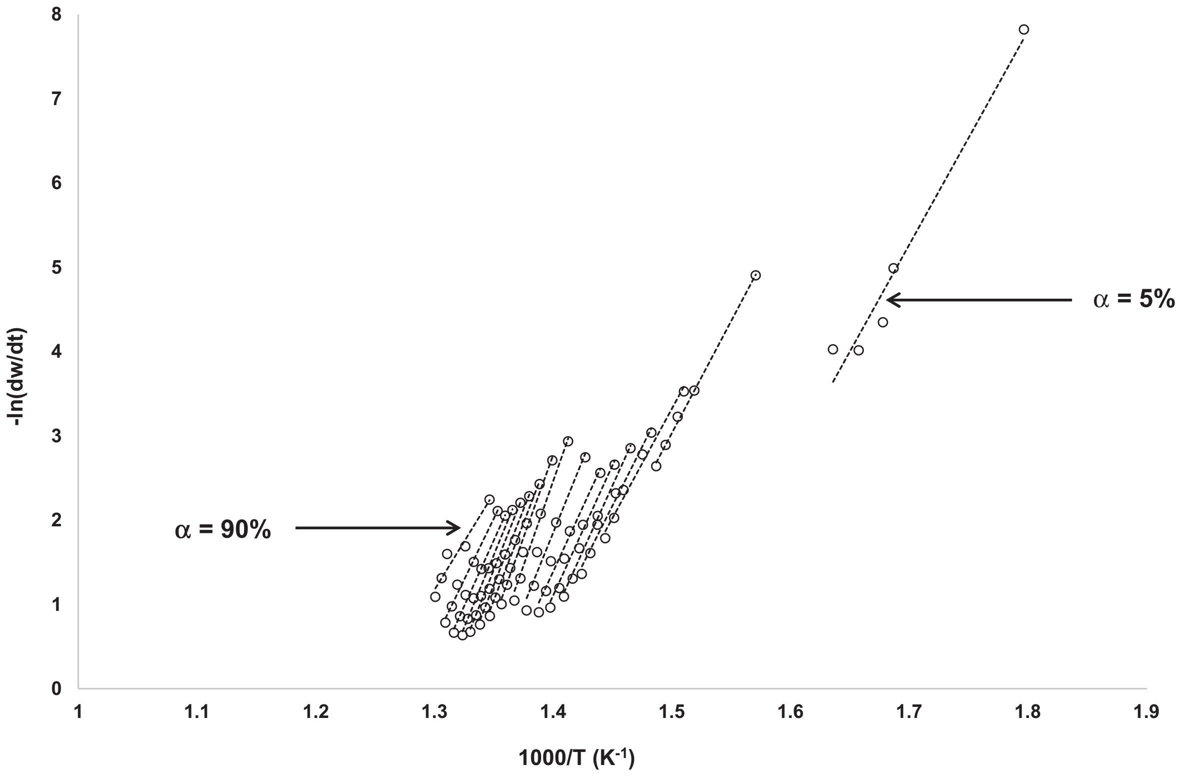


Fig. 3. Determination of Apparent Activation Energy (Ea) using Friedman's Isoconversion Method for The Reclaimed PSW Showing Range of Conversion (a) Results From Right To Left Starting With 5% to 90% with a 5% Conversion Rate Increment.

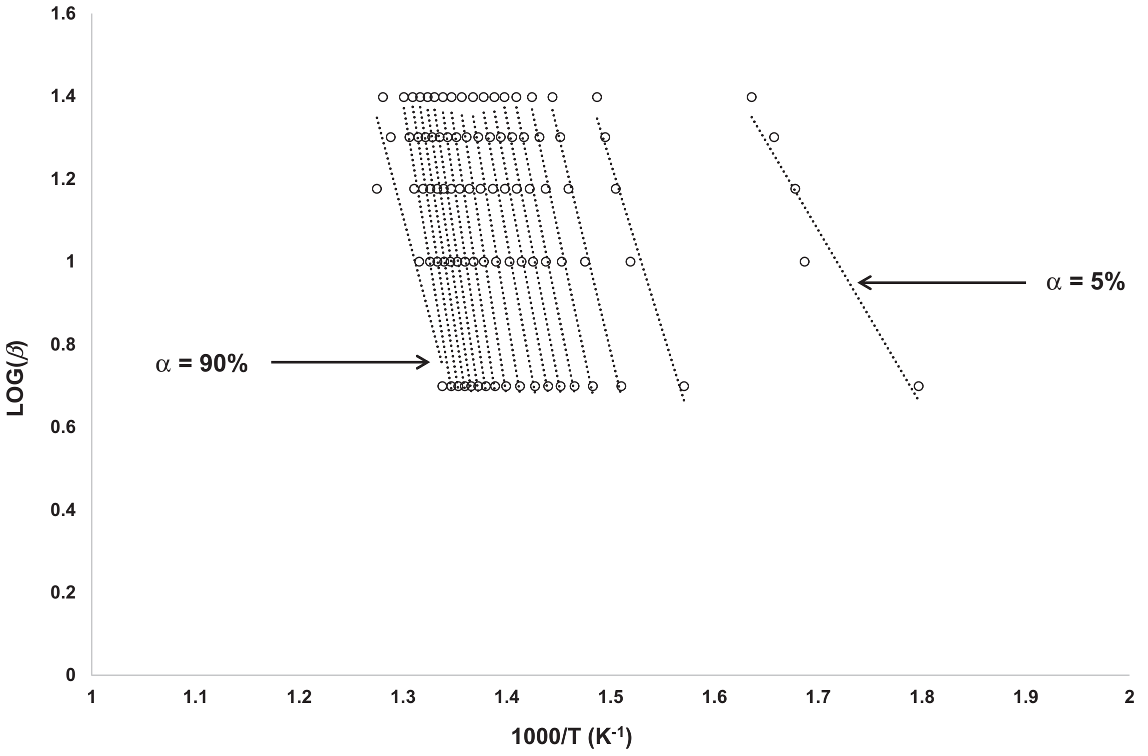


Fig. 4. Determination of Apparent Activation Energy (Ea) using FWO Method for The Reclaimed PSW Showing Range of Conversion (a) Results From Right To Left Starting With 5% to 90% with a 5% Conversion Rate Increment.

relationship was obtained between the conversion fraction and the estimated value of E_a. This was also previously observed by Nisar et al. [7] in their study. In general terms, the Friedman method yielded a higher estimate of energy than those determined using the FWO method. The compensation effect on the dataset studied could also yield different results of kinetic parameters for similar datasets as observed by Ceamanos et al. [73]. Chen et al. [65] referred to the ICTAC recommendations in their work, where they

Please cite this article as: S. M. Al-Salem, H. J. Karam, M. H. Al-Wadi et al., Thermal degradation kinetics of *real-life* reclaimed plastic solid waste (PSW) from an active landfill site: The mining of an unsanitary arid landfillreal-life reclaimed plastic solid waste (PSW) from an active landfill site –>, Ain Shams Engineering Journal, https://doi.org/10.1016/j.asej.2020.05.011

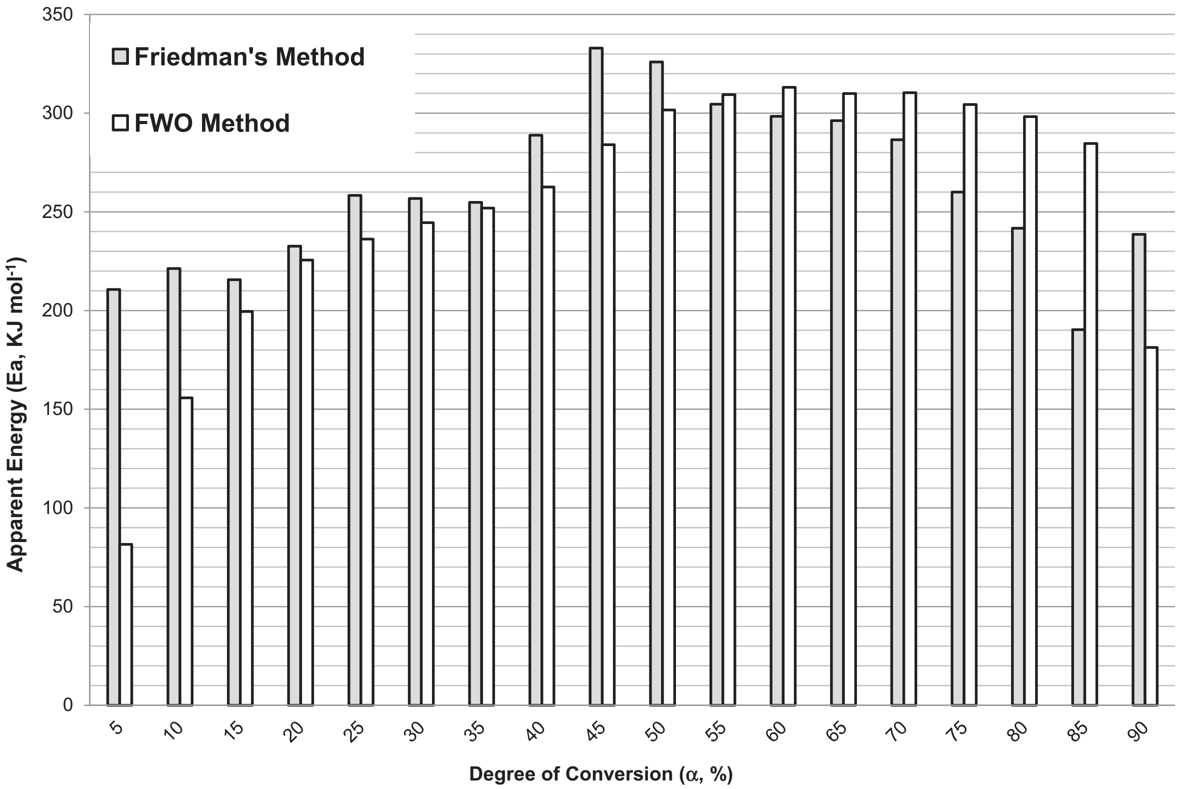


Fig. 5. Variation in Apparent Energy (Ea) Estimated Using Isoconversional Methods With Respect to Degree of Conversion In This Study.

have stated that if the variation between the minimum and maximum E_a values is over 30% a more complex differential method is required for the dataset analysis [48,49]. In this work, the overall variation between the obtained E_a values was estimated as 42% and 73% for the Friedman and FWO methods, respectively. Therefore, both methods are rendered inadequate for the obtention of kinetic parameters in this instance. Nonetheless, the variation of Friedman's method up to 40% of conversion was estimated to 27%, making it adequate for low conversion rates. This could also be attributed to a change in mechanism of the studied waste material has on the obtained results. The large variation in the FWO could also be explained by the expected errors in the results of integral methods [65].

Fig. S9 shows the fitting curve of the Kissinger method employed in this study. It is quite evident from the obtained curve that the regression is equal to near unity which indicated high accuracy resulting from the employment of this method. The method is based on the assumption that the maximum point, whether it be on the derivative or thermogram curve, of a single step reaction is reached independently of the employed heating rate at the same value of α [36]. Naskar et al. [74] used this method to determine the E_a value for the degradation of PSW resulting from carrier bags. The degradation reaction of the PSW resulted in an E_a value of 180 kJ mol^{-1}. Rana et al. [75] determined the E_a value of rejected PP waste, plastic films and pellets as 108, 98 and 132 kJ mol^{-1}, respectively. This work resulted in an E_a estimate of 226 kJ mol^{-1} with a high accuracy of the regression fit. The ICTAC committee explicitly state in their kinetics computations recommendations that the Kissinger method should be backed up by other isoconversional ones [48]. The Friedman method used in this work results in a value that is approximately similar to the Kissinger method namely for lower conversion rates. In addition to the high accuracy of the data fitting curve, this provides a good reliability of this method when compared to others.

3.5. Degradation mechanism determination of plastic solid waste using Criado's masterplots

The method of Cridao was implemented in this work by using Z(α)/Z(0.5) with respect to each conversion value (α), as previously described. The aim was to compare the generated masterplots (theoretical ones) with the experimental data produced at a β value of 5 °C min^{-1} as it is the slowest rate which in reality can produce the most reliable data for mechanism determination [62]. The models of degradation mechanism were depicted previously in Appendix B. The plot of mastercurves are typically performed by overlapping theoretical and experimental curves from the dataset generated as a function of the conversion to produce the pseudo component plots [46]. Fig. S10 shows the master and experimental plots produced for the PSW reclaimed from the landfill site. The experimental curve nearly overlaps and coincides with the A_3 model master curve. This is a clear indication that *Avarami-Erofeve* degradation mechanism represents the best representative to the case at hand. The data produced also confirms that the degradation is of a single step reaction as the curve doesn't overlap or simulate other curves as well as the A_3 model or follows two stage degradation curves previously shown by Xu et al. [76]. The estimated E_a is about 109 ± 9 kJ mol^{-1} which is in the same order of magnitude as the FWO method.

4. Conclusion

There is little information available on the actual value and appropriate treatment methods for landfilled waste namely plastic solid waste (PSW) resulting from landfilling mining operations. These operational conditions represent real life reclaimed waste that needs to be treated in accordance with appropriate conditions based on technical findings that can stretch to design aspects in the

Please cite this article as: S. M. Al-Salem, H. J. Karam, M. H. Al-Wadi et al., Thermal degradation kinetics of *real-life* reclaimed plastic solid waste (PSW) from an active landfill site: The mining of an unsanitary arid landfillreal-life reclaimed plastic solid waste (PSW) from an active landfill site –>, Ain Shams Engineering Journal, https://doi.org/10.1016/j.asej.2020.05.011

future. Furthermore, PSW also shows potential as a feedstock material for various thermo-chemical conversion (TCC) technologies namely pyrolysis, based on previous works. In this work, the nature of reclaimed landfill mined PSW was determined after excavating an active unsanitary landfill site in Kuwait. The PSW was determined to be of PE in nature and its properties determined experimentally have shown that the reclaimed waste was of high integrity and could be used as a feedstock material for pyrolysis units. The thermal profile of the material showed a clear shift in the degradation thermograms in response to a change in heating rates used in thermogravimetric analysis which indicated that the degradation level, duration of landfilling of the material and properties are of major impact on the obtained results. The apparent activation energy (E_a) resulting from the model free and model dependent methods applied ranged from 199 to 266 kJ mol^{-1} which is in-line with pyrolytic reactions applicable for future use in fuel recovery units. In addition, the degradation mechanism of the feedstock material was determined to be *Avarami-Erofeve* which can be used for future design of units that handle similar feedstock materials. The characteristics of the materials tested in this work, also favours TCC treatment over other conventional options such as physical (mechanical) recycling or incineration, and is attractive from a circular economy perspective. It should be noted that TCC technologies for such feedstock materials will also utilise less resources for segregation and can result in valuable hydrocarbon products. The work in this research could be extended in various directions to satisfy the gaps in current knowledge. Investigations into the use of landfill recovered feedstocks with different levels of contamination could be studied using micro and macro techniques, such as thermogravimetry coupled with mass spectroscopy and subjecting the feedstock to bench and pilot scale processes to further understand the behaviour of materials in larger scale operation. Furthermore, modelling and optimising the operation of such process and their integration with the oil and gas industry, may be beneficial to oil-at reducing our dependence on virgin feedstocks. Furthermore, mathematically optimising the operation of such process to present an integrated platform with oil and gas industry, could be of a certain benefit to oil based economies worldwide.

CRediT authorship contribution statement

S.M. Al-Salem: Conceptualization, Formal analysis, Funding acquisition, Investigation, Methodology, Writing - original draft, Writing - review & editing. **H.J. Karam:** Formal analysis, Investigation, Methodology. **M.H. Al-Wadi:** Formal analysis, Investigation, Methodology. **S. Alsamaq:** Formal analysis, Investigation, Methodology. **G. Jiang:** Formal analysis, Investigation, Methodology. **J. Wang:** Formal analysis, Investigation, Methodology. **G.A. Leeke:** Formal analysis, Writing - original draft, Writing - review & editing.

Acknowledgments

The authors would like to thank the Kuwait Institute for Scientific Research (KISR) and The British Council/UK-Gulf Institutional Links for funding and supporting this research through Grant no. 2793-5936-4.

Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.asej.2020.05.011.

References

[1] Eurostat. Municipal waste generation and treatment, by type of treatment method; 2015. Available at: https://ec.europa.eu/eurostat/statistics-explained/index.php?title=File:Breakdown_of_total_waste_generation_by_waste_category;_coverage_of_waste_generation_indicator,_EU-28,_2012_new_.png [accessed on 15 October 2019].

[2] Canopoli L, Fidalgo B, Coulon F, Wagland ST. Physico-chemical properties of excavated plastic from landfill mining and current recycling routes. Waste Mange 2018;76:55–67.

[3] Council of the European Union, European Parliament Council Directive 1999/31/EC of 26 April 1999 on the landfill of waste.

[4] Council of the European Union, European Parliament Directive 2008/98/EC of the European Parliament and of the Council of 19 November 2008 on waste and repealing certain Directives.

[5] Jones G. Asia's waste management failures reach crisis levels Japan offers lessons in how to handle the challenge quickly and cost-effectively. Nikkei Asian Rev 2018.

[6] Al-Salem SM, Al-Hazza'a A, Karam HJ, Al-Wadi MH, Al-Dhafeeri AT, Al-Rowaih AA. Insights into the evaluation of the abiotic and biotic degradation rate of commercial pro-oxidant filled polyethylene (PE) thin films. J Environ Mange 2019;250.

[7] Nasir S. You dump 2.5kg of garbage daily, where do you think it goes?. Khaleej Times; 2019.

[8] Kaza S, Yao L, Bhada-Tata P, Van Woerden F. What a waste 2.0: a global snapshot of solid waste management to 2050. In: Urban development series. Washington, DC: World Bank; 2018. doi: https://doi.org/10.1596/978-1-4648-1329-0.

[9] Bosmans A, Vanderreydt I, Geysen D, Helsen L. The crucial role of Waste to-Energy technologies in enhanced landfill mining: a technology review. J Clean Produc 2013;55:10–23.

[10] Van Passel S, Dubois M, Eyckmans J, De Gheldere S, Ang F, Jones PT, et al. The economics of enhanced landfill mining: private and societal performance drivers. J Clean Produc 2013;55:92–102.

[11] Jones PT, Geysen D, Tielemans Y, Pontikes Y, Blanpain B, Mishra B, et al. Closing material loops: the enhanced landfill mining concept. J Miner Metals Mater Soc 2012;64:743–4.

[12] Savage GM, Gouleke CG, Stein EL. Landfill mining: past and present. BioCycle 1993;34(5):58–62.

[13] Hogland W, Marques M, Nimmermark S. Landfill mining and waste characterization: a strategy for remediation of contaminated areas. J Mater Cycle Waste Mange 2004;6:119–24.

[14] Jasso-Gastinel CF, Soltero-Martínez JFA, Mendizábal E. Introduction: modifiable characteristics and applications. In: Jasso-Gastinel CF, Kenny JM, editors. Modification of polymer properties. Oxford: William Andrew; 2017. p. 1–21.

[15] Al-Salem SM, Lettieri P. Kinetic study of high density polyethylene (HDPE) pyrolysis. Chem Eng Res Des 2010;88(12):1599–606.

[16] Al-Salem SM, Lettieri P, Baeyens J. Recycling and recovery routes of plastic solid waste (PSW): a review. Waste Mange 2009;29(10):2625–43.

[17] He P, Chen L, Shao L, Zhang H, Lü F. Municipal solid waste (MSW) landfill: a source of microplastics? Evidence of microplastics in landfill leachate. Water Res 2019;159:38–45.

[18] Canopoli L, Coulon F, Wagland ST. Degradation of excavated polyethylene and polypropylene waste from landfill. Sci Total Environ 2020;698:134125.

[19] Kamura K, Omori M, Kurokawa M, Tanaka H. Estimation of the potential of landfill mining and exploration of metal-enriched zones. Waste Mange 2019;93:122–9.

[20] Mönkäre T, Palmroth MRT, Sormunen K, Rintala J. Scaling up the treatment of the fine fraction from landfill mining: mass balance and cost structure. Waste Mange 2019;87:464–71.

[21] Quaghebeur M, Laenen B, Geysen D, Nielsen P, Pontikes Y, Van Gerven T, et al. Characterization of landfilled materials: screening of the enhanced landfill mining potential. J Clean Produc 2013;55:72–83.

[22] Al-Salem SM, Sharma BK, Khan AR, Arnold JC, Alston SM, Chandrasekaran SR, et al. Thermal degradation kinetics of virgin polypropylene (PP) and PP with starch blends exposed to natural weathering. Indus Eng Chemst Res 2017;56:5210–20.

[23] Trninić M, Jovović A, Stojiljković D. A steady state model of agricultural waste pyrolysis: a mini review. Waste Mange Res 2016;34(9):851–65.

[24] Bosmans A, De Dobbelaere C, Helsen L. Pyrolysis characteristics of excavated waste material processed into refuse derived fuel. Fuel 2014;122:198–205.

[25] Chhabra V, Bhattacharya S, Shastri Y. Pyrolysis of mixed municipal solid waste: characterisation, interaction effect and kinetic modelling using the thermogravimetric approach. Waste Mange 2019;901:152–67.

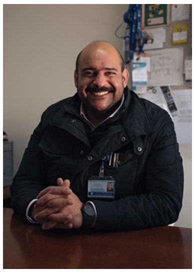
[26] Gunasee SD, Carrier M, Gorgens JF, Mohee R. Pyrolysis and combustion of municipal solid wastes: evaluation of synergistic effects using TGA-MS. J Anal App Pyrolysis 2016;121:50–61.

[27] Miteva K, Slavcho A, Bogoeva-Gaceva G. Kinetic analysis of pyrolysis of waste polyolefin mixture. Arab J Sci Eng 2016;41:2601–9.

[28] Al-Salem SM. Thermal pyrolysis of high density polyethylene (HDPE) in a novel fixed bed reactor system for the production of high value gasoline range hydrocarbons (HC). Process Safe Environ Protec 2019;127:171–9.

Please cite this article as: S. M. Al-Salem, H. J. Karam, M. H. Al-Wadi et al., Thermal degradation kinetics of *real-life* reclaimed plastic solid waste (PSW) from an active landfill site: The mining of an unsanitary arid landfillreal-life reclaimed plastic solid waste (PSW) from an active landfill site –>, Ain Shams Engineering Journal, https://doi.org/10.1016/j.asej.2020.05.011

[29] Chen R, Li Q, Xu X, Zhang D. Comparative pyrolysis characteristics of representative commercial thermosetting plastic waste in inert and oxygenous atmosphere. Fuel 2019;246:212–21.
[30] Salaudeen S, Al-Salem SM, Heidari M, Acharya B, Dutta A. Eggshell as a carbon dioxide sorbent: kinetics of the calcination and carbonation reactions. Energy Fuel 2019;33(5):4474–86.
[31] Biryan F, Demirelli K. Thermal degradation kinetic, electrical and dielectric behavior of brush copolymer with a polystyrene backbone and polyacrylate-amide side chains/nanographene-filled composites. J Moluc Struc 2019;1186:187–203.
[32] Al-Jarallah R, Aleisa E. A baseline study for municipal solid waste characterization for the state of Kuwait. Waste Mange 2014;34:952–60.
[33] Al-Salem SM, Al-Nasser A, Al-Dhafeeri AT. Multi-variable regression analysis for the solid waste generation in the State of Kuwait. Process Safe Environ Protec 2018;119:172–80.
[34] Al-Salem SM, Leeke GA, Al-Enezi R, Sultan HH, Karam HJ, Al-Wadi MH et al. Potential for thermal and solar power pyrolysis in treating reclaimed real life solid waste from a landfill disposal site. In: Proc: 17th international waste management and landfill symposium (Sardinia'19). Sardinia, Italy, 30th September–4th October 2019.
[35] Mor S, Ravindra K, De Visscher A, Dahiya RP, Chandra A. Municipal solid waste characterization and its assessment for potential methane generation: a case study. Sci Total Environ 2006;371:1–10.
[36] Al-Salem S, Al-Nasser A, Al-Wadi M, Al-Foudaree M, Al-Qassimi M, Al-Dhafeeri A et al. Established protocols and research methods acquired in the waste management research unit (WMRU), technical report, KISR no. 14854, Project Code: P-KISR-06-11; April 2018.
[37] Al-Ahmad MDS. Optimization of the assessment and rehabilitation of old landfills in Kuwait PhD thesis. Rostock University; 2012.
[38] Al-Sarawi MA, Massoud MS, Wahba SA. Physical properties as indicators of oil penetration in soils contaminated with oil lakes in the Greater Burgan oil fields, Kuwait. Water Soil Air Pollut 1998;102:1–15.
[39] Al-Khatib IA, Fkhidah IA, Khatib JI, Kontogianni S. Implementation of a multi-variable regression analysis in the assessment of the generation rate and composition of hospital solid waste for the design of a sustainable management system in developing countries. Waste Mange Res 2016;34(3):225–34.
[40] Al-Khatib IA, Monou M, Abu Zahra ASF, Shaheen HQ, Kassinos D. Solid waste characterization, quantification and management practices in developing countries. A case study: Nablus district – Palestine. J Environ Mange 2010;91:1131–8.
[41] WHO. World Health Organization, Handling solid wastes in developing countries. Egypt, Alexandria; 1998.
[42] ASTM D 5373. American society for testing & materials, standard test methods for determination of carbon, hydrogen and nitrogen in analysis samples of coal and carbon in analysis samples of coal and coke, Pennsylvania; 2016.
[43] ASTM D 5291. American society for testing & materials, standard test methods for instrumental determination of carbon, hydrogen, and nitrogen in petroleum products and lubricants, Pennsylvania; 2016.
[44] ASTM D 5630, American society for testing & materials, standard test method for ash content in plastics, Pennsylvania; 2013.
[45] ISO 1762. Paper, board, pulps and cellulose nanomaterials, determination of residue (ash content) on ignition at 525 °C; 2019.
[46] Mumbach GD, Alves JLF, Da Silva JCG, De Sena RF, Marangoni C, Machado RAF, et al. Thermal investigation of plastic solid waste pyrolysis via the deconvolution technique using the asymmetric double sigmoidal function: determination of the kinetic triplet, thermodynamic parameters, thermal lifetime and pyrolytic oil composition for clean energy recovery. Energy Conserv Mange 2019;200:112031.
[47] Regmi B, Dutta A, Pradhan RR, Arku P. Physicochemical characteristics and pyrolysis kinetics of raw and torrefied hybrid poplar wood (NM6 – *Populus nigra*). Biofuels 2017. doi: https://doi.org/10.1080/17597269.2017.1368058.
[48] Vyazovkin S, Burnham AK, Criado JM, Pérez-Maqueda LA, Popescu C, Sbirrazzuoli N. Thermochim Acta 2011;520:1–19.
[49] Vyazovkin S, Chrissafis K, Di Lorenzo ML, Koga N, Pijolat M, Roduit B, et al. Thermochim Acta 2014;590:1–23.
[50] ISO 11358. 2014. Plastics: thermogravimetry (TG) of polymers, Part 1: General principles.
[51] Dewil, R., Everaert, K., Baeyens, J., 2006. The European plastic waste issue: trends and toppers in its sustainable re-use. In: Proceedings of the 17th international congress of chemical and process engineering, 27–31 August 2006, Prague, Czech Republic.
[52] Al-Salem SM. Establishing an integrated databank for plastic manufacturers and converters in Kuwait. Waste Mange 2009;29:479–84.
[53] Al-Salem SM, Abraham G, Al-Qabandi OA, Dashti AM. Investigating the effect of accelerated weathering on the mechanical and physical properties of high content plastic solid waste (PSW) blends with virgin linear low density polyethylene (LLDPE). Polym Test 2015;46:116–21.
[54] SDS. Safety data sheet according to 1907/2006/EC, article 31, revision: version number 2 09.02.2016, trade name: polyethylene EFDC-7050; EFDC-7087; EFDA-7048; EFDA-7047; EHF-2818; EFDA- 7055, CAS number: 25087-34-7, 25213-02-9; 2006.
[55] Johari A, Hashim H, Mat R, Alias H, Hassim MH, Rozainee M. Generalization, formulation and heat contents of simulated MSW with high moisture content. J Eng Sci Technol 2012;7(6):701–10.
[56] Adrados A, de Marco I, Caballero BM, López A, Laresgoiti MF, Torres A. Pyrolysis of plastic packaging waste: a comparison of plastic residuals from material recovery facilities with simulated plastic waste. Waste Mange 2012;32:826–32.
[57] López A, de Marco I, Caballero BM, Laresgoiti MF, Adrados A. Pyrolysis of municipal plastic wastes: influence of raw material composition. Waste Mange 2010;30:620–7.
[58] Zhou C, Fang W, Xu W, Cao A, Wang R. Characteristics and the recovery potential of plastic wastes obtained from landfill mining. J Clean Produc 2014;80:80–6.
[59] Hashem FS, Razek TA, Mashout HA. Rubber and plastic wastes as alternative refused fuel in cement industry. Constr Build Mater 2019;212:275–82.
[60] Al-Salem SM. Introduction, Chapter 1. In: S.M. Al-Salem, editor. Plastics to energy: fuel, chemicals & sustainable implications, Elsevier; 2019. ISBN: 978-0-12-813140-4. https://doi.org/10.1016/B978-0-12-813140-4.00001-7.
[61] Fox JA, Stacey NT. Process targeting: an energy based comparison of waste plastic processing technologies. Energy 2019;170:273–83.
[62] Aboulkas A, El harfi K, El Bouadili A. Thermal degradation behaviors of polyethylene and polypropylene. Part I: Pyrolysis kinetics and mechanisms. Energy Convers Manage 2010;51:1363–9.
[63] Al-Salem SM, Bumajdad A, Khan AR, Sharma BK, Chandrasekaran SR, Al-Turki FA, et al. Non-isothermal degradation kinetics of virgin linear low density polyethylene (LLDPE) and biodegradable polymer blends. J Polym Res 2018;25:111.
[64] Al-Salem SM. Kinetic studies related to polymer degradation and stability, Chapter 9. In: Plastics to energy: fuel, chemicals, and sustainability implications. Elsevier, 1st ed. 2019. p. 233–68. https://doi.org/10.1016/B978-0-12-813140-4.00009-1.
[65] Chen G, He S, Cheng Z, Guan Y, Yan B, Ma W, et al. Comparison of kinetic analysis methods in thermal decomposition of cattle manure by themogravimetric analysis. Bioresour Technol 2017;243:69–77.
[66] Bach Q, Chen W, Eng CF, Wang C, Liang K, Kuo J. Pyrolysis characteristics and non-isothermal torrefaction kinetics of industrial solid wastes. Fuel 2019;251:118–25.
[67] Al-Salem SM, Khan AR. On the degradation kinetics of poly(ethylene terephtalate) (PET)/poly(methyl methacrylate) (PMMA) blends in dynamic thermogravimetry. Polym Degrad Stab 2014;104:28–32.
[68] Khedri S, Elyasi S. Kinetic analysis for thermal cracking of HDPE: a new isoconversional approach. Polym Degrad Stab 2016;129:306–18.
[69] Agrawal RK. Analysis of non-isothermal reaction kinetics: Part 1. Simple reactions. Thermochimica Acta 1992;203:93–110.
[70] Park JW, Oh SC, Lee HP, Kim HT, Yoo KO. A kinetic analysis of thermal degradation of polymers using a dynamic method. Polym Degrad Stab 2000;67:535–40.
[71] Hato MJ, Ray SS, Luyt AS. Nanocomposites based on polyethylene and polyhedral oligomeric silsesquioxanes, 1 – microstructure, thermal and thermomechanical properties. Macromol Materi Eng 2008;293:752–62.
[72] Bockhorn H, Hornung A, Hornung U, Schawaller D. Kinetic study on the thermal degradation of polypropylene and polyethylene. J Anal Appl Pyrol 1999;48:93–109.
[73] Ceamanos J, Mastral JF, Millera A, Aldea ME. Kinetics of pyrolysis of high density polyethylene. Comparison of isothermal and dynamic experiments. J Anal Appl Pyrol 2002;65:93–110.
[74] Naskar M, Chaki TK, Reddy KS. Effect of waste plastic as modifier on thermal stability and degradation kinetics of bitumen/waste plastics blend. Thermochim Acta 2010;509:128–34.
[75] Rana S, Parikh JK, Mohanty P. Thermal degradation and kinetic study for different waste/rejected plastic materials. Korean J Chem Eng 2013;30(3):626–33.
[76] Xu F, Wang B, Yang D, Hao J, Qiao Y, Tian Y. Thermal degradation of typical plastics under high heating rate conditions by TG-FTIR: Pyrolysis behaviors and kinetic analysis. Energy Conserv Mange 2018;171:1106–15.



Dr. Sultan Majed Al-Salem specializes in polymer degradation kinetics, which is a particular research interest of his. His research interests also include polymers weathering, waste management, reactor design, thermal engineering, life cycle assessment and biodegradable polymers. Dr. Al-Salem has authored a number of book chapters, refereed journal and conference articles. He currently holds the position of a Research Scientist at the Environment & Life Sciences Research Centre of KISR leading a number of national and international R&D funds. He is also the Environmental Pollution & Climate Program manager and has established the Waste Management Research Unit at KISR; and is currently supervising this research unit.

Engr. Hajar Jawad Karam is a Research Associate working under the supervision of Dr. Al-Salem at KISR. He has joined the institute back in 2016 with a Chemical Engineering BSc degree and has been part of various waste management research projects ever since as part of the Environmental Pollution & Climate Program. She is

Please cite this article as: S. M. Al-Salem, H. J. Karam, M. H. Al-Wadi et al., Thermal degradation kinetics of *real-life* reclaimed plastic solid waste (PSW) from an active landfill site: The mining of an unsanitary arid landfillreal-life reclaimed plastic solid waste (PSW) from an active landfill site –>, Ain Shams Engineering Journal, https://doi.org/10.1016/j.asej.2020.05.011

also an active member of the Analytical Characterization Laboratory of the Waste Management Research Unit, and has a special interest in thermal characterisation methods.

Mr. Majed Hameed Al-Wadi is a Senior Principle Research Technician at KISR, and has a special interest in waste management research projects for which he has devoted his time since 2015. He has over 30 years' experience in analytical methods and environmental laboratory hand-on analysis including various physical and thermal characterisation methods. He is also part of the research team working under the supervision of Dr. Al-Salem from which this research article was derived from.

Dr. Suzan Alsamaq is a post-doctoral research fellow at the Chemical Engineering Department of Aston University working in the research group of Dr. Jiawei Wang.

Dr. Guozan Jiang is a post-doctoral research fellow at the Chemical Engineering Department of Birmingham University working in the research group of Prof. Gary Leeke.

Dr. Jiawei Wang (JW) is a Senior Lecturer in Chemical Engineering at Aston University and a member of the Energy and Bioproducts Research Institute (EBRI). His research interests are on biomass/waste thermal treatment, utilisation of biomass-derived products and carbon capture and utilisation.

Prof. Gary Anthony Leeke is Professor of Chemical Engineering at the University of Birmingham. He is internationally leading in sustainable carbon processing and has >20 years' expertise in developing processes that enable the recovery, upgrading and remanufacture of materials and chemicals at the chemical engineering/chemistry/materials interface. He is expert in the engineering and science of advanced thermal conversion technologies and supercritical fluids and their integration with processes at lab, pilot and near-commercial scale. His work is interdisciplinary spanning engineering applications in oil, bioenergy, waste utilisation, biorefining, particle technology, polymer and composites, bioprocessing and the circular economy.

Please cite this article as: S. M. Al-Salem, H. J. Karam, M. H. Al-Wadi et al., Thermal degradation kinetics of *real-life* reclaimed plastic solid waste (PSW) from an active landfill site: The mining of an unsanitary arid landfillreal-life reclaimed plastic solid waste (PSW) from an active landfill site –>, Ain Shams Engineering Journal, https://doi.org/10.1016/j.asej.2020.05.011