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Kinetic study of municipal plastic waste

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ABSTRACT

Municipal Plastic Waste (MPW) comprises a mixture of thermoplastics (high and low density polyethylene, HDPE and LDPE; polypropylene, PP; polystyrene, PS; and polyethylene terephthalate, PET). The rate of MPW generation has increased steadily at 5% per year whilst that of MPW recycling is only at 3% per year. The remains are either incinerated or disposed in landfills. Pyrolysis, a thermochemical decomposition, provides an excellent alternative to valorise MPW into valuable products, such as hydrogen and hydrocarbons which could be further processed for fuels and chemicals like syngas (steam reforming). However, most MPW pyrolysis studies oversimplify the mechanism of reaction by assuming a first order decomposition, leading to inaccurate predictions of the process. This could cause big challenges in designing pyrolysers for MPW or scaling up pyrolysis process. This study was to develop a kinetic model to discover the true reaction mechanism of MPW pyrolysis experimentally and numerically by applying thermogravimetric analysis (TGA) and Matlab software. Several methods such as Kissinger–Akahira–Sunose, KAS; Málek and linear model fitting were applied to predict the mechanism of MPW pyrolysis and valuated by experimental data obtained from TGA. All components in MPW were decomposed in N₂ atmosphere over a set of heating rates (5, 10, 20 and 40 °C/min), temperatures of 30–700 °C and sample size range of 1–4 mm. The results confirmed that a complex mechanism rather than simple 1st order occurs during the decomposition because the variation in the apparent activation energy with conversion and kinetic model with heating rate. The assumption that MPW decomposition mechanism is a mixture of series and parallel reactions agreed well with experimental data and was confirmed by the results obtained from Málek method and linear model fitting.

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Introduction

Plastics products are highly convenient due to their resistance to degradation, versatility, light weight and low price. As a result, their use has increased by twenty fold in the past 60 years and so has the amount of plastic waste generated. EPA (U.S. Environmental Protection Agency) estimates that global

carbon footprint of plastic waste is somewhere between 100 and 300 million tonnes of CO₂ equivalent. To put those figures into context, plastics waste carbon footprint is equivalent to the carbon emissions of 21–63 million cars driven for one year [1], which represents 0.7–2 times the total number of vehicles registered in the UK at the end of 2015 [2].

Waste management is one of the European Union key priorities. Environmental waste policies try to maximise the

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efficient use of resources moving towards zero waste as stated by the waste hierarchy. Despite these efforts, over 50% of Europe's plastic waste were disposed in landfills during the past year. Every year the amount of plastic waste from packaging increases at a higher rate than the recycled fraction, meaning more plastic waste are diverted to landfill and incineration. Recycling of plastics is constrained by the addition of substances during their manufacture to improve the product quality and properties. At the end of the product life, those substances cannot be separated or removed and they decrease the quality of recycled products or even eliminate the possibility of recycling completely [3].

During 2013, only 26% of plastic waste was recycled/re-used in the UK whilst 29% was incinerated (142,353 tonnes of CO₂ equivalent) and 43% disposed in landfills (27,197 tonnes of CO₂ equivalent) [1,4,5]. Disposing plastic waste in landfills presents two problems: firstly, as they are not biodegradable, they break into small particles harmful for human and wild life; and secondly, 4% of the global oil production is used to manufacture plastics products [6], 50% of which have a short life so useful raw materials are disposed as waste in less than a year. Thermal treatments such as pyrolysis or gasification are excellent alternatives for sustainable energy recovery from MPW into fuels and chemicals [7].

Municipal Plastic Waste (MPW) consists mainly of high and low density polyethylene (HDPE and LDPE), polypropylene (PP), polyethylene terephthalate (PET) and polystyrene (PS) [5,8,9]. They present an average calorific value of 39.87 MJ/kg, representing an energy content of 80–90% of that of diesel fuel (45.30 MJ/kg) [10] so they must be considered as an energy source rather than waste required treatment. Pyrolysis presents a number of advantages over gasification for plastic feedstock: pyrolysis operation temperature (450–550 °C) is lower than gasification (700–900 °C) reducing energy requirements; and unlike pyrolysis, gasification of MPW generates CO or CO₂.

Pyrolysis is a complex process under an inert environment. Plastics decomposes as the temperature of the system increases, transforming into gas, liquid and solid residue. A catalyst (acid zeolites or transition metal oxides) can be added during the pyrolysis or to the liquid product for upgrading into synthetic fuels. The characteristics of the pyrolysis products strongly depend on the type and size of the feedstock, pyrolysis temperature, residence time and heating rate.

Plastic waste pyrolysis gas comprised mainly of light hydrocarbons (C₁–C₄) and hydrogen [11–14]. The liquid product is similar to crude oil and comprise of a mixture of aromatic, aliphatic and olefins from C₉ to C₃₅ [11–15]. Its proportion highly depends on the type of plastic. PS yields dark liquids with higher aromatic content. PET also presents higher aromatic content but the product has a yellow waxy appearance. HDPE, LDPE and PP yield light colour waxy products with low aromatic and higher aliphatic and olefin content.

Unlike incineration with energy recovery or mechanical recycling, pyrolysis products present a wide range of applications. Gases present a high calorific value (49.5 MJ/kg [13]) so they could be reused to decrease pyrolysis heat requirements; however they contain hydrogen and, in the case of HDPE and LDPE, the monomer that could be recovered. Light hydrocarbons (C₁–C₄) could be directed into steam reforming to maximise

hydrogen yield [16,17]. Liquid products are similar to crude oil and could be distilled to recover gasoline, diesel, and other fractions [13]. They can also be used for steam reforming [18].

The proportion of HDPE, LDPE, PP, PS and PET in the MPW mixture is unpredictable. It is important to understand decomposition behaviour of individual and mixtures to enable the development of a kinetic model that fully captures interplay between components. Several studies reported kinetic studies for either individual fractions comprising the MPW mixture [19–25] or focused on simple binary and tertiary mixtures [23,26–28].

Results obtained from kinetic studies are scattered and inconsistent. Sorum et al. [20] reported the activation energy (E_a) for commercial grade HDPE, LDPE, PP and PS as 445.1 kJ/mol, 340.8 kJ/mol, 336.7 kJ/mol, and 311.5 kJ/mol. However, Wu et al. [19] reported values of 233–326 kJ/mol for HDPE, 194–206 kJ/mol for LDPE, 184–265 kJ/mol for PP, and 172 kJ/mol for PS. Saha and Ghoshal [24] found that E_a and pre-exponential values for different PET drinking bottles were in a range of 162.15–338.98 kJ/mol and 2.83·10¹¹–1.18·10²⁵ depending on the bottle type and the method applied. Even though plastic products are made of the same type of plastic, they could behave differently during pyrolysis due to different manufacturing processes and incorporation of additives to improve their properties.

HDPE, LDPE, PP and PS kinetic studies are more common than PET [21] as they represent over half of the total plastic waste stream [15]. Most of them assumed a simple decomposition mechanism (first order reaction) and some performed single heating rate experiments [20,22,28,29] to obtain the kinetic model leading to inaccurate results. According to Westerhout et al. [21] this is only true for high degrees of conversion (over 70%) and low pyrolysis temperatures (<450 °C).

More complex models were developed. However, although they are more accurate they are also extremely complex and not really usable [21]. The most common ones are the infinite number of parallel reactions [30], the weak bond model [31], the consecutive reaction model [32,33], and the Simha and Wall model [34]. Sánchez-Jiménez et al. [35] suggested that MPW pyrolysis followed the Simha and Wall decomposition model [34] where random scissions occurred along hydrocarbon chains. This model was confirmed by Pérez-Maqueda et al. [29] whom also proved that the first order models could not accurately predict the actual plastic waste decomposition as they oversimplify MPW pyrolysis. There are strong interactions between pyrolysis products yielding to increasing E_a as the reaction proceeds [24] and therefore these must take into account. Vyazovkin [36] explained that the variation was due to the residue becoming more refractory at higher temperatures. The inconsistency in results found in literature suggests that thermal decomposition of MPW occurs through a complex mechanism and is required a thorough study to capture all possible steps in the process.

Experimental

Materials

Five types of MPW (HDPE, LDPE, PP, PET and PS) were used during this study. They were collected from O'Brien Recycling

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