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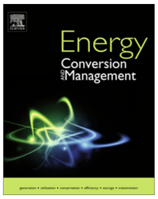

# Analysis of thermal degradation kinetics and carbon structure changes of co-pyrolysis between macadamia nut shell and PET using thermogravimetric analysis and $^{13}$C solid state nuclear magnetic resonance

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## ABSTRACT

Thermal degradation kinetics of co-pyrolysis of polyethylene terephthalate (PET) blended with macadamia nut shell were investigated using a large-scale customised thermogravimetric analysis (TGA) and $^{13}$C solid-state nuclear magnetic resonance (NMR) spectroscopy. Blending ratios ranging 20–80 wt.% of PET with macadamia nut shell were analysed at heating rates of 3, 5 and 8 °C/min up to 1273 K in the presence of $N_2$ atmosphere with a flow rate of 1 L/min. The differential thermogravimetric analysis (DTG) data was analysed by the Freeman–Carroll method to yield kinetic parameters which were correlated with chemical analysis by $^{13}$C solid-state NMR. The results indicated that two synergistic effects occurred between PET and macadamia nut shell during co-pyrolysis, which were characterised by an enhanced carbon yield of the co-pyrolysis products. The secondary reaction occurring between primary products of macadamia nut shell and PET was identified as the cause of the synergistic effect and this effect varied with weight fraction of macadamia nut shell in the blend and the heating rate. The measured changes in activation energy and reaction order indicated that the thermal degradation mechanism of co-pyrolysis is different to that of the individual components. The NMR results indicated that macadamia nut shell catalysed the degradation behaviour of PET leading to growth of polycyclic aromatic hydrocarbons (PAHs) through cross-linking reaction and enhancing the carbon yield from the PET.

## 1. Introduction

The co-pyrolysis of fossil fuel derived polymers with biomass in an inert atmosphere presents an alternative route to recycle waste polymers while implementing carbon capture of the renewable biomass. Intensive farming of crops such as macadamia can produce large quantities of waste biomass (exceeding 40,000 tonnes annually for the macadamia crop) [1]. Similarly nearly 15 million tonnes annually, of polymers such as polyethylene terephthalate (PET) are produced, primarily for the manufacture of disposable plastic drink bottles [2]. Instead of disposal in landfills or being used as an energy source in thermal power generation, co-pyrolysis technology enables the conversion of waste plastics and biomass into high value chemical feedstock that can replace dependence on fossil fuel [3,4]. The thermal treatment of plastics and biomass yields two fractions. The volatile light liquid fraction, known as tar can be downstream processed into various chemical feed stock. The condensed, high molecular weight fraction know as char, which is almost pure carbon has a variety of applications such as the carbon anode in aluminium production and graphite anode in lithium ion batteries [5,6]. Indeed the carbon derived from the pyrolysis of biomass and polymers at 1000 °C has outstanding electrochemical properties, comparable to those of graphite in some cases [7,8]. As a result, biomass and polymers have the potential to become an important alternative to replace petroleum coke as the carbon source for such applications.

The thermal degradation behaviour of synthetic polymers is relatively simple, even though the product yields from distinct polymers can be very different. For example, although both PET and polyolefins have single step primary degradation behaviour, the char yield of the PET pyrolysis is ca. ten times higher than that of polyolefins [9]. In comparison to synthetic polymers, biomass is predominantly a mix of three biopolymer components viz. cellulose, hemicellulose, and lignin. As expected from its multi-component nature, the thermal degradation of biomass is quite complex.

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TGA of macadamia nut shell in an inert atmosphere shows two main degradation regions from 565 K to 1075 K corresponding to the thermal degradation of hemicellulose and cellulose respectively [10]. Thermal degradation of lignin overlaps with that of both hemicellulose and cellulose. When biomass is heat treated in an inert atmosphere, the main components produce primary tar (primarily from the cellulose and hemicellulose) as well as primary char (from the lignin) over temperatures up to 820 K [11–13]. The primary char acts as a catalyst in converting the organic vapour to light gases by cracking reactions and then to secondary char by polymerisation reaction. The formation of char contributes to developing PAHs particularly during the low temperature (<800 K) stage of pyrolysis [12–16].

Co-pyrolysis of synthetic polymers with biomass enables the control of product distribution by varying the type and blend ratio of the raw materials. For example, previous studies on the co-pyrolysis of biomass and polyolefinic polymers have shown that the presence of biomass has a catalytic effect on the tar formation resulting in enhanced weight loss. The key factor for the enhanced weight loss is the hydrogen transfer from the degraded polyolefin (which have ca. 14 wt.% hydrogen) into the char-radical species (of the biomass) which prevents cross linking reactions to the char and thereby enhances the tar formation within the polyolefin [4,17–19]. On other hand polymers such as PET, which have a comparatively smaller weight fraction of hydrogen (4 wt.%), and produce high molecular weight aromatic products, may behave very differently in the presence of biomass during pyrolysis [9].

In the present work, we investigate the specific case of co-pyrolysis of macadamia nut shell biomass with PET to elucidate the co-pyrolysis kinetics and chemical structure which is at present poorly understood. We expect that due to its aromatic nature, PET has a distinct interaction with the biomass during co-pyrolysis which can enhance the end yield of the char residue.

The thermogravimetric analysis (TGA) is used to determine the overall thermal degradation kinetics which includes information such as the frequency factor, the activation energy and the overall reaction order [20]. Complementary to the TGA, $^{13}$C solid-state nuclear magnetic resonance (NMR) spectroscopy yields specific information regarding the chemical structure of the solid pyrolysis product at the relevant pyrolysis temperatures [21]. The resulting insights allow the significantly different kinetic mechanisms of PET-biomass co-pyrolysis to be determined along with a molecular level characterisation of the co-degradation process. This study of the carbonisation process of these materials in the manner of single and co-pyrolysis is expected to significantly contribute to understanding of char properties including electrochemical applications and the developing efficient char utilisation technologies [21,22].

## 2. Experimental

### 2.1. Raw materials

The materials used in this study were macadamia nut shell in the powder form and commercial available PET pellets. The macadamia collected in Queensland, Australia was milled the particle size ranging from 0.25 mm to 2 mm. The milled macadamia nut shell was dried in air at 60 °C for at least 48 h. The commercial PET did not contain any fibres or filler.

### 2.2. Weight reduction measurement in non-isothermal thermogravimetric analysis (TGA)

A customised large scale TGA was used to study thermal degradation behaviour of pure PET, macadamia nut shell and its blend. A sample weight of ca. 0.700 g (±0.001 g) was used for each experiment. In the current study, five different sample compositions were used: pure PET ($P_{100}$) and pure macadamia nut shell ($M_{100}$), a blend of 80 wt.% of macadamia nut shell and 20 wt.% of PET ($M_{80}P_{20}$ blend), a blend of 50 wt.% of macadamia nut shell and 50 wt.% of PET ($M_{50}P_{50}$ blend), and a blend of 20 wt.% of macadamia nut shell – 80 wt.% of PET ($M_{20}P_{80}$ blend). All samples were heated in an alumina crucible under an atmosphere of flowing nitrogen up to 1480 K at heating rates of 3 °C/min, 5 °C/min and 8 °C/min. Low heating rates were chosen because they yield more reliable results [23]. The flow rate of purge gas was kept at 1 L/min. Weight changes were automatically measured and simultaneously recorded by computer.

### 2.3. Determining the kinetic parameters

Thermal degradation kinetics of PET, macadamia nut shell and their blends were evaluated by the Freeman–Carroll method. All kinetics studies refer to the following basic rate equation [24]:

$$\frac{d\alpha}{dt} = kf(\alpha) = k(1-\alpha)^n \tag{1}$$

where $f(\alpha)$ is the reaction model implying the actual reaction mechanism and $k$ is the rate constant. According to Eq. (1), the rate of conversion at a constant temperature is a function of the reaction model and the rate constant. The conversion rate ($\alpha$) can be calculated using the following equation:

$$\alpha = \frac{W_o - W_t}{W_o - W_f} \tag{2}$$

where $W_o$, $W_f$ and $W_t$ are the initial weight, the final weight and the weight at any time ($t$) respectively. The rate constant ($k$) is obtained by the Arrhenius equation:

$$k = A\ \exp^{-E_a/RT} \tag{3}$$

where $A$ is the frequency factor, $E_a$ is the apparent activation energy (kJ/mol), $R$ is gas constant (8.314 J/mol), and $T$ is the absolute temperature (K). Eq. (1) can be converted as follows:

$$\frac{d\alpha}{dt} = A\ \exp^{-E_a/RT} f(\alpha) = A(1-\alpha)^n \exp^{-E_a/RT} \tag{4}$$

$$\ln\frac{d\alpha}{dt} = \ln\ A + n\ln(1-\alpha) - \frac{E_a}{RT} \tag{5}$$

The following equations can be used to study the thermal degradation kinetics at a constant heating rate by converting Eq. (5) if small changes in temperature lead to negligible change in the apparent activation energy [25]:

$$\Delta\ln\frac{d\alpha}{dt} = n\Delta\ln(1-\alpha) - \frac{E_a}{R} \times \frac{1}{\Delta T} \tag{6}$$

This equation is known as Freeman and Carroll method and it describes the reaction rate $\frac{d\alpha}{dt}$ (%/min) for degradation reaction.

$$\frac{\Delta\ln(\frac{d\alpha}{dt})}{\Delta\ln(1-\alpha)} = n - \frac{E_a}{R} \times \frac{\Delta T^{-1}}{\Delta\ln(1-\alpha)} \tag{7}$$

If the differences in $\Delta\ln\left(\frac{d\alpha}{dt}\right)$ and $\Delta\ln(1-\alpha)$ are obtained at regular intervals of $\frac{1}{T}$, the straight slope and intersect obtained from plot of $\frac{\Delta\ln\left(\frac{d\alpha}{dt}\right)}{\Delta\ln(1-\alpha)}$ against $\frac{\Delta T^{-1}}{\Delta\ln(1-\alpha)}$ produces $\frac{-E_a}{R}$ and reaction order ($n$) respectively. The apparent activation energy and reaction order can be determined from the best-fit lines. Frequency factor ($A$) is then calculated using $E_a$ and $n$ in Eq. (5) [26–28].