

## **Thermogravimetric analysis of face mask waste: kinetic analysis *via* iso-conversional methods.**

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**Abstract.** The surge of face mask waste in response to the global pandemic has proven to be a liability to the environment. Microfibers from plastic constituents of the face mask would cause microplastic pollution in the water bodies. Fortunately, these waste

could be converted into renewable source of energy *via* thermochemical method, i.e. pyrolysis. However, the studies on the thermal decomposition of face masks and their kinetic mechanisms are not well-established. The aim of this paper focuses on the prospects of pyrolysis at low to high heating rates ranging from 10 °C min<sup>-1</sup> to 100 °C min<sup>-1</sup>, to cater for the slow pyrolysis and fast pyrolysis modes. Following this, the thermal degradation behaviour of the face mask waste was studied via thermogravimetric analysis which determined the single peak temperature degradation range at 218 to 424 °C at 10 °C min<sup>-1</sup>, and maximum degradation rate was determined at 172.51 wt.% min<sup>-1</sup> at 520 °C, with heating rate of 100 °C min<sup>-1</sup>. Flynn-Wall-Ozawa (FWO) and Starink method was employed to determine the average activation energy and average pre-exponential factor of the pyrolysis process of face mask waste. i.e., 41.31 kJ mol<sup>-1</sup> and 0.9965, 10.43 kJ mol<sup>-1</sup> and 0.9901 for FWO and Starink method, respectively.

**Keywords:** Pyrolysis, Thermochemical, Polymer waste, FWO, Starink.

## 1. Introduction

The World Health Organisation (WHO) has made wearing a face mask a mandatory requirement, as a social distancing effort to combat the spread of the novel coronavirus disease 2019 (COVID-19). In response, the face mask production has rapidly increased to meet the demand globally. It is estimated that, face mask consumption could reach 129 billion per month [1]. These disposable face masks typically consist of 3-layered composites filter; the middle melt blown filter layer separating the inner and outer layers of non-woven polypropylene (PP) [2].

These face masks are often classified as single-use plastic waste made from petrochemical polymers such as PP and polyethylene (PE)[3]. The consequence of the accumulation of these plastic wastes is the microplastic pollution. Based on conducted studies, microfibrils (183 to 1247 particles piece<sup>-1</sup>) from face mask were being detected in the water bodies [4].

There are several methods to reduce these COVID-19 related wastes, i.e., reprocess, and recycling. In reprocessing strategies, there are studies on the sterilisation of used of face masks through supercritical CO<sub>2</sub> sterilisation [5] and photoactive antiviral self-sterilisation face masks [6]. In recycling strategies, studies have ventured in repurposing the face masks into sound porous absorbers [7].

Following this, there are studies that look into converting these wastes into renewable energy source. According to Nawaz and Kumar [8], pyrolysis is the preferred thermochemical conversion method as it is able to remove potential pathogens, while converting these wastes into valuable green fuels. However, in their studies, only low to moderate heating rates (10 °C min<sup>-1</sup> to 100 °C min<sup>-1</sup>) were utilised to study the pyrolytic behaviour of the face mask. Whereas the pyrolysis reactions, it is usually conducted in 2 modes, slow (<60 °C min<sup>-1</sup>), and fast pyrolysis (>60 to 1200 °C min<sup>-1</sup>) [9].

Therefore, this work focuses on the study of the pyrolysis of the three-layer samples of face mask via thermogravimetry. The thermogravimetric data is fit into an iso-conversional kinetic model, the Flynn-Wall-Ozawa (FWO), and Starink method.

## 2. Methodology

### 2.1. Sample Preparation and Characterisation

Face mask samples were collected from the brand *Pomerol*. The face mask components were divided into the outer layer, middle layer, inner layer, cotton straps, and metal strip. The components were individually weighed and recorded in **Table 1**. In this research project, only the plastic face mask layers were considered. The face mask layers were cut and sieved into 1 mm particle size.

*Table 1 Face mask components and its weights.*

Face mask components	Weight, g	Standard error, %
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Outer layer	0.9237	0.02%
Middle layer	0.8128	0.03%
Inner layer	0.7598	0.01%
Cotton strap	0.4141	0.06%
Metal strap	0.2711	0.01%

### 2.2. Thermogravimetric analysis (TGA)

Face mask pyrolysis was conducted with the *Seiko EXSTAR TG/DTA 6300* thermogravimetric analyser, with varying heating rates of 10, 20, 50, and 100 °C min<sup>-1</sup>. The inert gas (N<sub>2</sub>) supply was injected with a constant flow rate of 100 mL min<sup>-1</sup>. The samples were subjected to non-isothermal heating from room temperature to 900 °C.

### 2.3. Kinetic model

Iso-conversional methods such as Flynn-Wall-Ozawa (FWO) and Starink method are useful tools applied to compute the activation energies ( $E_a$ ) of the pyrolysis process. The model assumed that solid fuel follows a single step devolatilization reaction [10].

#### 2.3.1. Flynn-Wall-Ozawa (FWO)

$$\ln \beta = \left( \frac{\ln A \cdot E_a}{g(\alpha) \cdot R} \right) - 5.335 - \frac{1.0516E_a}{R \cdot T}$$

$\beta$ ,  $A$ ,  $E_a$ ,  $g(\alpha)$ ,  $R$ , and  $T$  are the heating rates, pre-exponential factor, activation energy, the integral form of the reaction model, universal gas constant and the temperature. The  $E_a$  can be determined by plotting  $\ln \beta$  vs  $1/T$ , at each of the conversion rate,  $\alpha$  at varying  $\beta$  [11].

#### 2.3.2. Starink method

$$\ln \left( \frac{\beta}{T^2} \right) = \left( \frac{\ln A \cdot E_a}{g(\alpha) \cdot R} \right) - 0.312 - \frac{1.008E_a}{R \cdot T}$$

The Starink method was employed to compare and validate the kinetic parameters determined from the FWO method.  $E_a$  is obtained from the slope of plot  $\ln \left( \frac{\beta}{T^2} \right)$  vs  $1/T$  [11].

## 3. Results and Discussion

### 3.1. TGA results

From **Figure 1**, the TG and DTG curves for the pyrolysis of face mask are observed to show only one degradation peak, at lower heating rate of 10 °C min<sup>-1</sup>, the degradation temperature range is determined to be 218 to 424 °C. A literature search was found that studied the thermal degradation range within 312 to 471 °C for the face mask, which is comparatively similar to the current study [8]. At 100 °C min<sup>-1</sup>, the degradation temperature range increased to 380 to 550 °C. This shift of temperature range is caused by the phenomenon called thermal lag, where temperature gradient is being formed at the surface to the center of the particle at high heating rates [12]. The start and end temperature of the major degradation of face mask (300 – 420 °C) were positioned between those of PP and PE (275 to 500 °C), which were the major components in the production of face masks [13]. Moreover, at all heating rates, the face mask achieved complete conversion into volatiles and non-condensable gases within the range of 364 °C and 540 °C at 10 °C min<sup>-1</sup> and 100 °C min<sup>-1</sup> respectively. The maximum degradation rates of the face mask waste samples were 10.65, 24.15, 83.82, 172.51 wt.%/min, for the heating rates of 10, 20, 50, and 100 °C min<sup>-1</sup> respectively.

### 3.2. Kinetic analysis

Following this, the TGA data was fitted into two kinetic models, i.e., FWO and Starink method to determine the kinetic parameters of the pyrolysis of face mask wastes. The Arrhenius plots are shown in **Figure 2**. Based on the summary of the results in **Table 2**, both models showed great fitting with the coefficient of determination ( $R^2$ ) ranging from 0.9722 to 0.9990 for FWO method, and 0.9954 to 0.9988 for Starink method.

Kinetic parameters such as activation energy ( $E_a$ ) and pre-exponential factor ( $A$ ) are important as  $E_a$  measures the energy required for the pyrolysis process to occur, enhancements of the process can also be reflected in the process i.e. catalyst, pre-treatment. The lower the  $E_a$ , the less energy is required [11]. The  $A$  refers to the frequency of collisions of particles within the system, where the higher the value, the quicker the reaction [14]. The  $E_a$  obtained from the results are  $41.31 \text{ kJ mol}^{-1}$  and  $10.43 \text{ kJ mol}^{-1}$  for FWO and Starink method, respectively. The  $A$  computed from the y-intercept of the Arrhenius plots are 0.9965 and 0.9901, respectively for FWO and Starink method. The discrepancies of both kinetic methods arise from its derivation methods and assumptions. The FWO method linearises the temperature integral using Doyle's approximation method [15]. While Starink method is an optimised expression of both FWO and Kissinger-Akahira-Sunose (KAS) method [15]. Further analyses by comparing the  $E_a$  and the  $\alpha$ ,  $A$  and  $\alpha$  were carried out, and illustrated in **Figure 3**. It was observed that FWO method showed more fluctuations in the activation energies, while Starink method showed a strong resistance to change at each conversion stage. Both methods showed similar trend for the pre-exponential factors determined at each conversion stage.

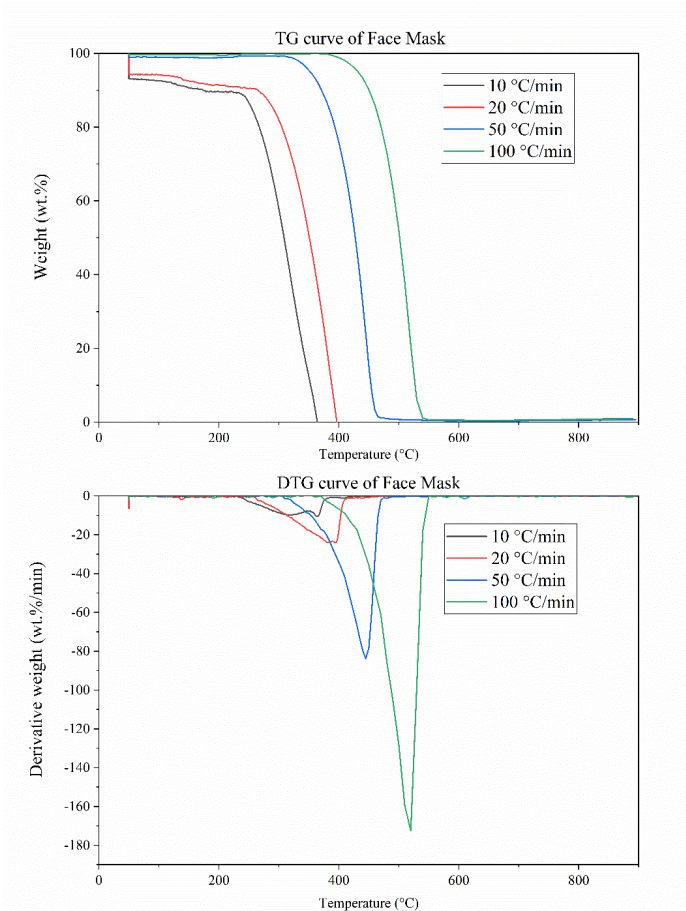


Figure 1 TG and DTG curve of non-isothermal heating of face mask samples.

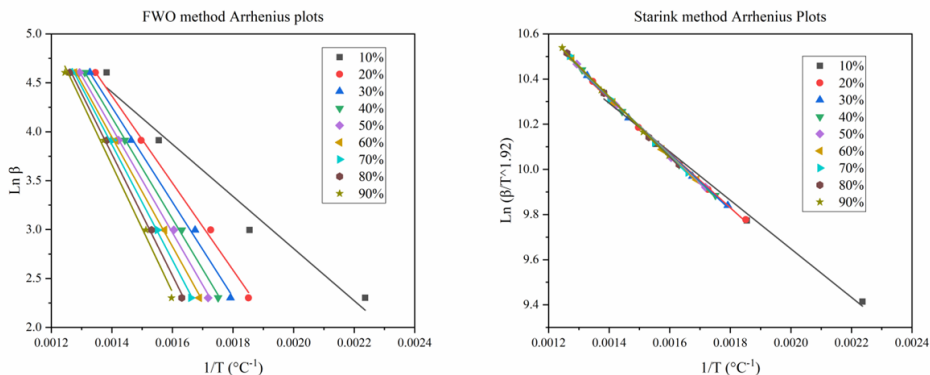


Figure 2 Comparison between FWO and Starink method kinetic models.

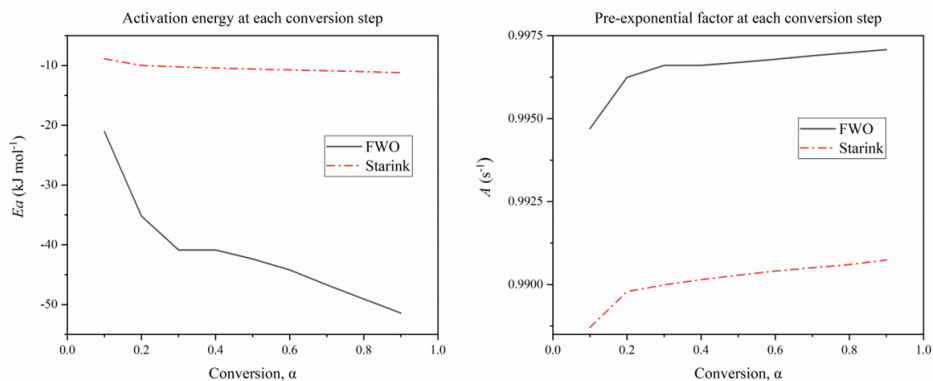


Figure 3 Comparison of  $E_a$  and  $A$  determined from FWO and Starink kinetic models.

Table 2 Kinetic model fitting for the pyrolysis of face mask waste samples via FWO and Starink method.

Conversion	$R^2$	Slope	Y-intercept	$E_a$ , $\text{kJ mol}^{-1}$	$A$ , $\text{s}^{-1}$
<b>FWO method</b>					
0.1	0.9722	-2665.4	8.1376	21.07	0.9947
0.2	0.9966	-4450.6	10.597	35.19	0.9962
0.3	0.9990	-5170.0	11.383	40.87	0.9966
0.4	0.9990	-5170.0	11.383	40.87	0.9966
0.5	0.9987	-5359.3	11.544	42.37	0.9967
0.6	0.9989	-5591.8	11.775	44.21	0.9968
0.7	0.9982	-5906.8	12.139	46.70	0.9969
0.8	0.9985	-6206.2	12.462	49.07	0.9970
0.9	0.9934	-6504.4	12.768	51.42	0.9971
			<b>Average</b>	<b>41.31</b>	<b>0.9965</b>
<b>Starink method</b>					
0.1	0.9954	-1075.2	11.799	8.87	0.9887
0.2	0.9983	-1210.2	12.008	9.98	0.9898
0.3	0.9985	-1239.2	12.052	10.22	0.9900
0.4	0.9985	-1262.5	12.087	10.41	0.9901
0.5	0.9986	-1283.1	12.117	10.58	0.9903
0.6	0.9985	-1303.0	12.146	10.75	0.9904
0.7	0.9986	-1318.8	12.169	10.88	0.9905
0.8	0.9987	-1335.1	12.192	11.01	0.9906
0.9	0.9988	-1358.5	12.224	11.20	0.9907
			<b>Average</b>	<b>10.43</b>	<b>0.9901</b>

#### 4. Conclusion

In summary, the thermal decomposition of face mask waste can be observed as a single peak DTG curve ranging from 218 to 424 °C at the lower heating rate of 10 °C min<sup>-1</sup>, with a maximum degradation rate of 10.65 wt.% min<sup>-1</sup>. Further, when the sample was subjected to a higher heating rate of 100 °C min<sup>-1</sup>, the maximum degradation rate was enhanced to 172.51 wt.% min<sup>-1</sup>. From the kinetic analysis, Starink method proves to be a much reliable model for the pyrolysis process, yielding higher average  $R^2$  value (0.9982) than FWO (0.9949) method. The kinetic parameters obtained from Starink method was 10.43

$\text{kJ mol}^{-1}$  and  $0.9901 \text{ s}^{-1}$  for  $E_a$  and  $A$  respectively. Future work for this study includes the determination of the reaction mechanism *via* model fitting methods, such as Criado method or Coats Redfern method. Furthermore, the effects of catalyst, as well as the co-pyrolysis technique with biomass could also be explored.

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