Pyrolysis and Combustion Kinetics of Disposable Surgical Face Mask Produced During Covid-19 Pandemic

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Research Article

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Pyrolysis and combustion kinetics of disposable surgical face mask produced during Covid-19 pandemic

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Abstract

In order to prevent the spread of Covid 19, most countries have made face masks compulsory. Millions of face mask are disposed of daily in the community. Therefore, the aim of the present paper is to study the thermo-chemical (pyrolysis and combustion) behavior of the face mask for its safe disposal. The kinetic parameter activation energy was calculated using both the model-based Coats–Redfern method and model-free methods (Flynn-Wall-Ozawa, Kissinger-Akihara-Sunose, and Starink) at four different heating rates (5, 10, 15, and 20 °C/min). Physical morphology with elemental analysis was performed using field-emission scanning electron microscopy and energy-dispersive X-rays. Results have shown that face masks decompose in the temperature range of 320–480 °C during pyrolysis with a maximum derivative weight loss of 2.5 %/°C. Combustion took place between 200 and 370 °C with a maximum derivative weight loss of 1.25 %/°C. The average activation energies calculated using model-free methods for pyrolysis and combustion were ~135 kJ/mol and ~65 kJ/mol, respectively. The leftover residue for both pyrolysis and

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combustion was in the range of 1.35 to 3.50 wt.%. In conclusion, thermo-chemical processes are a promising method for the safe disposal of face mask waste.

**Keywords:** Face mask; Waste; Pyrolysis; Combustion; Kinetics

**Statement of Novelty**

Covid 19 situation has created a huge impact on the society, economy, health and environment. There is a sudden rise in the generation of waste known as surgical medical Face Mask (FM) that is commonly used by the public to prevent the spread of pandemic. Continual use of this face mask during the Covid-19 pandemic has increased the littering and waste. So far, no study has investigated and compared the kinetic data of the FM under both pyrolysis and combustion process. Therefore, this study presents for the first time the pyrolysis and combustion of FM materials at four different heating rates with kinetics calculations that can be useful to design and optimize the process at large-scale. In contrast, combustion of FM has not been explored yet. We report a comprehensive kinetic and reaction mechanism analysis of FM in both inert and oxygen environments.

1. **Introduction**

   The outbreak of the SARS-CoV-2 epidemic and its rapid spread throughout the world has had a catastrophic impact on the social life, economy, and health of the community. At a global level, this deadly virus has taken more than 2.0 million human lives, with active cases reaching more than 87 million, and new cases continuing over 700,000 every day with third and fourth waves in some countries [1]. Fig. 1a shows the number of confirmed
Covid-19 cases across the world [2]. The USA recorded the highest number of Covid-19 cases, followed by India, Brazil, Russia, France, Spain, Argentina, the U.K.

**Fig. 1.** a) Confirmed cases of Covid 19 across the continents of the world, b) three layer/ply face mask materials, c) disposable FM waste littering the roadside and public places
Scientists are exploring cures and medicines with some success for Covid-19 pathogenesis, genetic evolution, and prevention. Face masking and physical distancing is the most appropriate control measure to reduce the severity of disease [3]. On January 29, 2020, the WHO advised using masks in the community to avoid contamination and the spread of this deadly virus. Therefore, most countries across the world made it compulsory to wear face masks (FMs) in public or crowded places.

Thus, the demand for personal protective equipment (PPE), including the FM, has increased markedly. Disposable surgical FMs are generally assumed to be effective for a few hours only. The global market for disposable masks was worth $75 billion in the first quarter of this year and is expected to grow at a rate of over 50% for the next seven years [4]. This surge in demand of the FM for both healthcare and public use has put a strain on the global of mask production supply chain and distribution system [5]. For instance, Sangkham [6] reported that approximately 4.6 billion FM units were used in 49 Asian countries, with the highest use in China (989,103,299 units), followed by India, Indonesia, Bangladesh, Japan, Pakistan, Iran, the Philippines, and Vietnam. Although the use of FMs plays an important role in a crisis like Covid-19, its significance will remain even after life returns to normalcy.

The FM is a multi-layered (usually three-ply) structure made of non-woven polypropylene (PP) fabric. The first or outer layer that protects against liquid splash and the third or inner layer in contact with the mouth are usually made of PP, as illustrated in Fig. 1b. The second or middle layer that act as filter is made up of BFE 95 “melt-blown” cloth of micro-diameter fibers in a random pattern that can trap small particles. The nose wrap and ear string are made of plastic and elastic, respectively.
The continual and mass use of FM during the pandemic has increased the environmental consequences related to littering, waste, and unsafe disposal, as shown in Fig. 1c. However, the potential impacts of FM are far overshadowed by the more urgent health issues [7]. The unpredictable environmental aspect of Covid-19 has increased medical waste, including surgical FMs, by a considerable degree [8]. Currently, millions of contaminated surgical FM and other PPE materials related to the Covid-19 virus are becoming infectious waste [6] that can cause serious environmental and health problems if not handled properly [9]. Poor solid waste management in most of countries will impose a major threat of contamination in the general community, particularly for countries that still rely on open landfills for their waste management.

Thermochemical methods such as pyrolysis and combustion are promising processes that can safely dispose of waste materials as well as convert them into valuable products. While thermo-chemical and kinetic studies for biomass and waste materials are available in the literature [10-19], so far, few studies [20-22] are available on the kinetic data for the FM, but these are limited to pyrolysis process only. None have presented and compared the kinetics of pyrolysis with combustion process in the literature. Recently, Jung et al. [20] used nitrogen and carbon dioxide environments in a thermogravimetric analyzer (TGA) from 35 to 900 °C with a constant heating rate of 10 °C/min. They also carried out one-stage, two-stage, and catalytic pyrolysis of FMs in a tubular reactor and analyzed the chemical compounds of the gaseous product. This study was limited to pyrolysis only with one heating rate. According to them [20], it is difficult to recycle FMs because of the FM materials and the high probability of cross-contamination. Very recently, Chen et al. [21] published an article on the pyrolysis characteristics, kinetics, thermodynamics, and volatile
products of waste medical surgical mask rope made up of elastic. Thus, kinetic analysis provides crucial information on the decomposition behavior of any feedstock, mechanism of reaction that can help to design the reactor [16], optimization of the process, and scale-up [16, 23].

Therefore, this study presents and compares for the first time the pyrolysis and combustion behavior and kinetics analysis of FM waste materials. The temperature was varied from room temperature to 750 °C at four different heating rates. The activation energy was calculated using model-based (Coats–Redfern, CR) and model-free (Flynn-Wall-Ozawa (FWO) and Kissinger-Akihara-Sunose (KAS), and Starink (STK)) methods. The surface morphology and elemental analysis of FMs using field-emission scanning electron microscopy (FE-SEM) and energy-dispersive X-ray (FE-SEM-EDX) are also presented. This study provides useful data for disposing of FM waste materials in a controlled manner.

2. Methodology

2.1. Materials

New disposable surgical FM obtained from the local market were used in this study due to safety and health concerns of the students and staff. In actual conditions, the waste FM generated from both domestic and medical facilities can be sorted and collected with great care and can then be sent for thermo-chemical processing. FM samples were manually hand-cut into small particles in the size range of 1 to 3 mm and kept in airtight sealed bags for further analysis. It should be noted that the combination of three layers of FM (inner,
outer, and middle) was utilized in the analysis as received. Table 1 presents the proximate and ultimate analysis of FM sample. The carbon content in FM is about ~180%, ~75%, and ~40%, higher than the sewage sludge [18], variety of biomasses [16], and bituminous coal [10], respectively. However, it is almost similar to electronic keyboard keys waste [17], and low-density polyethylene [18]. The chemical composition of FM clearly indicates its potential to convert it into energy, fuels and chemicals with minimal environmental impact since the sulphur and nitrogen contents are very low.

Table 1
Proximate and ultimate analysis of FM waste sample

| Proximate analysis, wt.% (this study) | Reference [22] |
|--------------------------------------|----------------|
| Moisture content                     | 0.12           |
| Volatile matter                      | 97.0           |
| Ash                                  | 3.0            |

| Ultimate analysis |          |
|-------------------|----------|
| C                 | 84.71    |
| H                 | 14.35    |
| N                 | <0.01    |
| S                 | <0.01    |
| O*                | 0.94     |

*Oxygen is by difference = 100% - [C%+H%+N%]

2.2. Pyrolysis and combustion of FM using TGA machine

The experiments were conducted in a TGA (TA Instrument Q50, USA). In each experiment, about 5 to 6 mg of FM samples were placed in a ceramic pan and loaded into the TGA. The temperature was ramped from room temperature to 750 °C at different heating rates (β) of 5, 10, 15, and 20 °C min⁻¹ in an inert (nitrogen) and oxygen (air) environment under a constant gas flow rate of 60 ml/min. The effect of different β on the
thermal behavior was examined and the kinetic parameter was calculated for the decomposition temperature range.

2.3. **Kinetics analysis and reaction mechanism**

The activation energy \( (E_a) \) was calculated based on the TG data using model-fitting (CR) and model-free (FWO, KAS, and STK) methods. In the present study, the \( E_a \) was calculated in the main decomposition region.

The thermal degradation of the sample is a function of temperature and follows the fundamental Arrhenius law (Eq. 1).

\[
k(T) = Ae^{-\frac{E_a}{RT}}
\]  

(1)

Non-isothermal condition is typically expressed as a solid-state reaction rate as

\[
\frac{d\alpha}{dt} = \beta \frac{d\alpha}{dT} = Ae^{-\frac{E_a}{RT}(1 - \alpha)^n}
\]  

(2)

where \( A \) is the frequency or pre-exponential factor, \( E_a \) is the activation energy of the reaction, \( R \) is the universal gas constant, \( T \) is the absolute temperature, \( \beta \) is the heating rate, \( n \) is the order of reaction, \( t \) is time, and \( \alpha \) is the fraction of reactant decomposed at time \( t \) (min) and is given as follows:

\[
\alpha = \frac{w_i - w}{w_i - w_f}
\]  

(3)

where \( w_i \), \( w \), and \( w_f \) are the initial, actual, and final weights of the sample, respectively.

The integral form of Eq. 2 is

\[
g(\alpha) = \int_0^\alpha \frac{d(\alpha)}{f(\alpha)} = \frac{A}{B} \int_0^T \exp \left( -\frac{E}{RT} \right) dT = \frac{AE}{\beta R} \rho(x)
\]  

(4)
where \( p(x) \) is an approximation equation, with \( x = E/RT \). Several approximations will eventually lead to the following final equations.

**CR:** \[
\ln \left( \frac{g(\alpha)}{T^2} \right) = \ln \left( \frac{AR}{\beta E_a} \right) - \frac{E_a}{RT} \tag{5}
\]

**KAS:** \[
\ln \left( \frac{\beta}{T^2} \right) = \ln \left( \frac{AR}{E_a g(\alpha)} \right) - \frac{E_a}{RT} \tag{6}
\]

**FWO:** \[
\ln \beta = \ln \left( \frac{AE_a}{Rg(\alpha)} \right) - 2.315 - 0.457 \frac{E_a}{RT} \tag{7}
\]

**STK:** \[
\ln \left( \frac{\beta}{T^{1.92}} \right) = C_s - 1.0008 \left( \frac{E_a}{RT} \right) \tag{8}
\]

In the CR method \([24]\), the plot of \( \ln(-\ln(1 - \alpha)/T^2) \) against \( 1/T \) results in a straight line with slope \( -E_a/R \) and intercept \( \ln\left(\frac{AR}{\beta E_a}\right) \). The plot of \( \ln\left(\frac{\beta}{T^2}\right) \) against \( 1/T \) in the KAS method \([22]\) shows a linear relationship, and the slope of the straight line is equal to \( -E_a/R \).

Similarly, in the FWO method \([25, 26]\), a linear relationship is established by plotting \( \ln(\beta) \) against \( 1/T \), and the resulting slope will be equal to \( -1.052E_a/R \). Lastly, a linear regression line plot of \( \ln\left(\frac{\beta}{T^{1.92}}\right) \) versus \( 1/T \) in the STK method \([27]\), provides a slope that will be equal to \( -1.0008E_a/R \).

Further, in the present study, 14 different types of reaction models/mechanism \([28]\), as listed in Table 2, are employed to calculate the global \( E_a \) of FM waste using a model-fitting Coats-Redfern (CR) method based on the thermogravimetric data at 5, 10, 15, and 20 °C min\(^{-1}\). Thus, the value of the \( E_a \) obtained by the CR method at different reaction models will be compared with that obtained using the three model-free methods. If the global \( E_a \) value of one certain reaction model (Table 3) is nearest to the value of the model-free
methods, then that reaction model will characterize the pyrolysis and combustion process of FM waste [29].

Table 2
The reaction models of solid-state kinetics [28, 29]

| No. | $g(\alpha)$                        | Reaction mechanism                      |
|-----|------------------------------------|----------------------------------------|
| 1   | $1 - (1 - \alpha)^{2/3}$           | Chemical reaction                       |
| 2   | $1 - (1 - \alpha)^{1/4}$           | Chemical reaction                       |
| 3   | $1 - (1 - \alpha)^2$               | Chemical reaction                       |
| 4   | $1 - (1 - \alpha)^3$               | Chemical reaction                       |
| 5   | $1 - (1 - \alpha)^4$               | Chemical reaction                       |
| 6   | $\alpha^{3/2}$                     | Nucleation                              |
| 7   | $\alpha^{1/2}$                     | Nucleation                              |
| 8   | $-\ln(1 - \alpha)$                | Assumed random nucleation               |
| 9   | $[-\ln(1 - \alpha)]^{2/3}$         | Assumed random nucleation               |
| 10  | $[-\ln(1 - \alpha)]^{1/3}$         | Assumed random nucleation               |
| 11  | $\alpha$                           | Contracting disk                        |
| 12  | $1 - (1 - \alpha)^{1/2}$           | Contracting cylinder                    |
| 13  | $1 - (1 - \alpha)^{1/3}$           | Contracting sphere                      |
| 14  | $\alpha^2$                         | One-dimensional diffusion               |

2.4. FE–SEM with EDX

The physical surface morphology and elemental analysis of FM samples was analyzed using FE-SEM), model Hitachi SU8020 UHR Cold-Emission and Oxford-Horiba Inca XMax50 EDX. Samples were coated with 2–6 nm of gold coating using a sputter coater in order to minimize sample charging by non-conducting materials. FE-SEM images were taken at several magnifications (20 μm scale @ 2000 magnification, 100 μm scale @ 300
magnification, and 1 mm scale @ 35 magnification) and at 5.0 kV. The EDX elements were estimated at 15 kV and at 200 µm scale.

3. Results and discussion

3.1 Physical and elemental analysis of FM samples using FE-SEM and EDX

The FE-SEM micrographs from Fig. 2 clearly illustrates that FM is made up of fibrous materials. The fibers are longitudinal cylindrical structures that are differently sized, randomly oriented, and nonwoven (entangling in each other). Similar physical surface morphology was reported by Zheng et al. [30] for PP nonwoven fabric. All three layers (inner, middle, and outer) are made up of fibers.

The EDX spectrum of the FM samples and the elements on weight percentages (Table S1) suggests the exclusive presence of C and some traces of O in all the individual (inner, middle, and outer) and mixed layers of FM samples consisting of a large quantity of the fibers. These elements could be the result of their parent material, such as viscose and polyester [31-33]. The presence of high carbon and hydrogen with low content of oxygen element in the FM material is also confirmed by recent study [22]. Inorganic materials were not detected, or if present, might have been traces.
Fig. 2. FE-SEM images of disposable FM fabric materials
3.2 Pyrolysis of disposable surgical FMs

Pyrolysis TG and DTG profiles of the FM samples showed one major decomposition region, as presented in Fig. 3. There was no weight loss below 300 °C in both TG and DTG profiles, indicating a total absence of moisture in the FM sample. Typically, PP non-woven textile fabrics have the capability to retain and quickly transfer heat and moisture away from the FM for higher levels of wear comfort [34]. Apparently, new FMs do not contain moisture as they are manufactured in a controlled environment and packed to avoid contamination. However, used FMs may contain some moisture, which is absorbed by the inner layer of the FM (Fig. 1b) from the exhaled air due to respiration [35]. The moisture can be absorbed by the FM fabric in two ways: either by diffusion, and/or by wicking by capillary transport [36]. The presence of a small amount of moisture in the used FM does not affect thermochemical processing.

The major weight loss of the FM sample occurred during the main pyrolysis stage within a temperature range of 320–500 °C. Only one major derivative peak was detected in this temperature range for FM pyrolysis, as seen in Fig. 3b (DTG curve), unlike biomass materials [15, 37, 38], which showed two or more peaks. The initial and final degradation temperature of the FM in the main pyrolysis region was delayed, with the increase in heating rate as presented in Table 3. This is due to a slower decomposition process at higher heating rates, as the heat transfer is not as effective at higher heating rates compared with lower heating rates [39]. The sample heats gradually at lower heating rates and thus has more effective and improved heat transfer.
In the present study, only one sharp DTG peak (Fig. 3b) in the range of 315 to 490 °C was observed that clearly indicated the presence of PP \((\text{C}_3\text{H}_6)_n\) consists of a thermoplastic polymer chain that is usually crystalline) as the major constituent in the FM. This agrees with the TG and DTG profiles of PP studied by other researchers [22, 40-42]. Moreover, industrial nonwoven fabrics are embedded with cellulose and are used for manufacturing cosmetics, masks, medical accessories, and other things [43]. A high degradation temperature (>300 °C) during pyrolysis designates a higher thermal stability of the FM materials.

Another prominent region was located above 400 °C (Fig. 3), also known as the char region, where no significant weight loss was observed. No peak was noted beyond 450 °C
in the DTG curves, which indicate a complete degradation of sample with very minimal leftover residue at a temperature of 500 °C (Table 3). It should be noted that FM is a very light (low density) material and the remaining residue or char (left after TGA analysis) might fly away with the purge gas.

Table 3

Degradation temperatures and residue obtained after pyrolysis and combustion of FM

| Process heating rate | $T_i$, °C$^1$ | $T_f$, °C$^2$ | $DTG_{max}$, %/°C$^3$ | $T_{peak\_DTG\_max}$, °C$^4$ | Residue @ 500 °C, wt. % |
|----------------------|---------------|---------------|------------------------|-----------------------------|-------------------------|
| Pyrolysis            |               |               |                        |                             |                         |
| 5                    | 395           | 438           | 2.34                   | 425                         | 2.73                    |
| 10                   | 415           | 452           | 2.85                   | 440                         | 1.34                    |
| 15                   | 420           | 465           | 2.10                   | 450                         | 2.73                    |
| 20                   | 435           | 475           | 2.60                   | 462                         | 3.41                    |
| Combustion           |               |               |                        |                             |                         |
| 5                    | 218           | 325           | 1.04                   | 260                         | 2.73                    |
| 10                   | 252           | 335           | 1.20                   | 303                         | 2.22                    |
| 15                   | 260           | 340           | 1.31                   | 306                         | 1.80                    |
| 20                   | 280           | 355           | 1.35                   | 335                         | 2.00                    |

$^1T_i$ – initial degradation temperature according to intersection method applied to TG curves

$^2T_f$ – final degradation temperature according to intersection method applied to TG curves

$^3DTG_{max}$ – maximum degradation rate (DTG curve)

$^4T_{peak\_DTG\_max}$ – peak temperature at maximum degradation rate (DTG curve)

3.3 Combustion of disposable surgical FMs

The combustion behavior of FM was different from the pyrolysis process (Fig. 4). For instance, the initial degradation temperature during combustion was much lower (200 to 240 °C) than pyrolysis. There was no obvious weight loss below 200 °C, thus showing an absence of moisture content as during the pyrolysis process (Section 3.2). This would be
quite beneficial to the combustion process, as it can save energy needed to evaporate the water content and can cause earlier ignition of the sample [44].

![TG, DTG, and conversion degree profiles of FM during combustion]

Fig. 4. TG, DTG, and conversion degree profiles of FM during combustion

The second event or major combustion happened in the temperature range of 200 to 370 °C. The ignition temperatures were 218, 252, 260 and 280 °C at 5, 10, 15, and 20 °C/min, respectively, according to the intersection method applied on the TG curves [45]. These ignition temperatures are much lower than anthracite (~800 °C), bituminous (~600 °C), and brown (~450 °C) coals, but are comparable to some biomass such as date palm seed (200 °C) [38], sunflower shell (201 °C), pine cone (201°C), and cotton refuse (150 °C) [46], and amazon biomass (140–200 °C) [44]. It was reported by Rybak et al. [47] that ignition temperature is related to the volatile matter content and the chemical composition of the
material. For instance, the ignition temperature decreases when the volatile content is high. The volatile matter of the FM sample was found to be higher than 90 wt.% (TGA curve), which attributes to lower ignition or combustion temperature. The ignition temperature of pure PP material is ~270 °C at a 10 °C/min heating rate [48], which is somewhat higher than the FM material.

The DTG thermograms of the combustion process for FM samples showed only one peak (Fig. 4b) similar to pyrolysis (Fig. 3b), however the maximum degradation rate ($DTG_{\text{max}}$) and peak temperature ($T_{\text{max,DTG}}$) (Table 3) are different. Further, the presence of small peaks between 400 and 450 °C during the combustion process as seen in the DTG profile (Fig. 4b) is due to the oxidation of char to ash. The maximum degradation rate (from the DTG curve) of FM samples at 5, 10, 15, and 20 °C/min was 1.04, 1.20, 1.31, and 1.35 wt.%/°C, respectively. This signifies that the rate of combustion is faster than the rate of pyrolysis [49]. The oxygen environment facilitated the early decomposition of carbon, and oxygen content in the sample. It is worth noting that the remaining residue (1.3 to 3.5 wt.% in Table 1) at 500 °C was almost similar for both the pyrolysis and combustion processes. Notably, the FM char was difficult to breakdown in the combustion process which might be due to presence of inorganic and mineral components that might have limited the further oxidation and thus the residue leftover is comparable to the pyrolysis. FM contains majorly (~97 wt.%) of carbon (Table 1) that reacts with available oxygen during combustion process to produce gases and ash residues.

Typically, PP materials contain a high amount of volatile matter (~99 wt.%) and low ash (~0.15 wt.%), as reported in [49]. Therefore, they produce very minimal char at the end of a
thermo-chemical process. The decomposition process was almost finished at 500 °C, as the residual weight at 500 °C and at 600 °C were similar. The degradation temperature, peak degradation temperature, and residue left over from the present FM sample was close to that of pure PP material studied by previous researchers [49]. This proves that the thermal behavior and stability of the FM sample resembles that of PP materials, which are the primary material for manufacturing the FM.

3.4 Conversion degree of FM samples during pyrolysis and combustion

The conversion degree shows only one principle stage of reaction consistent with TG and DTG profiles, as presented in Fig. 3c and 4c. Surprisingly, it took a long time (60 min at 5 °C/min) to start the initial pyrolysis degradation of FM sample, as compared with 30 min at 10 °C/min, 21 min at 15 °C/min, and 16 min at 20 °C/min. In comparison, the initial combustion degradation of the FM sample started at 35 min for 5 °C/min, 18 min at 10 °C/min, 14 min at 15 °C/min, and 10 min at 20 °C/min. After the FM sample began to degrade, the complete conversion or reaction degree was more rapid. For instance, the FM samples took 25 min at 5 °C/min to completely pyrolyze, 13 min at 10 °C/min, 9 min at 15 °C/min, and 7 min at 20 °C/min, whereas it took 45 min at 5 °C/min, 23 min at 10 °C/min, 13 min at 15 °C/min, and 12 min at 20 °C/min for the complete combustion of FM samples. Much less time would be required for them to completely pyrolyze or combust in an actual large-scale reactor operating at a high temperature and heating rate.

The conversion degree at peak degradation temperature ($T_{\text{max,DTG}}$) for the pyrolysis of the FM was, on average, 31% for all heating rates. However, it varied during the
combustion process with 56% @ 5 °C/min, 40% @ 10 °C/min, 41% @ 15 °C/min, and 26% @20 °C/min. The time to reach the $T_{max_{DTG}}$ from the initial degradation temperature during the pyrolysis process was 20, 11, 7, and 6 min at 5, 10, 15, and 20 °C/min, respectively, whereas it took 11, 10, 5, and 5 min at 5, 10, 15, and 20 °C/min, respectively, to reach $T_{max_{DTG}}$ from the initial degradation temperature during the combustion process. Finally, it can be concluded that the degree of conversion highly depends on the heating rate. The maximum conversion of the FM sample during pyrolysis and combustion shows great potential for fuel and chemical applications [20].

3.5 Kinetics analysis and reaction mechanism

The data from the TGA were used to calculate the activation energy ($E_a$) for all the kinetic methods by linear regression, as mentioned earlier in Section 2.3. An example of these linear regressions for different kinetic methods is shown in Fig. 5. The parallel linear regression lines are attributed to similar kinetic behavior and reaction mechanisms [50]. Table 4 shows the coefficient of determination ($R^2$) obtained for each kinetic method, and it is commonly greater than 0.9. The models used to calculate $E_a$ were applied to the main decomposition region (320–480 °C for pyrolysis and 200–360 °C for combustion).

Remarkably, the average $E_a$ values for FWO, KAS, and STK were quite comparable, and that for KAS and STK were similar. This is because Starink [27] presented a more accurate approximation of the temperature of the FWO and KAS equations. While values obtained by CR method were quite high compared with model-free methods. Only the $E_a$ obtained at a lower heating rate (5 °C/min for CR) were somewhat close to the model-free
methods. It can be observed in Table 4 that $E_a$ was also influenced by the heating rate in the case of the CR method.

Table 4

Activation energy ($E_a$, kJ/mol) during pyrolysis and combustion of FM

| Heating rate | CR* (R²)  | FWO* (R²) | KAS@ (R²) | STK$^\$ (R²) |
|--------------|-----------|-----------|-----------|--------------|
| Pyrolysis    |           |           |           |              |
| 5            | 155.95 (0.980) |           |           |              |
| 10           | 214.89 (0.985) | 139.23 (0.953) | 135.06 (0.942) | 134.45 (0.942) |
| 15           | 168.48 (0.984) |           |           |              |
| 20           | 214.21 (0.992) |           |           |              |
| Combustion   |           |           |           |              |
| 5            | 77.40 (0.988) |           |           |              |
| 10           | 96.95 (0.982) | 70.28 (0.980) | 64.65 (0.973) | 64.51 (0.974) |
| 15           | 111.93 (0.980) |           |           |              |
| 20           | 115.04 (0.986) |           |           |              |

# CR – Coats Redfern for reaction order (n = 1)
*FWO - Flynn-Wall-Ozawa
@KAS - Kissinger-Akihara-Sunose
$STK - Starink

The variation in $E_a$ between model-fitting (CR) and model-free (FWO, KAS, and STK) methods has also been reported in a previous study [51]. They [51] found an $E_a$ of 167.05 and 169.31 kJ/mol using the KAS and FWO methods, respectively, for used pure ramie yarn fabrics. The value of $E_a$ obtained from the CR method largely depends on the reaction mechanism or order, and therefore it can vary with the reaction order [51]. In the case of model-free methods, $E_a$ is calculated by building a relationship between the heating rate and decomposition temperatures at the conversion degree, and thus a series of $E_a$ at a different conversion degree can be obtained. Therefore, errors in CR methods are relatively larger than for model-free methods [52]. Very recently, Singh and Sawarkar [53] found the average $E_a$ for garlic stalk to be 95.11 and 94.54 kJ/mol for the KAS and FWO methods,
respectively. A higher $E_a$ will slow the reaction rate, and vice versa. The average value of $E_a$ for cotton stalk was found to be in the range of 100 to 120 kJ/mol for the KAS, FWO, and CR methods [13]. They also reported that the particle size of the biomass sample could play a role in the variation in $E_a$ values. Further, the difference in $E_a$ may also be attributed to the operating conditions of the pyrolysis process, heating conditions, and the chemical composition of the FM.

The distribution of $E_a$ against the FM conversion degree with model-free methods is compared in Fig. 6. This provides an important investigation of the change in activation energy with the varying conversion degree [50]. As can be observed, the $E_a$ profiles are quite similar to each other, except that the value of $E_a$ obtained from the FWO values were slightly higher than those from the KAS and STK values. The FWO method is simply based on the heating rate and involves no temperature function. The variation in $E_a$ distributions clearly indicates the complex multi-step reactions as discussed previously [16]. Moreover, FM is composed of different materials (non-woven fabric and melt blown filter) which might vary the $E_a$ as a whole, since the $E_a$ of each of FM component differs in value [22, 51]. In general terms, $E_a$ changes with the conversion degree. Interestingly, the profile of $E_a$ for pyrolysis is opposite to that of the combustion conversion process. The $E_a$ of the present study during pyrolysis of FM was lower than reported by recent study [22]. This could be due to physio-chemical content, experimental and data analysis methodologies that can cause substantial variations.
Fig. 5. Linear fit plots of different kinetic models for pyrolysis and combustion of FM
An abrupt increase in the $E_a$ (from 95 kJ/mol to 140 kJ/mol) was observed in the case of FM pyrolysis when the FM sample was converted from 10 % to 40 %, with a brief increase (from 140 kJ/mol to 155 kJ/mol) from 40 % to 90 %. This is because the thermal degradation rate is high from 10 to 40 %, as seen in the DTG curve corresponding to temperature between 300 and 450 °C. Moreover, a sharp increase in the $E_a$ for a 10 to 40 % conversion degree depicts multi-step reactions due to the mixture of FM layers (non-woven PP fabric with cotton filter fabrics). This specifies that it may be difficult for the FM material to decompose during the initial pyrolysis process. Hence, it took a higher temperature to initially degrade the FM sample (Fig. 3), as evident from the TG and DTG profiles.

![Graph showing activation energy profile against conversion degree of FM during pyrolysis and combustion](image)

**Fig. 6.** Activation energy profile against conversion degree of FM during pyrolysis and combustion.

A relatively short variation in $E_a$ after 40 % conversion shows a change in kinetic mechanism with reactions moving to a single step. Comparison of the obtained $E_a$ shows that KAS and STK methods provided results similar to the FWO for an $\alpha$ between 10 and
90%. The profile of $E_a$ for FM pyrolysis conversion was quite unique when compared with other biomass [13, 16, 52, 53], and waste materials [19, 50, 51]. The model-free methods also prove that the reaction mechanism of the FM lies in the major conversion region (0.3 to 0.7) as reported in [22].

The average value of $E_a$ for the FWO, KAS, and STK methods during the combustion of the FM sample was ~71.0, 64.6 and 65.5 kJ/mol, respectively. The $E_a$ increased slowly in the case of combustion conversion from 58 to 68 kJ/mol from 10 to 60 % conversion, and after that it increased rapidly until a conversion of 90% to a maximum of 95 kJ/mol.

The profile of $E_a$ during FM combustion conversion somewhat resembled that of rice husk and pine wood biomass samples [16], whereas the $E_a$ was stable within a wide conversion range (10% to 80%) and increased at a high conversion (around 80%). Two main decomposition regions (devolatilization and char oxidation) can be observed from the $E_a$ profiles of the combustion process [19]. Devolatilization occurring between 10 to 60 % conversion and char oxidation between 60 to 90 % conversion corresponds to a temperature of approximately 200 to 320 °C and 280 to 350 °C, respectively. These was in close agreement with Fernandez-Lopez [19]. A high $E_a$ above 80 % conversion at temperatures higher than 350 °C is related to the decomposition of the strongest bonds in the sample, which is usually difficult to degrade [16]. Another fact is that the heat transfer inside the particle is enhanced as the heating rate increases, and consequently, so is the reactivity of the sample [15]. Like pyrolysis, the values of $E_a$ obtained from FWO method were slightly higher than KAS and STK. The values of $E_a$ for combustion of the FM samples are lower than the values reported in the literature for the combustion of pine wood chips [11] and
manure [19]. However, the present result of $E_a$ during combustion is in line with the combustion values of cotton stalk [13]. A lower $E_a$ during the combustion process is desirable so that the reaction initiates more quickly. This could be due to the presence of an oxygen environment in the combustion process, whereas with pyrolysis, a higher $E_a$ delays the initiation of reaction due to the inert environment.

The variation in the values of the global $E_a$ is observed using different reaction models and at different heating rate obtained by CR method (Table 5). These values when compared with the model-free methods (Table 4) provides different reaction models associated with respective heating rates. For instance, if the value of $E_a$ obtained from all the three model-free method (FWO, KAS and STK) is considered for combustion of FM at 5 °C/min, then reaction model No. 13 (Table 5), contracting sphere best describe the combustion reaction mechanism. However, if only FWO method is considered, then reaction model No. 2 and 12 might better define the combustion reaction mechanism at 5 °C/min. If only model-free method is considered then reaction model No. 12 and 13 should characterize the combustion mechanism with a deviation of ±3.50 kJ/mol. According to [23], such a shift in reaction model is apparent because material conversion is not a single-step process, and at each step the reaction models might get change. Therefore, the application of multiple model-free methods is more accurate than a single method. The corresponding to the models of No. 2 and No. 15 is closest to 138.39 kJ/mol. The $R^2$ values > 0.9 for reaction models indicate the high desirability of that particular reaction mechanism. The poor value of $R^2$ < 0.8 might be due to heterogeneous and complex nature of reactions as well as the diffusion mechanism.
Table 5

Calculated activation energy based on CR method at different heating rate and reaction models

a) Combustion of FM

| No. | $g(\alpha)$ | Reaction mechanism | 5 °C/min | 10 °C/min | 15 °C/min | 20 °C/min |
|-----|--------------|-------------------|----------|-----------|-----------|-----------|
|     |              | $E_a$, kJ/mol     | $R^2$    | $E_a$, kJ/mol | $R^2$    | $E_a$, kJ/mol | $R^2$    |
| 1   | $1 - (1 - \alpha)^{2/3}$ | Chemical reaction | 56.18 | 0.95 | 74.83 | 0.93 | 81.73 | 0.90 | 91.50 | 0.96 |
| 2   | $1 - (1 - \alpha)^{1/4}$ | Chemical reaction | 72.17 | 0.98 | 89.10 | 0.97 | 99.60 | 0.96 | 108.91 | 0.98 |
| 3   | $1 - (1 - \alpha)^2$ | Chemical reaction | 32.04 | 0.77 | 52.30 | 0.80 | 54.66 | 0.75 | 64.50 | 0.85 |
| 4   | $1 - (1 - \alpha)^3$ | Chemical reaction | 22.45 | 0.65 | 42.91 | 0.71 | 44.00 | 0.65 | 53.10 | 0.76 |
| 5   | $1 - (1 - \alpha)^4$ | Chemical reaction | 16.02 | 0.54 | 36.33 | 0.64 | 36.68 | 0.58 | 44.93 | 0.70 |
| 6   | $\alpha^{3/2}$ | Nucleation Assumed random nucleation | 76.52 | 0.92 | 105.56 | 0.90 | 113.50 | 0.87 | 128.57 | 0.93 |
| 7   | $\alpha^{1/2}$ | Nucleation Assumed random nucleation | 19.55 | 0.86 | 29.05 | 0.86 | 31.51 | 0.82 | 36.48 | 0.91 |
| 8   | $-\ln(1 - \alpha)$ | Assumed random nucleation | 77.40 | 0.99 | 96.95 | 0.98 | 111.93 | 0.98 | 115.05 | 0.99 |
| 9   | $[-\ln(1 - \alpha)]^{2/3}$ | Assumed random nucleation | 48.07 | 0.99 | 60.88 | 0.98 | 70.68 | 0.97 | 72.71 | 0.98 |
| 10  | $[-\ln(1 - \alpha)]^{1/2}$ | Assumed random nucleation | 34.27 | 0.98 | 43.91 | 0.97 | 51.30 | 0.97 | 52.78 | 0.98 |
b) Pyrolysis of FM

| No. | Reaction mechanism | $g(\alpha)$ | $5 \, ^{\circ}C/min$ | $10 \, ^{\circ}C/min$ | $15 \, ^{\circ}C/min$ | $20 \, ^{\circ}C/min$ |
|-----|-------------------|-------------|----------------------|----------------------|----------------------|----------------------|
|     |                   | $E_a$, kJ/mol | $R^2$               | $E_a$, kJ/mol | $R^2$               | $E_a$, kJ/mol | $R^2$               |
| 1   | $1 - (1 - \alpha)^{2/3}$ | Chemical reaction | 132.88 | 0.99 | 188.77 | 0.99 | 146.75 | 0.99 | 195.05 | 0.99 |
| 2   | $1 - (1 - \alpha)^{1/4}$ | Chemical reaction | 152.63 | 0.98 | 214.18 | 0.99 | 168.85 | 0.98 | 216.83 | 0.99 |
| 3   | $1 - (1 - \alpha)^{2}$  | Chemical reaction | 102.00 | 0.95 | 150.14 | 0.97 | 112.45 | 0.93 | 161.33 | 0.98 |
| 4   | $1 - (1 - \alpha)^{3/2}$ | Chemical reaction | 133.10 | 0.94 | 97.12 | 0.89 | 145.91 | 0.96 |
| 5   | $1 - (1 - \alpha)^{4}$  | Chemical reaction | 134.21 | 0.93 | 120.43 | 0.92 | 85.75 | 0.85 |
| 6   | $\alpha^{3/2}$        | Nucleation    | 189.54 | 0.98 | 269.71 | 0.99 | 209.00 | 0.97 | 281.91 | 0.99 |
| 7   | $\alpha^{1/2}$        | Nucleation    | 55.86  | 0.97 | 82.36  | 0.99 | 62.10  | 0.97 | 86.26  | 0.99 |
| 8   | $-\ln(1 - \alpha)$ | Assumed random nucleation | 155.95 | 0.98 | 214.89 | 0.98 | 168.50 | 0.98 | 214.21 | 0.99 |
| 9   | $[-\ln(1 - \alpha)]^{2/3}$ | Assumed random nucleation | 138.01 | 0.98 | 107.34 | 0.98 | 137.47 | 0.99 |
| 10  | $[-\ln(1 - \alpha)]^{1/2}$ | Assumed random nucleation | 101.83 | 0.98 | 78.60  | 0.98 | 101.36 | 0.99 |
| 11  | $\alpha$                | Contracting disk          | 176.03 | 0.98 | 154.03 | 0.99 | 184.10 | 0.99 |
| 12  | $1 - (1 - \alpha)^{1/2}$ | Contracting cylinder      | 197.10 | 0.99 | 154.03 | 0.99 | 202.20 | 0.99 |
| 13  | $1 - (1 - \alpha)^{1/3}$ | Contracting sphere        | 207.72 | 0.99 | 163.26 | 0.99 | 211.30 | 0.99 |
| 14  | $\alpha^2$              | One-dimensional diffusion | 363.38 | 0.99 | 282.50 | 0.98 | 379.73 | 0.99 |
4. **Conclusions**

Physically, the FM sample was composed of entangled, irregularly wound, cylindrical, smooth-surface fiber materials. The major element present in FM is carbon. The profiles of pyrolysis and combustion of FM showed only a single degradation peak (320–480 °C and 200–370 °C, respectively). The average $E_a$ values obtained from the FWO, KAS, and STK methods during pyrolysis were ~139, 135, and 134 kJ/mol, respectively, whereas for the combustion process, the values were ~70, 64, and 64 kJ/mol, respectively. The $E_a$ calculated using the model fitting method (CR) overestimated the values. Interestingly, the residual char obtained after the pyrolysis and combustion process of the FM was minimal (in the range of 1.35–3.50 wt.%). In conclusion, thermo-chemical conversion processes such as pyrolysis and combustion have the potential to convert FM waste into energy in addition to offering safe disposal. The immediate solution to dispose the FM would be through combustion process, because most of the power plant are based on combustion process that uses solid fuels such as coal, biomass, waste etc. Therefore, it would be suitable to co-combust FM waste with existing solid fuels to generate power and heat. Overall, the present study provides new knowledge and data on understanding the pyrolysis and combustion behavior to help scale up a waste processing system for the FM and similar waste generated from the pandemic.

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Not applicable

Authors’ contributions
Arshad Adam Salema: supervision, writing–original draft, reviewing and editing;
Yasmin Mohd Zaifullizan: methodology, formal analysis and investigation, data analysis, review and editing; Wong Wai Hong: methodology, formal analysis and investigation, data analysis.
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