

Thermal Decomposition and Combustion Analysis of Malaysian Peat Soil Samples Using Coats Redfern Model-free Method

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ABSTRACT

This research investigates the thermal decomposition behaviour of Malaysian peat soil through thermogravimetric analysis at varying heating rates. The study aims to analyse the thermal kinetics of decomposition for distinct peat soil types under inert and oxidative atmospheres while considering the role of available oxygen. The investigation encompasses virgin and agricultural peat, employing a non-isothermal thermogravimetric analysis technique to evaluate thermal decomposition characteristics and compute kinetic parameters using the Coats Redfern model-free approach. The pyrolysis profiles reveal three primary stages: moisture evaporation (30–180°C), organic component decomposition (200–500°C), and mineral decomposition (600–800°C). Virgin peat experiences a 43% mass loss during pyrolysis, while agricultural peat shows a 46% mass loss, emphasising insights into thermal behaviour and consistent decomposition patterns across peat types. Combustion profiles exhibit three main stages: dehydration (30–180°C), oxidative pyrolysis transforming organic matter into volatiles and char (200–300°C), and subsequent char oxidation (300–500°C). The

study determines average activation energy trends, measuring 14.87 kJ/mol for virgin peat and 5.37 kJ/mol for agricultural peat under an inert atmosphere, and 28.89 kJ/mol for virgin peat and 36.66 kJ/mol for agricultural peat under an oxidative atmosphere. The research introduces an innovative two-step reaction model elucidating peat thermal decomposition kinetics (excluding dehydration), including a

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discussion on the impact of oxygen availability on kinetic parameters. These findings essential peat fire smouldering modelling, contributing to peat combustion behaviour for effective strategies to reduce peat fire risks.

Keywords: Coats Redfern, combustion, peat, pyrolysis, thermal decomposition, thermogravimetric analysis

INTRODUCTION

Peat is an important component representing a carbon-rich organic soil that contains at least 12% organic carbon (Rezanezhad et al., 2016), accompanied by a mineral content ranging from 20% to 35% (Turetsky et al., 2015). A brownish-black colour peat is formed through the partial decomposition of organic matter accumulated over thousands of years within oxygen-deprived, water-logged conditions derived from plant material (Lourenco et al., 2022). Precisely, peat is defined as soil containing no less than 65% organic matter and reaching a thickness of at least 50 cm (Adon et al., 2012; Lourenco et al., 2022).

Malaysian peatlands cover an area of about 2.6 Mha (Melling, 2015). Sarawak, one of two Malaysian states on the island of Borneo, possesses the largest extent of peat, over 1.6 Mha. They represent about 70% of all Malaysian peatlands (Melling, 2015) Emphasising tropical peat is of great significance due to its millennia-long peat accumulation, encompassing around 15%–19% of the total peat carbon and playing a role in 90% of carbon emissions from combustion (Azmi et al., 2021; Dommain et al., 2011; Sundari et al., 2012). However, the high carbon content in peat makes it easy to ignite (Rein, 2013), with the presence of oxygen and ignition sources (Melling, 2015). Especially when it is below its critical ignition point, the fire on the peat is called smouldering fire, which is a flameless and slow combustion process (Rein, 2013).

Peat is classified as a subsurface fuel beneath the ground's surface (Rein, 2013). During dry seasons, the peat's surface rapidly dries out, rendering it susceptible to easy ignition (Huang & Rein, 2014). Among the elements forming the fire triangle, fuels, oxygen, and ignition heat are the final elements needed for peat to catch fire. This heat can originate from various sources, including human activities, whether intentional or accidental, that act as potential ignition points (Fawzi et al., 2021). Examples include discarding lit cigarettes or neglecting to properly extinguish smouldering wood. Furthermore, external natural factors such as extremely hot weather, wind dispersion, or other influences can also contribute to ignition, leading to smouldering peat fires (Hu et al., 2018; Rein, 2013).

Smouldering combustion is the slow, low-temperature, flameless burning of porous fuels and is the most persistent type of combustion phenomenon (Rein, 2013). Upon ignition, smouldering peat fires possess the potential to persist for hours initially and then continue to smoulder over extended periods, spanning months to even years (Goldstein et al., 2020; Rein, 2013). Within controlled laboratory conditions, the persistence of smouldering peat

fires can extend over several weeks (Qin et al., 2022). This observation emphasises the need for further research on their thermal behaviour in this domain. The global impact of smouldering fires leads to forest degradation and localised haze occurrences with associated mortalities (Mezbahuddin et al., 2023; Othman et al., 2014). The main concern surrounding these events is their potential to desiccate the environment, disrupt natural ecosystems, and release harmful carbon emissions, ultimately contributing to haze formation. This particular setting provided the reasoning behind our research endeavour.

Smouldering occurs in the presence of ample oxygen; nonetheless, as the fire goes downward, the availability of oxygen is limited, and it may eventually disappear (Rein, 2013; Zhao et al., 2014). Consequently, at elevated temperatures and in the absence of oxygen, peat pyrolysis predominates the reaction. The smouldering peat fire emerges due to limited oxygen intake, resulting from the peat's organic materials undergoing pyrolysis (Kosyakov et al., 2020). Oxygen affects the peat's thermal decomposition process and subsequent smouldering combustion (Zhao et al., 2014). Various experimental studies have explored smouldering peat combustion under differing oxygen concentrations. For example, previous studies have examined the influence of different oxygen concentrations on the thermal decomposition of peat and the kinetics of thermal decomposition for peat samples within the atmosphere of Nitrogen and air, which are two of the most common atmospheres during the smouldering of peat fires (Chen et L., 2011; Zhao et al., 2014). These atmospheric conditions represent two common scenarios during peat smouldering. Another study examined three distinct peat types: two high-moor peat types collected in Edinburgh (Scotland) and Tomsk (Siberia), along with a transitional peat from Tomsk. Significantly different degradation patterns have been identified for the various peat forms of peat through a kinetic approach to estimate the sample temperature at high heating rates (Cancellieri et al., 2012).

This paper studies peat soil decomposition from two different locations in Malaysia using thermogravimetric analysis under oxidative and inert atmospheres. Peat properties influence its chemical reaction, including combustion and pyrolysis. Moisture content is one of the main factors contributing to the smouldering peat fire when the moisture decreases on the peat surface caused by evapotranspiration (Taufik et al., 2022; Prat et al., 2015). The peat soil types are characterised by their carbon content, and data for carbon and moisture are in Table 1. Model-free methods of Coats Redfern is used to calculate the activation energy of peat decomposition, and the two-step reaction model is applied. The role of oxygen on kinetic parameters is extensively discussed in this paper.

Table 1
Peat sample's carbon and moisture content

Type of Peat	Carbon content (wt%)	Moisture content (wt%)
Virgin Peat	80.48	70.97
Agricultural Peat	68.27	76.66

METHODOLOGY

The area for the sample collection has been identified around Selangor, Malaysia. The first sample, a virgin peat sample, was taken from Hutan Simpan Raja Musa, Selangor. The second agricultural peat sample was taken from a plantation site in Banting, Selangor.

Peat soil is distinctively characterised by its high carbon content, a primary marker of its identity. According to Ekono (1981), for soil to qualify as peat, it should possess a carbon content above 55% by weight percentage. Any value below this benchmark may indicate that the sample is not purely peat or could have been adulterated with other soil types. In the provided sample, the carbon content stands prominently at 80.48%, well above the standard value, affirming its status as peat soil. Other sample constituents include oxygen at 11.20%, aluminium at 2.69%, and silicon at 5.63%, with carbon being the predominant element, as expected for peat soils.

The sample was required to be weighed before (W_1), and after (W_2), the sample was dried in the oven to measure the moisture content. The weight of the sample before it dried contains the original moisture content of the sample ($MC = ((W_1 - W_2) / W_2) \times 100\%$). Post-drying, the peat sample's weight indicated the absence of moisture. The sample was dried in the oven at 105°C for 24 hours, allowing water to evaporate and leaving only the dry content of the peat. The sample's moisture content was recorded, and the dried samples were sent to the Laboratory for thermalgravimetric analysis (TGA).

The tests were conducted under two conditions, air atmosphere and nitrogen atmosphere, for both virgin peat and agricultural peat samples. The heating rate was set to be 5, 10 and 20°C min⁻¹ and the temperature range from 30°C to 1000°C for virgin peat samples. Two runs were performed with the same experimental conditions, and the experiment's reproducibility was verified. The same conditions were applied for agricultural peat but with a heating rate of 10°C min⁻¹.

The Coats-Redfern method is applied to calculate the pet decomposition activation energy (A_c), and the two-step reaction model is applied (Ali et al., 2021). Every kinetic model obeys the same Arrhenius equation (Yan et al., 2019) and conversion rate equation as in Equations 1 and 2:

$$K(T) = A \exp\left(-\frac{E}{RT}\right) \quad (1)$$

$$\frac{da}{dt} = A e^{-E/RT} (1 - a)^n \quad (2)$$

where T = absolute temperature; R is the universal gas constant; A is the frequency or pre-exponential factor; E is the activation energy of the reaction; n is the order of reaction; and t is the time.

RESULTS AND DISCUSSION

In a thermogravimetric analyser, the most valuable signal arising from a reaction is the curve derivative, DTG. This study employed DTG to pinpoint inflexion points on the TG curve, serving as a reference for calculating weight changes in each peat sample (Cancellieri et al., 2012). The activation energy (E_a) represents the energy required for a reaction, indicating a component's reactivity level.

For this study, E_a and pre-exponential values were determined through the Coats Redfern method and the Microsoft Excel Solver. From TGA results, three regions were identified on each thermograph. These regions were defined by the approximate starting and ending points of the DTG curve, which visualises the thermal breakdown of the organic matter and the volatiles in the samples. The first region on the DTG curve, associated with the moisture and low boiling point of the organic matter in the sample, will not be further elaborated.

Pyrolysis for Virgin Peat

Peat organic material falls under the biomass category (Kosyakov et al., 2020), allowing the application of the three-component reaction scheme to model organic material pyrolysis kinetics (Chen et al., 2011). In this study, peat pyrolysis unfolds in three main mass loss stages of mass loss: moisture evaporation (Stage 1), organic component decomposition (Stage 2), and mineral decomposition (Stage 3). Illustrated in Figure 1 are the experimental TG and derivative thermogravimetry (DTG) plots for virgin peat pyrolysis under Nitrogen at heating rates of 5, 10 and 20°C min⁻¹.

Examining the DTG plot at a heating rate of 5°C min⁻¹ provides details about the thermal decomposition. Stage 2 occurred within the temperature range of about 250–500°C, which signifies the important phase of organic material transformation. As the temperature rises from 200°C, the decomposition rate of organic materials increases and reaches the first peak temperature at 378°C. Following this, the rate decreases slightly before reaching the secondary peak temperature at 400°C. After 500°C, the sample's mass decreases gradually, making the culmination of the organic materials decomposition process, accounting for 43% mass loss during this phase.

In the absence of oxygen, the organic material does not combust; instead, it decomposes into combustible gases and char, encompassing chemical compounds like cellulose, hemicellulose, and lignin (Rein et al., 2008). During this stage, the organic components of the peat undergo a transition into ash and charred fragments, and the resulting volatile substances are carried away by the flowing gas (Chen et al., 2011; Khoroshavin et al., 2012). At this stage, the impact of ash in the biomass char becomes significant in the context of the gasification procedure (Jayaraman & Gökalp, 2015). This observation highlights the complexity of peat decomposition but also the role of oxygen in dictating the organic material outcome.

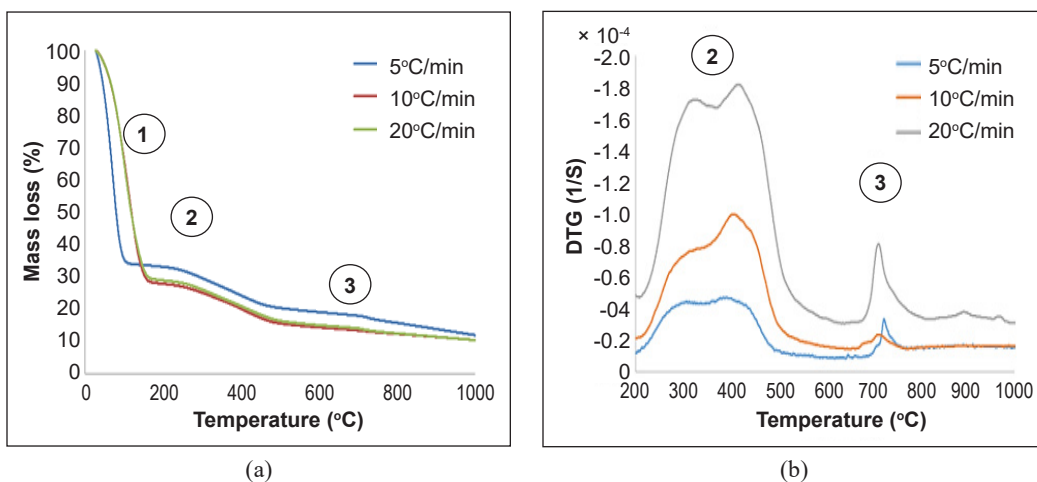


Figure 1. (a) TG and (b) DTG plots for virgin peat pyrolysis in Nitrogen at 5, 10 and 20°C min⁻¹

The third stage of mass loss under the heating rate of 5°C min⁻¹ begins at 600°C and becomes more obvious between 660°C and 800°C. Such a high temperature facilitates the decomposition of peat materials, leading to a reduction in char production (Chen et al., 2011; Khelkhal et al., 2021). In Figure 1(b), the DTG curve illustrates a mass loss peak at about 780°C for a 5°C min⁻¹ heating rate. This finding aligns with the decomposition traits of certain minerals, such as calcium carbonate (Chen et al., 2011). The manifestation of this stage results in a total mass loss of 21%, providing a quantitative representation of the relationship between temperature and the decomposition process of the virgin peat. The calculated kinetic parameters for all heating rates of virgin peat in an inert atmosphere are tabulated in Table 2. The data offers comprehensive findings of the observed reaction and lays the groundwork for future studies into the kinetic complexities that influence peat's decomposition behaviour.

It was summarised that the pyrolysis kinetics of virgin peat were classified into moisture evaporation (Stage 1), organic component decomposition (Stage 2), and mineral

Table 2

Kinetic parameters pyrolysis of virgin peat under different heating rates

Heating Rate (°C min ⁻¹)	5	10	20
Ea ₂ (kJ mol ⁻¹)	4.405	10.09	52.46
Ea ₃ (kJ mol ⁻¹)	21.88	19.66	10.52
Average Ea (kJ mol ⁻¹)	13.14	14.87	31.49
A ₂ (s ⁻¹)	-0.00030	-0.05058	215.1
A ₃ (s ⁻¹)	0.03550	0.09343	-0.01841
n	2	2	2

Note. Subs 2 and 3 indicate the parameters at Stages 2 and 3, respectively

decomposition (Stage 3). Stage 2 at 250–500°C results in 43% mass involving organic material decomposing into combustible gases and char. The subsequent ash and chare are carried away by flowing gas in the third stage at 600–800°C, leading to significant peat material decomposing, reducing char production and resulting in a 21% mass loss. The data will offer insights into the behaviour of virgin peat under elevated temperature conditions, particularly in the context of smouldering peat fires.

Pyrolysis of Agricultural Peat. Figure 2 shows the experimental thermogravimetry (TG) and derivative thermogravimetry (DTG) plots depicting agricultural peat pyrolysis under a nitrogen atmosphere with a heating rate of 10°C min⁻¹. Similar to virgin peat, agricultural peat also undergoes three primary mass loss stages for pyrolysis: moisture evaporation (Stage 1), organic component decomposition (Stage 2) and mineral decomposition (Stage 3).

DTG curve analysis reveals that Stage 2 transpires within a temperature range of about 270–530°C. As temperature rises from 200°C, the decomposition rate of organic materials increases, reaching its first peak temperature at 323°C. Subsequently, the rate experiences a minor decline, followed by a secondary peak temperature at 415°C. As the temperature exceeds 450°C, the gradual decrease in the sample's mass signifies the completion of the decomposition process for organic materials, resulting in an overall mass loss of 46% during this phase.

Moving to the third stage of mass loss, it initiates at 800°C and reaches its peak temperature at 915°C, leading to a total mass loss of 20%. These findings emphasise the complex condition of agricultural peat decomposition under diverse temperature conditions. The presence of certain mineral constituents within the peat could contribute

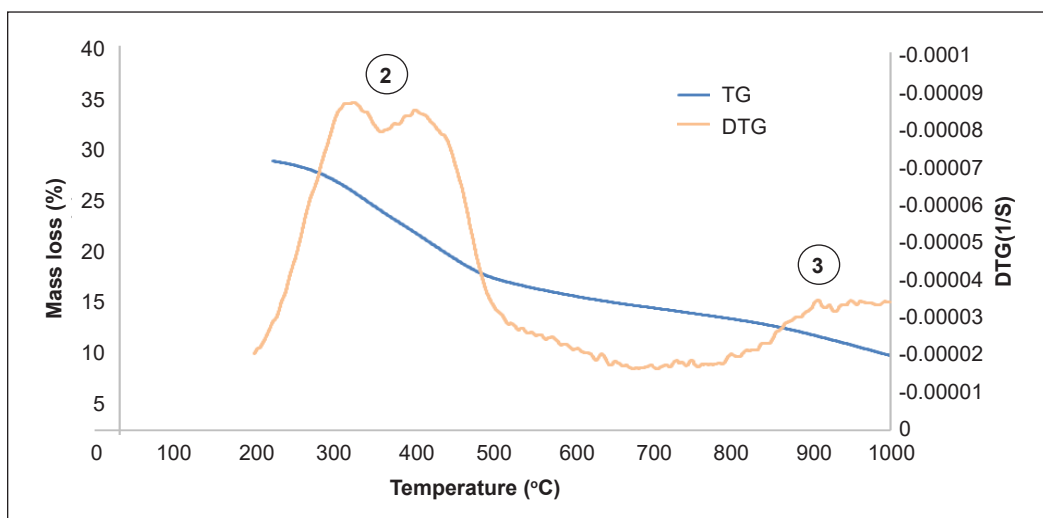


Figure 2. TG and DTG plots for agricultural peat pyrolysis in Nitrogen at a heating rate of 10°C min⁻¹

to the decomposition behaviours. Table 3 presents the calculated kinetic parameters for agricultural peat under an inert atmosphere with a heating rate of $10^{\circ}\text{C min}^{-1}$, explaining the distinct thermal behaviour of the virgin peat under specified conditions.

The findings elucidate that agricultural peat shares resemblances with virgin peat, manifesting three distinct stages of mass loss throughout the pyrolysis process. Stage 2, unveiled through the DTG curve analysis, is notable within the temperature

span of $270\text{--}530^{\circ}\text{C}$. This stage showcases escalated decomposition rates as the temperature increases, leading to a substantial percentage mass loss of 46%. The third stage, which unfolds at higher temperatures, specifically starting at 800°C and reaching its peak at 915°C , brings about a significant 20% mass loss. These observations highlight the intricate thermal behaviour of agricultural peat during pyrolysis, contributing to a more comprehensive understanding of its decomposition characteristics.

Comparison Pyrolysis of Virgin Peat and Agricultural Peat. Figure 3 displays the DTG plots of virgin and agricultural peat under an inert atmosphere at a heating rate of $10^{\circ}\text{C min}^{-1}$. The graph shows that virgin peat exhibits a higher decomposition rate than agricultural peat within the same temperature range ($200\text{--}500^{\circ}\text{C}$). This discrepancy is attributed to the higher carbon content in virgin peat. Consequently, the organic decomposition transpires more swiftly in virgin peat compared to agricultural peat, even when subjected to the same heating rate.

The study on the activation energy values for virgin and agricultural peat offers valuable insights into their respective thermal behaviours. Activation energy represents the minimum energy required to initiate a chemical reaction (Hänninen, 2017). The contrast between the average activation energy value was 14.87 kJ mol^{-1} for virgin peat and 5.37 kJ mol^{-1} for agricultural peat, underscoring a significant distinction in both peat types of reactivity. Particularly, the lower activation energy of agricultural peat suggests that the initiation of its pyrolysis might transpire at comparatively lower temperatures, indicative of a propensity for earlier decomposition. As evidenced by the results, the peak temperature in Stage 2 was 405°C for virgin peat and 323°C for agricultural peat. Generally, this peak temperature can be seen as the ignition temperature, which can be reached even with a relatively weak heat source. In light of this, it becomes evident that virgin peat could potentially present a heightened risk compared to agricultural peat due to its lower ignition

Table 3
Kinetic parameters pyrolysis of virgin peat under different heating rates

Heating Rate ($^{\circ}\text{C min}^{-1}$)	10
Ea_2 (kJ mol^{-1})	5.74
Ea_3 (kJ mol^{-1})	5.00
Average Ea (kJ mol^{-1})	5.37
A_2 (s^{-1})	-0.15318
A_3 (s^{-1})	-0.00958
n	2

Note. Subs 2 and 3 indicate the parameters at Stages 2 and 3, respectively

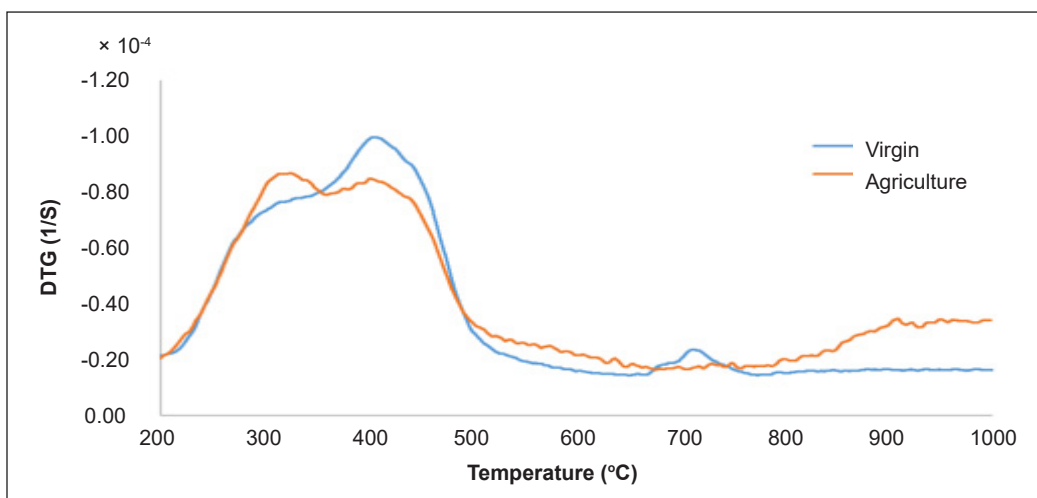


Figure 3. DTG curve of Virgin and Agricultural Peat under an inert atmosphere at $10^{\circ}\text{C min}^{-1}$ heating rate

Table 4

Kinetic parameters of virgin peat and agricultural peat under an inert atmosphere under $10^{\circ}\text{C min}^{-1}$

Parameters	E_a (kJ mol^{-1})	A (s^{-1})	R^2
Virgin Peat	14.87	-0.05058	0.9313
Agricultural Peat	5.37	-0.09128	0.9692

threshold. A comparison of kinetics can be found detailed in Table 4 for comprehensive reference and analysis.

The discussion focused on virgin and agricultural peat under an inert atmosphere. Upon observing the graph, it becomes apparent that virgin peat displays a higher decomposition rate than agricultural peat in the temperature range of 200°C to 500°C , indicative of its elevated carbon content, which poses a significant risk of environmental pollution. These findings imply faster organic decomposition in virgin peat, displaying an average activation energy of $14.87 \text{ kJ mol}^{-1}$ than agricultural peat's 5.37 kJ mol^{-1} . Agricultural peat's lower activation energy suggests possible pyrolysis at lower temperatures, making it more susceptible to ignition. The ignition points occur in Stage 2, at 405°C for virgin peat and 323°C for agricultural peat.

Combustion of Virgin Peat

Figure 4 depicts the TG and DTG plots for illustrating peat decomposition within the atmosphere of the air. These tests were conducted using 5 , 10 and $20^{\circ}\text{C min}^{-1}$ heating rates. The first region on the DTG curve indicates the process of dehydration and water elimination. This first stage, which occurs from room temperature to approximately 180°C , is linked to the dehydration of samples and requires no further elaboration. The second

region (Stage 2) is linked to the oxidation and removal of volatile matter within the samples. Following this, the third region (Stage 3) corresponds to the oxidation of residual char after the volatiles were removed from the samples (Varol et al., 2010).

At a heating rate of $5^{\circ}\text{C min}^{-1}$, Stage 2 occurred between $200\text{--}300^{\circ}\text{C}$, becoming notably obvious at 270°C . As the temperature rises from 200°C , the decomposition rate of organic materials increases, culminating in a prominent peak temperature at 272°C (Figure 4b). It signifies the decomposition of peat's organic components into volatiles, semi-volatiles, and char residues. The combustible components of the generated volatiles can then be oxidised by the influx of air, accompanied by substantial heat release (Kosyakov et al., 2020; Chen et al., 2011). In the second stage, the hemicellulose, cellulose, and lignin within the samples underwent decomposition. Subsequently, the third stage involved the combustion of structures possessing greater complexity and thermal stability, as well as char oxidation (Jayaraman et al., 2017b). As the temperature surpassed 300°C , a gradual decline in the virgin peat sample's mass was discerned, effectively encapsulating the culmination of the decomposition processes concerning organic and volatile constituents. A total mass loss of 44% resulted at this stage, bearing testimony to the extensive transformation during the combustion process. Biomass reactivity is linked to its light volatile content, while energy release is influenced by fixed carbon combustion (Jayaraman et al., 2017a).

Stage 3 is estimated to begin within the $340\text{--}400^{\circ}\text{C}$ temperature range at a heating rate $5^{\circ}\text{C min}^{-1}$. At this stage, the peak occurs at 350°C , with a corresponding peak on the DTG graph. Here, the total mass loss reaches 27%. Beyond 600°C , the variations in the sample's mass alteration become imperceptible. According to Kosyakov et al. (2020), this pyrolysis range of $200\text{--}600^{\circ}\text{C}$ resembles actual peat fire conditions. However, Chen et al. (2011)

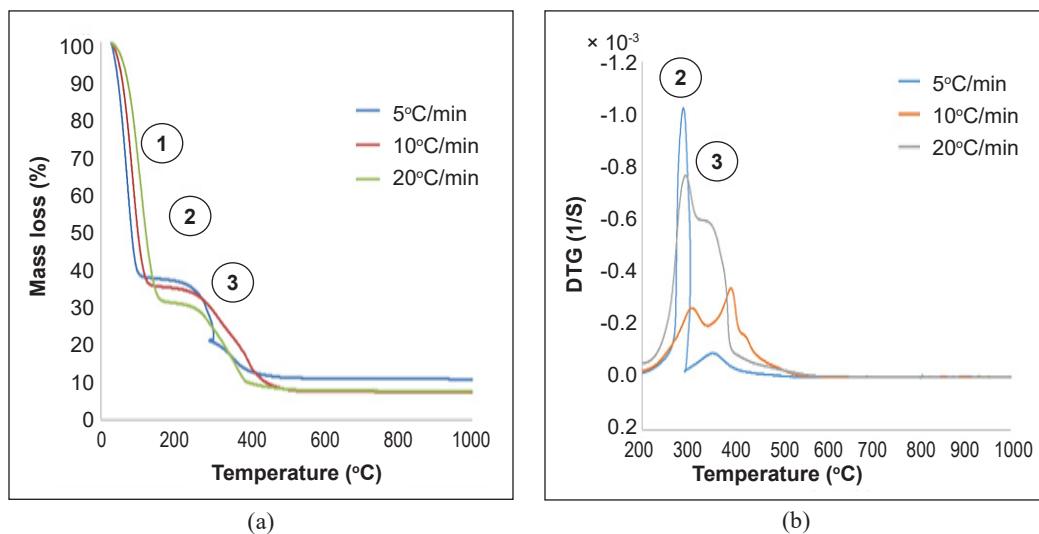


Figure 4. TG and DTG curves of virgin peat under an oxidative atmosphere at heating rates of 5, 10 and $20^{\circ}\text{C min}^{-1}$

suggest that the phase of mineral decomposition is less discernible in an air environment. Table 5 presents the calculated kinetic parameters for all heating rates of virgin peat under an oxidative atmosphere. Additionally, the quality of the fitted lines was evaluated based on the R^2 value assessment.

The findings regarding peat decomposition in an air atmosphere under heating rates of 5, 10, and 20°C min⁻¹ were summarised. The first stage signifies dehydration and water elimination up to 180°C. In the second stage, at a heating rate of 5°C min⁻¹, oxidation and removal of volatile matter occur at 270°C, indicating the decomposition of peat's organic components. The third stage corresponds to char oxidation following volatile removal, commencing around 340–400°C, resulting in a 27% mass loss. This condition mirrors actual peat fire conditions, and these findings contribute to the understanding of peat combustion for the virgin peat, which is related to the forest reserve area.

Table 5
Kinetic parameters of virgin peat under different heating rates

Heating Rate (°C min ⁻¹)	5	10	20
Ea ₂ (kJ mol ⁻¹)	34.64	11.92	16.57
Ea ₃ (kJ mol ⁻¹)	64.74	45.87	62.11
Average Ea (kJ mol ⁻¹)	49.69	28.89	39.34
A ₂ (s ⁻¹)	4.708	0.06555	0.2631
A ₃ (s ⁻¹)	1416	25.62	1118
n	2	2	2

Note. Subs 2 and 3 indicate the parameters at Stages 2 and 3, respectively

Combustion of Agricultural Peat. Figure 5 displays the thermogravimetry (TG) and derivative thermogravimetry (DTG) plots depicting the decomposition of agricultural peat within an oxygen environment, using heating rates of 10°C min⁻¹. Similar to virgin peat, the decomposition of agricultural peat under oxygen exhibits three primary mass loss stages. The first stage occurs from room temperature up to about 150°C, which was attributed to the dehydration process of the peat samples.

Upon reviewing the DTG curve, Stage 2 occurred in the temperature range of approximately 270–350°C. As the temperature surpasses 200°C, the decomposition rate of organic materials escalates, culminating in a peak temperature of 326°C. Beyond 330°C, the sample's mass decreases, indicating the completion of the decomposition process for organic and volatiles. The total mass loss recorded at this stage is 30%.

The onset of the third stage of mass loss is estimated at 360°C, reaching its peak temperature at 398°C. Beyond 400°C, the sample's mass experiences a notable decline and achieves another minor peak at 430°C. The second appears to correspond to a maximum decomposition of hemicellulose. At this stage, less stable compounds created in the first stage, along with the cellulose and lignin, decompose due to heat, forming more complex

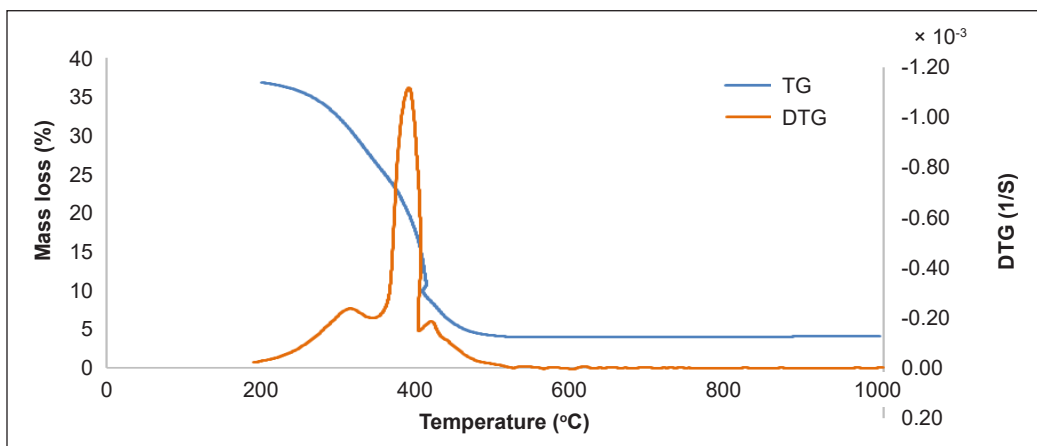


Figure 5. TG and DTG curves of agricultural peat under an oxidative atmosphere at heating rates of $10^{\circ}\text{C min}^{-1}$

substances that need less heat to form (Khelkhal et al., 2022). The overall mass loss at this stage totals 44%. The kinetic parameters calculated for agricultural peat within an oxidative atmosphere are presented in Table 6.

The analysis of agricultural peat combustion is summarised in its decomposition at a rate of $10^{\circ}\text{C min}^{-1}$. It is important to highlight the presentation of kinetic parameters that illustrate the oxidative behaviour of agricultural peat. Similar to virgin peat, three stages occur in the mass loss process. The first stage involves peat sample dehydration at around 150°C . Stage 2 reveals an increase in organic decomposition, resulting in a 30% mass loss at a peak temperature of 326°C . Stage 3 demonstrates further mass loss corresponding to significant hemicellulose decomposition, accompanied by the decomposition of less stable compounds under heat, forming complex substances that require less heat. This finding underscores the importance of efficient thermal utilisation for agricultural peat samples, particularly as the mass loss in the third stage reaches 44%.

Comparison Combustion of Virgin Peat and Agricultural Peat. Figure 6 illustrates the derivative thermogravimetry (DTG) of virgin and agricultural peat subjected to a heating rate of $10^{\circ}\text{C min}^{-1}$ within an oxidative atmosphere. Based on the graph, agricultural peat displays a higher decomposition rate within the temperature range of $350\text{--}420^{\circ}\text{C}$. Notably, the DTG curve diverges between the Nitrogen and oxidative atmosphere due to the absence

Table 6
Kinetic parameters combustion of agricultural peat at $10^{\circ}\text{C min}^{-1}$

Heating Rate ($^{\circ}\text{C min}^{-1}$)	10
Ea_2 (kJ mol^{-1})	8.75
Ea_3 (kJ mol^{-1})	64.58
Average Ea (kJ mol^{-1})	36.66
A_2 (s^{-1})	-0.02706
A_3 (s^{-1})	709.96
n	2

Note. Subs 2 and 3 indicate the parameters at Stages 2 and 3, respectively

of oxidation reactions in Nitrogen. Moreover, virgin peat's decomposition rate was lower than agricultural peat's under oxidative conditions.

By exploring the activation energy values, a differential pattern emerges between the two types of peat samples. The average activation energy value for virgin peat was $28.89 \text{ kJ mol}^{-1}$, while agricultural peat records a value of $36.66 \text{ kJ mol}^{-1}$. Higher activation energy values for agricultural peat suggest that agricultural peat requires more energy in comparison to virgin peat to undergo the same process. The activation energy of virgin peat indicated that it was easier for the peat to reach oxygen (Palamba et al., 2018). In simpler terms, virgin peat exhibits a higher flammability contrasted with agricultural peat. This contrast can be attributed to the higher carbon content in virgin peat. Comprehensive kinetic comparisons of the virgin peat and agricultural peat under an oxidative atmosphere are detailed in Table 7.

The combustion characteristics of virgin and agricultural peat, observed under a $10^\circ\text{C min}^{-1}$ heating rate within an oxidative atmosphere, have been summarised to provide insights into peat fire behaviour. The importance of carbon content in combustion behaviour is also evident, as it indicates that virgin peat is more flammable than agricultural peat due to its reaction with oxygen. The higher activation energy observed in agricultural peat

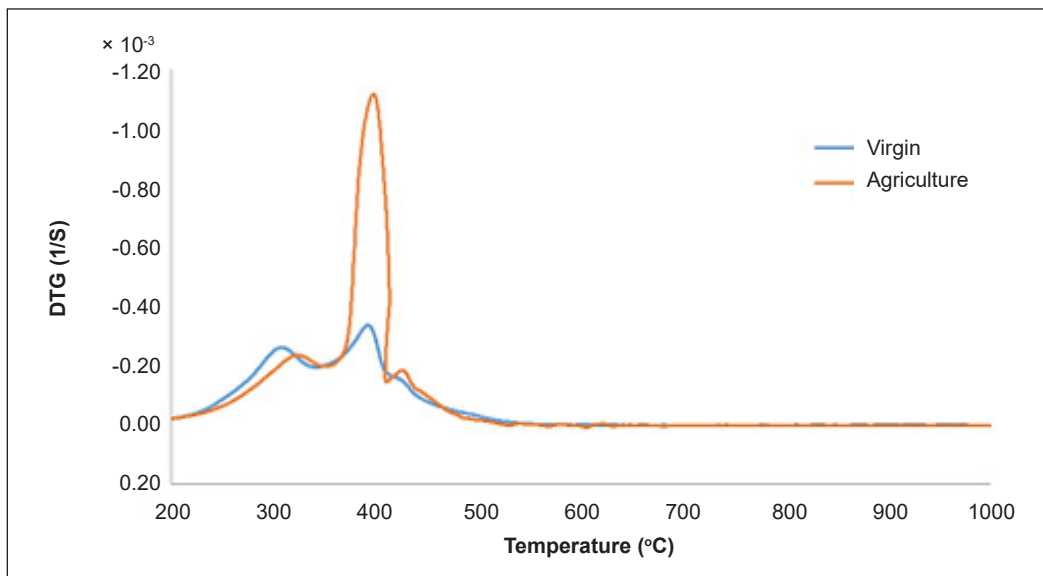


Figure 6. DTG curve of virgin and agricultural peat under an oxidative atmosphere at $10^\circ\text{C min}^{-1}$ heating rate

Table 7

Kinetic parameters of virgin peat and agricultural peat under an oxidative atmosphere at $10^\circ\text{C min}^{-1}$

Parameters	Ea (kJ mol^{-1})	A (s^{-1})	R ²
Virgin Peat	28.89	4.708	0.9405
Agricultural Peat	36.66	-0.02706	0.9444

suggests that it requires more energy compared to virgin peat for the same process. Virgin peat exhibits a slower decomposition rate than agricultural peat, with average activation energy values of $28.89 \text{ kJ mol}^{-1}$ for virgin peat and $36.66 \text{ kJ mol}^{-1}$ for agricultural peat. These findings imply that the higher flammability of virgin peat leads to increased carbon release during peat fire events compared to agricultural peat.

Comparison of Pyrolysis and Combustion of Peat

As stated earlier, peat can break down in environments within inert or oxidative atmospheres, like in-ground fires. The presence of oxygen influences this decomposition process. Thus, this study compares the TG and DTG curves of peat decomposition in air and nitrogen atmospheres to see how oxygen plays a role in influencing the decomposition process. This study has redrawn the TG-DTG curves for nitrogen and air atmospheres of virgin peat under a heating rate of $10^\circ\text{C min}^{-1}$ to clarify the comparison. These can be found in Figures 1 and 4 and were redrawn in Figure 7.

Up to the temperature mark around 200°C , the two TG curves in Figure 7 closely match, indicating similar mass loss rates for peat decomposition in air and Nitrogen environments. This similarity arises because the initial mass loss is due to moisture evaporation, where the influence of oxygen is minimal. Therefore, the mass loss was mainly based on the heating rate rather than the moisture content of the sample (Jayaraman et al., 2020).

Within the temperature range of approximately $200\text{--}500^\circ\text{C}$, the mass loss rate is higher in the presence of air, and the starting temperature is lower compared to Nitrogen. It suggests that the reactions occurring in an oxidative atmosphere are more active within this temperature range. During this phase, a crucial decomposition process commences as

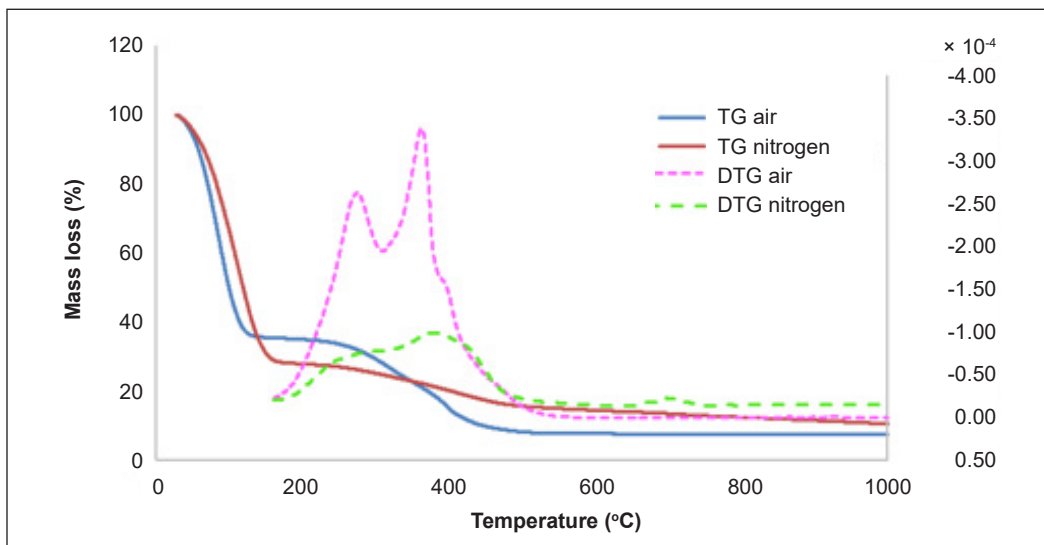


Figure 7. TG-DTG curve of virgin peat Nitrogen and air atmosphere at $10^\circ\text{C min}^{-1}$ heating rate

hemicellulose and cellulose decompose (Chen et al., 2011). In particular, oxygen availability leads to the combustion of volatile gases, thus intensifying the volatilisation rate.

Additionally, after reaching 600°C, nitrogen still allows the decomposition process to proceed, involving the decomposition of minerals in peat. However, this high-temperature effect is not noticeable in an oxidative atmosphere. At such high temperatures, oxygen does not significantly impact peat decomposition (Chen et al., 2011). Nevertheless, the presence of oxygen does result in the peak pyrolysis phase to lower temperatures and an earlier onset of the decomposition stage (Jayaraman & Gökalp, 2015). This complex interaction of temperature, oxygen, and decomposition processes is clarified through these observations.

Hence, the impact of oxygen on peat decomposition is examined in both inert and oxidative atmospheres, with specific relevance for environments such as in-ground fires. The study notes that mass loss rates primarily due to moisture evaporation, where oxygen's influence is minimal, occur around 200°C. Mass loss is subsequently expedited in the presence of air, with a slightly lower starting temperature within the 200–500°C range, indicating heightened reaction activity in an oxidative atmosphere. Beyond 600°C, nitrogen continues to support decomposition, including mineral breakdown, while oxidative atmospheres lack notable high-temperature effects. However, the presence of oxygen shifts peak pyrolysis to lower temperatures and advances the onset of decomposition. These findings emphasise the complex role of oxygen in peat decomposition, especially in the context of peat fire behaviour.

Heating Rate Effect. The thermal degradation patterns of virgin peat were examined at different heating rates of 5, 10 and 20°C min⁻¹ under both inert and oxidative atmospheres. Figures 1(b) and 4(b) showcase these profiles. Specifically, as the heating rate increased, the temperature range for thermal decomposition moved to a higher temperature zone. For example, the peak temperature for peat pyrolysis (Stage 2) was observed at 378°C, 405°C, and 415°C under heating rates of 5, 10 and 20°C min⁻¹, respectively. One reason for the change in the DTG curve could be the poor heat conduction ability of peat, causing a lag in temperature distribution across its cross-section during heating.

Mishra and Mohanty (2018) have put forth an interesting proposition regarding the influence of heating rates on the temperature distribution within biomass particles. Their study suggests that at a lower heating rate, the temperature profile along the cross-section of biomass is assumed to be linear, as both the outer surface and the inner core of biomass gradually attain the same temperature over time. Recent studies have shown that lower heating rates enhance heat transfer within the particle surface (Mishra & Mohanty, 2018). Its heightened heat transfer efficiency at lower heating rates leads to more homogeneous temperatures within the peat samples, thus having implications for the kinetics and thermal behaviours during the pyrolysis or combustion process.

On the contrary, Gogoi et al. (2018) argue that a higher heating rate generally leads to less char formation during biomass pyrolysis. Moreover, the increased heating rate impacts the activation energy values of biomass decomposition reactions under an inert atmosphere (Gogoi et al., 2018). Besides, the completion of combustion was closely linked to the heating rate (Dong et al., 2023). Based on the result from Table 2 reveals that the average activation energy of virgin peat under an inert atmosphere was 13.14 kJ mol⁻¹, 14.87 kJ mol⁻¹ and 31.49 kJ mol⁻¹ for heating rates of 5, 10 and 20°C min⁻¹, respectively. Mishra and Mohanty (2018) propose that higher heating rates lead to a peak decomposition rate due to an increase in thermal energy. It will cause the ignition and combustion index to increase when the heating rate increases (Jayaraman et al., 2020)

In summary, this study examined the thermal degradation pattern of virgin peat under varying heating rates (5, 10 and 20°C min⁻¹) in both inert and oxidative atmospheres. The altered DTG curve shape may arise from the poor heat conduction of virgin peat, resulting in temperature distribution delays during heating. The study also revealed the average activation energies for virgin peat under inert atmospheres, where higher heating rates induce peak decomposition rates due to increased thermal energy, impacting ignition and combustion indices. This research offers valuable insights into the complex relationship between heating rates, thermal behaviour, and peat combustion characteristics, contributing to a deeper understanding of peat fire behaviour under various conditions.

CONCLUSION

In conclusion, this study delves into the thermal degradation of two distinct varieties of Malaysian peat soils and their associated kinetic parameters under varied experimental conditions, encompassing peat type, heating rates, and surrounding atmospheric composition. The samples analysed include virgin peat from a forest reserve and agricultural peat from a cultivated area, exhibiting different carbon contents due to potential elemental mixtures in agricultural peat. The research uncovers that the pyrolysis patterns of both peat types are similar, yet virgin peat displays a higher decomposition rate at Stage 2 due to its elevated carbon content. This higher carbon content leads to a greater heating value (Jayaraman et al., 2017b) and significantly influences the organic component decomposition process. Notably, virgin peat experiences a 43% mass loss during pyrolysis, while agricultural peat demonstrates a 46% mass loss, highlighting insights into thermal behaviour and consistent decomposition patterns across peat types.

Furthermore, the investigation unveils altered DTG curve shapes and activation energy trends, with 14.87 kJ mol⁻¹ for virgin peat and 5.37 kJ mol⁻¹ for agricultural peat under an inert atmosphere, and 28.89 kJ mol⁻¹ for virgin peat and 36.66 kJ mol⁻¹ for agricultural peat under an oxidative atmosphere. It deepens our understanding of the intricate relationships between heating rates, thermal behaviours, and peat combustion characteristics. By contrasting

the decomposition behaviours of virgin and agricultural peat under inert atmospheres, the differential influence of carbon content on their combustion characteristics becomes evident. Oxygen's presence significantly affects thermal decomposition and smouldering combustion, particularly pertinent to the deep soil layers with limited oxygen availability. The study underscores the higher flammability of virgin peat due to its elevated carbon content, impacting ignition points and decomposition rates, which in turn emphasises the need for tailored management strategies based on peat type to mitigate fire risks.

The significance of this research lies in Malaysia's vast peatland extent, approximately 2.5 million hectares, constituting 7.5% of the total land area and frequently encountering smouldering peat fire events. Despite existing research on peat soil thermal and kinetic decomposition, there remains a dearth of Malaysian peat soil studies. This study contributes to understanding and potentially simulating smouldering peat fires in Malaysia and holds relevance for global peatland management. The insights from investigating peat pyrolysis kinetics offer a comprehensive understanding of its behaviour under diverse conditions. The delineation of distinct mass loss stages, including moisture evaporation, organic component decomposition, and mineral breakdown, offers foundational knowledge. Moreover, the research highlights the paramount influence of heating rates on decomposition, influencing ignition, combustion, and flammability dynamics. By elucidating oxygen's role in peat decomposition, particularly in the context of ground fires, this research updates the potential research on management strategies to mitigate the environmental risks associated with peat fires.

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REFERENCES

- Adon, R., Bakar, I., Wijeyesekera, D. C., & Zainorabidin, A. (2012). Overview of the sustainable uses of peat soil in Malaysia with some relevant geotechnical assessments. *International Journal of Integrated Engineering*, 4(4), 38-46.
- Azmi, N. A. C., Apandi, N. M., & Ahmad, A. S. (2021). Carbon emissions from the peat fire problem - A review. *Environmental Science and Pollution Research*, 28(14), 16948-16961. <https://doi.org/10.1007/s11356-021-12886-x>
- Cancellieri, D., Leroy-Cancellieri, V., Leoni, E., Simeoni, A., Kuzin, A. Y., Filkov, A. I., & Rein, G. (2012). Kinetic investigation on the smouldering combustion of boreal peat. *Fuel*, 93, 479-485. <https://doi.org/10.1016/j.fuel.2011.09.052>
- Chen, H., Zhao, W., & Liu, N. (2011). Thermal analysis and decomposition kinetics of Chinese forest peat under nitrogen and air atmospheres. *Energy and Fuels*, 25(2), 797-803. <https://doi.org/10.1021/ef101155n>

- Dommain, R., Couwenberg, J., & Joosten, H. (2011). Development and carbon sequestration of tropical peat domes in south-east Asia: Links to post-glacial sea-level changes and Holocene climate variability. *Quaternary Science Reviews*, 30(7-8), 999-1010. <https://doi.org/10.1016/j.quascirev.2011.01.018>
- Dong, H., Hu, X., Yu, A., Wang, W., Zhao, Q., Wei, H., Yang, Z., Wang, X., & Luo, C. (2023). Study on the mechanism of an enteromorpha-based compound inhibitor for inhibiting the spontaneous combustion of coal using in situ infrared spectroscopy and thermal analysis kinetics. *Journal of Environmental Chemical Engineering*, 11(2), Article 109577. <https://doi.org/10.1016/j.jece.2023.109577>
- Fawzi, N. I., Qurani, I. Z., & Darajat, R. (2021). Alleviating peatland fire risk using water management trinity and community involvement. In *IOP Conference Series: Earth and Environmental Science* (Vol. 914, No. 1, p. 012037). IOP Publishing. <https://doi.org/10.1088/1755-1315/914/1/012037>
- Gogoi, M., Konwar, K., Bhuyan, N., Borah, R. C., Kalita, A. C., Nath, H. P., & Saikia, N. (2018). Assessments of pyrolysis kinetics and mechanisms of biomass residues using thermogravimetry. *Bioresource Technology Reports*, 4, 40-49. <https://doi.org/10.1016/j.biteb.2018.08.016>
- Goldstein, J. E., Graham, L., Ansori, S., Vetruta, Y., Thomas, A., Applegate, G., Vayda, A. P., Saharjo, B. H., & Cochrane, M. A. (2020). Beyond slash-and-burn: The roles of human activities, altered hydrology and fuels in peat fires in Central Kalimantan, Indonesia. *Singapore Journal of Tropical Geography*, 41(2), 190-208. <https://doi.org/10.1111/sjtg.12319>
- Hänninen, K. I. (2017). A chemical mechanism for self-ignition in a peat stack. *Environment and Ecology Research*, 5(1), 6-12. <https://doi.org/10.13189/eer.2017.050102>
- Hu, Y., Fernandez-Anez, N., Smith, T. E. L., & Rein, G. (2018). Review of emissions from smouldering peat fires and their contribution to regional haze episodes. *International Journal of Wildland Fire*, 27(5), 293-312. <https://doi.org/10.1071/WF17084>
- Huang, X., & Rein, G. (2014). Smouldering combustion of peat in wildfires: Inverse modelling of the drying and the thermal and oxidative decomposition kinetics. *Combustion and Flame*, 161(6), 1633-1644. <https://doi.org/10.1016/j.combustflame.2013.12.013>
- Jayaraman, K., & Gökalp, I. (2015). Pyrolysis, combustion and gasification characteristics of miscanthus and sewage sludge. *Energy Conversion and Management*, 89, 83-91. <https://doi.org/10.1016/j.enconman.2014.09.058>
- Jayaraman, K., Kok, M. V., & Gokalp, I. (2017a). Combustion properties and kinetics of different biomass samples using TG-MS technique. *Journal of Thermal Analysis and Calorimetry*, 127(2), 1361-1370. <https://doi.org/10.1007/s10973-016-6042-1>
- Jayaraman, K., Kok, M. V., & Gokalp, I. (2017b). Thermogravimetric and mass spectrometric (TG-MS) analysis and kinetics of coal-biomass blends. *Renewable Energy*, 101, 293-300. <https://doi.org/10.1016/j.renene.2016.08.072>
- Jayaraman, K., Kök, M. V., & Gökalp, I. (2020). Combustion mechanism and model free kinetics of different origin coal samples: Thermal analysis approach. *Energy*, 204, Article 117905. <https://doi.org/10.1016/j.energy.2020.117905>

- Khelkhal, M. A., Lapuk, S. E., Buzyurov, A. V., Krapivnitskaya, T. O., Peskov, N. Yu., Denisenko, A. N., & Vakhin, A. V. (2022). Thermogravimetric study on peat catalytic pyrolysis for potential hydrocarbon generation. *Processes*, *10*(5), Article 974. <https://doi.org/10.3390/pr10050974>
- Khelkhal, M. A., Lapuk, S. E., Ignashev, N. E., Eskin, A. A., Glyavin, M. Y., Peskov, N. Y., Krapivnitskaia, T. O., & Vakhin, A. V. (2021). A thermal study on peat oxidation behavior in the presence of an iron-based catalyst. *Catalysts*, *11*(11), Article 1344. <https://doi.org/10.3390/catal11111344>
- Khoroshavin, L. B., Medvedev, O. A., Belyakov, V. A., & Bezzaponnaya, O. V. (2012). *Peat Fires and their Extinguishing*. ResearchGate. https://www.researchgate.net/publication/324694093_PEAT_FIRES_AND_THEIR_EXTINGUISHING
- Kosyakov, D. S., Ul'yanovskii, N. V., Latkin, T. B., Pokryshkin, S. A., Berzhonskis, V. R., Polyakova, O. V., & Lebedev, A. T. (2020). Peat burning - An important source of pyridines in the earth atmosphere. *Environmental Pollution*, *266*, Article 115109. <https://doi.org/10.1016/j.envpol.2020.115109>
- Lourenco, M., Fitchett, J. M., & Woodborne, S. (2022). Peat definitions: A critical review. *Progress in Physical Geography*, *47*(4), 506-520. <https://doi.org/10.1177/03091333221118353>
- Melling, L. (2015). Peatland in Malaysia. In *Tropical Peatland Ecosystems* (pp. 59-73). Springer. https://doi.org/10.1007/978-4-431-55681-7_4
- Mezbahuddin, S., Nikonovas, T., Spessa, A., Grant, R. F., Imron, M. A., Doerr, S. H., & Clay, G. D. (2023). Accuracy of tropical peat and non-peat fire forecasts enhanced by simulating hydrology. *Scientific Reports*, *13*(1), 1-10. <https://doi.org/10.1038/s41598-022-27075-0>
- Mishra, R. K., & Mohanty, K. (2018). Pyrolysis kinetics and thermal behavior of waste sawdust biomass using thermogravimetric analysis. *Bioresource Technology*, *251*, 63-74. <https://doi.org/10.1016/j.biortech.2017.12.029>
- Othman, J., Sahani, M., Mahmud, M., & Ahmad, M. K. S. (2014). Transboundary smoke haze pollution in Malaysia: Inpatient health impacts and economic valuation. *Environmental Pollution*, *189*, 194-201. <https://doi.org/10.1016/j.envpol.2014.03.010>
- Palamba, P., Ramadhan, M. L., Pamitran, A. S., Prayogo, G., Kosasih, E. A., & Nugroho, Y. S. (2018). Drying Kinetics of Indonesian Peat. *International Journal of Technology*, *9*(5), Article 1006. <https://doi.org/10.14716/ijtech.v9i5.805>
- Prat, N., Belcher, C. M., Hadden, R. M., Rein, G., & Yearsley, J. M. (2015). A laboratory study of the effect of moisture content on the spread of smouldering in peat fires. *Flamma*, *6*(1), 35-38.
- Qin, Y., Musa, D. N. S., Lin, S., & Huang, X. (2022). Deep peat fire persistently smouldering for weeks: A laboratory demonstration. *International Journal of Wildland Fire*, *32*(1), 86-98. <https://doi.org/10.1071/wf22143>
- Rein, G. (2013). Smouldering fires and natural fuels. In *Fire Phenomena and the Earth System: An Interdisciplinary Guide to Fire Science* (pp. 15-33). John Wiley & Sons, Inc. <https://doi.org/10.1002/9781118529539.ch2>

- Rezanezhad, F., Price, J. S., Quinton, W. L., Lennartz, B., Milojevic, T., & Van Cappellen, P. (2016). Structure of peat soils and implications for water storage, flow and solute transport: A review update for geochemists. *Chemical Geology*, 429, 75-84. <https://doi.org/10.1016/j.chemgeo.2016.03.010>
- Sundari, S., Hirano, T., Yamada, H., Kusin, K., & Limin, S. (2012). Effect of groundwater level on soil respiration in tropical peat swamp forests. *Journal of Agricultural Meteorology*, 68(2), 121-134. <https://doi.org/10.2480/agrmet.68.2.6>
- Taufik, M., Widyastuti, M. T., Sulaiman, A., Murdiyarso, D., Santikayasa, I. P., & Minasny, B. (2022). An improved drought-fire assessment for managing fire risks in tropical peatlands. *Agricultural and Forest Meteorology*, 312, Article 108738. <https://doi.org/10.1016/j.agrformet.2021.108738>
- Turetsky, M. R., Benscoter, B., Page, S., Rein, G., Van Der Werf, G. R., & Watts, A. (2015). Global vulnerability of peatlands to fire and carbon loss. *Nature Geoscience*, 8, 11-14. <https://doi.org/10.1038/ngeo2325>
- Varol, M., Atimtay, A. T., Bay, B., & Olgun, H. (2010). Investigation of co-combustion characteristics of low quality lignite coals and biomass with thermogravimetric analysis. *Thermochimica Acta*, 510(1-2), 195-201. <https://doi.org/10.1016/j.tca.2010.07.014>
- Zhao, W., Chen, H., Liu, N., & Zhou, J. (2014). Thermogravimetric analysis of peat decomposition under different oxygen concentrations. *Journal of Thermal Analysis and Calorimetry*, 17(1), 489-497. <https://doi.org/10.1007/s10973-014-3696-4>