ผลกระทบของกระบวนการทอร์รีแฟคชันต่อการเกิดความร้อนด้วยตัวเองของสนที่ผ่านกระบวนการทอร์รีแฟคชัน

Effect of torrefaction process on self-heating of torrefied pine

ฐณพล เวียงทอง

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ชื่อเรื่อง ผลกระทบของกระบวนการทอร์รีแฟคชันต่อการเกิดความร้อนด้วยตัวเองของสนที่ผ่านกระบวนการทอร์รีแฟคชัน
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บทคัดย่อ

งานวิจัยนี้ศึกษาผลกระทบของอุณหภูมิและความรุนแรงของกระบวนการทอร์รีแฟคชันต่อพฤติกรรมการเกิดความร้อนด้วยตัวเองของไม้สนที่ผ่านการทอร์รีแฟคชัน โดยมีเป้าหมายเพื่อศึกษาปัจจัยที่มีอิทธิพลต่อการเกิดความร้อนด้วยตัวเองในกระบวนการทอร์รีแฟคชัน ผลการศึกษาพบว่า ที่อุณหภูมิที่ 60 ℃ น้ำหนักของไม้สนที่ผ่านการทอร์รีแฟคชันยังคงเสถียรในระหว่างกระบวนการออกซิเดชัน ทั้ง 10% และ 30% ของการลดลงของน้ำหนักเริ่มต้น ซึ่งบ่งชี้ถึงการเกิดกระบวนการออกซิเดชันที่น้อยมาก ในขณะที่ 120 ℃ มีการเพิ่มขึ้นเล็กน้อยของน้ำหนักซึ่งเกิดจากการดูดซับออกซิเจน แต่ที่ 180 ℃ พบว่ามีการเพิ่มขึ้นของน้ำหนักในระยะเริ่มต้นตามด้วยการลดลงอย่างมีนัยสำคัญเนื่องจากการสลายตัวของออกซิเจนและกระบวนการออกซิเดชันของคาร์บอนโดยตรง ผลลัพธ์เหล่านี้ชี้ให้เห็นว่าอุณหภูมิที่สูงขึ้นเพิ่มโอกาสในการเกิดความร้อนด้วยตัวเอง จึงแนะนำให้ใช้อุณหภูมิต่ำกว่า 120 ℃ เพื่อลดความเสี่ยงนี้ นอกจากนี้การศึกษายังเน้นถึงความรุนแรงของกระบวนการทอร์รีแฟคชันที่มีผลต่อการเกิดความร้อนด้วยตัวเอง อุณหภูมิทอร์รีแฟคชันที่สูงขึ้นจะเพิ่มแนวโน้มในการเกิดปฏิกิริยาออกซิเดชัน ทำให้ชีวมวลมีความเสี่ยงต่อการเกิดความร้อนด้วยตัวเองมากขึ้น งานวิจัยนี้แสดงให้เห็นถึงความสัมพันธ์ระหว่างอุณหภูมิ ความรุนแรงของกระบวนการทอร์รีแฟคชัน และพฤติกรรมการเกิดความร้อนด้วยตัวเอง ซึ่งเป็นประโยชน์สำหรับการจัดการและการแปรรูปชีวมวลที่ผ่านการทอร์รีแฟคชันอย่างปลอดภัย

Title Effect of torrefaction process on self-heating of torrefied pine

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Abstract

This study investigates the effects of temperature and torrefaction severity on the self-heating behavior of torrefied pine. It aims to explain how these factors influence self-heating phenomena during the torrefaction process. The findings reveal that at a cooling temperature of 60 °C, mass stability was maintained during air oxidation for both 10% and 30% mass loss, indicating minimal oxidation activity. At 120 °C, a slight mass increase was observed, attributed to oxygen chemisorption. In contrast, at 180 °C, an initial mass increase was followed by a significant decline due to the decomposition of oxygen surface complexes and direct carbon oxidation. These results indicate that higher cooling temperatures enhance the likelihood of self-heating, suggesting that cooling temperatures should remain below 120 °C to mitigate this risk. Additionally, the study highlights that torrefaction severity impacts self-heating susceptibility. Higher torrefaction temperatures increase the tendency for oxidation reactions, making the biomass more prone to self-heating. This research underscores the complex interplay between temperature, torrefaction severity, and self-heating behavior, providing insights for safer handling and processing of torrefied biomass.

กิตติกรรมประกาศ

ผู้วิจัยขอขอบพระคุณ กองทุนเพื่อการวิจัย มหาวิทยาลัยเทคโนโลยีราชมงคลพระนคร ที่สนับสนุนงบประมาณในการทำวิจัย

ฐณพล เวียงทอง

สารบัญ

สารบัญ (ต่อ)

สารบัญตาราง

ตารางที่ หน้า

สารบัญรูป

รูปที่ หน้า

บทที่ 1

บทนำ

1.1 ความเป็นมาและความสำคัญของปัญหา

The utilization of biomass as a renewable energy source is on the rise in Thailand, with the Thai government promoting the bio-circular-green (BCG) economic model. The BCG model capitalizes on the country's strengths in biological diversity and cultural wealth while leveraging technology and innovation to transform Thailand into an economy centered on value and driven by innovation. This BCG model is implemented with a focus on promoting four key industries. Particularly in the bioenergy, biomaterials, and biochemistry sector, this sector holds significant growth potential due to the government's policy aimed at making renewable energies represent 30% of the total final energy consumption by 2036.

However, certain properties of biomass still fall below those of fossil fuels. The high moisture content of biomass is one of the main drawbacks, resulting in low energy density, low bulk density, and a low calorific value. Therefore, biomass requires a pretreatment process to overcome these issues and achieve higher energy densities than fossil fuels. Torrefaction is one of the pretreatment methods used to enhance the properties of biomass.

Torrefaction is carried out within a temperature range of 200 to 300°C under an inert atmosphere [1]. After torrefaction, the biomass acquires new energy, mechanical, and physico-chemical properties, such as higher energy density, hydrophobicity, increased friability, and more.

Cooling, a critical step in any thermal treatment, involves bringing the torrefied biomass to a temperature below 200°C before releasing it into the air, as 200°C is considered the ignition temperature of wood [2]. After cooling, self-heating can occur, leading to spontaneous combustion of the torrefied biomass.

This risk of self-ignition is encountered during the production, storage, and transportation of torrefied biomass. Although limited regarding torrefied biomass, the literature has shown that this process increases the susceptibility to self-heating in torrefied products compared to untreated biomass [3], [4].

Spontaneous combustion is a thermal runaway caused by the self-heating of materials, leading to a transition from a slow internal exothermic reaction to rapid oxidation without an external heat source, such as a spark or flame. Self-heating is part of the spontaneous combustion process that occurs before the material ignites. It results from an imbalance between the heat generated by the internal exothermic reaction and the heat dissipated into the environment. The heat source for self-heating is classified into three phenomena: biological reaction, chemical oxidation, and physical reactions like hydro-thermal migration of moisture [5]. These three processes can occur independently or in combination. This study focuses on the heat generated by chemical.

Chemical oxidation, also known as low-temperature oxidation (below 200°C), is the main source of heat for the self-heating of carbonaceous materials. Low-temperature oxidation involves an interaction between the cellulosic components and oxygen molecules, resulting in an exothermic reaction that generates heat. This reaction takes place on the surface of the materials. It produces carbon dioxide (CO_2), carbon monoxide (CO), methane (CH_4), and aldehydes [6].

The objective of this study is to examine the impact of temperature on the chemical oxidation of torrefied pine, which is the main cause for self-heating. The aim is to gain a deeper understanding of this process and, furthermore, to implement measures that can prevent self-heating and spontaneous combustion while storing torrefied biomass.

1.2 วัตถุประสงค์ของโครงการวิจัย

1.2.1 To study the effect of temperature on chemical oxidation of torrefied pine

1.2.2 To understand the self-heating of torrefied biomass

1.3 ประโยชน์ที่คาดว่าจะได้รับ

1.3.1 To gain knowledge about the self-heating process of biomass that has undergone torrefaction.

1.3.2 To learn about the effect of temperature on the oxidation reaction of torrefied pine wood and used as a guideline for preventing the spontaneous combustion of torrefied biomass.

บทที่ 2
ทฤษฎีและวรรณกรรมที่เกี่ยวข้อง

2.1 Biomass

Biomass is primarily made up of cellulose, hemicellulose, and lignin. In biomass, cellulose and lignin form a matrix that is surrounded by hemicellulose chains. Cellulose, a polysaccharide-based organic compound, is the main chemical component of plant primary cell walls. Hemicellulose, another group of carbohydrates, consists of various sugar units, including xylose, arabinose, mannose, galactose, and glucose. Together, cellulose and hemicellulose provide structural support to the cell wall. Lignin, the third key component, is a polymer made up of phenylpropane units, connected by ether or carbon-carbon bonds. Lignin enhances the mechanical strength of the cell wall through covalent linkages [7].

Although all types of biomass share these three major components, their compositions vary, as shown in Table 2.1. Biomass contains different amounts of cellulose (30% to 51%), hemicellulose (17% to 31%), and lignin (17% to 44%). These variations in composition are influenced by factors such as climatic conditions, seasonal changes, harvesting time, and the specific type of biomass, including species and plant parts [8]–[10].

Biomass can be classified into two categories: woody and non-woody biomass. Woody biomass is derived from trees, while non-woody biomass comes from herbaceous plants, agricultural sources, and aquatic organisms. Non-woody biomass generally has lower lignin content and energy value [8], but it is abundant and cost-effective. Table 2.2 provides examples of woody and non-woody biomass, along with their uses.

Table 2.ผิดพลาด! ไม่มีข้อความของสไตล์ที่ระบุในเอกสาร Properties of biomass (%) [8]

Biomass	Cellulose	Hemicellulose	Lignin
Sugarcane top	29.85	18.85	25.69
Cornstalk	34.45	27.55	21.81
Bagasse	30	35	18
Wheat straw	38.7	19	17.3
Rice straw	35.8	21.5	24.4
Rapeseed	51.3	17.3	44
Corn stover	36.3	31.4	17.2

Table 2.2 Biomass groups and examples of utilisation [8], [29]

Groups	Biomass sub-groups, species and varieties coniferous	Example of utilisation
Woody biomass	i.e. barks, branches (twigs), leaves (foliage), bushes (shrubs), chips, lumps, pellets, briquettes, sawdust, sawmill	Wood chips, particles, firewood briquettes and pellets
Non-woody biomass	**Herbaceous and agricultural biomass** i.e. grasses and flowers, straws, stalks, fibres, Shells and husks, pit	**Oilseed crops**: for biodiesel production **Sugar and starch crops**: for bioethanol **Lignocelluloses**: for heat and power production
	Aquatic biomass i.e. marine or freshwater, macroalgae, etc.	Algae: production of biogas for energy production

2.2 Torrefaction

Some properties of biomass are inferior to coal for fuel use. They have high moisture content, high oxygen content and low energy density. To overcome these limitations, thermochemical pretreatment such as torrefaction is used to improve the biomass properties. Torrefaction process was first investigated in France in 1930's [11]. This process is considered to be similar to the roast coffee beans technique that had been started in the late 13th century [12], [13].

Torrefaction consists of the slow heating of biomass at temperatures ranging between 200 °C and 300 °C in an atmosphere with no oxygen. Prins et al. [14] suggested the torrefaction temperature should below 300 °C to prevent a fast thermal cracking of cellulose which may cause tar formation that occurred above 300 °C. Rousset et al. [15] divided the torrefaction process into two categories including light torrefaction with torrefaction temperature is below 240 °C and severe torrefaction with torrefaction temperature is above 270 °C. Unlike pyrolysis, the maximisation of the solid yield is the major motivation of torrefaction, biomass weight reduced while the energy content sustained [16]. The high solid yield can be accomplished with the removal of water and carbon dioxide by heating biomass at low heating rate (below 50 °C/min) [17]. A consequence of torrefaction is to remove oxygen from biomass. As the result, torrefied biomass has lower O/C ratio compared to raw biomass [18] and higher energy density.

During torrefaction, biomass undergoes physicochemical changes, especially the three main components (cellulose, hemicellulose, and lignin). Tumuluru et al. [19] divided torrefaction into three zones: nonreactive zone (50 - 150 °C), reactive drying zone (150 - 200 °C), and destructive drying (200 - 300 °C). During the temperature range 50 to 150 °C, the moisture content is eliminated and no chemical reaction occur. At the end of this range (120 - 150 °C), lignin starts softening. In reactive drying zone (150 - 200 °C), the hydrogen and carbon bonds begin to break and the structural deformation and depolymerisation of hemicellulose occur. Depolymerisation of hemicellulose causes shortened and condensed solid polymers. In destructive drying (200 - 300 °C), complete degradation of hemicellulose and partial degradation of cellulose and lignin take place. The degradation of cellulose might have enhanced by acids and water vapour generated from degradation of hemicellulose. Thus, torrefied biomass has more lignin content, which is more stable than the other two components. However according to Bergman et al. [20], torrefaction can be divided into five stage with the drying process is subdivided into two stages, as described in Table 2.3.

Torrefaction process improve the chemical and physical properties of raw biomass and changes these properties closer to those of bituminous coal [21]. Torrefaction can produce a torrefied biomass with an energy density higher than those of wood and with a solid denser than wood, make the properties of biomass fall in between those of coal and wood [22]. Rousset et al. [15] found the characteristics of torrefied bamboo is close to low-rank coal. The same finding also found in Tapasvis [23], where the characteristics of torrefied birch and spruce were closer to coal. Thus, the torrefied biomass can be used in some application such as domestic heating, residential cooking stoves, to substitute charcoal.

Table 2.3 Five stages of torrefaction process, adapted from [20]

Stages	Description
1 Heating	Biomass is heated until the drying temperature is reached and at the end of this stage moisture starts to evaporate.
2 Pre-drying	Over 100 °C, free water in biomass is evaporated at constant temperature.
3 Post-drying	Temperature is increased to 200 °C, physically bound water present on biomass chemical bonds is completely evaporated. During this stage, light organic compounds can evaporate result in the presence of some mass loss.
4 Torrefaction	Main stage of the torrefaction process. This stage is entered when the temperature exceeds 200 °C and is ends when the temperature becomes below 200 °C again. The torrefaction temperature is the maximum temperature used during this process.
5 Cooling	The torrefied biomass is cooled down to a temperature below 200 °C, which is the ignition temperature of wood, before it contacts the air and until room temperature is reached.

2.3 Spontaneous combustion

Similar to coal, heat-treated biomass such as torrefied biomass and biochar has the risk of self-heating and spontaneous combustion. Whatever the thermal modification process used to improve biomass quality, a stabilization step is needed for new material. During storage step, torrefied biomass or biochar took place many industrial sites. It is possible, sometimes, that biomass underwent the auto-ignition during production process [24]. To date, despite considerable efforts to understand and predict the self-heating and spontaneous combustion of biomass and coal in recent decades, literature on these phenomena in torrefied biomass is limited.

Spontaneous combustion, also known as spontaneous ignition, self-ignition or auto-ignition is one major problem of several carbonaceous materials such as coal, lignocelluloses biomass, and wastes, especially in their storage and transportation [25], [26]. Spontaneous combustion causes not only safety problem and energy losses but also the emission of pollutant gas [26], [27]. According to Kim and Sohn [28], the four conditions for coal spontaneous combustion are presented, including a sufficient and continuous supply of oxygen; accumulation of coal with spontaneous combustion tendency in broken form, accumulation of heat and sufficient time to happen. Spontaneous combustion is delayed or terminated if one of these conditions is prevented.

According to Bowes [29], the thermal explosion analysis by Semenov (1940) and Frank Kamenetskii (1939) are the basis theory of spontaneous combustion and self-heating in stockpile. Spontaneous combustion is a thermal runaway occurring from self-heating of the materials resulted in a transition from slow internal exothermic reaction to a rapid oxidation without external heat source such as spark or flame. Self-heating is a part of spontaneous combustion process that happened before the ignition of material. Self-heating results from the imbalance between the heat generated by the internal exothermic reaction and the heat dissipated to the surrounding via conduction, convection and radiation.

According to Blijderveen et al. [30], Figure 2.1 represents the classic graphic of the relationship between heat generation and three possible rates of heat loss using Semenov diagram to explain spontaneous combustion of packed beds reactor.

The heat generated by the internal exothermic reaction is plotted as Q_{react}. The three parallel straight lines represent the convective heat loss from the fuel bed to the air stream for three primary air stream temperatures (Q_{conv}). These lines cross the x-axis at the air temperature (T_0). The fuel bed is heated by the primary air stream when Q_{conv} is negative.

Spontaneous combustion may or may not occur depending on the air temperature (T_0). There are three possible following situations:

In situation (a), the air temperature is too low to ignite the fuel bed and a heat loss rate greater than the heat generated as a consequence spontaneous combustion will not take place.

In situation (b), the heat loss rate is never larger than the heat generated, so spontaneous combustion will take place. This situation gives the critical condition at which spontaneous combustion will take place. The air temperature (T_0) corresponds to the critical air temperature (T_{crit}). At point 2, where the heat loss is equal the heat generated, the ignition temperature is presented.

In situation (c), the air stream temperature (T_0) is highest among other situations. The heat loss rate is much lower than the heat generated as a consequence spontaneous combustion is already occurring.

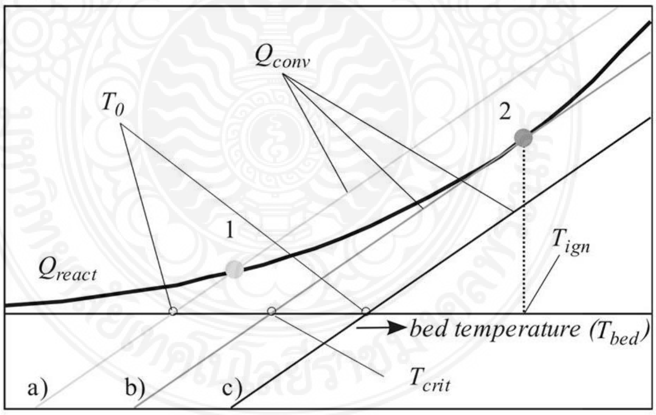


Figure 2.1 Heat produced by the reaction (thick curved line) and the heat lost (positive values) or gained (negative values) due to convective heat transfer by the air stream for three values of T_0, adapted *from* **[30]**

Many scholars proposed that the coal spontaneous combustion phenomenon can be divided into three stages (Figure 2.2): 1) the incubation stage, the temperature was relatively low and the oxidation rate was slow; 2) the self-heating stage, the heat generated from oxidation increases the coal temperature and exceed the critical temperature (60-80°C); 3) the combustion stage, the coal temperature rose rapidly and reached the ignition temperature. [31]–[33]

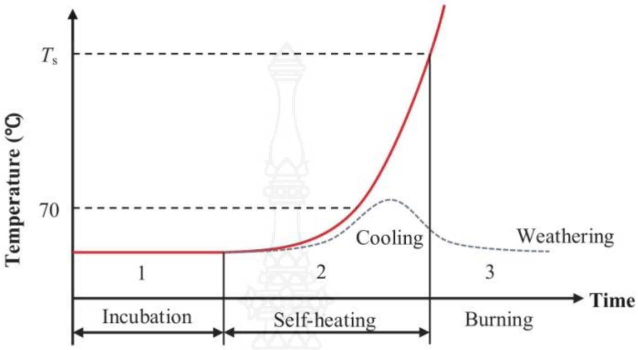
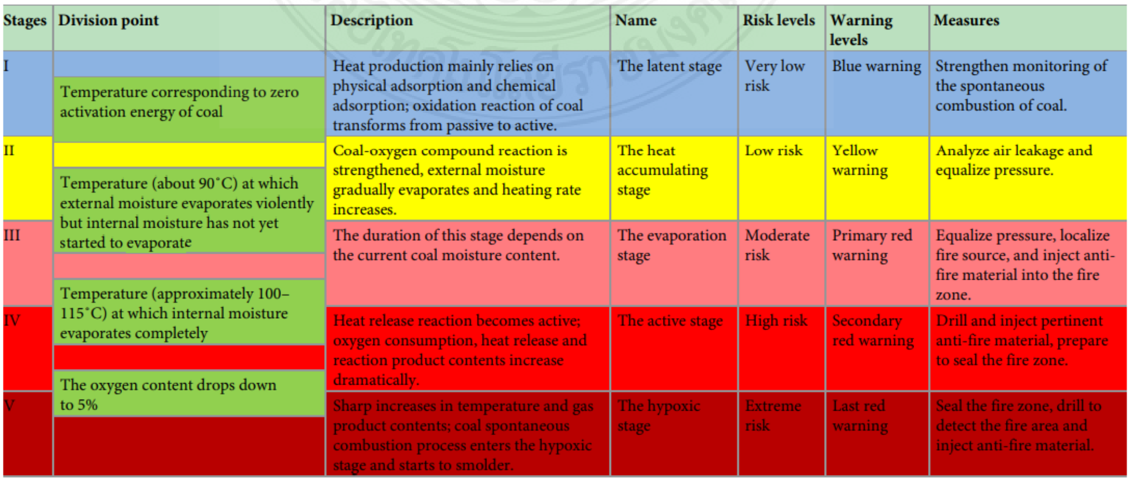


Figure 2.2 Three stages division method, adapted from [33]

However, the three stages division method is difficult to prevent accurately the coal spontaneous combustion in early stage and the targeted prevention measures for each stage have not described. Zhu et al.[31] proposed the five stages division method as presented in Table 2.4. In 2021, Zhang et al. [32] provided the seven stages division method for coal spontaneous combustion. Both methods gave more details for early warning criteria to prevent the coal spontaneous combustion.

Table 2.4 Five stages warning of the spontaneous combustion of coal, adapted from [31]



Stages	Division point	Description	Name	Risk levels	Warning levels	Measures
I	Temperature corresponding to zero activation energy of coal	Heat production mainly relies on physical adsorption and chemical adsorption; oxidation reaction of coal transforms from passive to active.	The latent stage	Very low risk	Blue warning	Strengthen monitoring of the spontaneous combustion of coal.
II	Temperature (about 90°C) at which external moisture evaporates violently but internal moisture has not yet started to evaporate	Coal-oxygen compound reaction is strengthened, external moisture gradually evaporates and heating rate increases.	The heat accumulating stage	Low risk	Yellow warning	Analyze air leakage and equalize pressure.
III	Temperature (approximately 100–115°C) at which internal moisture evaporates completely	The duration of this stage depends on the current coal moisture content.	The evaporation stage	Moderate risk	Primary red warning	Equalize pressure, localize fire source, and inject anti-fire material into the fire zone.
IV	The oxygen content drops down to 5%	Heat release reaction becomes active; oxygen consumption, heat release and reaction product contents increase dramatically.	The active stage	High risk	Secondary red warning	Drill and inject pertinent anti-fire material, prepare to seal the fire zone.
V		Sharp increases in temperature and gas product contents; coal spontaneous combustion process enters the hypoxic stage and starts to smolder.	The hypoxic stage	Extreme risk	Last red warning	Seal the fire zone, drill to detect the fire area and inject anti-fire material.

2.4 Self-heating

Self-heating in a material is the initial step in spontaneous combustion process that might followed by rapidly accelerating temperatures or thermal runaway which finally results in spontaneous combustion. The heat source of self-heating is classified into three phenomena; biological reaction; chemical oxidation and physical reaction such as hydro-thermal moisture migration. These three processes can occur alone or in combination [34].

2.4.1 Self-heating mechanism

2.4.1.1 Biological reaction

Biological reaction that leads to heat generation includes the respiration of living cells and the growth and respiration of micro-organism, such as bacteria, moulds and fungi. The surrounding environment and the material characteristics such as moisture content determine the concentration of micro-organism [34]. Materials that have high moisture content allow a suitable environment for micro-organism because they use the nutrients in water [34].

Forestry products can also initially have biological reaction such as respiration of living cells to produce heat [34]. Conversely, respiration does not occurred for biomass pellet or torrefied biomass pellet since drying at high temperatures during making pellet biomass or torrefying pellet biomass kill the respiration cells [34].

This biological reaction occurs at lower temperatures than chemical oxidation but may increase the temperature to a sufficiently high temperature to start chemical oxidation reaction [35]. Biological activity is known to work efficiently in the temperature range of 50-80°C, may be found in a few days or a few months. Beyond this range, above 80°C, micro-organism will decrease or die [35].

In case of wood pellets, there is very limited or no presence of micro-organism. As described above, during the production process, the micro-organism already dies at high temperature. In addition, biomass pellets have low moisture content compared to raw material, which is normally 7-10% [36], that limits the growth of micro-organisms. However, there is no report that micro-organisms are involved in significant degree in self-heating of wood pellet.

2.4.1.2 Chemical oxidation

Chemical oxidation, also known as low temperature oxidation (below 200°C), is the main heat source for self-heating of carbonaceous materials. The low temperature oxidation, the interaction between cellulosic materials and the oxygen molecules, is an exothermic reaction which generates heat. This reaction takes place on the surface of the materials and exothermic heart is produced when biomass is oxidized. This reaction also generates carbon dioxide (CO_2), carbon monoxide (CO), methane (CH_4), also including aldehydes and other emissions that might have a negative impact on the environment [34], [36].

During storage period, biomass fuels have potentials to absorb oxygen and produce exothermic reactions. The oxidation of wood normally starts at 40°C and generally becomes the dominating process at temperature above 50°C. At temperature above 80°C, the low temperature oxidation is the only source of heat for self-heating [37]. As the temperature increases, the rate of low temperature oxidation increases and the heat generation rate also rapidly rises. As a result, spontaneous combustion is able to take place within a biomass pile [38].

The oxidation process is a complicate mechanism and still not well understood. According to Hotova et al., [39], three reactions are believed to occur during the carbon oxidation process: (i) the chemisorption process that create oxygen surface groups with generalized composition COx, (ii) oxidation process or sample burn off connected with the evolution of CO_2 and (iii) decomposition of created oxygen surface groups that generates CO_2.

$$i. C + O_2 \rightarrow CO_x$$

$$ii. C + O_2 \rightarrow CO_2$$

$$iii. CO_x + O_2 \rightarrow CO_2$$

Figure 2.3, from [39], illustrates TG curves of the isothermal experiments for the oxidation of carbon cryogels at constant temperature. They found that at lower temperature (180-240°C), the increase of mass of the carbon sample is observed and the reaction (i) predominates. A further increase in temperature results a change in the trend (260-280°C). At the beginning of the oxygen injection, the mass of carbon sample still increases, afterward the two remaining reactions ((ii) and (iii)) start to occur, which lead the decrease of sample mass.

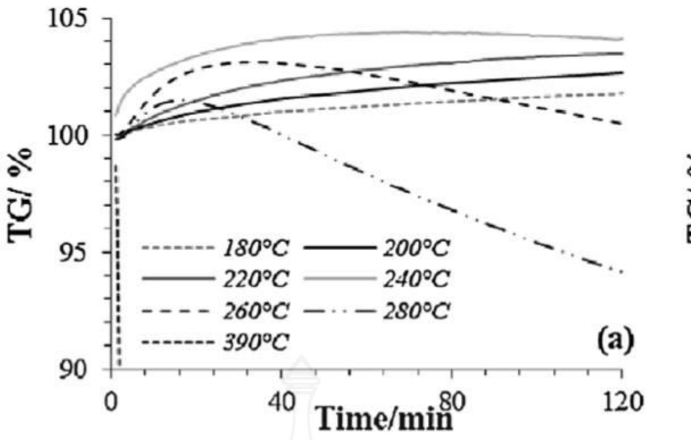


Figure 2.3 TG curve of the isothermal experiments for the oxidation of carbon cryogels under 20% oxygen atmosphere, adapted from [39].

Some researchers suggested two parallel reactions occurred during carbon oxidation: sorption and direct burn-off (Figure 2.4) [40]. The sorption reaction consists of the three following steps: (i) oxygen chemisorption on carbon surfaces, when the free radicals chemically adsorb oxygen to form unstable carbon-oxygen complexes, e.g. peroxides and hydroperoxides; (ii) decomposition of unstable carbon-oxygen complexes to form stable solid complexes, e.g. carboxyl (-COOH), carbonyl (C=O) and hydroxyl (-OH), and gaseous products; and (iii) degradation of these stable solid complexes and the generation of new active sites for carbon oxidation. Oxidation stops when all the active sites are saturated. Carbon oxidation is favoured by the high vibrational kinetic energy which increases with an increase in temperature. Oxygen chemisorption and the decomposition of hydroperoxides are exothermic reactions whereas the decomposition of carboxyl and carbonyl is endothermic [41]. However, more heat is generated during carbon oxidation than that consumed by endothermic reactions, making oxidation an exothermic reaction. The direct burn-off reaction is hypothesised to be similar to the direct combustion reactions of solid fuels, which depend on temperature. This reaction only occurs at certain active sites, and involves rapid interaction with oxygen, followed by the rapid desorption of the gaseous products and the production of heat [41].

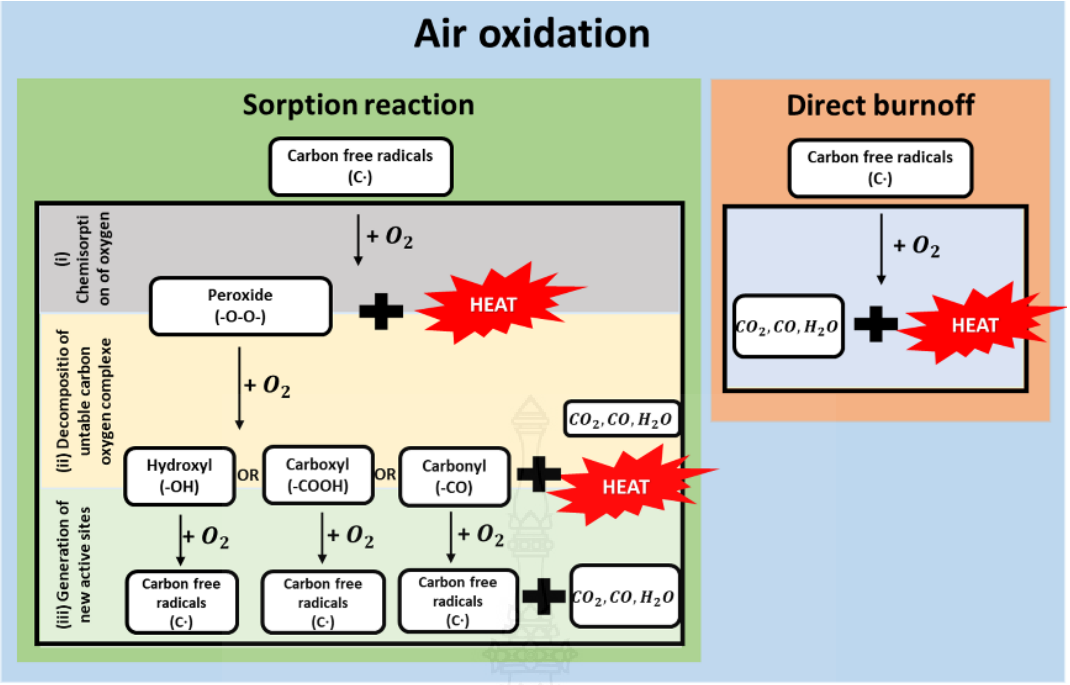


Figure 2.4 Mechanism of air oxidation process

2.4.1.3 Physical reactions

Carbonaceous materials cannot evitable contact with moisture in the atmosphere during their storage or transportation. As a result, material will normally absorb moisture in the atmosphere that lead to the moisture content increase and the decrease of heating value of materials. But not only the problem of decreasing of heating value of materials but physical reactions such as hydro-thermal moisture migration is also one heat source for self-heating that occur in a pile of material [42]. In tropical countries, the first safety aspect of coal that should be considered is the effects of high relative humidity and ambient temperature, especially in rainy season, the influence of humidity to self-heating is important [43].

Water adsorption is a physical interaction between water molecules and carbonaceous materials. It is an exothermic reaction which generates heat. Water molecules are initially adsorbed on hydrophilic sites, including oxygen functional groups on the carbonaceous surface such as carboxyl (-COOH), carbonyl (C=O) and hydroxyl (-OH), by hydrogen bonds. This reaction is known as primary adsorption. The secondary adsorption occurs with an increase in relative humidity. New hydrogen bonds are formed between free water vapour molecules and the primary adsorbed water molecules. This results in the formation of water clusters and pore filling [44], as shown in Figure 2.5.

The adsorption of water vapour from the atmosphere plays an important role in raising the temperature of biochar [83].

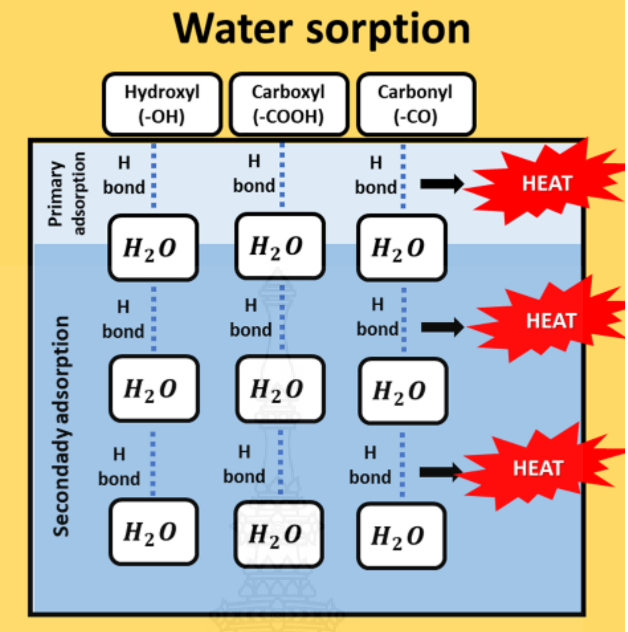


Figure 2.5 Mechanism of water adsorption process

Bastistella et al. [45] provided a more comprehensive in adsorption of water vapor of biochar. Their results showed the adsorption of water vapor from ambient atmosphere plays an important role in raising the temperature of a biochar. The raise in temperature of a biochar increases with the increase of air humidity. In large scale storage, migration of moisture through the material will create both absorption and desorption of moisture and absorption of moisture which is exothermic reactions that can cause the self-heating [37]. The quantity of heat generated by absorption of moisture depends on the phase of the moisture adsorbed (liquid water or water vapour) and the materials. According to Back [46], the heat generated from wetting dry wood by liquid water is approximately 1170 J/g of water. However, the heat of condensation is twice of this amount (2440 J/g of water at 20°C) when wood absorbs moisture from the air. Wood pellet with low initial moisture content and high air humidity will increase the risk of heat generation by moisture absorption. To reduce the risk for self-heating due to absorption of moisture, it is important to store pellets indoors in order to limit the contact with air humidity and avoid water wetting [47].

บทที่ 3

วิธีดำเนินงานวิจัย

3.1 วิธีการดำเนินการวิจัย

This research follows a procedure, comprising four main steps, which are as follows:

Step 1 Pine preparation

Firstly, pine is ground using a ball mill, Retsch PM100, to achieve a fine particle size. The ground rice straw is then sieved to obtain particles that are smaller than 100 μm in size. These finely ground particles are then used in the subsequent torrefaction process and to study the chemical oxidation.

Step 2 Torrefaction and chemical oxidation study

The experimental procedures for isothermal analysis to observe the heat source of self-heating and spontaneous combustion, specifically air oxidation (using dry air), are as follows (Figure 3.1):

Torrefaction: The pine biomass is subjected to torrefaction at 280°C until reaching the desired mass loss levels of 10% and 30%.

TGA/DSC Setup: The torrefaction process is carried out using a TGA/DSC 1 Mettler-Toledo instrument with a continuous flow of nitrogen at a rate of 50 ml/min to prevent biomass combustion.

Cooling: After completing the torrefaction process for each temperature and mass yield combination, the torrefied biomass is cooled down to one of the predetermined cooling temperatures (60°C, 120°C, or 180°C) at a cooling rate of 20°C per minute until the temperature stabilizes.

Isothermal Analysis: The stabilized torrefied biomass is exposed to dry air (oxidation) at the specified cooling temperature (60°C, 120°C, or 180°C). The heat evolution and mass changes during this process are monitored and recorded for observation and analysis.

Through these experimental procedures, the heat source responsible for self-heating and spontaneous combustion during air oxidation can be thoroughly investigated. Each experiment was conducted three times at three different cooling temperatures (60°C, 120°C, and 180°C).

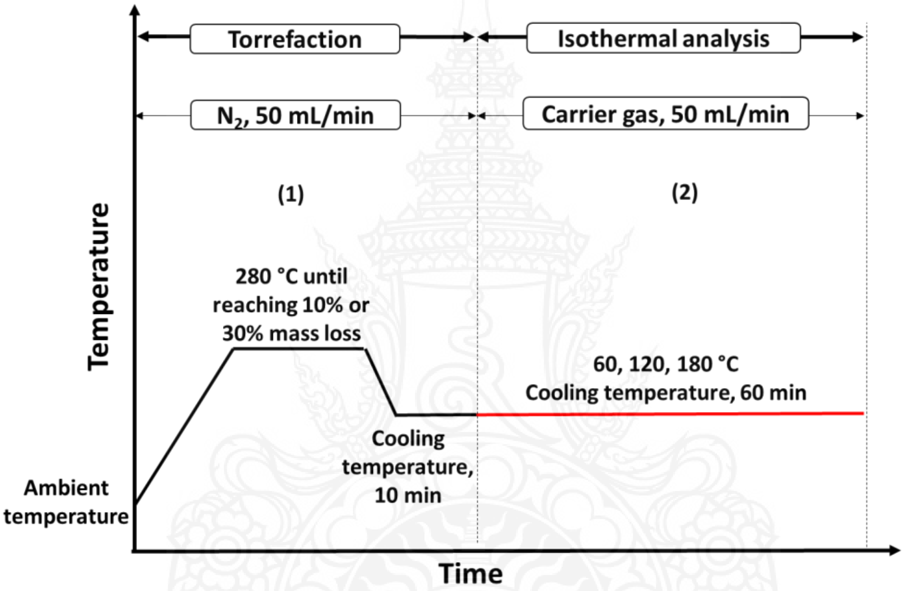


Figure 3.1 Isothermal analysis procedure using TGA/DSC

Step 3 Analysis the results

Once all the experimental tests are completed, and the data is collected, a comprehensive analysis will be carried out to investigate the influence of cooling temperature and torrefaction severity on the chemical oxidation of torrefied pine, which is the primary heat source for self-heating. The obtained results will be thoroughly examined to comprehend how different temperatures and mass loss affect the self-heating process of biomass.

These findings will offer valuable insights into the self-heating and spontaneous combustion tendencies of torrefied pine, and will also contribute to devising preventive measures against fires caused by self-heating and spontaneous combustion.

บทที่ 4

ผลการศึกษา

This study examines the impact of temperature on the self-heating of torrefied pine and the influence of torrefaction severity on self-heating, aiming to understand how the torrefaction process affects self-heating behaviour.

4.1 Effect of temperature on self-heating of torrefied pine

Hotová et al. [39] proposed that the carbon oxidation process involves three interactions between the solid (C or CO_x) and oxygen: (i) oxygen chemisorption, which forms oxygen surface complexes (CO_x) (reaction 1), (ii) the breakdown of these oxygen surface complexes (reaction 2), and (iii) oxidation or direct burn-off, leading to CO_2 release.

$$C + \left(\frac{x}{2}\right) O_2 \rightarrow CO_x \quad + \text{HEAT} \qquad \text{reaction 1}$$

$$CO_x + \left(\frac{2-x}{2}\right) O_2 \rightarrow CO_2 \quad + \text{HEAT} \qquad \text{reaction 2}$$

$$C + O_2 \rightarrow CO_2 \quad + \text{HEAT} \qquad \text{reaction 3}$$

Figure 4.1 and 4.2 presents various mass trends produced by torrefied pine at different cooling temperatures when the gas stream was switched from nitrogen to dry air for 10% and 30% mass loss respectively.

For torrefied pine cooled at 60 °C, the mass remained stable during air oxidation for both 10% and 30% mass loss. This suggests that, if any oxidation mechanisms were present, they occurred at a very slow rate. Oxygen-carbon interactions are typically minimal at ambient temperatures and may take several days to months to initiate self-heating or spontaneous combustion.

At a cooling temperature of 120 °C, a slight increase in mass was observed at the end of the dry air exposure for both 10% and 30% mass loss. This mass increase resulted from the oxygen chemisorption reaction, which led to the formation of oxygen surface complexes.

At 180 °C, the sample's mass initially increased upon exposure to dry air, followed by a sharp decline. Early in the exposure, the oxygen chemisorption reaction (reaction 1) was still active. However, the subsequent mass decrease was due to the decomposition of the oxygen surface complexes (reaction 2) and direct burn-off (reaction 3), which became the dominant processes, causing the downward mass trend.

In conclusion, higher cooling temperatures increase the likelihood of self-heating. To prevent self-heating, the cooling temperature should be kept below 120 °C.

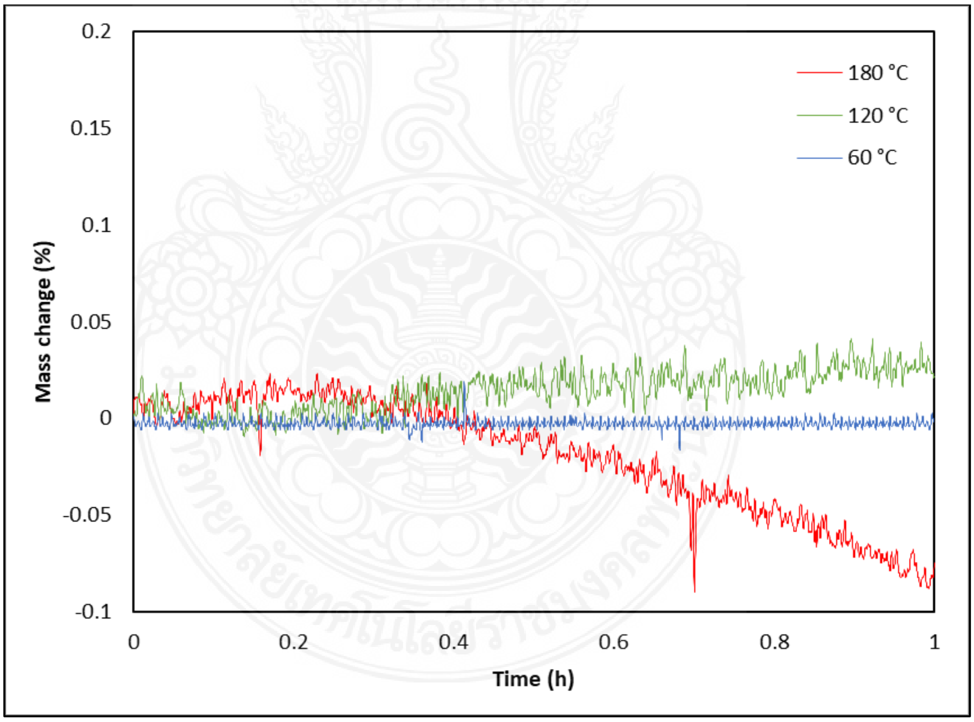


Figure 4.1 Mass change during chemical oxidation process of torrefied pine with 10 % mass loss

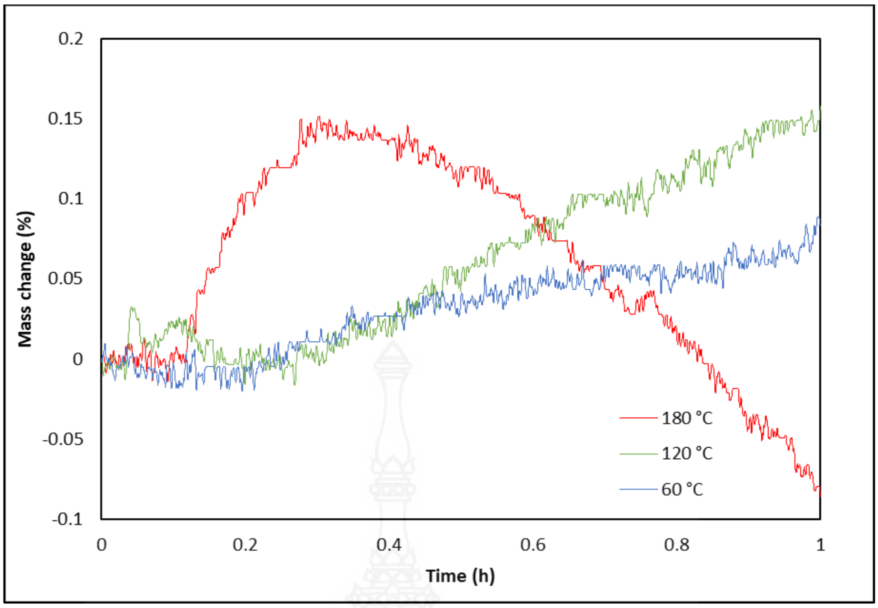


Figure 4.2 Mass change during chemical oxidation process of torrefied pine with 30 % mass loss

4.2 Effect of torrefaction severity on self-heating

Rousset et al. [48] investigated the self-ignition of biochar treated at 500 °C and found that its mass increased rapidly after exposure to dry air at 60 °C, accompanied by heat generation. This finding suggests that the severity of thermal treatment influences the likelihood of self-heating. Candelier et al. [49] noted that the more wood is thermally degraded, the more susceptible it becomes to oxidation reactions. This implies that biochar treated at higher temperatures is more prone to air oxidation than torrefied biomass.

Figures 4.3, 4.4, and 4.5 compare the mass trends of torrefied pine with 10% and 30% mass loss when the gas stream was switched from nitrogen to dry air at cooling temperatures of 60 °C, 120 °C, and 180 °C, respectively.

At 60 °C, the mass remained stable during air oxidation for both 10% and 30% mass loss. However, a slight mass increase was observed for the 30% mass loss. At 120 °C, a slight mass increase occurred toward the end of the dry air exposure for both 10% and 30% mass loss, with the mass increase for 30% being greater than that for 10%, similar to the pattern at 60 °C. At 180 °C, the mass initially increased upon exposure to dry air, followed by a sharp decline for both 10% and 30% mass loss. However, the initial mass increase for 30% was higher than that for 10%, confirming that the more severe the torrefaction, the more sensitive the torrefied pine becomes to oxidation reactions, increasing the risk of self-heating.

Low-temperature oxidation of coal typically progresses through three stages: (i) slow oxidation, (ii) a transition stage, and (iii) rapid oxidation. Slow oxidation occurs at temperatures below 65 °C. The transition stage, involving oxygen chemisorption (reaction 1), takes place during the early phase of coal oxidation (65 °C – 80 °C). At temperatures above 80 °C, the rapid oxidation stage, referred to as direct burn-off (reaction 3), dominates [50], [51]. In the current study, the slow oxidation stage was clearly evident at 60 °C, where air oxidation reactions were very slow. The transition stage occurred at 120 °C, indicated by the mass increase and heat generation due to oxygen chemisorption. The rapid oxidation stage was observed at 180 °C, with mass decrease and significant heat generation resulting from the three carbon oxidation reactions [52].

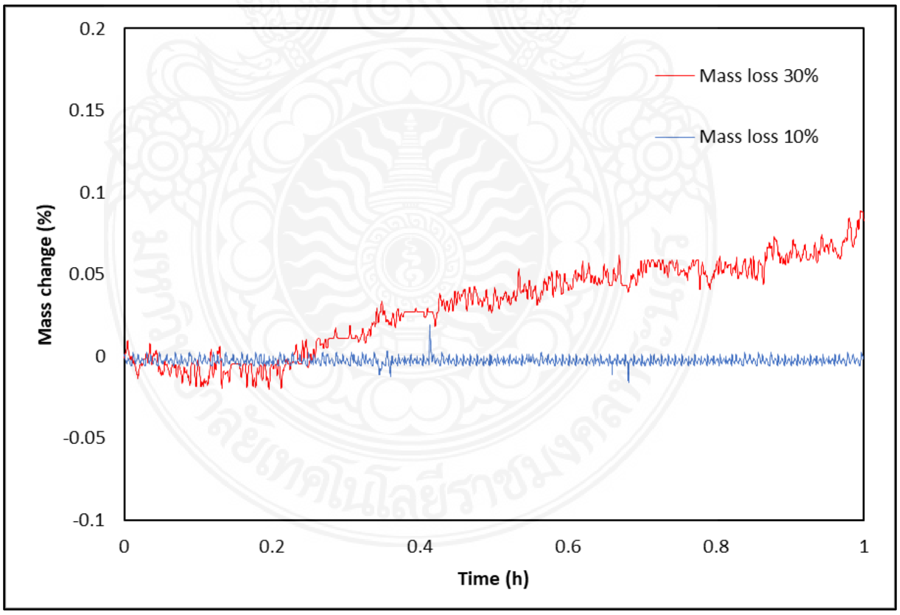


Figure 4.3 Mass change during chemical oxidation process of torrefied pine at 60 °C cooling temperature

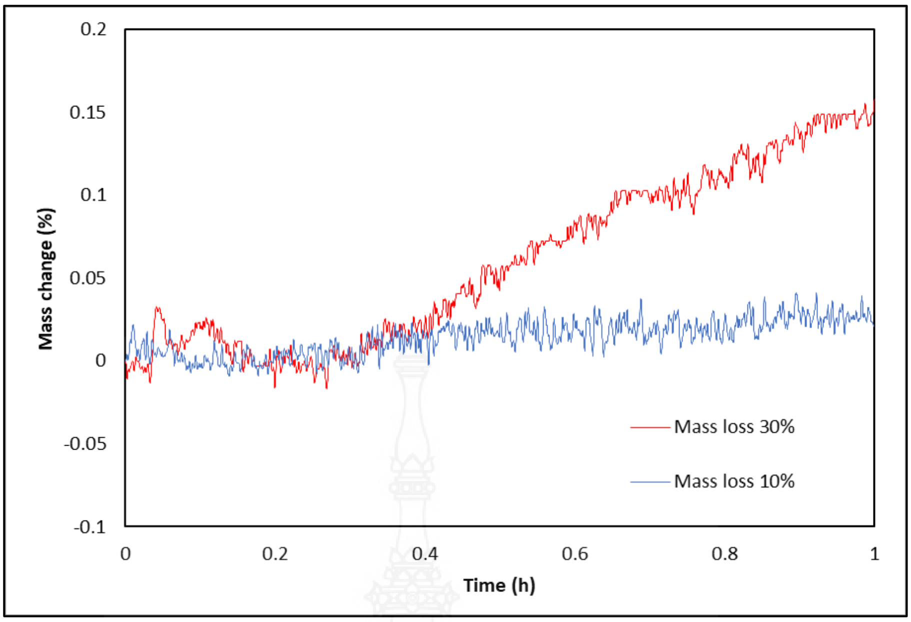


Figure 4.4 Mass change during chemical oxidation process of torrefied pine at 120 °C cooling temperature

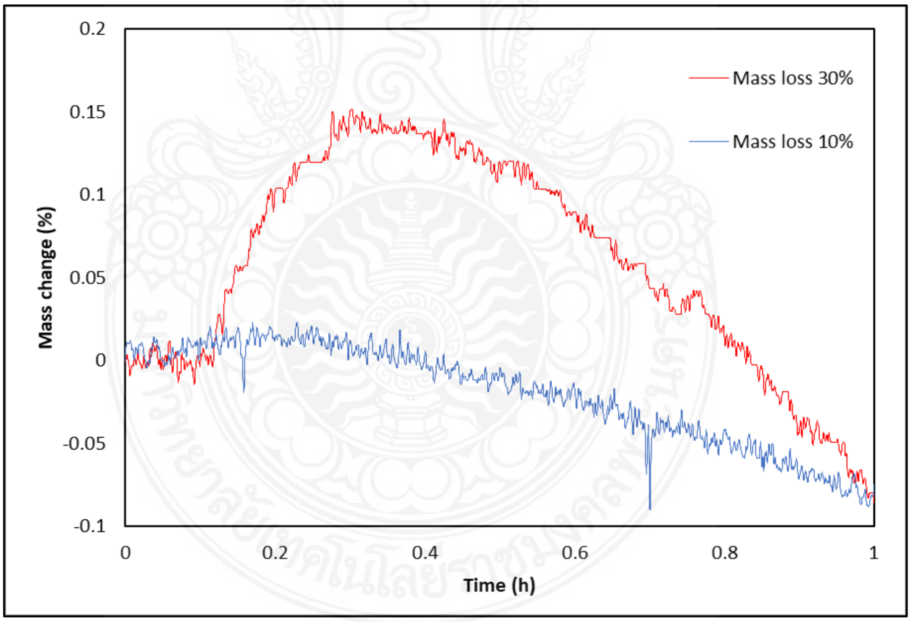


Figure 4.5 Mass change during chemical oxidation process of torrefied pine at 180 °C cooling temperature

ทที่ 5

สรุปผลงานวิจัย

5.1 สรุปผลการทดลอง

This study investigates the effects of temperature and torrefaction severity on the self-heating behavior of torrefied pine, aiming to clarify how these factors influence self-heating risks. The carbon oxidation process, as outlined by Hotová et al. [39], comprises three key interactions between carbon (C or COx) and oxygen: oxygen chemisorption, decomposition of oxygen surface complexes, and oxidation or direct burn-off.

Mass trend analyses at various cooling temperatures (60 °C, 120 °C, and 180 °C) revealed important insights. At 60 °C, the mass remained stable during air oxidation, indicating minimal oxidation and slow interactions that could take days or months to lead to self-heating. Conversely, at 120 °C, a slight mass increase was observed, indicating active oxygen chemisorption and the formation of oxygen surface complexes. At the highest temperature, 180 °C, the mass initially increased but subsequently declined sharply as decomposition of the oxygen surface complexes and direct burn-off became dominant, leading to significant heat generation and mass loss.

Furthermore, the study explored the impact of torrefaction severity. Rousset et al. [48] noted that biochar treated at elevated temperatures (e.g., 500 °C) exhibited a rapid increase in mass and heat generation upon exposure to dry air, underscoring the importance of thermal treatment in self-heating susceptibility. Candelier et al. [49] highlighted that increased thermal degradation heightens wood's vulnerability to oxidation reactions.

The findings for torrefied pine further confirmed these observations. At 60 °C, the mass remained stable, with a slight increase for samples experiencing 30% mass loss. At 120 °C, both 10% and 30% mass loss samples showed increased mass, with the 30% loss demonstrating a more pronounced sensitivity to oxidation. By 180 °C, the mass of both samples initially increased before sharply declining, with the 30% mass loss sample exhibiting an even greater sensitivity to oxidation reactions and a heightened risk of self-heating.

The study also aligned with the established stages of coal oxidation: slow oxidation (below 65 °C), transition (oxygen chemisorption between 65 °C and 80 °C), and rapid oxidation (direct burn-off above 80 °C) [50], [51]. The observations revealed that slow oxidation dominated at 60 °C, with minimal reactions, while at 120 °C, the transition stage was evident due to increased mass and heat generation. The rapid oxidation stage became apparent at 180 °C, characterized by significant heat generation and mass loss driven by carbon oxidation reactions [52].

In conclusion, the results demonstrate that both higher cooling temperatures and increased torrefaction severity significantly elevate the likelihood of self-heating. This underscores the critical need for meticulous control of cooling processes and torrefaction conditions to mitigate combustion risks associated with torrefied biomass.

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