



Review Paper

Oxidative torrefaction and torrefaction-based biorefining of biomass: a critical review

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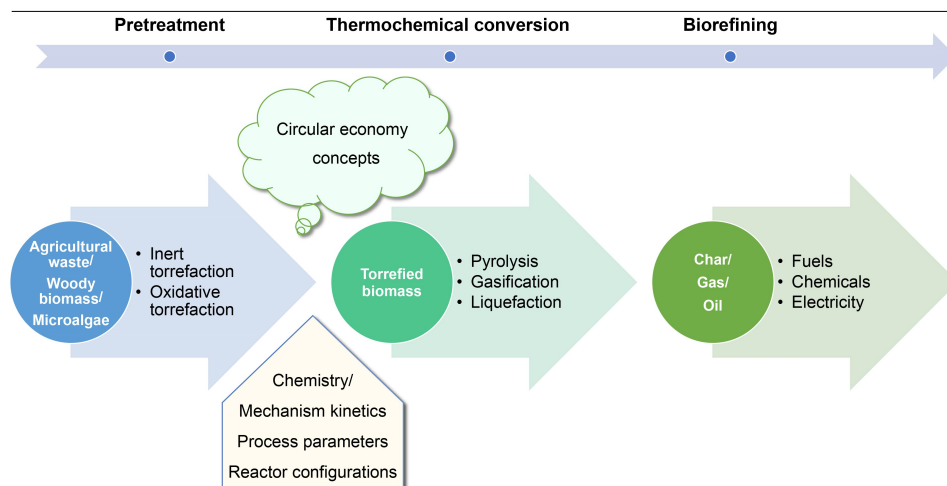
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HIGHLIGHTS

- Torrefaction is a vital pretreatment technology for thermochemical biorefinery applications.
- Oxidative torrefaction is an economical version of torrefaction.
- Woody biomass equally benefits from oxidative or inert torrefaction.
- Inert torrefaction is more suitable for agricultural wastes and microalgae.
- Significant challenges in oxidative torrefaction are identified, and solutions are presented.

GRAPHICAL ABSTRACT



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ABSTRACT

Torrefaction is a vital pretreatment technology for thermochemical biorefinery applications like pyrolysis, gasification, and liquefaction. Oxidative torrefaction, an economical version of torrefaction, has recently gained much attention in the renewable energy field. Recent literature on inert and oxidative torrefaction was critically reviewed in this work to provide necessary guidance for future research and commercial implementations. The critical performance parameters of torrefaction for thermochemical biorefinery applications, such as solid yield, energy yield, carbon enhancement, higher heating value (HHV) enhancement, and energy-mass co-benefit index (EMCI), were also analyzed. Agricultural waste, woody biomass, and microalgae were considered. The analysis reveals that woody biomass could equally benefit from oxidative or inert torrefaction. In contrast, inert torrefaction was found more suitable for agricultural wastes and microalgae. Using flue gas as the oxidative torrefaction medium and waste biomass as the feedstock could achieve a circular economy, improving the sustainability of oxidative torrefaction for thermochemical biorefineries. The significant challenges in oxidative torrefaction include high ash content in torrefied agricultural waste, the oxidative thermal runaway of fibrous biomass during torrefaction, temperature control, and scale-up in reactors. Some proposed solutions to address these challenges are combined washing and torrefaction pretreatment, balancing oxygen content, temperature, and residence time, depending on the biomass type, and recirculating torrefaction gases.

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Contents

| | |
|--|------|
| 1. Introduction..... | 1673 |
| 2. Biomass pretreatment technologies..... | 1674 |
| 3. Torrefaction chemistry/mechanism for different lignocellulosic and non-lignocellulosic biomass..... | 1674 |
| 4. Classification of torrefaction: inert torrefaction and oxidative torrefaction..... | 1675 |
| 5. Torrefaction kinetics..... | 1675 |
| 6. Oxidative torrefaction parameters and the effect on properties of torrefied biomass..... | 1675 |
| 6.1. Effect on solid yield..... | 1679 |
| 6.2. Effect on carbon enhancement..... | 1679 |
| 6.3. Effect on higher heating value enhancement..... | 1683 |
| 6.4. Effect on energy yield..... | 1685 |
| 6.5. Effect on energy mass co-benefit index..... | 1687 |
| 7. Torrefaction in the flue gas atmosphere..... | 1687 |
| 8. Reactor configurations..... | 1690 |
| 8.1. Fixed bed reactor..... | 1690 |
| 8.2. Rotary drum reactor..... | 1691 |
| 8.3. Moving bed reactor..... | 1691 |
| 8.4. Screw reactor..... | 1691 |
| 9. Application of torrefied product in thermochemical-based biorefineries..... | 1691 |
| 10. Circular economy concepts of torrefaction-based thermochemical biorefinery..... | 1691 |
| 11. Challenges towards commercialization and future perspectives..... | 1692 |
| 12. Conclusions..... | 1693 |
| Acknowledgements..... | 1693 |
| References..... | 1693 |

1. Introduction

A biorefinery integrates biomass conversion processes to produce biofuels, power, and chemicals. The primary objective of biorefineries is to replace petroleum oil with biomass as raw material for fuels and chemicals. Different types of biomass feedstocks can be converted to different fuels and chemicals in a biorefinery through different conversion technologies (Balagurumurthy et al., 2015). Biorefineries are classified into two groups: biochemical and thermochemical. Biochemical conversion processes produce specific products like biogas and bioethanol, and the conversion is relatively slow. Thermochemical conversion processes produce various products relatively quickly (Seo et al., 2022). During thermochemical conversion processes, biomass is transformed into intermediate products such as syngas, bio-oil, and biochar in a reactor, depending on the conversion technology applied. These intermediate products can then be used to produce bioalcohols (methanol and ethanol), hydrogen, and Fischer-Tropsch diesel (Foust et al., 2009). Biochar can be used as a soil amendment, catalyst, or adsorbent. The major technologies for biomass conversion in thermochemical processing are pyrolysis, gasification, and liquefaction (Tursi, 2019; Rodionova et al., 2021).

For economic conversion, the most important requirement is the quality and quantity of biomass feedstocks. First-generation feedstocks are out of the scope due to direct competition with human food and animal feed. Second-generation feedstocks are mainly agricultural waste and energy crops, and the conversion processes are complex due to the nature of lignocellulosic biomass. Third-generation feedstocks include a wide range of photosynthetic microalgae and have a large potential in the future; the current conversion processes are still

technically immature, though (Balagurumurthy et al., 2015).

Biomass properties directly affect thermochemical biorefinery applications. Compared to petroleum, biomass generally has less hydrogen and carbon and high oxygen, moisture, and alkali metal contents. This compositional difference adversely affects the processing and product qualities of a thermochemical biorefinery. Further, low bulk density, low energy density, hydrophilic nature, and poor grindability of biomass also create logistic and processing issues. Therefore, pretreatment plays an important role in all thermochemical biorefinery applications, and torrefaction is considered a vital pretreatment step.

Torrefaction is a current hot topic in the renewable energy field. After years of research on torrefaction in an inert atmosphere, current efforts are focused on making it practical on a commercial scale. In this regard, oxidative torrefaction plays a vital role. Several reviews on biomass torrefaction have been reported, covering the areas of process, product, and uses, as summarized in Table 1. All these reviews addressed torrefaction chemistry, mechanism, and effect of different process parameters on product properties. Some reviews also covered kinetics, reactor configurations, applications, environmental and economic aspects, and challenges and prospects. However, to the best of the authors' knowledge, oxidative torrefaction, an economical version of traditional torrefaction technology for thermochemical biorefinery applications, is yet to be comprehensively reviewed. Further, considering the importance of a closed-loop economic system in which there is no considerable loss of material values, circular economy approaches of the oxidative torrefaction-based thermochemical biorefinery along with challenges and future

Table 1.
A comparison of the present review with the previously published reviews on torrefaction.

| Aspect | Chen et al. (2015) | Barskov et al. (2019) | Niu et al. (2019) | Mamvura and Danha (2020) | Cahyanti et al. (2020) | Ong et al. (2021) | Abdulyekeen et al. (2021) | Chen et al. (2021) | This review |
|---|--------------------|-----------------------|-------------------|--------------------------|------------------------|-------------------|---------------------------|--------------------|-------------|
| Torrefaction chemistry/mechanism | √ | √ | √ | √ | √ | √ | √ | √ | √ |
| Analysis of both inert and oxidative torrefaction | - | - | - | - | - | - | - | - | √ |
| Torrefaction kinetics | √ | - | - | - | - | √ | - | √ | √ |
| Parameters and effects on the product | √ | √ | √ | √ | √ | √ | √ | √ | √ |
| Reactor configurations | - | - | - | √ | - | - | √ | √ | √ |
| Applications | √ | - | √ | √ | √ | - | √ | √ | √ |
| Environmental aspects | - | - | - | - | √ | - | - | √ | - |
| Economic aspects | - | - | √ | - | √ | - | - | - | - |
| Circular economy aspects | - | - | - | - | - | - | - | - | √ |
| Challenges and prospects | - | - | √ | - | - | √ | √ | √ | √ |

√: Included

-: Not included

perspectives are also introduced in the present work. The analyzed results of inert and oxidative torrefaction of different biomass classes such as agricultural waste, woody biomass, and microalgae reveal the expected performance and the operational limits, offering essential guidance, especially for commercial applications.

2. Biomass pretreatment technologies

The limitations of raw biomass can be reduced to a certain extent by pretreatment such as drying, pelletizing, grinding, milling, etc. Biomass pretreatments can be studied under five categories: chemical, mechanical, thermal, hydrothermal, and biological. Catalyzed steam-explosion, ammonia fiber/freeze explosion, and acid-alkaline, pH-controlled liquid hot water treatment are categorized under common chemical pretreatments. They remove hemicelluloses and lignin to improve biomass biodegradability (Nhuchhen et al., 2014). Mechanical pretreatments such as grinding, milling, pelletizing, and extrusion can improve the physical properties of biomass. Pelletization increases the handling ability but does not increase the hydrophobicity. The surface area of biomass can be increased by milling and grinding processes (Nhuchhen et al., 2014; Ribeiro, 2018). Hydrothermal carbonization, a biomass thermochemical conversion process, is carried out under high pressures at 180–230 °C. This process overcomes the major limitations of raw biomass, but the process is more complex due to the high-pressure requirement (Pang, 2019). Hydrothermal carbonization occurs in the water medium; hence, it is best suited for wet biomass. In biological pretreatments, microorganisms modify the chemical composition and biomass structure. However, this process is very slow and requires a controlled environment (Nhuchhen et al., 2014). Biomass' physical, structural, and chemical properties can be modified using thermal treatment methods. Drying is a simple thermal pretreatment method that removes biomass moisture. Torrefaction is the latest thermal pretreatment technology and is defined as a mild pyrolysis process (Nhuchhen et al., 2014). A comparison of different biomass pretreatment technologies is presented in Table 2.

3. Torrefaction chemistry/mechanism for different lignocellulosic and non-lignocellulosic biomass

Torrefaction is a recently developed technology carried out at 200–300 °C and normally in an inert environment under atmospheric pressure producing a dark-coloured solid product with non-condensable gases and liquid products (Nhuchhen et al., 2014). There are three torrefaction types called light (200–235 °C), mild (235–275 °C), and severe (275–300 °C) torrefaction (Chen et al., 2015). Torrefaction generally happens in five phases: heating, pre-drying, post-drying, torrefaction, and cooling (Nhuchhen et al., 2014; Ribeiro et al., 2018), as shown in Figure 1. At the initial heating stage, biomass is heated until it reaches the drying temperature (100 °C), and all free water is evaporated at the pre-drying stage. Then the temperature increases to 200 °C, and the remaining water in biomass is evaporated. This stage is called the post-drying stage, and significant mass loss can be observed due to the decomposition of several biomass components during the post-drying stage. The major mass loss occurs during the torrefaction stage and temperature above 200 °C. Finally, biomass should be cooled down below 200 °C, the ignition point of wood, and is called the cooling stage (Ribeiro et al., 2018).

Table 2.
A comparison of biomass pretreatment technologies*.

| Pretreatment technology | Methods | Advantages | Disadvantages | Commercial status |
|---------------------------|--|--|--|---|
| Chemical pretreatment | Catalyzed steam explosion, ammonia fiber/freeze explosion, and acid-alkaline, pH-controlled liquid hot water treatment | Improves biomass biodegradability | Inhibitor generation, corrosive, high cost, use of chemicals | The most applied method on the commercial scale |
| Mechanical pretreatment | Grinding, milling, pelletizing, and extrusion | Improves the physical properties; handling ability, increases surface area, low cost | High energy consumption | Commonly applied, mostly alongside other pretreatment methods |
| Thermal pretreatment | Drying and torrefaction | The physical, structural, and chemical properties of biomass can be modified | High energy consumption | Gaining commercial attention |
| Hydrothermal pretreatment | Hydrothermal carbonization, liquefaction, and gasification | Suited for wet biomass, high energy conversion, low corrosion, and no catalyst requirements | More complex due to the high-pressure, high process cost | Limited commercial applicability |
| Biological pretreatment | Treatment by bacteria, fungi, insects, worms, and gastropods | Low cost, low energy input, no chemical application, and working under mild environmental conditions | The process is very slow and requires a controlled environment | Less attractive commercially |

* Based on Cheah et al. (2020) and Nhuchhen et al. (2014).

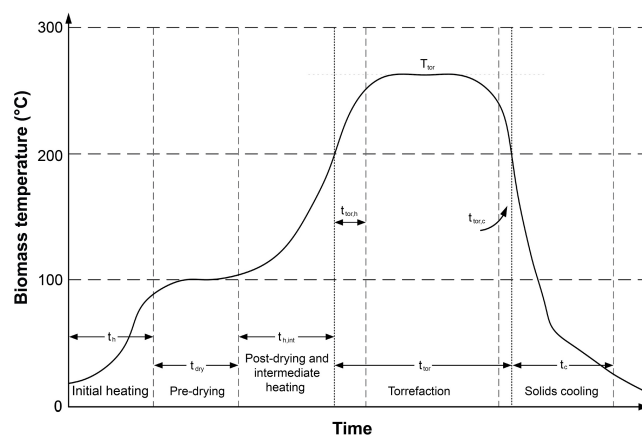


Fig. 1. Schematic description of the different torrefaction stages with time and temperature (Ribeiro et al., 2018).

The biomass chemical changes from the torrefaction process have been characterized based on Fourier-transform infrared spectroscopy (FTIR) analysis, solid-state ¹³C NMR, fiber analysis, and ultimate analysis (Acharya et al., 2015; Ong et al., 2021). The study of raw and torrefied pinewood has shown that the intensity of the FTIR broadband correlates with the decrease of O-H functional groups when the torrefaction temperature is increased. At 300 °C, this band does not appear, implying the hydrophobicity enhancement of the wood due to torrefaction (So and Eberhardt, 2018). Moreover, C-H, C-O-C, and C=O groups are also shifted to lower wave numbers as a result of hemicellulose and cellulose degradation (Eseyin et al., 2016; So and Eberhardt, 2018). A study done for cotton stalk and corn stalk has discussed the top three susceptible bonds as H-bond and C-O bond of primary alcohol group and C-O bond of secondary alcohol group (Chen et al., 2014b). Moreover, it has been revealed that the path of bond breaking in hydroxyl depends on the feedstock's constituents. Due to the higher content of hemicelluloses in corn stalk, the C-O bond in alcohol breaks preferentially compared to cotton stalk. The higher contents of cellulose and lignin in the cotton stalk, which are difficult to decompose, tend to break the O-H bonds in primary alcohol groups (Chen et al., 2014b).

The overall torrefaction process is governed by the heat transfer of particles and the heat of the chemical reactions. The heat transfer within a particle varies based on the biomass type, and the heat transfer among particles depends on the type of reactor. Both exothermic and endothermic chemical reactions can be observed during torrefaction. One of the thermal analysis-based experimental studies has shown that up to 230 °C, the overall system shows an endothermic behaviour. After that, it shifted to an exothermic behaviour (Balat, 2008). It has been found that hemicelluloses and lignin decompose exothermically, whereas cellulose decomposition

happens endothermically (Balat, 2008). Further, the analysis of the differential scanning calorimetry (DSC) curve of cellulose has shown a comparatively high endothermic peak at 355 °C (Yang et al., 2007). A study on torrefaction of a single wood particle revealed that the internal temperature gradient over radius direction decreased while heating the wood particle. After that, due to intra-particle exothermic reactions, a comparatively higher temperature can be observed in the core of wood particles than in the surrounding (van der Stelt, 2011). Due to the depolymerisation reactions, the volatiles liberated from biomass particles help break the resistance to mass transfer inside the particles. After that, the volatiles travel from the biomass surface to the reactor through an external mass transfer mechanism that depends on the reactor type.

4. Classification of torrefaction: inert torrefaction and oxidative torrefaction

To prevent biomass oxidation during torrefaction, inert conditions are maintained by numerous studies. However, some have used partially oxidative or oxygen-lean conditions as non-inert torrefaction to minimize the process cost. Nitrogen is the most commonly used inert gas, and a few studies have investigated the torrefaction in the CO₂ environment (Thanapal et al., 2014; Su et al., 2018). The study on Mesquite and Juniper wood has revealed that the CO₂ medium enhances the grindability of the biomass because of the increased surface area caused due to the formation of pores on the biomass samples (Thanapal et al., 2014). In non-oxidative torrefaction, only thermal decomposition happens. However, oxidative torrefaction leads to both thermal decomposition and oxidation due to the participation of oxygen in torrefaction reactions (Uemura et al., 2015). Oxidative torrefaction experiments have been conducted for various feedstocks such as agricultural waste, woody biomass, and microalgae. It has been observed by analyzing SEM images that woody biomass has higher stability at oxidative torrefaction than fibrous biomass (Chen et al., 2014a). Further, the use of simulated or real flue gas for torrefaction has been carried out for cedarwood (Mei et al., 2015), corn residue pellets (Onsree et al., 2019), corn straw (Liu et al., 2021), distilled spirit lees (Zhu et al., 2021), oil palm empty fruit bunches (EFB) (Sulaiman et al., 2015; Sellappah et al., 2016), oil palm kernel shells (Uemura et al., 2018), rice husk (Zhang et al., 2021c), and spruce (Tran et al., 2016). The torrefaction processes have been categorized as wet torrefaction (Li et al., 2015; Bach et al., 2016), steam torrefaction (Sui et al., 2012), and microwave torrefaction (Gronnow et al., 2013). In addition, the effect of potassium carbonate to modify the microstructure of the torrefied biomass and improve the torrefaction performance has been recently studied (Zhang et al., 2022).

5. Torrefaction kinetics

Torrefaction involves a series of complex chemical reactions. It is vital to analyze torrefaction kinetics to recognize biomass thermodegradation characteristics and determine the rate constants such as pre-exponential factor and activation energy (Chen et al., 2021). The two main modes of torrefaction kinetics are isothermal kinetics and non-isothermal kinetics. Further development of the kinetics is based upon the modes mentioned above.

According to the latest research findings, the weight loss of the woody biomass starts at 250 °C. There are two types of kinetic models that have been developed by the researchers: one-step kinetics and multi-step kinetics. The one-step torrefaction kinetics model can predict xylan, cellulose, and lignin thermal decompositions at 200-300 °C and can predict the torrefaction reaction well over a long residence time. But it predicts poorly over a short residence time with a low weight loss during torrefaction (Chen et al., 2015).

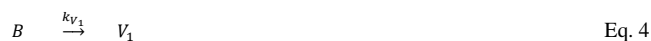
For this one-step kinetic model, the overall reaction equation can be expressed as in Equation 1, and the one-step kinetic model with nth order torrefaction reaction can be given as in Equation 2.



$$\frac{d\alpha}{dt} = k(1 - \alpha)^n \quad \text{Eq. 2}$$

The multi-step kinetic model has been used for biomass pyrolysis to predict the reaction rates and the product yields. According to a study on willow wood, torrefaction reaction can be presented as a two-step reaction mechanism. In this model, biomass (B) decomposes to volatiles (V₁) and intermediate product (C). Then, the intermediate product (C) decomposes to the final char (D), and

volatiles (V₂) are formed according to Equations 3-6 (Shoulaifar, 2016). The reaction rates are given in Equations 7-9. Kinetic parameters of different biomass types have also been previously reviewed (Perera et al., 2021).



$$r_B = (k_c + k_{V_1}) \times [B] \quad \text{Eq. 7}$$

$$r_C = k_c \times [B] - (k_D + k_{V_2}) \times [C] \quad \text{Eq. 8}$$

$$r_D = k_D \times [C] \quad \text{Eq. 9}$$

As for the oxidative torrefaction, according to a study carried out using EFB, two parallel reactions have been found. The decomposition of hemicelluloses or ordinary torrefaction and the oxidation of biomass is presented in Equation 10 (Uemura et al., 2013).

$$-r_{\text{overall}} = (-r_{\text{tor}}) + (-r_{\text{oxy}}) = k_{\text{tor}} C_{\text{HC}}^l + k_{\text{oxy}} C_{\text{biomass}}^m C_{\text{O}_2}^n \quad \text{Eq. 10}$$

where r is the reaction rate in kg/m³s, k_{tor} stands for the rate constant of torrefaction in s⁻¹, k_{oxy} denotes the rate constant of oxidation in m³/mol s, C_{HC} is the concentration of hemicellulose in biomass in kg/m³, C_{EFB} is the concentration of biomass in kg/m³, and C_{O_2} is the concentration of oxygen in mol/m³.

In a study about oxidative torrefaction of biomass residues, this parallel reaction mechanism was extended by dividing the biomass into two reactive components: the fast reaction group and the medium reaction group (Eqs. 11-13). The fast reaction group represents the decomposition of hemicelluloses, and the medium reaction group accounts for cellulose and lignin decomposition (Wang et al., 2013).

$$-r_{\text{overall}} = (-r_{\text{tor}}) + (-r_{\text{oxy}}) \quad \text{Eq. 11}$$

$$-r_{\text{tor}} = (-r_{\text{tor,fast group}}) + (-r_{\text{tor,medium group}}) \quad \text{Eq. 12}$$

$$-r_{\text{oxy}} = (-r_{\text{oxy,fast group}}) + (-r_{\text{oxy,medium group}}) \quad \text{Eq. 13}$$

6. Oxidative torrefaction parameters and the effect on properties of torrefied biomass

The product properties of torrefaction are directly affected by process parameters such as temperature, residence time, particle size, composition and flow rate of carrier gas, and catalyst availability (Chen et al., 2021). Some studies on oxidative torrefaction of agricultural waste, woody biomass, and microalgae are summarized in Table 3. The tabulated performance parameters (solid yield, carbon enhancement, higher heating value (HHV) enhancement, and energy yield) are the values reported with maximum HHV enhancement in inert and oxidative conditions. The colour scale of the cells in Table 3 depicts the severity of the treatment varying from green to red, where red is most severe. Both agricultural waste and woody biomass have gone through a range of severities from low to high, and microalgae have gone through a medium severity treatment. In the case of agricultural waste, coconut fiber, oil palm fiber, and sugar cane residues have gone through severe degradation, whereas, in the case of woody biomass, Cryptomeria japonica and Eucalyptus show the most severe degradation. Even though most of these studies have done comparative analysis between inert and oxidative torrefaction, most have fixed one or two parameters from temperature, residence time, and oxygen content. Very few studies have analyzed the effect of particle size (Uemura et al., 2015), superficial velocity of carrier gas (Chen et al., 2013), or operating pressure (Nhuuchen and Basu, 2014) as well. Overall, these studies gave a general understanding of the trends in oxidative torrefaction.

Table 3.
Operating conditions and performance parameters of the reviewed inert and oxidative torrefaction studies.

| Biomass Type | O ₂ (%) in torrefaction medium | Temperature (°C) | Time (min) | Particle Size | Process Condition | Solid Yield (%) | Carbon Enhancement | HHV Enhancement | Energy Yield (%) | EMCI* | Reference |
|----------------------------------|---|--------------------|------------------------|---|---|-----------------|--------------------|-----------------|------------------|---------------------|------------------------|
| Agricultural Waste | | | | | | | | | | | |
| Corn cob pellets | 0, 6, 12, 18 | 220, 260, 300 | 5, 10, 15, 20 | Diameter-7 mm, length-20 mm | 300°C, 10 min, 0% O ₂ 300 °C, 20 min, 12% O ₂ | 90.6** | 1.03 | 1.03 | 92.9 | 2.3 | Tanyaket et al. (2020) |
| | | | | | | 34.3 | 1.46 | 1.42 | 48.8 | 14.5 | |
| Coconut fiber | 0, 21 | 250, 300, 350 | 60 | Length < 30mm | 350 °C, 60 min, 0% O ₂ 350 °C, 60 min, 21% O ₂ , 0.82 cm/min | 40.9 | 1.48 | 1.43 | 58.8 | 17.9 | Chen et al. (2013) |
| | | | | | | 37.2 | 1.53 | 1.41 | 52.5 | 15.3 | |
| | 0, 5, 10, 15, 21 | 300 | 60 | Length < 30mm | 300 °C, 60 min, 0% O ₂ 300 °C, 60 min, 5% O ₂ | 47.1 | 1.4 | 1.37 | 64.6 | 17.5 | Chen et al. (2014a) |
| | | | | | | 38.9 | 1.47 | 1.34 | 52 | 13.1 | |
| Oil palm empty fruit bunch (EFB) | 0, 3, 9, 15 | 220, 250, 300 | 30 | 0.375 mm | 300 °C, 30 min, 0% O ₂ 300 °C, 30 min, 3% O ₂ | 79.7 | - | 1.19 | 95 | 15.3 | Uemura et al. (2013) |
| | | | | | | 79.1 | - | 1.19 | 94.5 | 15.4 | |
| | 0, 3, 9, 15, 21 | 220, 260, 300 | 30 | 0.25-0.5 mm | 300 °C, 30 min, 0% O ₂ 300°C, 30 min, 21% O ₂ | 72.7 | - | 1.24 | 90.2 | 17.5 | Hisham, et al. (2016) |
| | | | | | | 51.1 | - | 1.44 | 73.6 | 22.5 | |
| | 0, 21 | 300 | 30 | 0.25-0.5 mm | 300°C, 30 min, 0% O ₂ 300°C, 30 min, 21% O ₂ | 72.4 | 1.12 | 1.25 | 90.5 | 18.1 | Sulaiman et al. (2015) |
| | | | | | | 59.8 | 1.31 | 1.38 | 82.5 | 22.7 | |
| 0, 21 | 150, 170, 190 | 30 | <0.5 mm | 170°C, 30 min, 0% O ₂ 190°C, 30 min, 21% O ₂ | 92.1 | - | 0.98 | 90.6 | -1.5 | Adnan et al. (2017) | |
| | | | | | 91.4 | - | 1.04 | 95.3 | 3.9 | | |
| Oil palm fiber | 0, 21 | 250, 300, 350 | 60 | Length < 30 mm | 350°C, 60 min, 0% O ₂ 350°C, 60 min, 21% O ₂ , 0.82 cm/min | 43.9 | 1.48 | 1.39 | 61.4 | 17.5 | Chen et al. (2013) |
| | | | | | | 43.4 | 1.5 | 1.31 | 56.8 | 13.4 | |
| | 0, 5, 10, 15, 21 | 300 | 60 | Length < 30 | 300°C, 60 min, 0% O ₂ 300°C, 60 min, 5% O ₂ | 51.7 | 1.35 | 1.37 | 70.9 | 19.2 | Chen et al. (2014a) |
| | | | | | | 48 | 1.31 | 1.21 | 58.4 | 10.4 | |
| 0, 21 | 250, 275, 300, 325, 350 | 60 | length less than 30 mm | 350°C, 60 min, 0% O ₂ 250°C, 60 min, 21% O ₂ | 43.9 | 1.37 | 1.4 | 61.3 | 17.4 | Lu et al. (2012) | |
| | | | | | 42.4 | 1.17 | 1.19 | 50.1 | 7.7 | | |
| Oil palm fiber pellets | 0, 5, 10 | 275, 300, 325, 350 | 30 | Length 30mm diameter 8 mm | 350°C, 30 min, 0% O ₂ 350°C, 30 min, 10% O ₂ | 45.9 | - | 1.22 | 55.9 | 10 | Chen et al. (2016a) |
| | | | | | | 43.1 | - | 1.23 | 53 | 9.9 | |
| Oil palm kernel shell (PKS) | 0, 21 | 210, 230, 250 | 30 | <0.5 mm | 250°C, 30 min, 0% O ₂ 250°C, 30 min, 21% O ₂ | 71 | - | 1.18 | 83.7 | 12.7 | Adnan et al. (2017) |
| | | | | | | 58.9 | - | 1.17 | 69.2 | 10.3 | |
| | 0, 3, 9, 12, 15 | 220, 250, 300 | 30 | 0.375 mm in average diameter | 300°C, 30 min, 0% O ₂ 300°C, 30 min, 15% O ₂ | 68.8 | - | 1.17 | 80.4 | 11.6 | Uemura et al. (2015) |
| Olive pomace pellets | 0, 21 | 200, 230, 250 | 15 | 6–7 mm diameter and about 2 cm length | 250°C, 15 min, 0% O ₂ 250°C, 15 min, 21% O ₂ | 56.3 | 1.2 | 1.34 | 75.2 | 18.9 | Brachi et al. (2019) |
| | | | | | | 53 | 1.16 | 1.29 | 68.4 | 15.4 | |
| Rice Husk | 0, 2, 5, 10, 15 | 220, 260, 300 | 30 | 0.125–0.3 mm | 300°C, 30 min, 0% O ₂ 300°C, 30 min, 2% O ₂ | 64.5 | 1.24 | 1.21 | 78.3 | 13.8 | Chen et al. (2020) |
| | | | | | | 59.3 | 1.22 | 1.18 | 70.1 | 10.8 | |
| | 0, 21 | 220, 270, 300 | 30, 60 | 0.1–0.2 mm | 300°C, 30 min, 0% O ₂ 300°C, 30 min, 21% O ₂ | 65.8 | 1.58 | 1.46 | 94 | 28.2 | Zhang et al. (2021c) |
| | | | | | | 38.3 | 1.38 | 1.38 | 52.2 | 13.9 | |
| Rice Straw | 0, 3, 6, 9 | 180, 210, 240, 270 | 30 | 0.085-0.250 mm | 270°C, 30 min, 0% O ₂ 270°C, 30 min, 9% O ₂ | - | 1.24 | 1.3 | - | - | Tan et al. (2021) |
| | | | | | | - | 1.31 | 1.35 | - | - | |
| <i>Sapindus mukorossi</i> shells | 0, 5, 15, 21 | 250, 300 | 10, 20, 30 | < 0.4 mm | 300°C, 30 min, 0% O ₂ 300°C, 30 min, 21% O ₂ | 67.6 | 1.31 | 1.23 | 83.4 | 15.8 | Zhang et al. (2019a) |
| | | | | | | 34.9 | 1.51 | 1.32 | 46.1 | 11.2 | |

Table 3.
Continued.

| Biomass Type | O ₂ (%) in torrefaction medium | Temperature (°C) | Time (min) | Particle Size | Process Condition | Solid Yield (%) | Carbon Enhancement | HHV Enhancement | Energy Yield (%) | EMCF* | Reference |
|--------------------------------------|---|-------------------------|-----------------------|-----------------------------------|---|-----------------|--------------------|-----------------|------------------|-------|-----------------------------|
| Sugarcane bagasse | 0, 1, 3, 5, 7, 10 | 250, 270, 290, 310 | 45 | - | 310°C, 45 min, 0% O ₂ | 37.6 | - | 1.19 | 44.7 | 7.1 | Joshi et al. (2015) |
| | | | | | 310°C, 45 min, 1% O ₂ | 33.6 | - | 1.11 | 37.2 | 3.6 | |
| Sugarcane leaves | 21 | 250, 300, 350 | 0, 15, 30, 45, 60, 75 | average particle size of 0.56 mm | 350°C, 75 min, 21% O ₂ | 39 | - | 1.54 | 60 | 21 | Conag et al. (2017) |
| | | | | | 300°C, 75 min, 21% O ₂ | 42 | - | 1.38 | 58 | 16 | |
| Walnut shells | 0, 5, 15, 21 | 250, 300 | 10, 20, 30 | < 0.4 mm | 300°C, 30 min, 0% O ₂ | 66.7 | 1.2 | 1.23 | 82 | 15.3 | Zhang et al. (2019b) |
| | | | | | 300°C, 20 min, 21% O ₂ | 54.2 | 1.33 | 1.32 | 71.3 | 17.1 | |
| <i>Xanthoceras sorbifolia</i> shells | 0, 5, 15, 21 | 250, 300 | 10, 20, 30 | < 0.4 mm | 300°C, 30 min, 0% O ₂ | 67.4 | 1.24 | 1.25 | 84.5 | 17.1 | Zhang et al. (2019b) |
| | | | | | 300°C, 30 min, 15% O ₂ | 58.5 | 1.28 | 1.27 | 74.2 | 15.7 | |
| Woody biomass | | | | | | | | | | | |
| Bamboo particles | 0, 2 | 230, 250 | 60 | 0.15 to 0.3 mm | 250°C, 60 min, 0% O ₂ | 74.7 | 1.09 | 1.11 | 83 | 8.3 | Su et al. (2018) |
| | | | | | 250°C, 60 min, 2% O ₂ | 67.2 | 1.11 | 1.13 | 76.1 | 8.9 | |
| <i>Cryptomeria japonica</i> | 0, 21 | 250, 300, 350 | 60 | 15*10*5 mm | 350°C, 60 min, 0% O ₂ | 35 | 1.5 | 1.53 | 53.6 | 18.6 | Chen et al. (2013) |
| | | | | | 350°C, 60 min, 21% O ₂ , 0.82 cm/min | 36.1 | 1.52 | 1.49 | 53.9 | 17.8 | |
| | 0, 5, 10, 15, 21 | 300 | 60 | 15*10*5 mm | 300°C, 60 min, 0% O ₂ | 41.8 | 1.42 | 1.52 | 63.4 | 21.6 | Chen et al. (2014a) |
| | | | | | 300°C, 60 min, 5% O ₂ | 40.6 | 1.45 | 1.43 | 58 | 17.4 | |
| Eucalyptus | 0, 21 | 250, 300, 350 | 60 | 15*10*5 mm | 350°C, 60 min, 0% O ₂ | 41.8 | 1.48 | 1.42 | 58.9 | 17.1 | Chen et al. (2013) |
| | | | | | 350°C, 60 min, 21% O ₂ , 0.82 cm/min | 41.1 | 1.47 | 1.42 | 58.6 | 17.5 | |
| | 0, 5, 10, 15, 21 | 300 | 60 | 15*10*5 mm | 300°C, 60 min, 0% O ₂ | 57.9 | 1.35 | 1.3 | 75.5 | 17.6 | Chen et al. (2014a) |
| | | | | | 300°C, 60 min, 5% O ₂ | 53.6 | 1.36 | 1.34 | 71.7 | 18.1 | |
| | 0, 21 | 250, 275, 300, 325, 350 | 60 | 10*15*8 mm | 325°C, 60 min, 0% O ₂ | 45.8 | 1.48 | 1.41 | 64.7 | 18.9 | Lu et al. (2012) |
| | | | | | 275°C, 60 min, 21% O ₂ | 52 | 1.36 | 1.27 | 66 | 14 | |
| <i>Eucalyptus grandis</i> | 2, 6, 10, 21 | 240, 280 | - | 10 mm ×40 mm ×80 mm | 280°C, 10% O ₂ | 79.8 | - | 1.3 | - | - | Rousset et al. (2012) |
| Fir pellets | 0, 21 | 200, 230, 250 | 15 | 6 mm diameter and 3-4 mm length | 250°C, 15 min, 0% O ₂ | 52.7 | 1.22 | 1.23 | 65.1 | 12.4 | Brachi et al. (2019) |
| | | | | | 250°C, 15 min, 21% O ₂ | 38.2 | 1.31 | 1.3 | 49.8 | 11.6 | |
| Patula pine | 21 | 180, 210, 240 | 30, 75, 120 | 10 - 20 mm | 240°C, 30 min, 21% O ₂ | 34.2 | 1.36 | - | - | - | Ramos-Carmona et al. (2018) |
| Poplar | 0, 21 | 220, 260, 300 | 15, 25, 35 | 50.5 mm length and 19 mm diameter | 300°C, 35 min, 0% O ₂ , 600 kPa | 55.5 | - | 1.34 | 74.3 | 18.8 | Nhuchhen and Basu, (2014) |
| | | | | | 300°C, 35 min, 21% O ₂ , 400 kPa | 50 | - | 1.42 | 71 | 21 | |
| Sawdust | 0, 3, 6, 9 | 240, 270, 300 | 50, 120 | 0.5-1 mm | 300°C, 120 min, 0% O ₂ | 61.8 | 1.2 | 1.24 | 76.8 | 15 | Wang et al. (2019) |
| | | | | | 300°C, 50 min, 3% O ₂ | 55.8 | 1.1 | 1.18 | 65.7 | 9.9 | |
| Schima wood | 0, 2, 4, 6, 8 | 200, 230, 260, 290 | 15 | 3.94 mm | 260°C, 15 min, 0% O ₂ | 76.5 | 1.05 | 1.06 | 81.4 | 4.9 | Li et al. (2021) |
| | | | | | 290°C, 15 min, 6% O ₂ | 46 | 1.26 | 1.26 | 57.7 | 11.7 | |
| Spruce and fir sawdust | 0, 3, 6 | 250, 270, 290 | 4-42 | 0.25-0.355 mm | 270°C, 30 min, 0% O ₂ | 64 | 1.12 | 1.13 | 72 | 8 | Wang et al. (2013) |
| | | | | | 290°C, 7 min, 3% O ₂ | 64 | 1.15 | 1.15 | 73.8 | 9.8 | |
| Spruce, pine, fir sawdust | 0, 3, 6, 9 | 240, 270, 300 | 50 | 0.5-1 mm | 300°C, 50 min, 0% O ₂ | 72.4 | 1.11 | 1.14 | 82.7 | 10.3 | Wang et al. (2018) |
| | | | | | 300°C, 50 min, 3% O ₂ | 68.1 | 1.11 | 1.15 | 78.3 | 10.2 | |
| | | | | | 230°C, 20 min, 21% O ₂ | 89.7 | - | 1.05 | 94.5 | 4.8 | |

Table 3.
Continued.

| Biomass Type | O ₂ (%) in torrefaction medium | Temperature (°C) | Time (min) | Particle Size | Process condition | Solid Yield (%) | Carbon Enhancement | HHV Enhancement | Energy Yield (%) | EMCI* | Reference |
|---------------------------------|---|-------------------------|----------------|-----------------------------------|-----------------------------------|-----------------|--------------------|-----------------|------------------|-------|-----------------------|
| Willow | 0, 21 | 200, 210, 220, 230, 240 | 20 | 0.71-1 mm | 240°C, 20 min, 0% O ₂ | 87.2 | - | 1.06 | 92.8 | 5.6 | Álvarez et al. (2021) |
| | | | | | 230°C, 20 min, 21% O ₂ | 89.7 | - | 1.05 | 94.5 | 4.8 | |
| Microalgae | | | | | | | | | | | |
| <i>Chlorella</i> sp. | 0, 21 | 200, 250, 300 | 15, 30, 45, 60 | - | 300°C, 60 min, 0% O ₂ | 58.5 | 1.35 | 1.27 | 74.2 | 15.7 | Zhang et al. (2019a) |
| | | | | | 300°C, 60 min, 21% O ₂ | 50.1 | 1.41 | 1.24 | 62.2 | 12.1 | |
| <i>Nannochloropsis Oceanica</i> | 0, 21 | 200, 250, 300 | 15, 30, 45, 60 | - | 300°C, 60 min, 0% O ₂ | 60.3 | 1.32 | 1.32 | 79.6 | 19.3 | Zhang et al. (2019a) |
| | | | | | 300°C, 60 min, 21% O ₂ | 49.6 | 1.42 | 1.25 | 62.2 | 12.6 | |
| | 21 | 200, 225, 250, 275, 300 | 15, 30, 45, 60 | - | 300°C, 60 min, 21% O ₂ | 60.8 | 1.17 | 1.24 | 75.7 | 14.9 | Zhang et al. (2021b) |
| | | | | | 300°C, 60 min, 0% O ₂ | 54.1 | - | 1.33 | 71.9 | 17.8 | Zhang et al. (2021a) |
| 0, 21 | 200, 250, 300 | 30, 45, 60 | - | 300°C, 60 min, 21% O ₂ | 50.3 | - | 1.22 | 61.6 | 11.3 | | |

Abbreviations: HHV: higher heating value; EMCI: energy-mass co-benefit index
* Calculated value.

** Performance parameters are reported at the maximum HHV enhancement in inert and oxidative conditions. The colour scale depicts the severity of the treatment varying from green to red, where red is most severe.

Agricultural waste is the most commonly studied feedstock of oxidative torrefaction, followed by woody biomass. There are only a few studies on oxidative torrefaction of microalgae. Most of the studies are within the temperature range of 200-300 °C, which is the typical torrefaction condition, and in most cases, residence time applied is 30 min or 60 min. Most oxidative torrefaction studies used air as the torrefaction medium, while agricultural waste and woody biomass have also been studied using different oxygen contents. Since the oxidative torrefaction of microalgae is only studied with air, it shows a narrow range of values for the performance parameters compared to the other two feedstock types. Figures 2 and 3 represent the ranges of performance parameters tabulated in Table 3.

Table 4 summarizes the performance parameters at the maximum HHV enhancement in inert and oxidative conditions, reported by the reviewed torrefaction studies using different biomass classes. It is worth noting that inert torrefaction gives a similar solid yield and energy yield for all the biomass types, whereas oxidative torrefaction always results in less solid yield and energy yield than inert torrefaction. The oxidative torrefaction of woody biomass leads to a slightly higher solid yield and energy yield than other biomass types due to the higher resistance of woody biomass to thermal degradation. Regarding carbon enhancement and HHV enhancement, inert torrefaction gives similar carbon enhancement and HHV enhancement for all the biomass types, whereas woody biomass

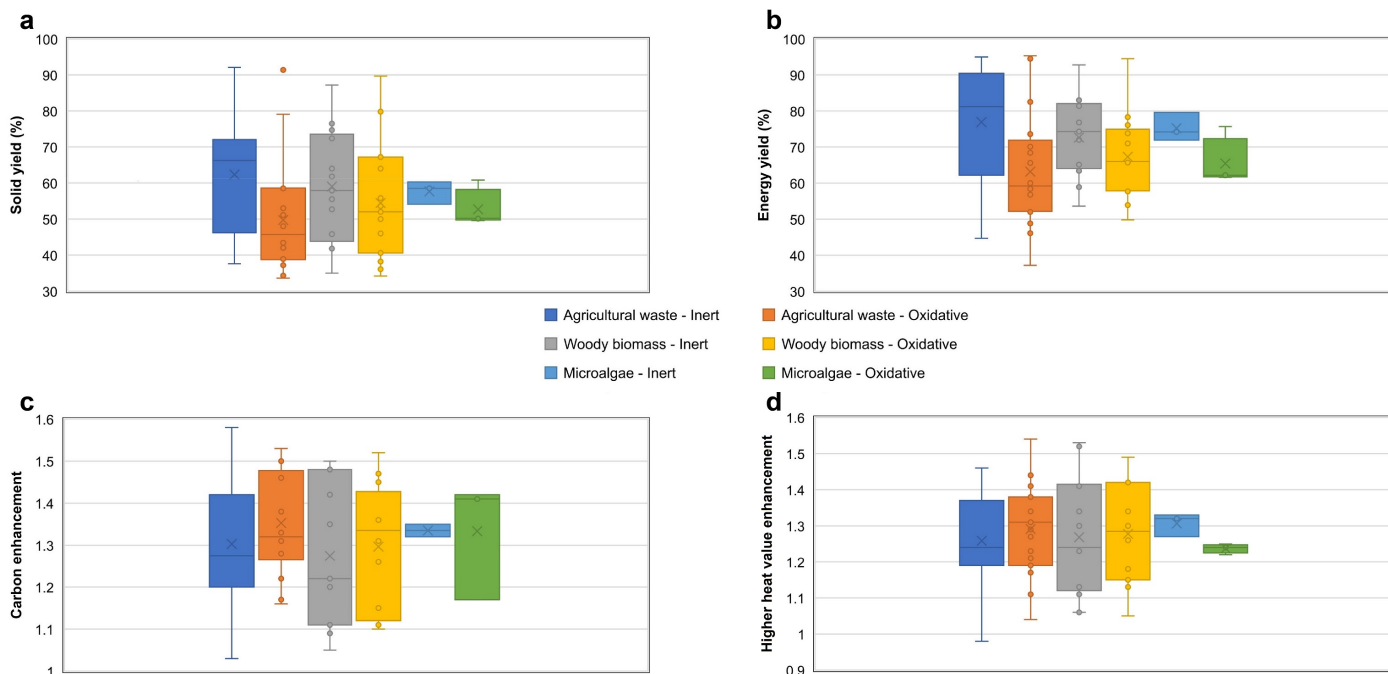


Fig. 2. The ranges of (a) solid yield, (b) energy yield, (c) carbon enhancement, and (d) HHV enhancement at the maximum HHV enhancement in inert and oxidative conditions of reviewed torrefaction studies relevant to different biomass classes. HHV: higher heating value. Data Source: Table 3.

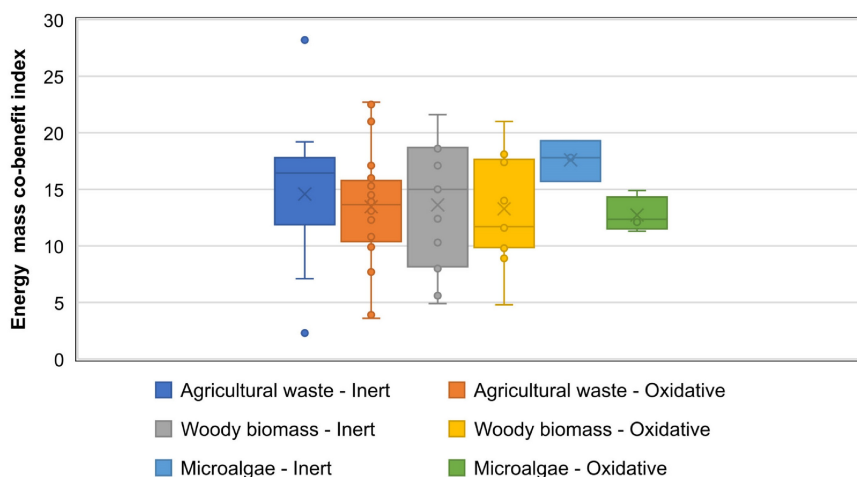


Fig. 3. The energy-mass co-benefit index (EMCI) range at the maximum HHV enhancement in inert and oxidative conditions of the reviewed torrefaction studies relevant to different biomass classes. Data Source: Table 3.

Table 4.

The performance parameters at the maximum HHV enhancement in inert and oxidative torrefaction conditions, reported by the reviewed torrefaction studies using different biomass classes.

| Solid yield | Carbon enhancement | HHV enhancement | Energy yield | EMCI |
|---|---|--|--|--|
| Similar solid yield irrespective of the biomass type during inert torrefaction. | Similar carbon enhancement irrespective of the biomass type during inert torrefaction. | Similar HHV enhancement irrespective of the biomass type during inert torrefaction. | Similar energy yield irrespective of the biomass type during inert torrefaction. | Similar EMCI irrespective of the biomass type during oxidative torrefaction. |
| Less solid yield during oxidative torrefaction compared to inert torrefaction. | Slightly higher carbon enhancement with agricultural waste compared to other types during oxidative torrefaction. | Less HHV enhancement with microalgae compared to other types during oxidative torrefaction. | Less energy yield during oxidative torrefaction compared to inert torrefaction. | Similar EMCI during oxidative and inert torrefaction of woody biomass. |
| Slightly higher solid yield with woody biomass compared to other types during oxidative torrefaction. | Similar carbon enhancement during oxidative and inert torrefaction of woody biomass. | Similar HHV enhancement during oxidative and inert torrefaction of agricultural waste and woody biomass. | Slightly higher energy yield with woody biomass compared to other types during oxidative torrefaction. | Slightly higher EMCI with agricultural waste and microalgae compared to woody biomass during inert torrefaction. |

Abbreviations: HHV: Higher heating value; EMCI: Energy mass co-benefit index

results in similar carbon enhancement and HHV enhancement during inert torrefaction and oxidative torrefaction. As measured by the energy-mass co-benefit index (EMCI), woody biomass can benefit equally from oxidative or inert torrefaction, whereas inert torrefaction is more suitable for agricultural waste and microalgae.

Only a few studies have analyzed the effects of torrefaction temperature, residence time, and oxygen concentration altogether on torrefaction performance. The studies on corncob pellets, rice husk, shells, poplar wood, and microalgae (*Nannochloropsis oceanica* and *Chlorella* sp.) with torrefaction time, temperature, and oxygen concentration are shown in Figures 4-8.

6.1. Effect on solid yield

The solid yield of torrefied rice husk, corncob pellets, three nutshells (walnut shells, *Xanthoceras sorbifolia* shells, and *Sapindus mukorossi* shells), poplar wood, and microalgae (*Nannochloropsis oceanica* and *Chlorella* sp.) with torrefaction time, temperature, and oxygen concentration are shown in Figures 4-8.

As expected, it has been shown that the solid yield of the torrefied product decreases progressively with increasing residence time and temperature due to accelerating the decomposition of hemicellulose and cellulose (Li et al., 2021). Further, during the oxidative torrefaction, the oxidizing agents consume the combustible components by surface oxidation; hence, massive mass loss can be observed (Tanyaket et al., 2020). Most severe degradation has happened to rice husk resulting in 45-60% mass loss under all of the air torrefaction conditions studied, mainly due to long residence time of 30-60 min. The effect of residence time seems weak in both the inert and oxidative torrefaction of rice husk; this could be due to the long residence time applied. Moreover, the torrefaction of shells has revealed that 15% and 21% oxygen environments

can significantly affect torrefaction severity leading to up to 60% mass loss in the most severe conditions. However, torrefaction at the 5% oxygen environment is almost similar to the 0% oxygen environment, with only 30-35% mass loss in the most severe condition.

Poplar wood shows a significant degradation even at inert torrefaction, and at air torrefaction conditions, up to 60% mass loss has happened in the most severe condition, which is similar to shells. Even though the applied residence time range is not so long, the effect of residence time seems weak in both inert and oxidative torrefaction of poplar wood. While in a 21% oxygen environment, the maximum mass loss of microalgae torrefaction is 45-50%, revealing that microalgae are more resistant to oxidative torrefaction than all other biomass types. The residence time range applied for corncob pellets torrefaction is comparatively low, ranging between 5 and 20 min. As a result, no significant degradation can be observed up to 260 °C. Further, at 300 °C, even with inert or low oxygen content, a significant mass loss is observed within 15-20 min of residence time with a maximum value of 60%. Microalgae have never recorded such a mass loss, nor have the inert torrefaction of other biomass types. The interesting point is that, not like other biomass types, while temperature and residence time both have a significant effect, oxygen content does not have a significant effect on the torrefaction severity of corncob pellets. Further, for corncob pellets, shells, and microalgae, where residence time has a significant effect on the degradation, the effect of residence time is more prominent at high temperatures.

6.2. Effect on carbon enhancement

Figures 9-11 represent the carbon enhancement of shells, rice husk, and microalgae against time, temperature, and oxygen concentration.

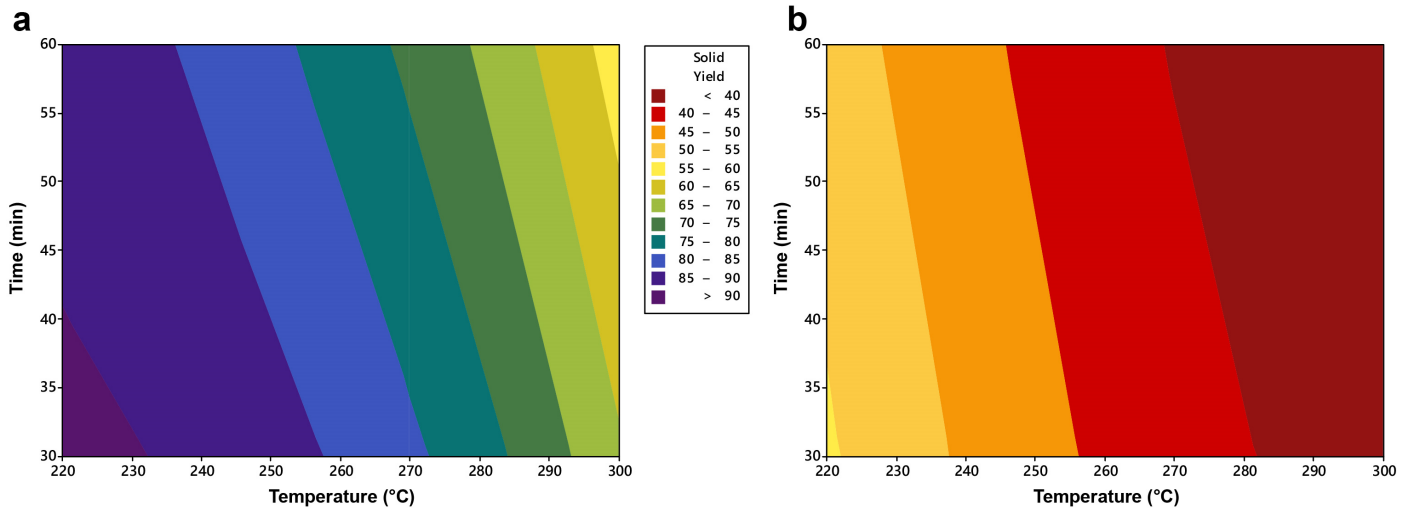


Fig. 4. Solid yield of Rice husk at different severities; (a) inert and (b) 21% Oxygen. Developed based on the data obtained from Zhang et al. (2021c).

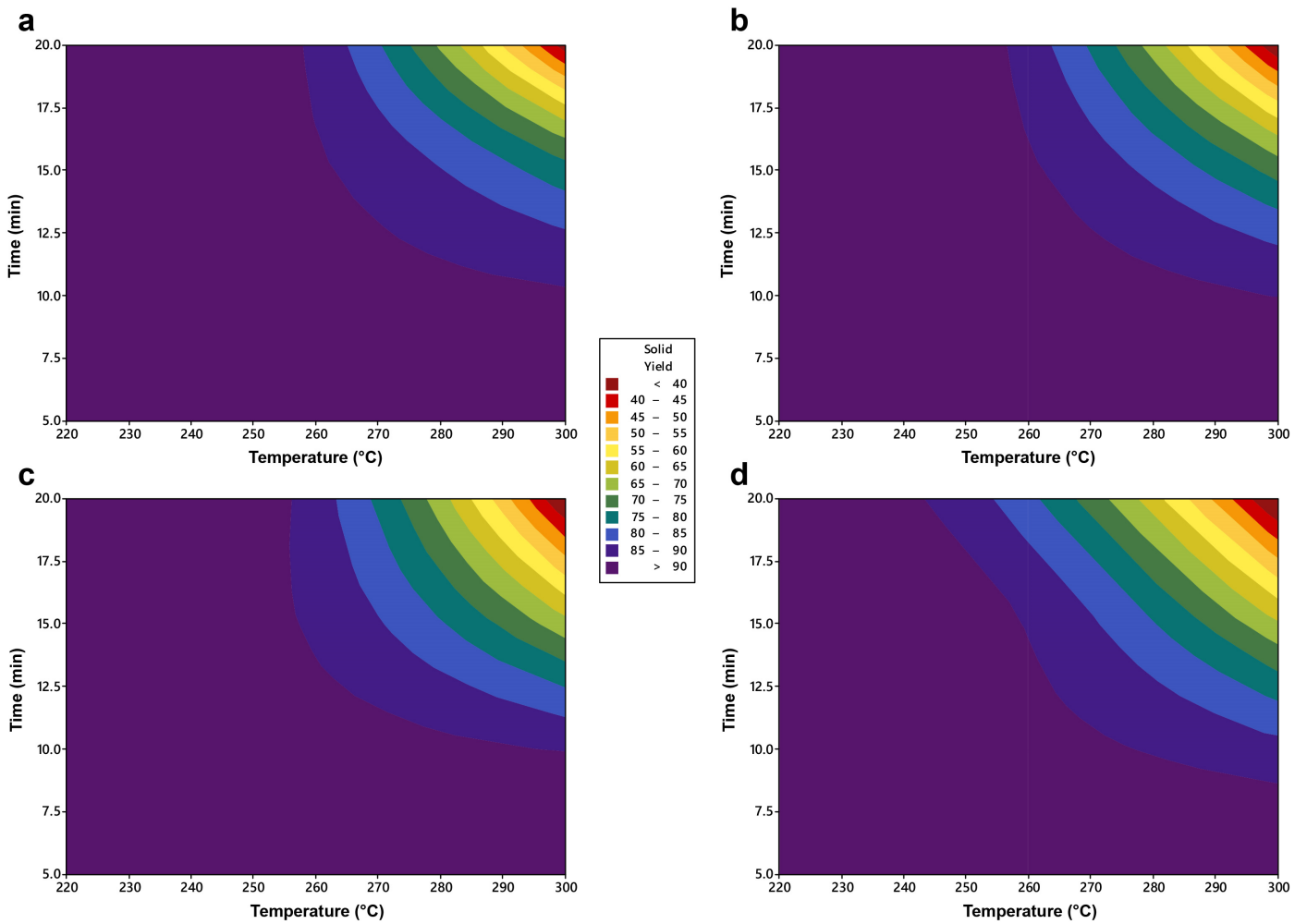


Fig. 5. Solid yield of corncob pellets at different severities; (a) inert, (b) 6% Oxygen, (c) 12% Oxygen, and (d) 18% Oxygen. Developed based on the data obtained from Tanyaket et al. (2020).

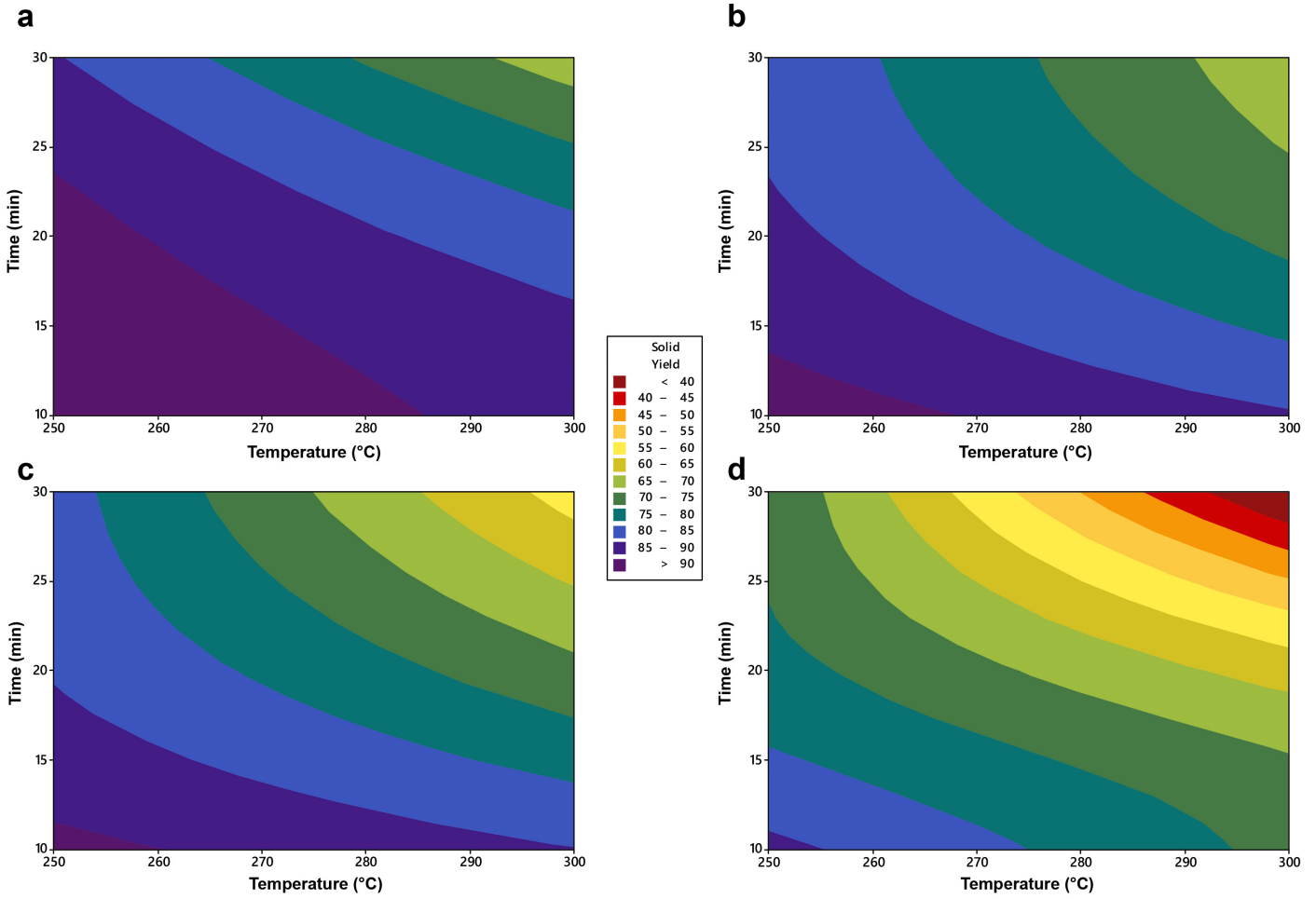


Fig. 6. Solid yield of Shells at different severities; (a) inert, (b) 5% Oxygen, (c) 15% Oxygen, and (d) 21% Oxygen. Developed based on the data obtained from Zhang et al. (2019b).

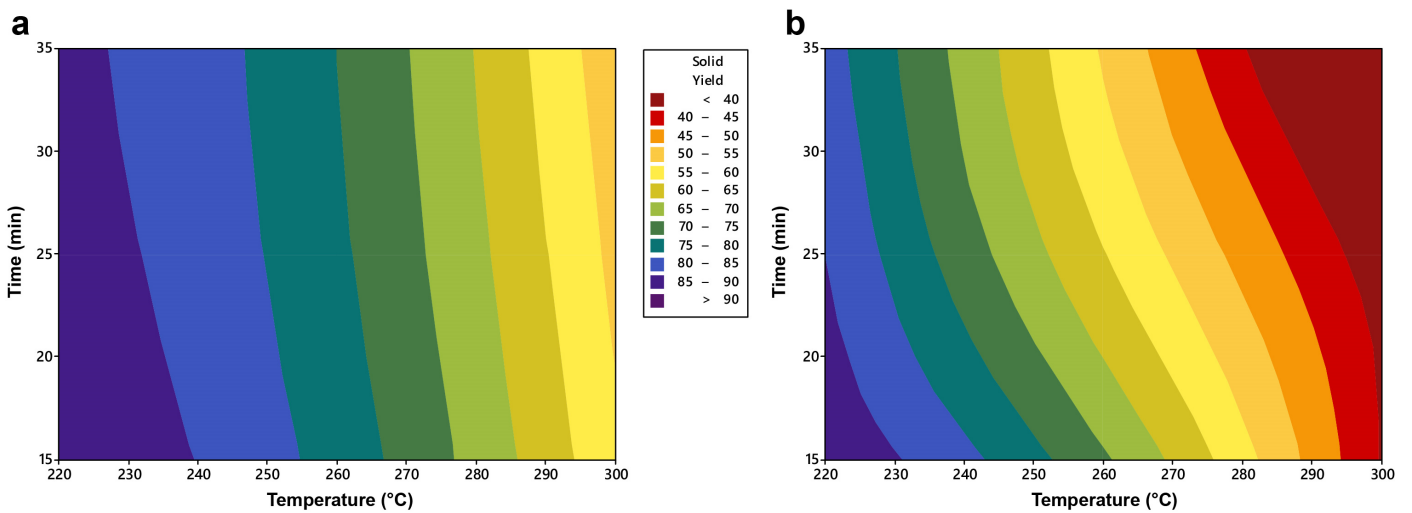


Fig. 7. Solid yield of Poplar wood at different severities (a) inert and (b) 21% Oxygen. Developed based on the data obtained from Nhuchhen and Basu (2014).

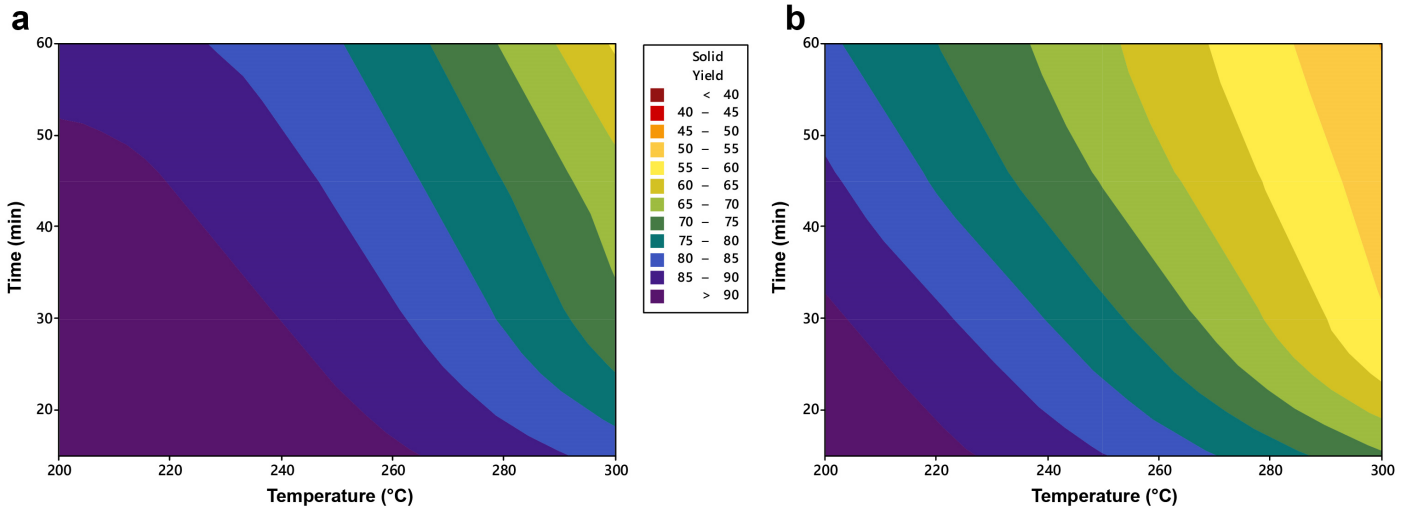


Fig. 8. Solid yield of Microalgae at different severities; (a) inert and (b) 21% Oxygen. Developed based on the data obtained from Zhang et al. (2019a).

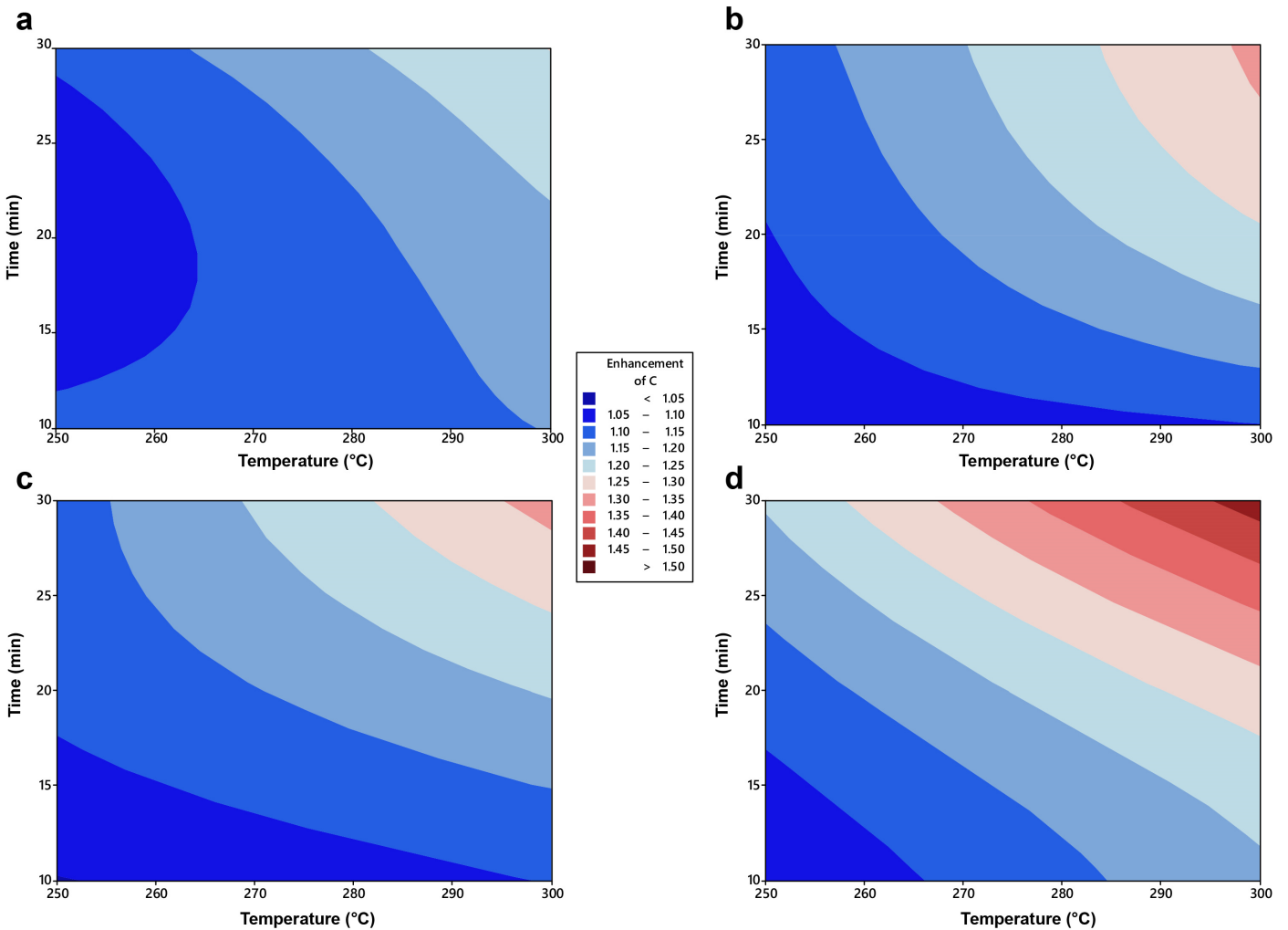


Fig. 9. Carbon enhancement of shells at different severities; (a) inert, (b) 5% Oxygen, (c) 15% Oxygen, and (d) 21% Oxygen. Developed based on the data obtained from Zhang et al. (2019b).

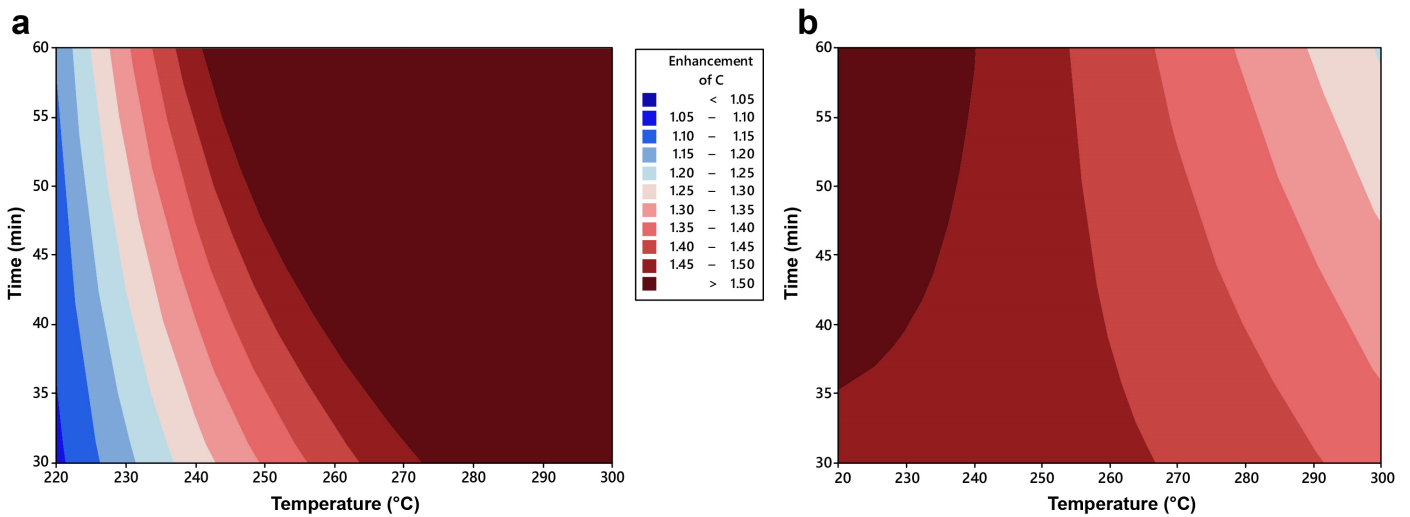


Fig. 10. Carbon enhancement of rice husk at different severities; (a) inert and (b) 21% Oxygen. Developed based on the data obtained from Zhang et al. (2021c).

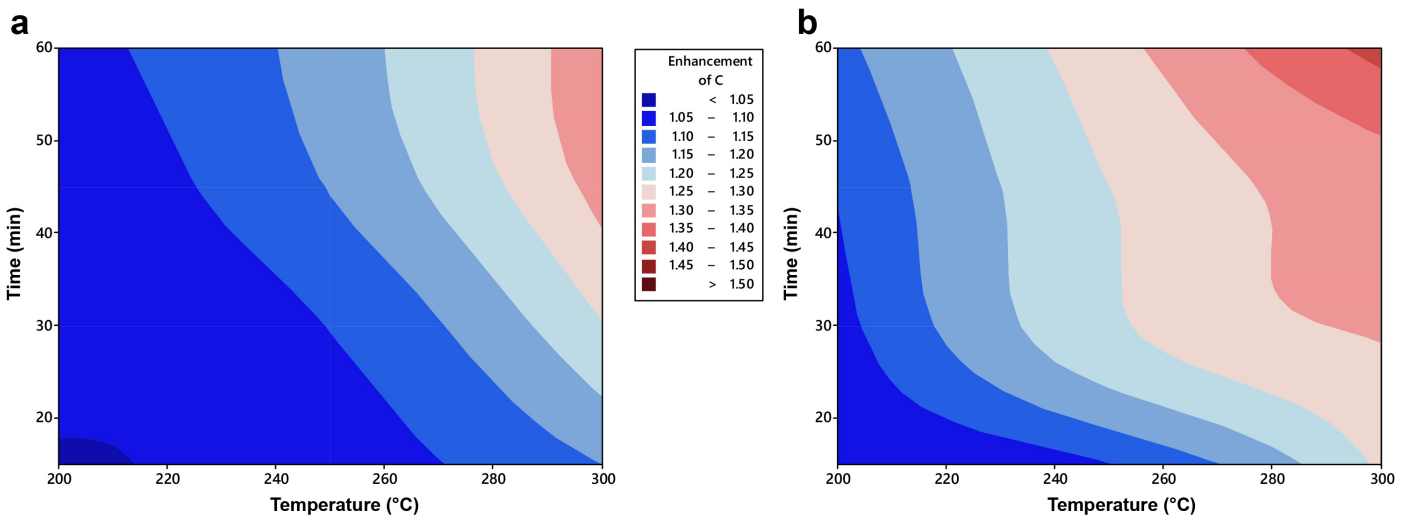


Fig. 11. Carbon enhancement of microalgae at different severities; (a) inert and (b) 21% Oxygen. Developed based on the data obtained from Zhang et al. (2019a).

The highest carbon enhancement profile is seen with both inert and oxidative torrefaction of rice husk, resulting in values standing at 1.25-1.5 and even greater ones at most of the studied torrefaction conditions. Interestingly, the lowest temperature and long residence time give the highest carbon enhancement during air torrefaction. This could be due to surface oxidation of rice husk at high temperatures releasing more carbon. Both shells and microalgae show high carbon enhancement in a high oxidative environment. Although some amounts of carbon are volatilized from torrefaction, the carbon yield increases due to the dehydrogenation and deoxygenation reactions. Therefore, this reflects that the oxidative environment impacts dehydrogenation and deoxygenation reactions (Zhang et al., 2019b). However, this seems to be true only if the surface oxidation is not dominant. Even though the mass loss of microalgae is comparatively less severe than shells, carbon enhancement at 21% oxygen content is almost comparable in both biomass types, with a maximum value of around 1.4-1.5. Even with inert torrefaction, microalgae show carbon enhancement of up to 1.3-1.35, similar to shells with 5-15% oxygen.

6.3. Effect on higher heating value enhancement

The variation of HHV enhancement with torrefaction conditions is presented in Figures 12-15.

Both shells and microalgae show the highest HHV enhancement in the most severe conditions reflecting energy densification. However, microalgae show higher HHV enhancement under inert conditions, whereas shells show improved HHV enhancement profiles with more oxygen. Rice husk and poplar wood show comparatively higher HHV enhancement (1.35-1.4) than shells and microalgae (1.2-1.3). The maximum HHV enhancement of poplar wood happens at high temperature and medium residence time of around 25 min in both inert and oxidative conditions and could be due to the release of more carbon in response to surface oxidation at long residence times. Surface oxidation seems more severe in rice husk's oxidative torrefaction, resulting in a lower maximum HHV enhancement at oxidative torrefaction than inert torrefaction. Further, maximum HHV enhancement during the oxidative torrefaction occurs at the lowest

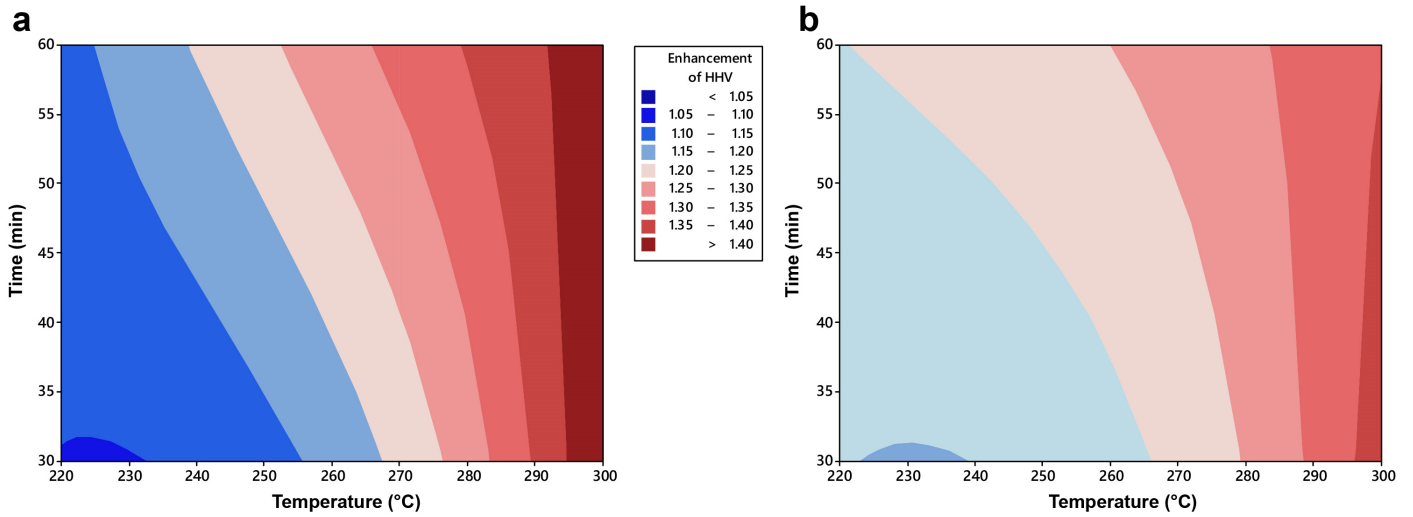


Fig. 12. HHV enhancement of rice husk at different severities; (a) inert and (b) 21% Oxygen. Developed based on the data obtained from Zhang et al. (2021c).

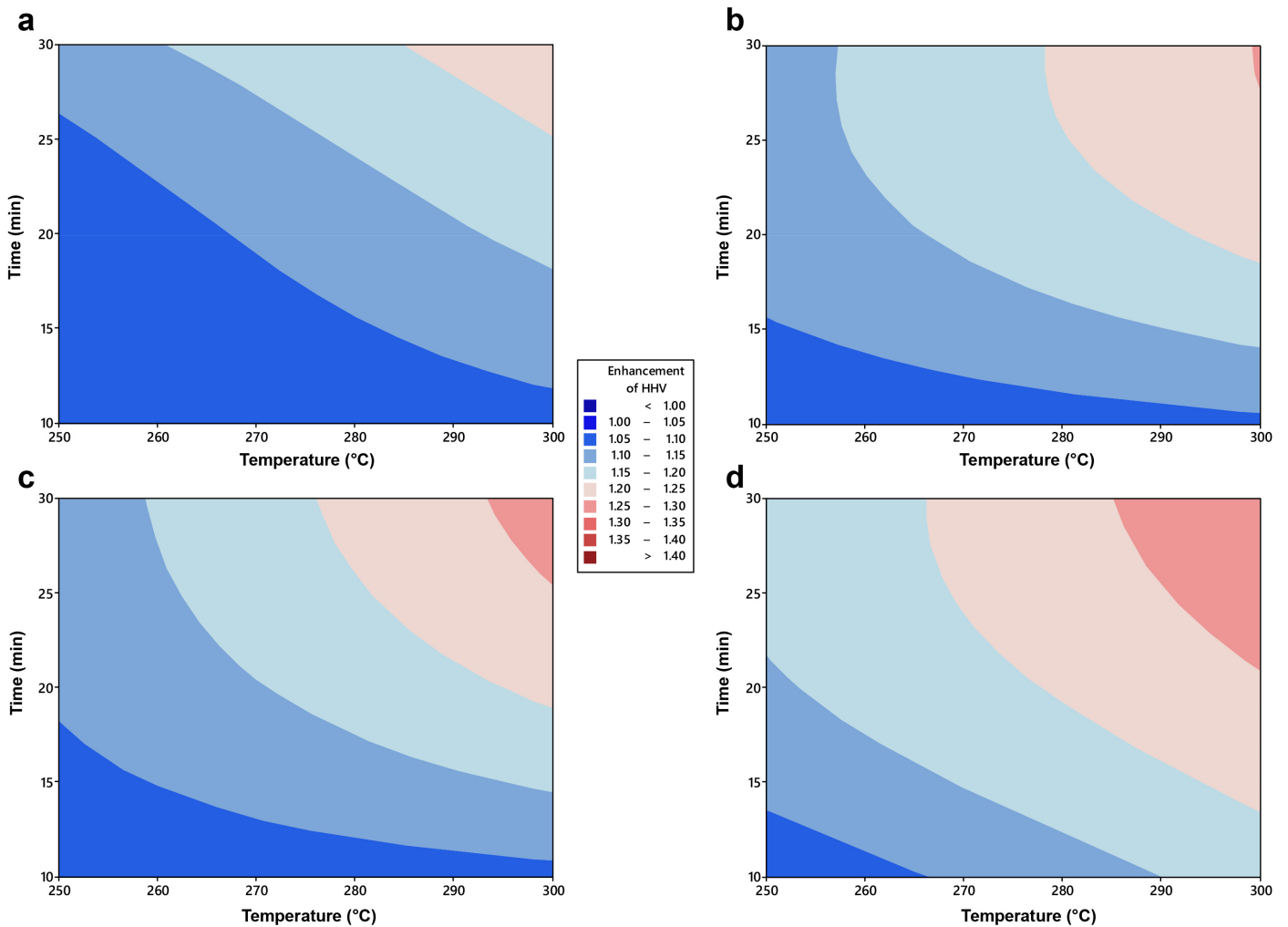


Fig. 13. HHV enhancement of shells at different severities; (a) inert, (b) 5% Oxygen, (c) 15% Oxygen, and (d) 21% Oxygen. Developed based on the data obtained from Zhang et al. (2019b).

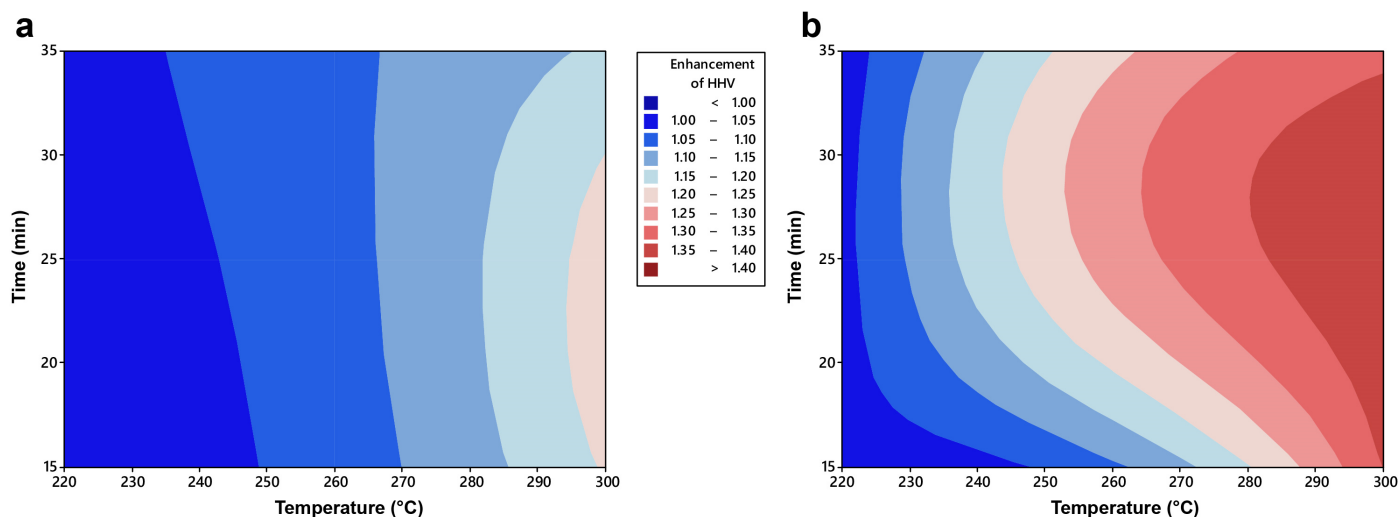


Fig. 14. HHV enhancement of poplar wood at different severities; (a) inert and (b) 21% Oxygen. Developed based on the data obtained from Nhuchhen and Basu (2014).

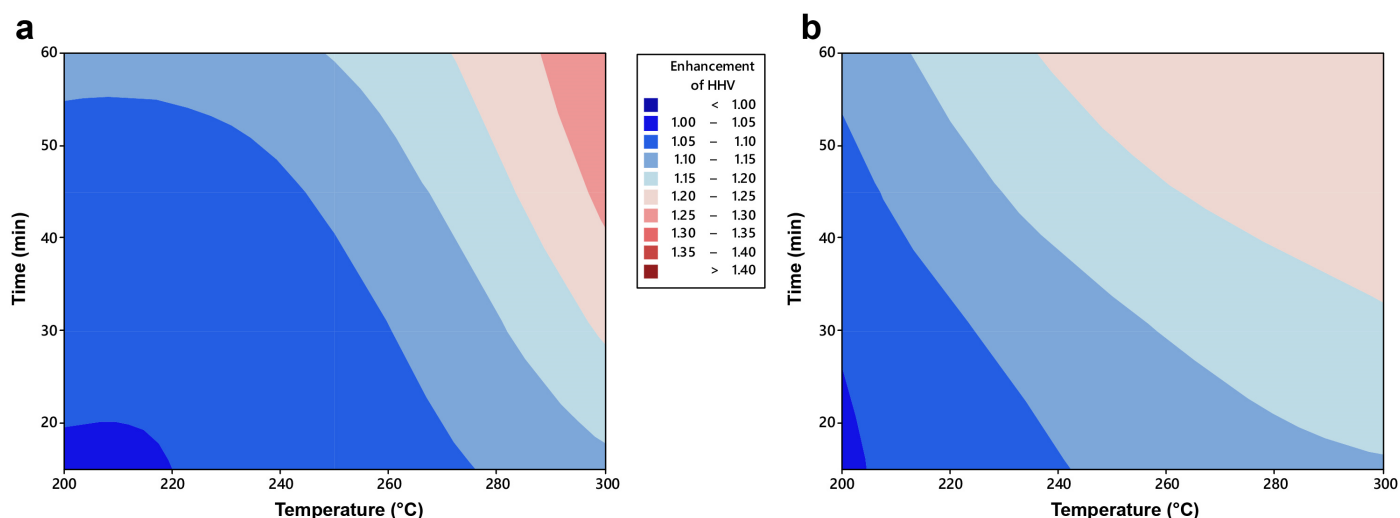


Fig. 15. HHV enhancement of microalgae at different severities; (a) inert and (b) 21% Oxygen. Developed based on the data obtained from Zhang et al. (2019a).

residence time studied, which is 30 min. The effect of residence time on the HHV enhancement of rice husk is weak at high temperatures and could be due to the long residence time range applied. According to the data presented in Table 3, almost all the times, the maximum HHV enhancement happens in the most severe condition during inert torrefaction. In contrast, oxidative torrefaction happens in moderately severe conditions (at a low oxygen content, temperature, or residence time). For example, the maximum HHV enhancement happens at the lowest tested oxygen content (1-5%) for sugarcane bagasse, rice husk, EFB, coconut fiber, and oil palm fiber. When only air is used as the oxidative torrefaction medium, the maximum HHV enhancement happens at the lowest temperature (at 250 °C for oil palm fiber) or lowest residence time (at 30 min for rice husk) tested.

6.4. Effect on energy yield

Figures 16-19 present the energy yield of four types of biomass, i.e., rice husk, shells, poplar wood, and microalgae, against time, temperature, and oxygen content. The energy yield of all the biomass types is lowest at the most

severe condition following the trend of solid yield, whereas the lowest energy yield of oxidative torrefaction of rice husk happens at an intermediate temperature around 280 °C due to opposite trends of solid yield and HHV enhancement. Rice husk, shells, and microalgae preserve at least 80% energy yield at most severe torrefaction conditions when the oxygen content is equal to or less than 5%. Poplar wood shows a significant energy loss at inert torrefaction, owing to high mass loss, even though the energy yield profile at air torrefaction is almost similar to shells, confirming the resistance of woody biomass to oxidative torrefaction. The effect of residence time seems to be weak in both rice husk and poplar wood torrefaction, similar to the solid yield observations. Moreover, at 60 min residence time, the effect of temperature on the energy yield of rice husk is negligible. Similar to the observations made on solid yield, the energy yield profile confirms that microalgae are more resistant to oxidative torrefaction than all the other biomass types preserving 60-65% energy yield at most severe torrefaction conditions with air. The effect of time and temperature on energy yield is also more prominent at high oxidative conditions, regardless of the type of feedstock.

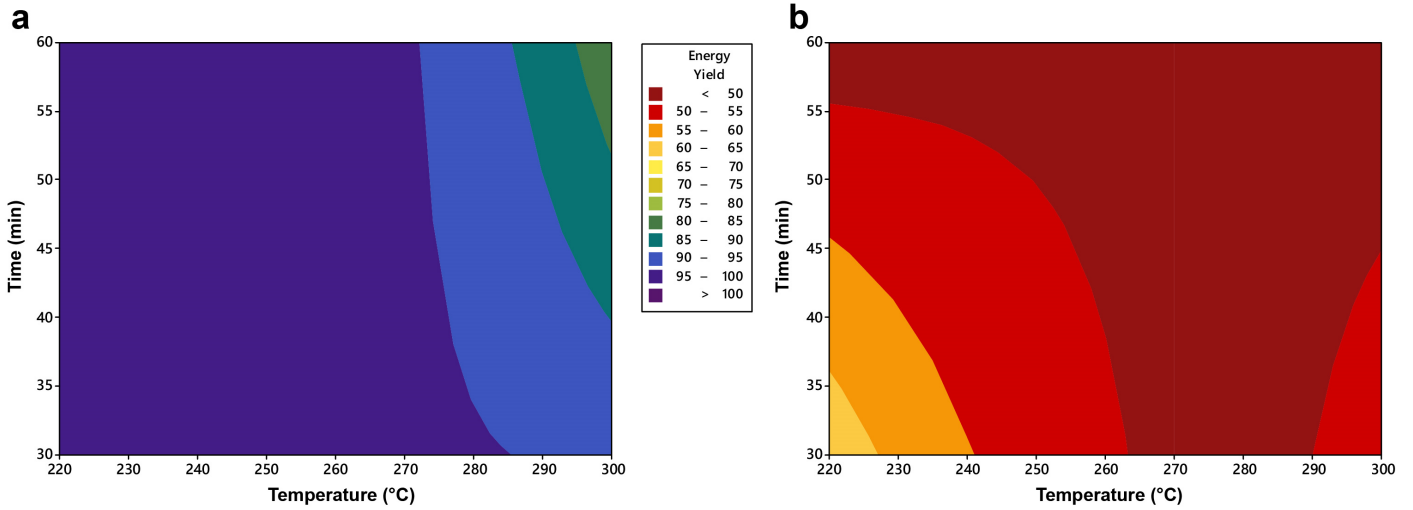


Fig. 16. Energy yield of rice husk at different severities; (a) inert and (b) 21% Oxygen. Developed based on the data obtained from Zhang et al. (2021c).

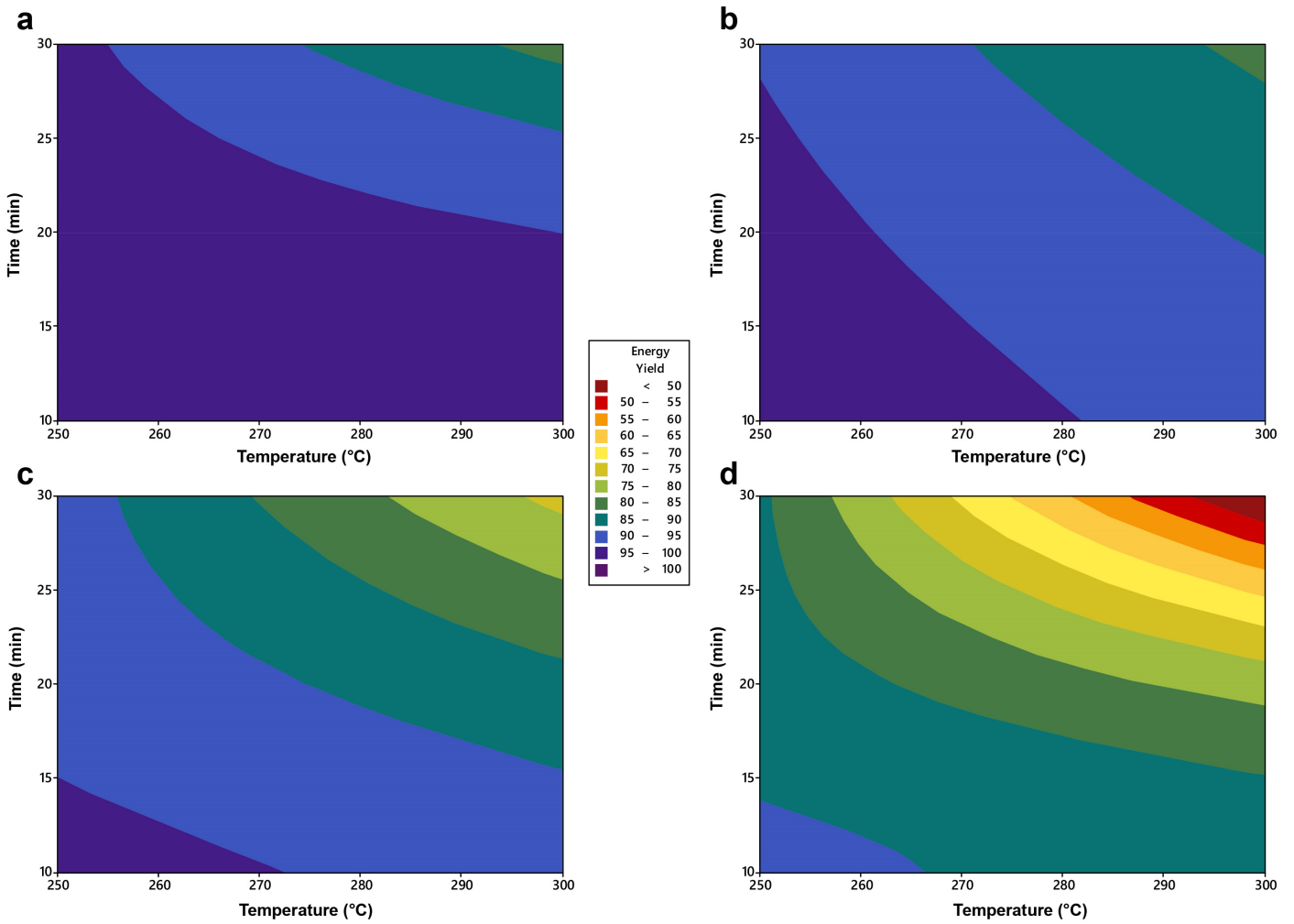


Fig. 17. Energy yield of shells at different severities; (a) inert, (b) 5% Oxygen, (c) 15% Oxygen, and (d) 21% Oxygen. Developed based on the data obtained from Zhang et al. (2019b).

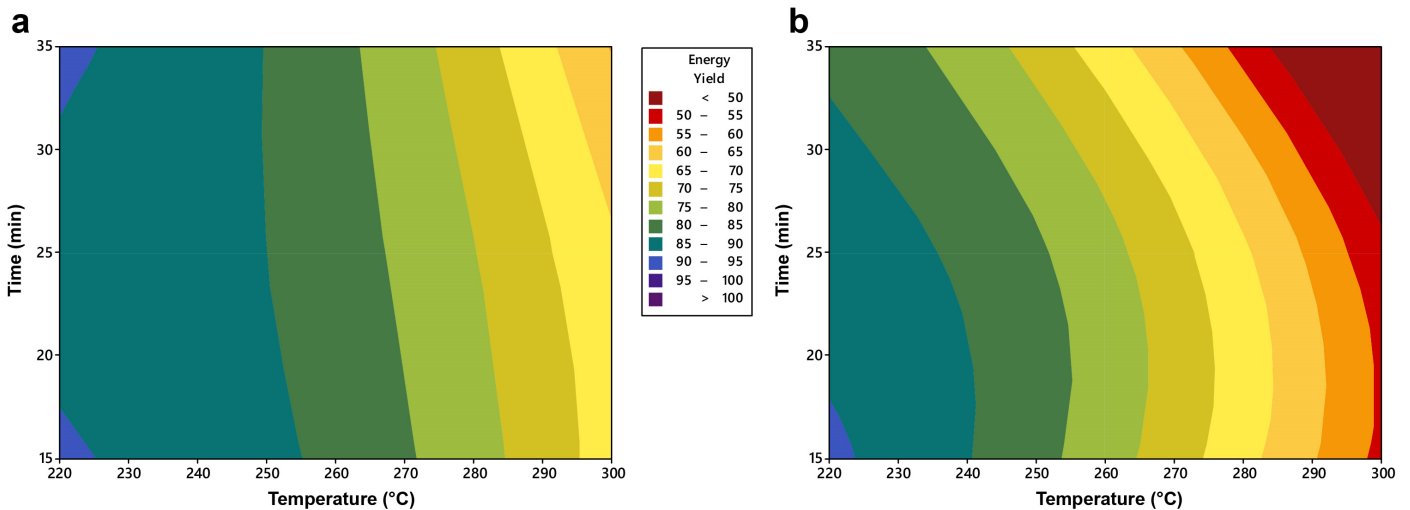


Fig. 18. Energy yield of poplar wood at different severities; (a) inert and (b) 21% Oxygen. Developed based on the data obtained from Nhuchhen and Basu (2014).

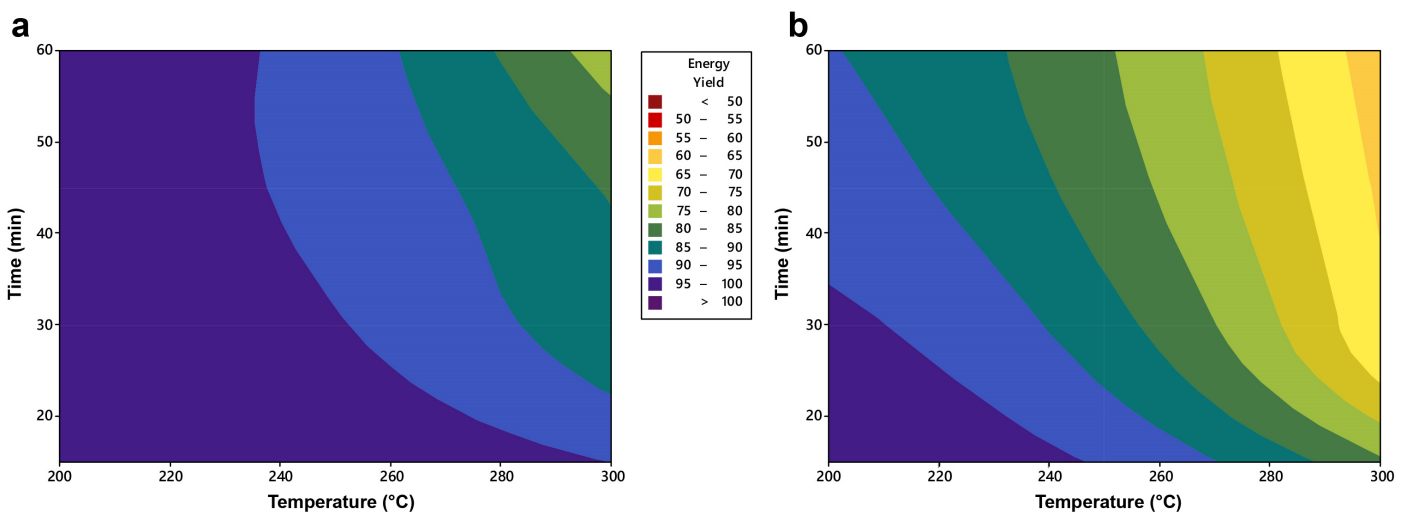


Fig. 19. Energy yield of microalgae at different severities; (a) inert and (b) 21% Oxygen. Developed based on the data obtained from Zhang et al. (2019a).

6.5. Effect on energy mass co-benefit index

In a study on oil palm fibers, the EMCI parameter (EMCI = energy yield – solid yield) was introduced, gradually decreasing with increasing oxygen concentration (Lu et al., 2012). High EMCI means high energy density and low volume of fuel. It is widely accepted that the optimal balance occurs in biomass torrefaction at around 80% solid yield and around 90% energy yield (Álvarez et al., 2021). This implies that an EMCI of 10 or higher is desirable. Low torrefaction severities preserve energy yield above 90%, but without a significant mass loss, the benefits of pretreatment cannot be obtained though. According to Table 3, this criteria satisfies EFB torrefaction at an inert or 3% oxygen environment with 300 °C temperature and 30 min of residence time with an EMCI of 15.3-18.1. Further, inert torrefaction of rice husk at 300 °C and 30 min of residence time give similar results with an EMCI of 28.2. Figures 20-23 present the EMCI of four types of biomass, i.e., rice husk, shells, poplar wood, and microalgae, against time, temperature, and oxygen content.

For rice husk, the EMCI of inert torrefaction is greater than that of oxidative torrefaction, whereas the opposite is true for poplar wood. For shells, the highest EMCI profile is obtained at an oxygen content of 5%. The EMCI of oxidative torrefaction is greater than inert torrefaction for poplar wood. Overall,

for agricultural waste, inert or mildly oxidative torrefaction is preferred for better performance, whereas oxidative torrefaction can be effectively used for woody biomass.

7. Torrefaction in the flue gas atmosphere

There are several studies on biomass torrefaction in flue gas or similar atmospheres, as summarized in Table 5. Simulated* dry or wet flue gas has been commonly used in these studies, while real flue gas has been occasionally used. Compared to the inert atmosphere, utilizing available wet flue gas at power plants or other industries as the torrefaction medium is of great interest in terms of practicality, affordability, and environmental sustainability (Onsree et al., 2019). Under real conditions, power plant wet flue gas typically contains steam (5–20% v/v), CO₂ (10–14% v/v), O₂ (4–6% v/v), and N₂ (Lasek et al., 2017). Both CO₂ and N₂ can be considered inert at low temperatures because the presence of CO₂ does not have a significant effect at low temperatures (Thanapal et al., 2014; Li et al., 2018). The CO₂ atmosphere has shown a minor influence at higher temperatures than N₂ (Uemura et al., 2015; Su et al., 2018). Several other studies have also observed faster biomass torrefaction in CO₂ than in the N₂ atmosphere

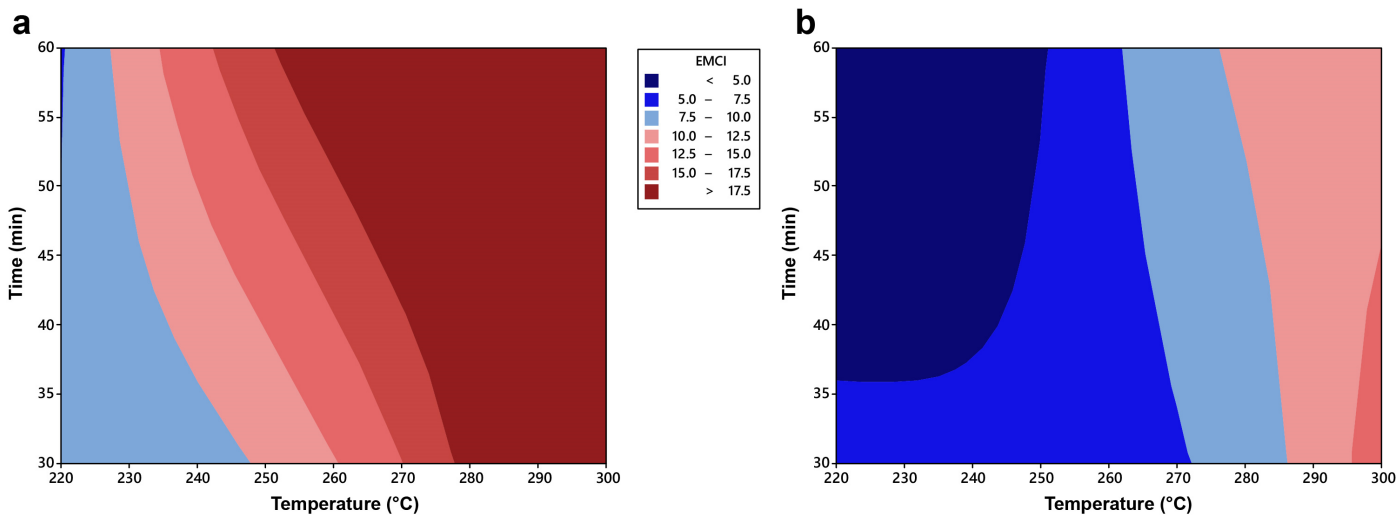


Fig. 20. EMCI of rice husk at different severities; (a) inert and (b) 21% Oxygen. Developed based on the data obtained from Zhang et al. (2021c).

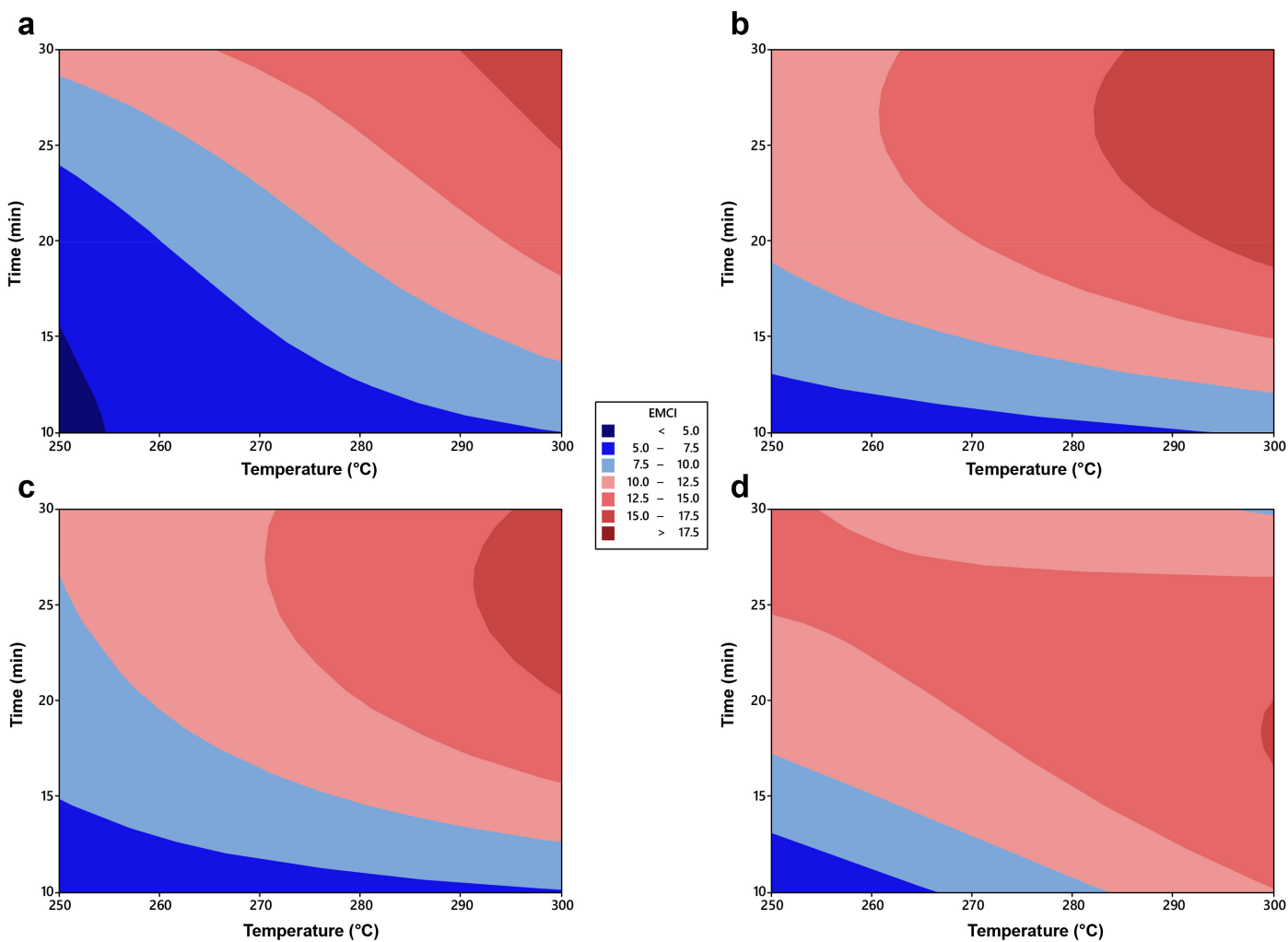


Fig. 21. EMCI of shells at different severities; (a) inert, (b) 5% Oxygen, (c) 15% Oxygen, and (d) 21% Oxygen. Developed based on the data obtained from Zhang et al. (2019b).

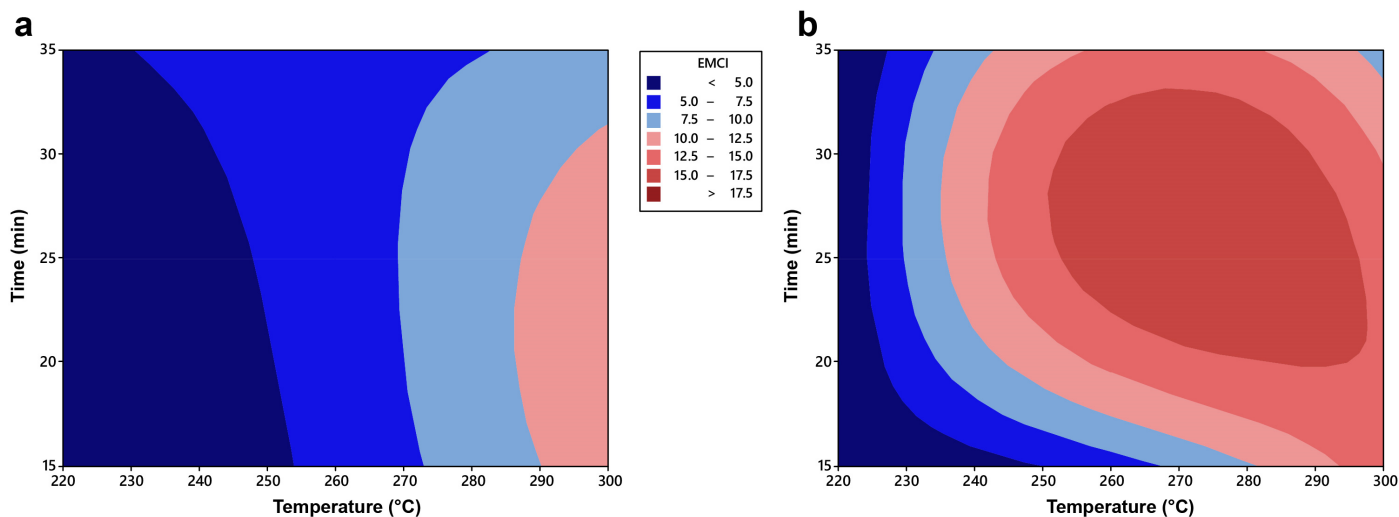


Fig. 22. EMCI of poplar wood at different severities; (a) inert and (b) 21% Oxygen. Developed based on the data obtained from Nhuchhen and Basu (2014).

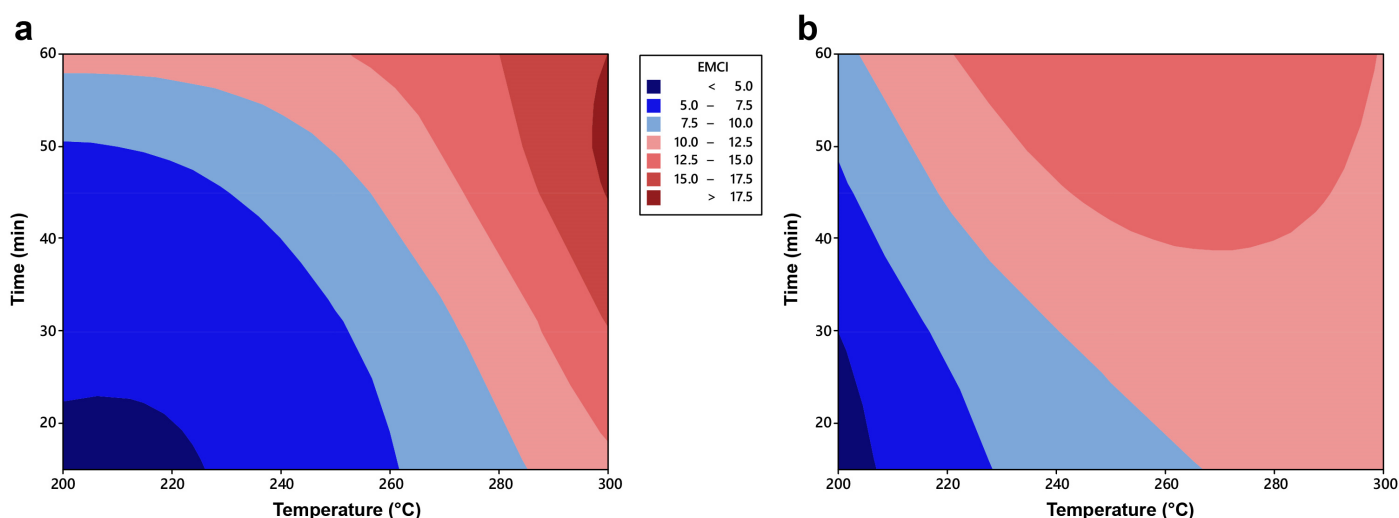


Fig. 23. EMCI of microalgae at different severities; (a) inert and (b) 21% Oxygen. Developed based on the data obtained from Zhang et al. (2019a).

(Chen et al., 2013; Tran et al., 2016). However, having steam with CO₂ negatively affects the torrefaction reaction, resulting in a slightly higher solid yield compared to the CO₂-only torrefaction (Tran et al., 2016). The presence of O₂ in the torrefaction medium, along with steam and CO₂ (which represents wet flue gas), results in a reduction in solid yield (Tran et al., 2016). This is attributed to the possible oxidation reaction of O₂ with biomass. In such a case, the overall torrefaction reaction happens in two ways; hemicellulose decomposition in ordinary torrefaction during devolatilization (inert atmosphere) and partial oxidation (oxidative atmosphere) (Uemura et al., 2015).

Low torrefied solid product yield and high liquid and gaseous product yields have been observed with increasing torrefaction temperature and residence time in the presence of O₂ (Su et al., 2018; Onsree et al., 2019). An increase in O₂ concentration results in a further reduction of solid product yield (Su et al., 2018). Partial combustion and Boudouard reactions under non-inert conditions increase gaseous products (Joshi et al., 2015). Here, O₂ and CO₂ in the torrefaction medium react with carbon in biomass to yield CO₂ and CO. Steam plays two roles by expediting the decomposition reaction and facilitating heat transfer. As a result, lower solid yields and reduced O₂ content in the gaseous products have been observed when the steam concentration increases (Onsree

et al., 2019). Further, the reaction of CO with steam, through the water gas shift reaction, results in increased CO₂ and H₂ in the gaseous product. Partial combustion, Boudouard, and water gas shift reactions generate heat inside the particles, which can be instantly utilized by the steam reforming and methanation reactions for producing H₂, CO, and CH₄ (Onsree et al., 2019). High torrefaction temperature promotes the thermal degradation of biomass, releasing more volatiles (Chen et al., 2020). The residence time primarily affects hemicellulose decomposition (Sarvaramini and Larachi, 2014; Negi et al., 2020). When the residence time is short, less than 30 min, hemicelluloses and cellulose decompose greatly, and the lignin fraction is enriched, resulting in high fixed carbon content in the product (Zhu et al., 2021). However, when the residence time is too long, around 60 min, the oxidation of fixed carbon could happen (Chen et al., 2013; Ramos-Carmona et al., 2018). During oxidative torrefaction of biomass, surface oxidation is the dominant mechanism (Chen et al., 2013). This intensifies the internal heat and mass transfer leading to severe degradation of volatile matter, resulting in a significant increase in fixed carbon content and a slight increase in ash content (Zhu et al., 2021).

Similar to torrefaction under an inert atmosphere where O/C and H/C ratios are reduced, the reduction of O improves the calorific value of the

Table 5.
Operating conditions and findings of torrefaction in flue gas or similar atmospheres.

| Biomass type | Torrefaction medium | Composition of torrefaction medium | | | | Temperature (°C) | Time (min) | Remarks | Reference |
|-------------------------------------|------------------------|------------------------------------|---------------------|--------------------|---|-------------------------|----------------|---|-------------------------|
| | | O ₂ (%) | CO ₂ (%) | N ₂ (%) | H ₂ O (%) | | | | |
| Cedarwood | Simulated dry flue gas | 6 | 10 | 84 | - | 200, 230, 260, 290 | 50 | Torrefaction temperature should not be higher than 260 °C for flue gas torrefaction. | Mei et al. (2015) |
| Corn residue pellets | Simulated wet flue gas | 4 | 12 | Balance | 0,7,14,21 | 260 | 10, 20, 30, 40 | The optimal torrefaction condition is 260 °C, 20 min, and 14% v/v steam giving 70% torrefied pellet yield with 23 MJ/kg of HHV. | Onsree et al. (2019) |
| Corn straw | Simulated dry flue gas | 3,5,7 | 17,15,13 | 80 | - | 275, 300, 325, 350, 375 | 20 | Mass and energy yield varies between 33-60% and 27-66%, respectively, and the effect of temperature is dominant. | Liu et al. (2021) |
| Distilled spirit lees | Simulated dry flue gas | 8 | 13 | 79 | - | 200, 250, 300 | 5, 30, 60 | For torrefaction at 250 °C, the flue gas requirement is about 1.41 tons/ton of raw distilled spirit lees and found to be technically and economically feasible. | Zhu et al. (2021) |
| Oil palm empty fruit bunches (EFB) | Real flue gas | 4 | 16.4 | 75.5 | - | 188-221 | 30 | Torrefaction in real flue gas results in 64.5% solid yield and 84.4% energy yield, as well as an increase of carbon content and calorific value by 15.1% and 30.9%. | Sellappah et al. (2016) |
| | Simulated dry flue gas | 9 | 12 | 79 | - | 220 | 30 | | |
| EFB | Simulated dry flue gas | 9 | 12 | 79 | - | 300 | 30 | An additional reaction occurs when O ₂ or CO ₂ is added to torrefaction gas, and the additional reaction by O ₂ is more significant than that by CO ₂ . | Sulaiman et al. (2015) |
| | | 12 | 9 | 79 | - | | | | |
| EFB and Oil palm kernel shell (PKS) | Simulated dry flue gas | 8-9 | 13-14 | 78 | - | 200, 250, 300 | 30 | For both biomass, the highest energy yield and highest energy density were obtained by torrefaction at 200 °C and 300 °C, respectively. | Uemura et al. (2018) |
| Rice husk | Simulated wet flue gas | 6 | 10 | 74 (Ar) | 10 | 220, 270, 300 | 30, 60 | Solid and energy yield of the upgraded samples remained at 47.98 – 70.56% and 64.82 – 78.96%, respectively. | Zhang et al. (2021c) |
| Spruce | Simulated wet flue gas | 5,10 | 95,90 | 100,0 | CO ₂ /H ₂ O = 1:0.7 | 250, 275, 300 | 30 | Energy yield in CO ₂ +H ₂ O atmosphere is higher than inert atmospheres, while the presence of O ₂ results in reduced energy yield. | Tran et al. (2016) |

fuel (Atienza-Martínez et al., 2013; Hu et al., 2020), leading to an increase in the energy density (Onsree et al., 2019). The HHV shows a growing trend with the increase in temperature and reactivity of the atmosphere in the order of N₂, CO₂, and O₂ (Su et al., 2018). Even though the energy yield in inert and flue gas atmospheres does not vary much at lower temperatures, the energy yield in flue gas atmospheres significantly decreases at higher temperatures (Mei et al., 2015). This is mainly because surface oxidation plays an important role at higher temperatures. Although high-temperature torrefaction shows many benefits, a higher torrefaction temperature does not necessarily produce a better energy yield. For optimum energy density and energy yield, the preferred temperature of flue gas torrefaction should not exceed 260 °C (Mei et al., 2015).

Overall, the temperature has the most significant effect on solid yield and energy yield. The residence time is also influential up to about 30 min but has no significant influence after that. Comparatively, the volumetric flow rate of the torrefaction medium is the least influential parameter (Zhu et al., 2021).

8. Reactor configurations

The various types of torrefaction reactors can be classified in several ways based on the heat exchange mechanism, mixing pattern, and assisted media (Nhuchhen et al., 2014; Chen et al., 2021). In the reactor configuration, the most important features are the heat transfer mechanism, biomass movement, and the working media. The heat transfer mechanism can be further classified into direct and indirect heating. Direct heating includes reactors for oxygen-free (inert) gas heating, low oxygen gas heating, and other reactor types. Reactor types used in inert gas heating are moving bed reactors, multiple-zone reactors, rotary drum types, and rotating packed bed reactors. Augur type, moving bed reactors, entrained flow, and spiral reactors are used in oxidative heating. Other reactor types include fluidized bed, microwave, and hydrothermal reactors. Augur and rotary drum reactors are used in indirect heating (Dhungana et al., 2012; Pillejera et al., 2017).

In the direct heating mechanism, heating media is in direct contact with the biomass, and it can be free of oxygen (inert) or a limited amount of oxygen. Hot gas, superheated steam, or hot solids can be used as heating media (Dhungana et al., 2012). In the indirect heating mechanism, biomass does not directly contact the heating media. Indirectly heated reactors have a low heat transfer coefficient and take high residence time to heat biomass. An experimental study on directly and indirectly heated reactors using 25–64 mm poplar wood particles has revealed that the core temperature of biomass particles is comparatively high in the indirectly heated reactor due to minimum dissipation of heat from inside to out by poor heat transfer (Dhungana et al., 2012). Hence, higher biomass conversion can be observed, and the final product has a high energy density but a lower solid and energy yield (Dhungana et al., 2012). In contrast, a directly heated reactor has a higher heat transfer ability resulting in low core temperature. Hence, it gives lower energy density but higher mass and energy yield. According to the basic classification, the most commonly used reactors are moving bed reactors, fluidized bed reactors, fixed bed reactors, rotary drum reactors, and microwave reactors. A brief introduction to those reactor types is given here, and the advantages and disadvantages of torrefaction reactors are listed in Table 6.

8.1. Fixed bed reactor

The reactor type most commonly used in laboratory experiments is the fixed bed reactor. It has a simple setup and can be built at a low cost. When the raw biomass is fed to the reactor and supplied with the heat, thermocouples are installed to measure the reactor temperature. A suitable carrier gas is provided to provide an inert or oxidative environment inside the reactor. A cooling unit is installed to cool down the reactor after the torrefaction process (Mamvura and Danha, 2020; Chen et al., 2021). Some studies used quartz tube fixed bed reactor type for oxidative torrefaction of

Table 6.
Advantages and disadvantages of different torrefaction reactor types.

| Reactor | Advantages | Disadvantages | Commercial Status | Reference |
|---------------|--|---|---|---|
| Fixed Bed | Simple setup Cost-effective | Poor heat transfer Poor temperature controlling | Commonly used in laboratories for preliminary tests | Chen et al. (2021) |
| Rotary Drum | Simple setup It can be used in both direct and indirect heating | Poor heat transfer Poor temperature controlling Bigger system size Difficult to scale up | Proven technology on a commercial scale by Torr-Coal B.V. (NL) | |
| Fluidized Bed | Higher heat transfer rates Easily scalable | Difficult to get plug flow Biomass particles should be small | Proven technology on a commercial scale by Topell Energy (NL) | Nhuchhen et al. (2014); Cremers et al. (2015) |
| Moving Bed | Higher heat transfer High bed density Simple setup | Higher pressure drops Poor temperature control | Proven technology on a demonstration scale by Andritz (DK) / ECN (NL) | |
| Screw Type | Mature technology Possible to get plug flow | Poor heat transfer Difficult to scale up Indirect heating only | Proven technology on a commercial scale by Solvay (FR) / New Biomass Energy (USA) | |

rice husk (Chen et al., 2020) and a vertical drop fixed-bed reactor for torrefaction of bamboo using flue gas (Su et al., 2018).

8.2. Rotary drum reactor

The rotary drum reactor can be used as a continuous torrefaction reactor. There are several parts in a rotary drum reactor, such as a feeding unit, external heater, and product collecting unit. An electric motor controls the rotary drum's rotation. Research findings indicate that the solid yield after torrefaction is lower in the rotary drum reactor compared to the fluidized bed reactor. Several disadvantages of the rotary drum reactors are scalability limitations, low thermal efficiency, and less plug flow (Tumuluru et al., 2011; Chen et al., 2021). A batch-type rotary kiln reactor has been used for torrefaction of Patula pine. According to the findings, this reactor system ensures consistent torrefied biomass quality compared to other reactors (Ramos-Carmona et al., 2018).

8.3. Moving bed reactor

The raw solid biomass particles are fed from the top of a vertical reactor. Then the biomass goes through the torrefaction process and exits at the bottom of the reactor. In the moving bed reactor, biomass is directly heated by recirculating the gases and vapours produced during torrefaction. A lab-scale moving bed reactor has been developed in a study conducted for parametric analysis of torrefaction. The biomass feed and the torrefied gas are transported in a countercurrent mode. The torrefied product goes out of the reactor by an auger regulated through a motor drive (Kung et al., 2019).

8.4. Screw reactor

Screw reactors also called auger reactors, use the principle of rotating to acquire an efficient torrefaction of the biomass. Biomass is fed continuously through a helical screw to a heated tubular shell. To achieve efficient heat transfer, smaller biomass particles should be used (Nachenius et al., 2013). A lab-scale batch-type screw reactor has been used to torrefy woody biomass with a bidirectional motor to mix the biomass and control the required temperature inside the reactor (Thanapal et al., 2014).

9. Application of torrefied product in thermochemical-based biorefineries

It has been revealed that torrefaction pretreatment is necessary to improve bio-oil properties from pyrolysis of biomass, which improves the economic feasibility of the pyrolysis process. Reduced bio-oil yield and increased char yield have to be expected from torrefied biomass (Chen et al., 2016b) because light compounds are decomposed to CO, CO₂, H₂O, acetic acid, and other minor constituents during torrefaction (Boateng and Mullen, 2013). Bio-oil from torrefied biomass has some definite advantages, such as low acidity and high energy content (Boateng and Mullen, 2013). The volatiles produced from torrefaction are undesirable oxygenated compounds during the pyrolysis process. Oxygenates result in high polarity, which hinders blending with fossil fuels. To deliver high-quality fuels or chemicals as the final product, it is worth improving the bio-oil quality even at the cost of reduced yields (Dai et al., 2019). Several studies have been conducted to analyze the pyrolysis behaviour of torrefied biomass and reviewed in several studies (Chen et al., 2018; Dai et

al., 2019). **Table 7** summarizes the benefits in pyrolysis applications associated with improved biomass properties from torrefaction.

Table 7.

A summary of the benefits in pyrolysis applications associated with improved biomass properties from torrefaction.*

| Torrefied biomass properties | Benefits in pyrolysis applications |
|---|---|
| Lower moisture content | Uniform small-size particles Improved and uniform heat transfer in the reactor |
| Grindability and pellet ability | Reduced water content due to decreased OH and COOH groups |
| Hydrophobicity | Lower moisture in the bio-oil |
| Higher heating value or calorific value | Increased C and low O/C ratio increase the higher heating value of the bio-oil |
| Homogeneity | Predictable conversion performance during the pyrolysis process |
| High density (after grinding) | Can be controlled to precise particle size and density |
| Thermal degradation | Lower acidity |

* Source: Tumuluru et al. (2021)

Further, it has been found that when torrefied biomass is used in the gasification process, syngas quality and yield are improved with higher H₂ and CO content and low CO₂ content. In addition, it has been observed that tar production during the gasification of torrefied biomass is slower, and a lower tar yield is expected compared to raw biomass. Biomass with high moisture, hemicellulose, and lignin content is more prone to tar formation. Torrefaction removes volatiles from raw biomass. Therefore, the primary tar formation during the devolatilization stage of gasification is limited. As a result, secondary and tertiary tar content is also expected to decrease. In addition, enhanced char reactivity due to increased alkali and alkaline earth metals, and a significant reduction in soot formation, are reported during torrefied biomass gasification (Lu et al., 2021). The gasification behaviour of torrefied biomass has been extensively studied in the literature.

Similar to the pyrolysis process, the bio-crude yield of hydrothermal liquefaction has been reportedly reduced due to torrefaction pretreatment (Tran et al., 2017). But less oxygenated compounds could be expected, which is beneficial. However, considering the applicability of this conversion technology specifically for wet biomass sources, dry torrefaction may not be an attractive option as pretreatment. This issue could be the reason for limited studies on the topic.

10. Circular economy concepts of torrefaction-based thermochemical biorefinery

According to the reviewed literature, torrefaction technology is of utmost importance for making biomass a sustainable resource for thermochemical biorefinery applications. Circular economy concepts can

add extra value to the sustainability of the torrefaction process, making it more economical. In better words, a circular economy can play a major role in thermochemical biorefinery applications. One of the circular economy concepts is using waste biomass sources in torrefaction-based thermochemical biorefineries. The majority of torrefaction studies reviewed were based on agricultural wastes, resulting in dual benefits providing economically-viable raw material along with the opportunity of waste management. The second circular economy concept would be the use of flue gas as the torrefaction medium. There are industries with flue gas temperatures within 200-300 °C and with limited oxygen content typically less than 10% suitable for the torrefaction process, and these industries have a good opportunity to recover this waste heat through the integrated torrefaction process.

The concepts of *in-situ* and *ex-situ* torrefaction of waste biomass are demonstrated in Figure 24. If the potential thermochemical biorefinery application is within a short distance, transporting raw biomass and *in-situ* torrefaction at the application site would be feasible. If the potential thermochemical biorefinery application is not within an economical distance, *ex-situ* torrefaction at a site where a waste heat source like flue gas is available in a short distance and long-distance transport of torrefied biomass would be beneficial. In either case, the circular bioeconomy concept is realized due to the use of waste heat in the flue gas as the torrefaction heat source. A comparative study of integrated (*in-situ*) and external (*ex-situ*) torrefaction for gasification-based biorefinery has revealed that *in-situ* torrefaction is much more beneficial at high torrefaction temperatures, whereas *ex-situ* torrefaction is not effective compared to raw biomass. The efficiency increases with the increase of torrefaction temperature in *in-situ* torrefaction. However, *in-situ* torrefaction makes it more difficult to transport, store, and handle biomass, while it also requires more complex plant designs. No net electricity production exists, and

reduced plant size may also hinder the economy of scale (Clausen, 2014). Depending on *in-situ* or *ex-situ* torrefaction, the type of reactor may vary. Energy yield is important in *in-situ* torrefaction, and for such a situation, directly heated reactors would be more suited as they have higher mass and energy yield. Indirectly heated reactors like rotating drum types are suitable for *ex-situ* torrefaction, where energy density is important to reduce transport costs (Dhungana et al., 2012).

11. Challenges towards commercialization and future perspectives

Even though torrefaction increases the energy density of biomass, a challenge remains because of the large amount of inorganic minerals remaining in the torrefied biomass. This is a typical problem arising with agriculture residues, which usually contain high contents of alkali and alkaline earth metals (Deng et al., 2013). It is well-known that alkali and alkaline earth metals in biomass significantly impact subsequent pyrolysis, gasification, or combustion performance. A decrease in liquid product yield and the formation of more water and organic acids have been reported, lowering bio-oil quality. Potassium and sodium, along with sulfur and chlorine, can cause fouling, slagging, and high-temperature corrosion during combustion applications. It has been reported that both inert and oxidative torrefaction increase the yield of PM10 during combustion (Cheng et al., 2022). Water washing is an effective pretreatment method to remove such troublesome elements from biomass (Deng et al., 2013). Therefore, combined pretreatment of water washing and torrefaction has been proposed, and the effect on subsequent pyrolysis has been evaluated in terms of bio-oil yield and composition, mainly for agricultural waste (Cen et al., 2016; Dong et al., 2018). Dilute acid washing by using

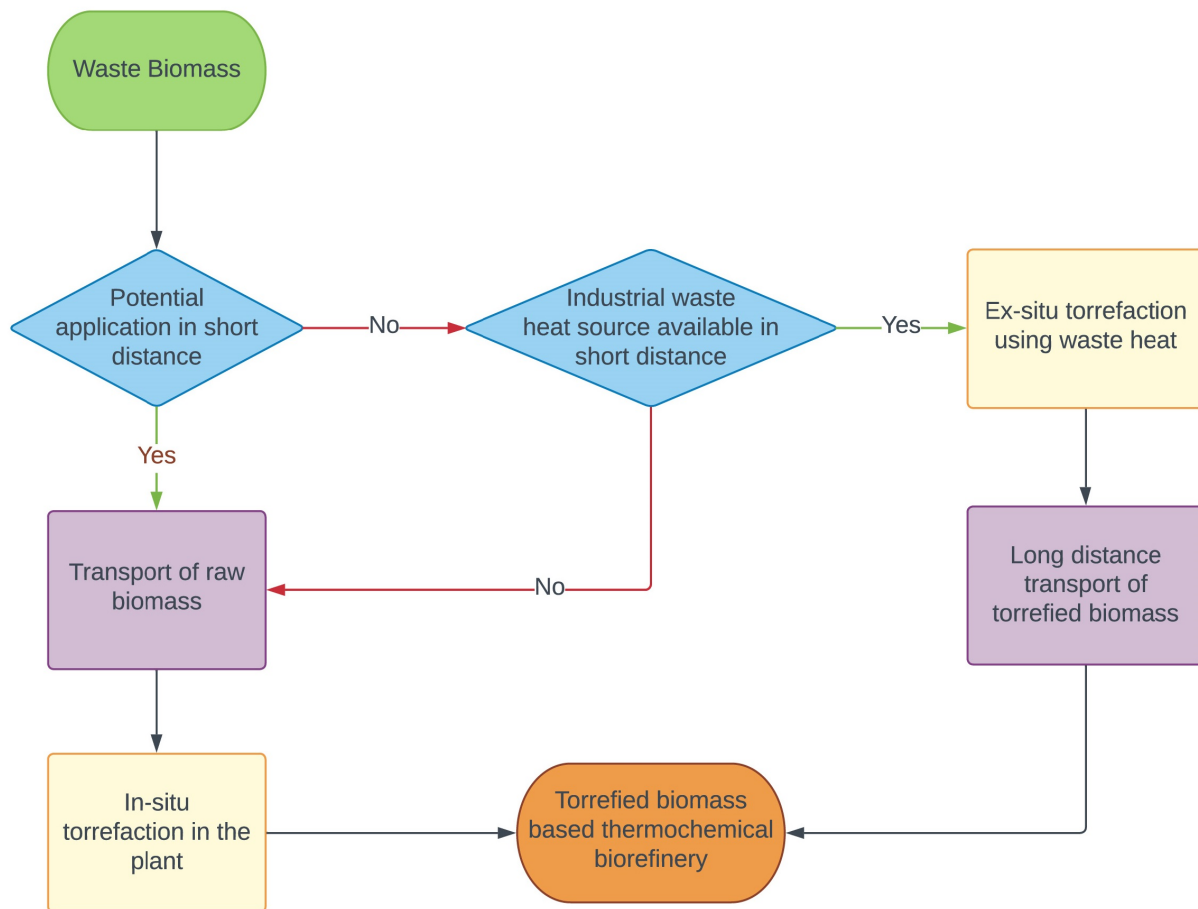


Fig. 24. *Ex-situ* and *in-situ* torrefaction integrated with the circular economy concept.

torrefaction liquid product (or a representative dilute acid solution) (Zhang et al., 2018a; Zhang et al., 2019c) or bio-oil obtained from fast pyrolysis (Zhang et al., 2016; Chen et al., 2017) has been successfully demonstrated. Both pre-washing and post-washing have been combined with torrefaction pretreatment (Zhang et al., 2018b). Further, reductions in NO_x emissions, high-temperature chlorine corrosion, fine particulate matter (submicron/aerosols) emissions, and alkali-induced fouling can be expected during combustion due to combined pretreatment (Abelha et al., 2019). With all these benefits, combined pretreatment of washing and torrefaction will be effective for agricultural waste. Agricultural waste can be first washed using mildly acidic torrefaction liquid, which originates from the water scrubber recovering the condensable part of the volatiles evolved during torrefaction. The majority of water can be removed by a subsequent pressing step, and further drying and torrefaction of washed agricultural waste can be achieved using industrial flue gas. The liquid removed in the pressing step could be used as a liquid fertilizer on agricultural land.

There are temperature-specific limits beyond which an increase in oxygen concentration leads to an oxidative thermal runaway when it comes to oxidative torrefaction. In a study of packed bed torrefaction of bagasse, the reported tolerable oxygen concentration was 5% for torrefaction at 270 °C, which was reduced to 1% for torrefaction at 290 °C (Joshi et al., 2015). In comparative studies, ligneous biomass has shown higher resistance against oxidative torrefaction than fibrous biomass (Lu et al., 2012; Chen et al., 2014a). For oil palm fibre torrefied in N₂ and air, the maximum values of the energy-mass co-benefit index were located at 300 and 250 °C; respectively, whereas for Eucalyptus torrefied in N₂ and air, the optimum operations took place at 325 and 275 °C, respectively (Lu et al., 2012), revealing the effect of biomass nature on the oxidative torrefaction. Therefore, it is important to operate at less oxygen content and low temperature for fibrous biomass like agricultural waste to minimize oxidative thermal runaway.

Practically, the oxygen content, temperature, and residence time should be balanced during oxidative torrefaction. When flue gas is used as the torrefaction medium, since there is limited control over oxygen content and temperature, it is important to operate at short residence times. Further, woody biomass types should be selected for such cases. In certain cases, recirculating torrefaction gases may also be a viable option that can effectively reduce oxygen content and temperature.

When it comes to torrefaction reactors, poor temperature control with fixed bed, moving bed, and rotary drum reactors, as well as limited scalability with fixed bed, moving bed, rotary drum, and screw-type reactors, are observed as the major limitations (Nhuchhen et al., 2014; Abdulyekeen et al., 2021). Most oxidative torrefaction studies are based on laboratory-scale fixed bed reactors. However, rotary drum, fluidized bed, and screw-type reactors are proven to be used on commercial scales, whereas moving bed reactors are on demonstration scales.

12. Conclusions

Oxidative torrefaction was extensively reviewed, focusing on thermochemical biorefinery applications. According to the reviewed literature focusing on the highest HHV enhancement, it was found that inert torrefaction gives similar solid yield, energy yield, carbon enhancement, and HHV enhancement for all the biomass types, whereas oxidative torrefaction always gives less solid yield and energy yield than inert torrefaction. Oxidative torrefaction of woody biomass results in slightly higher solid yield and energy yield than other biomass types. Further, woody biomass results in similar carbon enhancement and HHV enhancement during both inert and oxidative torrefaction. As a result, woody biomass can be equally benefitted from oxidative or inert torrefaction, whereas inert torrefaction is more suitable for agricultural waste and microalgae. Most oxidative torrefaction studies are based on agricultural waste and woody biomass, where limited studies are available for microalgae. *Ex-situ* and *in-situ* torrefactions with a circular economy approach, such as using waste biomass as the feedstock and flue gas as the torrefaction medium, were introduced. Identified challenges are mainly the increase of ash content in torrefied biomass, the oxidative thermal runaway of fibrous biomass during torrefaction, and temperature controlling and scale-up issues in the reactors. Some of the proposed remedies are combined washing and torrefaction pretreatment, balancing oxygen content, temperature, and residence time depending on the biomass type, and recirculating torrefaction gases.

Acknowledgements

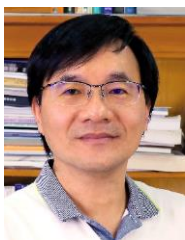
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References

- Abdulyekeen, K.A., Umar, A.A., Patah, M.F.A., Daud, W.M.A.W., 2021. Torrefaction of biomass: production of enhanced solid biofuel from municipal solid waste and other types of biomass. *Renew. Sust. Energy Rev.* 150, 111436.
- Abelha, P., Mourão Vilela, C., Nanou, P., Carbo, M., Janssen, A., Leiser, S., 2019. Combustion improvements of upgraded biomass by washing and torrefaction. *Fuel*. 253, 1018-1033.
- Acharya, B., Pradhan, R.R., Dutta, A. 2015. Qualitative and kinetic analysis of torrefaction of lignocellulosic biomass using DSC-TGA-FTIR. *AIMS Energy*. 3(4), 760-773.
- Adnan, M.A., Fuad, M.A.H.M., Hasan, M.F., 2017. Oxidative torrefaction for pulverized palm biomass using air. *J. Teknol.* 79(7-4).
- Álvarez, A., Migoya, S., Menéndez, R., Gutiérrez, G., Pizarro, C., and Bueno, J.L., 2021. Torrefaction of short rotation coppice willow. characterization, hydrophobicity assessment and kinetics of the process. *Fuel*. 295, 120601.
- Atienza-Martínez, M., Fonts, I., ábrego, J., Ceamanos, J., Gea, G., 2013. Sewage sludge torrefaction in a fluidized bed reactor. *Chem. Eng. J.* 222, 534-545.
- Bach, Q.V., Chen, W.H., Lin, S.C., Sheen, H.K., Chang, J.S., 2016. Wet torrefaction of microalga *Chlorella vulgaris* ESP-31 with microwave-assisted heating. *Energy Convers. Manage.* 141, 163-170.
- Balagurumurthy, B., Singh, R., Ohri, P., Prakash, A., Bhaskar, T., 2015. Chapter 6-Thermochemical biorefinery. *Recent Adv. Thermochem. Convers. Biomass*. 157-174.
- Balat, M., 2008. Mechanisms of thermochemical biomass conversion processes. Part I: reactions of pyrolysis. *Energy Sources A: Recovery Util. Environ. Eff.* 620-635.
- Barskov, S., Zappi, M., Buchireddy, P., Dufreche, S., Guillory, J., Gang, D., Hernandez, R., Bajpai, R., Baudier, J., Cooper, R., Sharp, R., 2019. Torrefaction of biomass: a review of production methods for biocoal from cultured and waste lignocellulosic feedstocks. *Renewable Energy*. 142, 624-642.
- Boateng, A.A., Mullen, C.A., 2013. Fast pyrolysis of biomass thermally pretreated by torrefaction. *J. Anal. Appl. Pyrolysis*. 100, 95-102.
- Brachi, P., Chirone, R., Miccio, M., Ruoppolo, G., 2019. Fluidized bed torrefaction of biomass pellets: a comparison between oxidative and inert atmosphere. *Powder Technol.* 357, 97-107.
- Cahyanti, M.N., Doddapaneni, T.R.K.C., Kikas, T., 2020. Biomass torrefaction: an overview on process parameters, economic and environmental aspects and recent advancements. *Bioresour. Technol.* 301, 122737.
- Cen, K., Chen, D., Wang, J., Cai, Y., Wang, L., 2016. Effects of water washing and torrefaction pretreatments on corn stalk pyrolysis: combined study using TG-FTIR and a fixed bed reactor. *Energy Fuels*. 30(12), 10627-10634.
- Cheah, W.Y., Sankaran, R., Show, P.L., Ibrahim, T.N.B.T., Chew, K.W., Culaba, A., Jo-Shu, C., 2020. Pretreatment methods for lignocellulosic biofuels production: Current advances, challenges and future prospects. *Biofuel Res. J.* 7(1), 1115-1127.
- Chen, W.H., Lu, K.M., Liu, S.H., Tsai, C.M., Lee, W.J., Lin, T.C., 2013. Biomass torrefaction characteristics in inert and oxidative atmospheres at various superficial velocities. *Bioresour. Technol.* 146, 152-160.

- [17] Chen, W.H., Lu, K.M., Lee, W.J., Liu, S.H., Lin, T.C., 2014a. Non-oxidative and oxidative torrefaction characterization and SEM observations of fibrous and ligneous biomass. *Appl. Energy*. 114, 104-113.
- [18] Chen, Y., Liu, B., Yang, H., Yang, Q., Chen, H., 2014b. Evolution of functional groups and pore structure during cotton and corn stalks torrefaction and its correlation with hydrophobicity. *Fuel*. 137, 41-49.
- [19] Chen, W.H., Peng, J., Bi, X.T., 2015. A state-of-the-art review of biomass torrefaction, densification and applications. *Renew. Sust. Energy Rev.* 44, 847-866.
- [20] Chen, W.H., Zhuang, Y.Q., Liu, S.H., Juang, T.T., Tsai, C.M., 2016a. Product characteristics from the torrefaction of oil palm fiber pellets in inert and oxidative atmospheres. *Bioresour. Technol.* 199, 367-374.
- [21] Chen, Y., Cao, W., Atreya, A., 2016b. An experimental study to investigate the effect of torrefaction temperature and time on pyrolysis of centimeter-scale pine wood particles. *Fuel Process. Technol.* 153, 74-80.
- [22] Chen, D., Cen, K., Jing, X., Gao, J., Li, C., Ma, Z., 2017. An approach for upgrading biomass and pyrolysis product quality using a combination of aqueous phase bio-oil washing and torrefaction pretreatment. *Bioresour. Technol.* 233, 150-158.
- [23] Chen, Z., Wang, M., Jiang, E., Wang, D., Zhang, K., Ren, Y., Jiang, Y., 2018. Pyrolysis of Torrefied Biomass. *Trends Biotechnol.* 36(12), 1287-1298.
- [24] Chen, D., Chen, F., Cen, K., Cao, X., Zhang, J., Zhou, J., 2020. Upgrading rice husk via oxidative torrefaction: characterization of solid, liquid, gaseous products and a comparison with non-oxidative torrefaction. *Fuel*. 275, 117936.
- [25] Chen, W.H., Lin, B.J., Lin, Y.Y., Chu, Y.S., Ubando, A.T., Show, P.L., Ong, H.C., Chang, J.S., Ho, S.H., Culaba, A.B., Pétrissans, A., Pétrissans, M., 2021. Progress in biomass torrefaction: principles, applications and challenges. *Prog. Energy Combust. Sci.* 82, 100887.
- [26] Cheng, W., Zhu, Y., Zhang, W., Jiang, H., Hu, J., Zhang, X., Yang, H., Chen, H., 2022. Effect of oxidative torrefaction on particulate matter emission from agricultural biomass pellet combustion in comparison with non-oxidative torrefaction. *Renewable Energy*. 189, 39-51.
- [27] Clausen, L.R., 2014. Integrated torrefaction vs. external torrefaction—a thermodynamic analysis for the case of a thermochemical biorefinery. *Energy*. 77, 597-607.
- [28] Conag, A.T., Villahermosa, J.E.R., Cabatingan, L.K., Go, A.W., 2017. Energy densification of sugarcane bagasse through torrefaction under minimized oxidative atmosphere. *J. Environ. Chem. Eng.* 5(6), 5411-5419.
- [29] Conag, A.T., Villahermosa, J.E.R., Cabatingan, L.K., Go, A.W., 2018. Energy densification of sugarcane leaves through torrefaction under minimized oxidative atmosphere. *Energy Sust. Dev.* 42, 160-169.
- [30] Cremers, M., Koppejan, J., Sokhansanj, S., Melin, S., Madrali, S., 2015. Status overview of torrefaction technologies. *IEA Bioenergy*. 32, 1-54.
- [31] Dai, L., Wang, Y., Liu, Y., Ruan, R., He, C., Yu, Z., Jiang, L., Zeng, Z., Tian, X., 2019. Integrated process of lignocellulosic biomass torrefaction and pyrolysis for upgrading bio-oil production: a state-of-the-art review. *Renew. Sust. Energy Rev.* 107, 20-36.
- [32] Deng, L., Zhang, T., Che, D., 2013. Effect of water washing on fuel properties, pyrolysis and combustion characteristics, and ash fusibility of biomass. *Fuel Process. Technol.* 106, 712-720.
- [33] Dhungana, A., Basu, P., Dutta, A., 2012. Effects of reactor design on the torrefaction of biomass. *J. Energy Resour. Technol.* 134(4), 1-11.
- [34] Dong, Q., Zhang, S., Ding, K., Zhu, S., Zhang, H., Liu, X., 2018. Pyrolysis behavior of raw/torrefied rice straw after different demineralization processes. *Biomass Bioenergy*. 119, 229-236.
- [35] Eseyin, A.E., Steele, P.H., Pittman, C.U., Ekpenyong, K.I., Soni, B., 2016. TGA Torrefaction Kinetics of Cedar Wood. *J. Biofuels*. 7(1), 20-27.
- [36] Foust, T.D., Aden, A., Dutta, A., Phillips, S., 2009. An economic and environmental comparison of a biochemical and a thermochemical lignocellulosic ethanol conversion processes. *Cellulose*. 16(4), 547-565.
- [37] Gronnow, M.J., Budarin, V.L., Mašek, O., Crombie, K.N., Brownsort, P.A., Shuttleworth, P.S., Hurst, P.R., Clark, J.H., 2013. Torrefaction/biochar production by microwave and conventional slow pyrolysis—comparison of energy properties. *Gcb Bioenergy*. 5(2), 144-152.
- [38] Hisham, S.M., Uemura, Y., Tazli, A.M., 2016. Effects of temperature and concentration of Oxygen on torrefaction of empty fruit bunches. *J. Jpn. Inst. Energy*. 95(12), 1110-1114.
- [39] Hu, J., Song, Y., Liu, J., Evrendilek, F., Buyukada, M., Yan, Y., Li, L., 2020. Combustions of torrefaction-pretreated bamboo forest residues: physicochemical properties, evolved gases, and kinetic mechanisms. *Bioresour. Technol.* 304, 122960.
- [40] Joshi, Y., Di Marcello, M., Krishnamurthy, E., De Jong, W., 2015. Packed-bed torrefaction of bagasse under inert and oxygenated atmospheres. *Energy Fuels*. 29(8), 5078-5087.
- [41] Kung, K.S., Thengane, S.K., Shanbhogue, S., Ghoniem, A.F., 2019. Parametric analysis of torrefaction reactor operating under oxygen-lean conditions. *Energy*. 181, 603-614.
- [42] Lasek, J.A., Kopczyński, M., Janusz, M., Iluk, A., Zuwała, J., 2017. Combustion properties of torrefied biomass obtained from flue gas-enhanced reactor. *Energy*. 119, 362-368.
- [43] Li, M.F., Shen, Y., Sun, J.K., Bian, J., Chen, C.Z., Sun, R.C., 2015. Wet torrefaction of bamboo in hydrochloric acid solution by microwave heating. *ACS Sust. Chem. Eng.* 3(9), 2022-2029.
- [44] Li, S.X., Chen, C.Z., Li, M.F., Xiao, X., 2018. Torrefaction of corncob to produce charcoal under nitrogen and carbon dioxide atmospheres. *Bioresour. Technol.* 249, 348-353.
- [45] Li, X., Lu, Z., Chen, J., Chen, X., Jiang, Y., Jian, J., Yao, S., 2021. Effect of oxidative torrefaction on high temperature combustion process of wood sphere. *Fuel*. 286, 119379.
- [46] Liu, Y., Rokni, E., Yang, R., Ren, X., Sun, R., Levendis, Y.A., 2021. Torrefaction of corn straw in oxygen and carbon dioxide containing gases: mass/energy yields and evolution of gaseous species. *Fuel*. 285, 119044.
- [47] Lu, H., Gong, Y., Areprasert, C., Ding, L., Guo, Q., Chen, W.H., Yu, G., 2021. Integration of biomass torrefaction and gasification based on biomass classification: a review. *Energy Technol.* 9(5), 2001108.
- [48] Lu, K.M., Lee, W.J., Chen, W.H., Liu, S.H., Lin, T.C., 2012. Torrefaction and low temperature carbonization of oil palm fiber and eucalyptus in nitrogen and air atmospheres. *Bioresour. Technol.* 123, 98-105.
- [49] Mamvura, T.A., Danha, G., 2020. Biomass torrefaction as an emerging technology to aid in energy production. *Heliyon*. 6(3), e03531.
- [50] Mei, Y., Liu, R., Yang, Q., Yang, H., Shao, J., Draper, C., Zhang, S., Chen, H., 2015. Torrefaction of cedarwood in a pilot scale rotary kiln and the influence of industrial flue gas. *Bioresour. Technol.* 177, 355-360.
- [51] Nachenius, R.W., Ronsse, F., Venderbosch, R.H., Prins, W., 2013. Biomass pyrolysis. *Adv. Chem. Eng. Academic Press*. 42, 75-139.
- [52] Nhuchhen, D.R., Basu, P., Acharya, B., 2014. A comprehensive review on biomass torrefaction. *Int. J. Renewable Energy Biofuels*. 2014, 1-56.
- [53] Nhuchhen, D.R., Basu, P., 2014. Experimental investigation of mildly pressurized torrefaction in air and nitrogen. *Energy Fuels*. 28(5), 3110-3121.
- [54] Niu, Y., Lv, Y., Lei, Y., Liu, S., Liang, Y., Wang, D., Hui, S., 2019. Biomass torrefaction: properties, applications, challenges, and economy. *Renew. Sust. Energy Rev.* 115, 109395.
- [55] Ong, H.C., Yu, K.L., Chen, W.H., Pillejera, M.K., Bi, X., Tran, K.Q., Pétrissans, A., Pétrissans, M., 2021. Variation of lignocellulosic biomass structure from torrefaction: a critical review. *Renew. Sust. Energy Rev.* 152, 111698.
- [56] Onsee, T., Tippayawong, N., Williams, T., McCullough, K., Barrow, E., Pogaku, R., Lauterbach, J., 2019. Torrefaction of pelletized corn residues with wet flue gas. *Bioresour. Technol.* 285, 121330.
- [57] Pang, S., 2019. Advances in thermochemical conversion of woody biomass to energy, fuels and chemicals. *Biotechnol. Adv.* 37(4), 589-597.
- [58] Perera, S.M., Wickramasinghe, C., Samarasinghe, B.K.T., Narayana, M., 2021. Modeling of thermochemical conversion of waste biomass—a comprehensive review. *Biofuel Res. J.* 8(4), 1481-1528.
- [59] Pillejera, M.K.V., Chen, W.H., De Luna, M.D.G., 2017. Bamboo torrefaction in a high gravity (Hige) environment using a rotating packed bed. *ACS Sust. Chem. Eng.* 5(8), 7052-7062.

- [60] Ramos-Carmona, S., Martínez, J.D., Pérez, J.F., 2018. Torrefaction of patula pine under air conditions: a chemical and structural characterization. *Ind. Crops Prod.* 118, 302-310.
- [61] Ribeiro, J.M.C., Godina, R., Matias, J.C.D.O., Nunes, L.J.R., 2018. Future perspectives of biomass torrefaction: review of the current state-of-the-art and research development. *Sustainability.* 10(7), 2323.
- [62] Rodionova, M.V., Bozieva, A.M., Zharmukhamedov, S.K., Leong, Y.K., Chi-Wei Lan, J., Veziroglu, A., Veziroglu, T.N., Tomo, T., Chang, J.S., Allakhverdiev, S.I., 2021. A comprehensive review on lignocellulosic biomass biorefinery for sustainable biofuel production. *Int. J. Hydrogen Energy.* 47(3), 1481-1498.
- [63] Rousset, P., Macedo, L., Commandré, J.M., Moreira, A., 2012. Biomass torrefaction under different oxygen concentrations and its effect on the composition of the solid by-product. *J. Anal. Appl. Pyrolysis.* 96, 86-91.
- [64] Sarvaramini, A., Larachi, F., 2014. Integrated biomass torrefaction-Chemical looping combustion as a method to recover torrefaction volatiles energy. *Fuel.* 116, 158-167.
- [65] Sellappah, V., Uemura, Y., Hassan, S., Sulaiman, M.H., Lam, M.K., 2016. Torrefaction of empty fruit bunch in the presence of combustion gas. *Procedia Eng.* 148, 750-757.
- [66] Seo, M.W., Lee, S.H., Nam, H., Lee, D., Tokmurzin, D., Wang, S., Park, Y.K., 2022. Recent advances of thermochemical conversion processes for biorefinery. *Bioresour. Technol.* 343, 126109.
- [67] Shoulaifar, T.K., 2016. Chemical changes in biomass during Torrefaction. PhD Dissertation, Åbo Akademi University.
- [68] So, C.L., Eberhardt, T.L., 2018. FTIR-based models for assessment of mass yield and biofuel properties of torrefied wood. *Wood Sci. Technol.* 52(1), 209-227.
- [69] Su, Y., Zhang, S., Liu, L., Xu, D., Xiong, Y., 2018. Investigation of representative components of flue gas used as torrefaction pretreatment atmosphere and its effects on fast pyrolysis behaviors. *Bioresour. Technol.* 267, 584-590.
- [70] Sui, P., Sokhansanj, S., Bi, X.T., Lim, C.J., Larsson, S.H., 2012. Drying characteristics and equilibrium moisture content of steam-treated Douglas fir (*Pseudotsuga menziesii* L.). *Bioresour. Technol.* 116, 396-402.
- [71] Sulaiman, M.H., Uemura, Y., Azizan, M.T., Iskandar, B.S., 2015. Effect of torrefaction condition the mass yield, elementary composition and calorific value of empty fruit bunches (EFB). *Aust. J. Basic Appl. Sci.* 9(37), 300-303.
- [72] Tan, M., Li, H., Huang, Z., Wang, Z., Xiong, R., Jiang, S., Zhang, J., Wu, Z., Li, C., Luo, L., 2021. Comparison of atmospheric and gas-pressurized oxidative torrefaction of heavy-metal-polluted rice straw. *J. Clean Prod.* 283, 124636.
- [73] Tanyaket, T., Onsree, T., Tippayawong, N., Baratieri, M., 2020. Effect of oxidative torrefaction on characteristics of treated corncob pellets. *Chin. J. Mech. Eng.* 41(1), 65-73.
- [74] Thanapal, S.S., Chen, W., Annamalai, K., Carlin, N., Ansley, R.J., Ranjan, D., 2014. Carbon dioxide torrefaction of woody biomass. *Energy Fuels.* 28(2), 1147-1157.
- [75] Tran, K.Q., Klemsdal, A.J., Zhang, W., Sandquist, J., Wang, L., Skreiberg, Ø., 2017. Fast hydrothermal liquefaction of native and torrefied wood. *Energy Procedia.* 105, 218-223.
- [76] Tran, K.Q., Trinh, T.N., Bach, Q.V., 2016. Development of a biomass torrefaction process integrated with oxy-fuel combustion. *Bioresour. Technol.* 199, 408-413.
- [77] Tumuluru, J.S., Sokhansanj, S., Hess, J.R., Wright, C.T., Boardman, R.D., 2011. A review on biomass torrefaction process and product properties for energy applications. *Ind. Biotechnol.* 7(5) 384-401.
- [78] Tumuluru, J.S., Ghiasi, B., Soelberg, N.R., Sokhansanj, S., 2021. Biomass torrefaction process, product properties, reactor types, and moving bed reactor design concepts. *Front Energy Res.* 462.
- [79] Tursi, A., 2019. A review on biomass: importance, chemistry, classification, and conversion. *Biofuel Res. J.* 6(2), 962-979.
- [80] Uemura, Y., Omar, W., Othman, N.A., Yusup, S., Tsutsui, T., 2013. Torrefaction of oil palm EFB in the presence of oxygen. *Fuel.* 103, 156-160.
- [81] Uemura, Y., Saadon, S., Osman, N., Mansor, N., Tanoue, K.I., 2015. Torrefaction of oil palm kernel shell in the presence of oxygen and carbon dioxide. *Fuel.* 144, 171-179.
- [82] Uemura, Y., Sellappah, V., Trinh, T.H., Komiyama, M., Hassan, S., Tanoue, K., 2018. Improvement of energy density and energy yield of oil palm biomass by torrefaction in combustion gas. *IOP Conf. Ser.: Mater. Sci. Eng.* 458(1), 012061.
- [83] van der Stelt, M.J.C., 2011. Chemistry and reaction kinetics of biowaste torrefaction. Technische Universiteit Eindhoven, Eindhoven.
- [84] Wang, C., Peng, J., Li, H., Bi, X.T., Legros, R., Lim, C. J., Sokhansanj, S., 2013. Oxidative torrefaction of biomass residues and densification of torrefied sawdust to pellets. *Bioresour. Technol.* 127, 318-325.
- [85] Wang, Z., Li, H., Lim, C.J., Grace, J.R., 2018. Oxidative torrefaction of spruce-pine-fir sawdust in a slot-rectangular spouted bed reactor. *Energy Convers. Manage.* 174, 276-287.
- [86] Wang, Z., Lim, C.J., Grace, J. R., 2019. A comprehensive study of sawdust torrefaction in a dual-compartment slot-rectangular spouted bed reactor. *Energy.* 189, 116306.
- [87] Yang, H., Yan, R., Chen, H., Lee, D.H., Zheng, C., 2007. Characteristics of hemicellulose, cellulose and lignin pyrolysis. *Fuel.* 86(12-13), 1781-1788.
- [88] Zhang, S., Dong, Q., Chen, T., Xiong, Y., 2016. Combination of light bio-oil washing and torrefaction pretreatment of rice husk: its effects on physicochemical characteristics and fast pyrolysis behavior. *Energy Fuels.* 30(4), 3030-3037.
- [89] Zhang, S., Su, Y., Xu, D., Zhu, S., Zhang, H., Liu, X., 2018a. Effects of torrefaction and organic-acid leaching pretreatment on the pyrolysis behavior of rice husk. *Energy.* 149, 804-813.
- [90] Zhang, C., Ho, S.H., Chen, W.H., Xie, Y., Liu, Z., Chang, J.S., 2018b. Torrefaction performance and energy usage of biomass wastes and their correlations with torrefaction severity index. *Appl. Energy.* 220, 598-604.
- [91] Zhang, C., Wang, C., Cao, G., Chen, W.H., Ho, S.H., 2019a. Comparison and characterization of property variation of microalgal biomass with non-oxidative and oxidative torrefaction. *Fuel.* 246, 375-385.
- [92] Zhang, C., Ho, S.H., Chen, W.H., Fu, Y., Chang, J.S., Bi, X., 2019b. Oxidative torrefaction of biomass nutshells: evaluations of energy efficiency as well as biochar transportation and storage. *Appl. Energy.* 235, 428-441.
- [93] Zhang, S., Zhu, S., Zhang, H., Liu, X., Zhang, H., 2019c. Evaluation of pyrolysis behavior and products properties of rice husk after combined pretreatment of washing and torrefaction. *Biomass Bioenergy.* 127, 105293.
- [94] Zhang, C., Ho, S.H., Chen, W.H., Wang, R., 2021a. Comparative indexes, fuel characterization and thermogravimetric-Fourier transform infrared spectrometer-mass spectrogram (TG-FTIR-MS) analysis of microalga *Nannochloropsis Oceanica* under oxidative and inert torrefaction. *Energy.* 230, 120824.
- [95] Zhang, C., Ho, S.H., Chen, W.H., Wang, R., Show, P.L., Ong, H.C., 2021b. Oxidative torrefaction performance of microalga *Nannochloropsis Oceanica* towards an upgraded microalgal solid biofuel. *J. Biotechnol.* 338, 81-90.
- [96] Zhang, L., Wang, Z., Ma, J., Kong, W., Yuan, P., Sun, R., Shen, B., 2021c. Analysis of functionality distribution and microstructural characteristics of upgraded rice husk after undergoing non-oxidative and oxidative torrefaction. *Fuel.* 310, 122477.
- [97] Zhang, C., Li, F., Ho, S., Chen, W., Sandamali, D., Loke, P., 2022. Oxidative torrefaction of microalga *Nannochloropsis Oceanica* activated by potassium carbonate for solid biofuel production. *Environ. Res.* 212, 113389.
- [98] Zhu, X., Zhou, S., Zhang, Z., Zhang, Y., Li, J., Ahmed, S., Yan, B., Chen, G., Li, N. 2021. Flue gas torrefaction of distilled spirit lees and the effects on the combustion and nitrogen oxide emission. *Bioresour. Technol.* 342, 125975.



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