



## Review

# A comprehensive review on the factors affecting thermochemical conversion efficiency of algal biomass to energy



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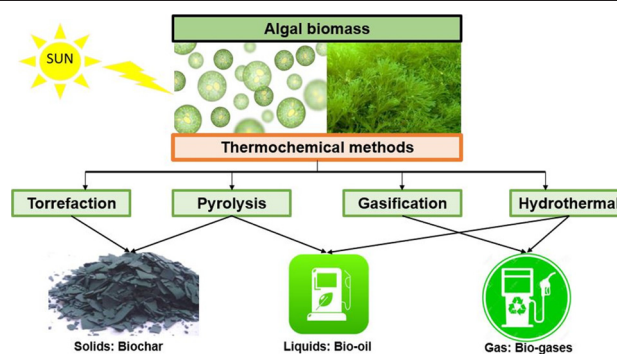
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## HIGHLIGHTS

- Factors affecting thermochemical conversion process of algal biomass were reviewed.
- Torrefaction, pyrolysis, gasification and hydrothermal processes were illustrated.
- Reaction temperature and residence time greatly influenced the process efficiency.
- Conversion process efficiency in terms of product yield and quality were spotlighted.
- Perspectives and challenges of algae biomass to biofuels were discussed.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Algae are one of the most viable feedstock options that can be converted into different bioenergies viz., bioethanol, biobutanol, biodiesel, biomethane, biohydrogen, etc. owing to their renewable, sustainable and economic credibility features. Algal biomass to fuel biorefining process is generally classified into three categories as chemical, biochemical and thermochemical methods. The present article aims to provide a state-of-the-art review on the factors affecting the thermochemical conversion process of algal biomass to bioenergy. Further, reaction conditions of each techniques (torrefaction, pyrolysis, gasification and hydrothermal process) influence biochar, bio-oil and syngas yield were discussed. Reaction parameters or factors such as reactor temperature, residence time, pressure, biomass load/feedstock composition, catalyst addition and carrier gas flow affecting process efficiency in terms of product yield and quality were spotlighted and extensively discussed with copious literature. It also presents the novel insights on production of solid (char), liquid (bio-oil) and gaseous (syngas) biofuel through torrefaction, pyrolysis and gasification, respectively. It is found that the energy intensive drying was more efficient mode involved in thermochemical process for wet algal biomass. However other modes of thermochemical process were having unique feature on improving the product yield and quality. Among the various factors, reaction temperature and residence time were relatively more important factors which affected the process efficiency. The other factors signposted in this review will lay a roadmap to researchers to choose an optimal thermochemical conditions for high quality end product. Lastly, the perspectives and challenges in thermochemical conversion algae biomass to biofuels were also discussed.

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## 1. Introduction

Algae are diverse group of aquatic living organism which perform photosynthesis to convert CO<sub>2</sub> and H<sub>2</sub>O into various energy rich products. Algae are broadly classified as either microalgae or macroalgae (Davis et al., 2011; Mohsenpour et al., 2021). Algae can grow in fresh water, seawater and brackish water and can be either autotrophic or heterotrophic or mixotrophic (Choudhary et al., 2020). The major advantages of algae are higher growth rate with lesser water consumption, high efficiency CO<sub>2</sub> mitigation, and cost effective farming. Furthermore, it produces more oil with less utilization of land for its cultivation and harvesting. All these mentioned benefits prove that the algae is third generation biofuel feedstock looks promising resource for biofuel production. Algae contain three principal components such as carbohydrates (4 to 57%), lipids (7 to 23%) and proteins (6 to 71%) (Prajapati et al., 2013). It is one of the most promising bio energies which further can be processed into various bio fuels such as bio ethanol, bio diesel, bio butanol, bio hydrogen etc. (Kumar et al., 2020). Biomass derived fuels are categorized into solid (Biochar), liquid (Bio-oil/Bio-crude, Bioethanol, Biodiesel) and gaseous (Syngas) fuels depending on the conversion process parameters and the type of feedstocks used (Saber et al., 2016). Algae biomass to biorefining process generally has three categories. They are; chemical conversion (transesterification for biodiesel production), biochemical (photo fermentation, dark fermentation, anaerobic digestion generally with the involvement of microbes) and thermochemical method (for biochar, bio-oil and syngas production).

Biochemical conversion process involves anaerobic digestion and fermentation which makes use of micro-organisms, enzymes, etc. to convert biomass to gaseous or liquid fuels (Demirbas, 2011). Conversely, thermochemical process involves combustion, gasification, hydrothermal processing, torrefaction, pyrolysis, etc., which converts biomass to value added fuels and chemicals under optimized operating conditions (Raheem et al., 2015; Tekin et al., 2014). Comparing to all three

biorefining process; thermochemical route looks simpler one for biofuel conversion from algal biomass. The chemical conversion route is complex and tedious as the biomass need to be further processed or purified. This is because transesterification process needs to be installed with the provision of methanol recycle (Huang et al., 2010). Similarly, in case of biochemical conversion route, the feedstock undergoes fermentation process which requires several days to convert into biofuels (Chen et al., 2015a). In view of increasing the efforts on cultivating and harvesting algal biomass and its conversion to bioenergy, thermochemical route looks promising. To avert the dewatering and harvesting expenses, thermochemical methods are being investigated by many researchers to obtain solid, liquid and gaseous products from algal biomass. This is due to its economic viability and high efficiency (Chen et al., 2015a).

Some recent review articles related to microalgae focused on optimizing the algal bio-refinery and discussed the challenges on thermochemical routes (Chandra et al., 2019; Fan et al., 2020). A critical review on biochemical and thermochemical conversions of waste grown algae was carried out by Choudhary et al. (2020). They discussed the scope of improvements in energy efficiency of each method. The production of hydrogen from algal biomass through thermochemical route was assessed by Kumar et al. (2019). The study reported that the gasification (supercritical) was a promising route for hydrogen production after analysing the initial techno-economic analysis. However, further process optimization is required to increase the fuel production. Pandey et al. (2019) revealed that higher temperature and suitable steam to biomass ratio were the major influential factors for getting higher hydrogen yield using thermochemical methods. Recent developments on pyrolysis process in specific to biochar and bio-oil production was reviewed by Sekar et al. (2021). It is reported that the microwave assisted pyrolysis process achieved more significance on yield of bio-oil and bio-gas due to higher and rapid heating during the process than other sub processes and also highlighted that product quality improved significantly with catalytic pyrolysis. The two-sub

thermochemical processes (pyrolysis and hydrothermal) were compared by Vardon et al. (2012). It is reported that hydrothermal process was more energy efficient thermochemical conversion route for handling wet biomass (Vardon et al., 2012). Arvindnarayan et al. (2017) analysed the challenges and opportunities of commercial scale algal to energy conversion through thermochemical conversion methods in specific hydrothermal and pyrolysis route. Most of the works paid attention on output products (Kumar et al., 2019; Pandey et al., 2019; Sekar et al., 2021; Wu et al., 2012) and its optimization (Chandra et al., 2019; Fan et al., 2020; Raheem et al., 2015; Tekin et al., 2014).

Mechanism underpinning the thermochemical conversion of biomass to fuel phenomena is still intricate. Further, each thermochemical process operates in different and its own reaction conditions based on the end product yield. Therefore, influence of all reaction conditions or parameters on the thermochemical process efficiency is prerequisite to choose an optimal process in maximizing the end product yield. Therefore, this article extensively reviewed the all-inclusive factors affecting the thermochemical process efficiency of biomass to fuel.

## 2. Thermochemical method

Thermochemical conversion method is one of the most efficient modes to convert biomass into bio-fuel (Chan et al., 2019). This process is more advantageous compared to biochemical route due to its flexibility in handling various types of biomass and it is also one of the direct, rapid and simple routes of conversion method. In this process, thermal decomposition of organic matters occurs at very high temperature where biomass yield decomposes and forms bio-oils and gases. This is one of the most promising one, which is subdivided in to four various processes such as torrefaction, pyrolysis, gasification and hydrothermal process (Chen et al., 2015a; Chiamonti et al., 2015) as mentioned in Fig. 1.

A schematic layout in Fig. 1 describes an overview of thermochemical process and its classifications. The main classifications again divided into sub-classifications such as torrefaction process is further classified as conventional, microwave, wet and oxidative torrefaction. Based on torrefaction temperature, it is further classified as light (200 to 235 °C), mild (235 to 275 °C) and intense (275 to 300 °C) torrefaction processes (Chen et al., 2014a). Conventional torrefaction process takes place in the presence of inert gas or carrier gas (mainly nitrogen) at a temperature of 200–300 °C and at time duration of 10–60 min with atmospheric pressure (Zhang et al., 2018). Oxidative torrefaction is similar to conventional torrefaction process and the air is used as carrier gas instead of N<sub>2</sub> and in some cases, other oxidative gases are used (Ho et al., 2020; Zhang et al., 2019). In microwave torrefaction process, the biomass is pyrolyzed from the interior material by utilizing microwave irradiation (Motasemi and Afzal, 2013). In wet torrefaction process, the biomass is treated in the hydrothermal or hot compressed water at a temperature of 180–260 °C for a duration of 10–240 min. The whole process of wet torrefaction occurs at a high-pressure condition that is above the saturated vapour pressure of water (Bach and Skreiberg, 2016). The key advantages of torrefaction process are higher reliability and stability with ease of control. Higher operational cost and residence time are the limitations in the process (Ho et al., 2020; Zhang et al., 2019). However, microwave torrefaction process is one of the method to save time to improve the physiochemical properties of the torrefied algal biomass but the investment cost is comparatively high (Zhang et al., 2019).

Pyrolysis process also is subdivided into four categories such as slow, fast, microwave and catalytic pyrolysis process. The fast pyrolysis process takes place in higher heating rate (600–36,000 °C/min) with less residence time (0.003–0.05 min) whereas, slow pyrolysis takes place in lower heating rate (3.5–10 °C/min) with very long residence time

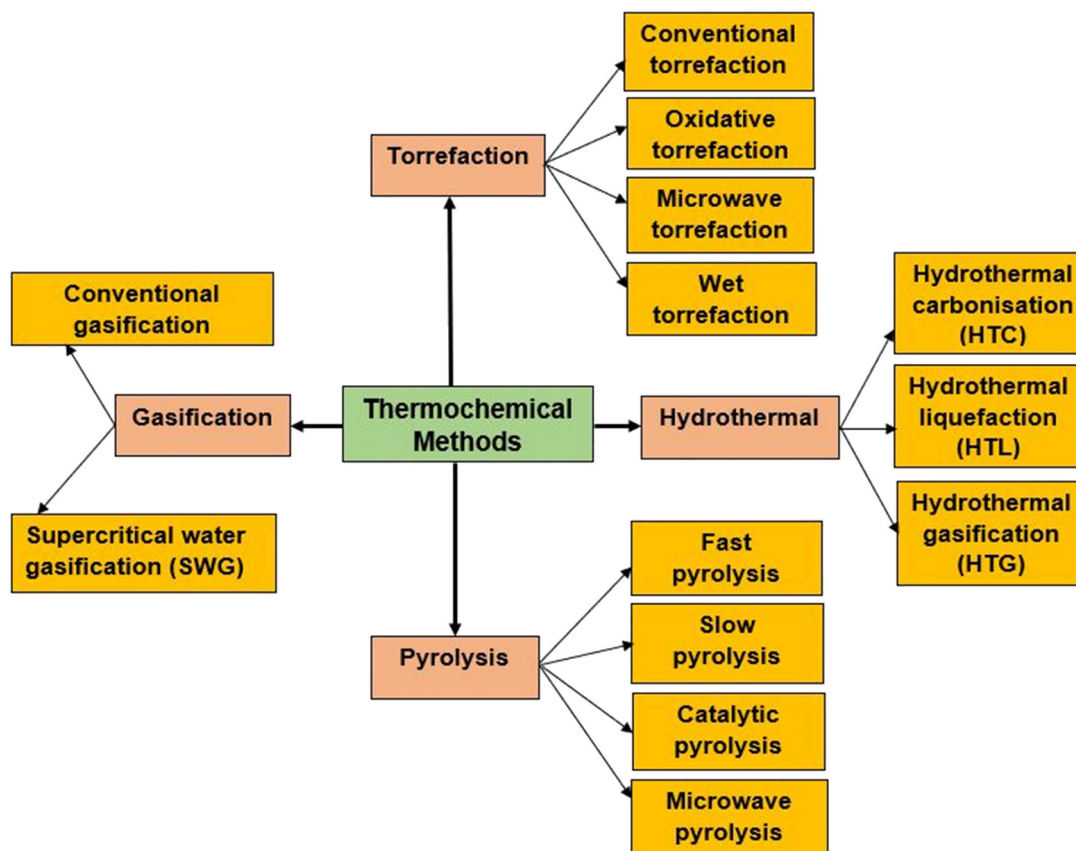


Fig. 1. Schematic layout of thermochemical process and its classifications.

(20–120 min). This process occurs at a temperature range of 300–800 °C. The maximum reaction temperature required for microwave pyrolysis is 800 °C whereas, in case of catalytic pyrolysis, it is low as 300 °C. But normally, pyrolysis takes place in the absence of oxygen at a temperature of 400–600 °C with atmospheric pressure (Auersvald et al., 2019; Lee et al., 2017). Overall, the fast pyrolysis process is one of the cost effective and highly efficient method. This process is more advantageous in terms of storage and transport of liquid fuels compared to other process whereas slow pyrolysis is advantageous for higher oil-yield applications (Chen et al., 2015a; Campanella and Harold, 2012). The major disadvantage of slow pyrolysis process is, its higher residence time. This process takes a higher energy input due to lower heating rate with high residence time. Compared to all sub pyrolysis processes, microwave pyrolysis is the energy efficient due to its less energy input required and fewer ash generation than other methods (Hu et al., 2012).

Hydrothermal process is another sub category of thermochemical process which classified into hydrothermal carbonization (HTC), hydrothermal liquefaction (HTL) and hydrothermal gasification (HTG). HTC takes the temperature of 200 °C and pressure less than 2 MPa within 60 min of residence time. Whereas, HTL takes 300 to 350 °C and pressure of 5–20 MPa with the residence time of 5 to 60 min. In HTG, the wet biomass (almost 80% of moisture) can be processed hydrothermally without drying so that the cost of drying is saved. In this mode, algal biomass can be directly converted into gas beyond the critical point of water (Jena and Das, 2011). Solid deposition and corrosion in the reactor are the major disadvantages of the process due to its operating conditions at critical temperature and pressure (Chiamonti et al., 2015).

Similarly, gasification process is subdivided into either conventional process or supercritical water gasification (SWG). The conventional gasification takes place with the temperature range of 800 to 1000 °C and the pressure range between 0.1 and 1 MPa. In SWG, algal biomass is directly converted into gas beyond the critical point of water (373.946 °C, 22.064 MPa). The major advantage of the process is that H<sub>2</sub> yield increases with increase in gasification temperature (Raheem et al., 2017). SWG process is an energy efficient one as biomass can be fed without drying, thus cost of drying is saved as the same as HTG method. The reported limitation is, the gasification efficiency decreases with repeated use of catalysts during the process (Duan et al., 2018; Guan et al., 2012). Based on the main product (solid/liquid/gas) from the algae feedstock to biofuel conversion, the processes are basically parted in to two categories such as dry processes and wet processes (Chen et al., 2014b). The various processes are discussed in detailed manner to explore further more on algal biomass to energy conversion.

### 3. Factors affecting the process efficiency of thermochemical method

The factors of process efficiency of different thermochemical methods such as torrefaction, pyrolysis and gasification processes are reviewed in further sections. Also, the factors affecting the hydrothermal treatment are also explained in this section. The microalgae conversion process is dependent on various operating conditions. As already highlighted in the Section 2, the important operating conditions are reaction temperature, residence time, and pressure. Apart from these three major variables, particle size, presence of catalyst, feedstock composition, etc. also affect the physical and chemical properties of biofuels. The effect of various factors affecting different modes of thermochemical process is discussed in the following sections.

#### 3.1. Factors affecting torrefaction process

Torrefaction is a pre-treatment process which is intended to improve the physiochemical properties of torrefied biomass. Due to the torrefaction process, fuel characteristics of algal biomass are improved

further because of changes in the physiochemical properties such as moisture content, ash, density, viscosity, grindability, fixed carbon and volatile content. Moisture content in the algal biomass is one of the important properties affecting the process efficiency. With higher content of moisture results in more energy loss during pre-drying or heat treatment process (Chen et al., 2011, 2015b). Solid yield, energy yield, higher heating value (HHV), energy efficiency and the enhancement on aforementioned physiochemical properties are also discussed in this section by keeping in mind about the various factors affecting the process. Torrefaction condition such as temperature, residence time, composition of biomass are the major influential factors affecting the process parameters and efficiency. The products after torrefaction process can be comparable with coal or wood due to its enhanced properties.

The operating condition of torrefaction process such as temperature, pressure and residence time are 200 to 300 °C, 0.1 MPa and 10 to 60 min, respectively. The major products from the torrefaction process are either in the form of solid, liquid or gas (Ho et al., 2020).

#### 3.1.1. Torrefaction temperature

Mass yield decreases with increase in torrefaction temperature and residence time (Phusunti et al., 2018). Many studies (Chen et al., 2015a, 2014b) observed that torrefaction temperature is the major influential parameter compared to residence time on decrease in mass yield. Increase in torrefaction temperature and time results in increase in HHV because of increase in carbon yield (or it can be said that fixed carbon content increases the post-torrefaction process). In conventional torrefaction process, increase in temperature results in significant decrease in solid yield and energy yields (Phusunti et al., 2018) due to moisture removal and volatile content released during thermal treatment of biomass. Energy yield is the amount of energy retained in post-torrefaction process. It is largely depending upon the mass yield values as energy yield is the product of mass yield and ratio of HHV of torrefied biomass to HHV of raw biomass (Matali et al., 2016). In wet torrefaction process, with increase in temperature and residence time, the solid and energy yields decrease significantly but there is an increase in calorific values and energy retention post-torrefaction. The ash content increases from 7.68 to 14.71% when temperature is increased from 150 to 300 °C also, the moisture content decreases during the increase in temperature. The moisture content is reduced to 2.34 wt % at 200 °C from an initial moisture of 5.47% (Phusunti et al., 2018) at the holding time of 30 min.

#### 3.1.2. Residence time/holding time

Apart from the reaction temperature, residence time or holding time is also one of the pivotal factors which affects the process efficiency of biomass conversion process. The effect of residence time is similar to temperature. The increase in residence time and torrefaction temperature decrease the volatile content significantly but fixed carbon content of the biomass increases (Wang et al., 2018). The carbon content of the torrefied biomass increases significantly and it can be compared with its parental (or raw) biomass. The elemental analysis on torrefied biomass (Bach and Skreiberg, 2016) proved that the volatile content decreased from 72.73% to 38.97% and the fixed carbon content increased from 15.9 to 40.5% of wt. when the temperature is increased from 150 to 300 °C and residence time is increased from 15 to 60 min, respectively.

#### 3.1.3. Particle size

The smaller particle size increases the quality of grindability which lowers the energy required for grinding (Basu, 2013). The biomass composition is changed due to variation in ash content. As there are both organic and inorganic matters present in the biomass composition, organic matters degrade easily, whereas decomposition of inorganic matters does not take place which leads to increase in ash content (Wu et al., 2012).

### 3.1.4. Carrier gas

Oxidative torrefaction process occurs in the presence of air or other oxidative gas as carrier gas (Leng et al., 2018; Zhang et al., 2019) whereas, all other torrefaction processes, N<sub>2</sub> is used as carrier gas (Chen et al., 2014b; Phusunti et al., 2018). For the thermal degradation of biomass, N<sub>2</sub> is more effective compared to CO<sub>2</sub> as carrier gas. With lesser residence time, oxidative torrefaction gives higher energy efficiency compared to non-oxidative process (Zhang et al., 2019). Another important observation is, the bio-char produced through oxidative process possess higher energy and solid yields compared to other processes with same torrefaction conditions. The studies suggested that microwave torrefaction gave better solid yield compared to conventional due to its shorter residence time and higher energy efficiency.

In summary, among the various factors affecting torrefaction process, reaction temperature is relatively more important factor compared to others. The HHV of torrefied biomass increases with increase in carbon yield. However other factors such as residence time, carrier gas and particle size also influence the overall product yield and quality.

### 3.2. Factors affecting pyrolysis process

The thermal decomposition of biomass through pyrolysis process divided into three major steps such as dehydration, devolatilization and decomposition. The main products are in the form of solid, liquid or condensable gases as mentioned earlier. Solid residues from the pyrolysis process are referred as bio-char and liquids are referred as bio-oil or bio-crude whereas gas product generated from the process referred as syngas or bio-syngas (Sirajunnisa and Surendhiran, 2016; Xiong et al., 2017). These products are used in different field of application such as waste water treatment, power generation, transportation and agricultural sector. The bio-oils produced from algal conversion through pyrolysis process are comparatively more stable than those produced from lignocellulosic biomass (Auersvald et al., 2019; Dai et al., 2020). The reaction temperature with bio-oil and bio-char yield for pyrolysis mode conversion of algal biomass are mentioned in Table 1.

Table 1 shows that the maximum bio-oil yields obtained during thermochemical process. The maximum bio-oil yield obtained are; *Chlorella vulgaris* - 72 wt% (Belotti et al., 2014), *Chlorella protothecoides*

- 57.9 wt% (Miao and Wu, 2004), *Nannochloropsis* sp. has the range of 41–59 wt% (Borges et al., 2014), *Chlorella* sp. - 35–55 wt% (Babich et al., 2011) etc. The bio-char yield obtained in the algae are; *Chlamydomonas reinhardtii* - 44% (Torri et al., 2011) and *Chlorella vulgaris* in the range of 19.3 to 43.4% (Yuan et al., 2015) etc. The reaction temperature maintained is 500 °C in most of the attempts (Aysu et al., 2016; Campanella and Harold, 2012; Grierson et al., 2009) however, the product yield increases at higher temperature of 900 °C (Yuan et al., 2015). There are various factors such as pyrolysis operating conditions, feedstock composition, types of reactors used are the major influential parameters which affect the performance of the process. Some other factors like catalytic loading rate, size of particle, carrier gas and gas flow rate also affect the process. By properly controlling these aforementioned factors during the process, quality and product yield can be optimized. In this study, all the factors affecting pyrolysis process are explored.

#### 3.2.1. Reaction temperature

Temperature plays an important role on the product yield and final output of the process. Dehydration of algal biomass occurs below 200 °C whereas, the devolatilization happens in the range of temperature between 200 and 550 °C and decomposition of solid biomass occurs above 550 °C (Adeniyi et al., 2018; Marcilla et al., 2013; Pragy et al., 2013). Secondary cracking reaction takes place above 550 °C which results in decrease in bio-oil yield as larger molecules of hydrocarbon are broken into smaller molecules. Further increase in the temperature results in increase in carbon content in the yields and leads to the formation of aromatic hydrocarbons.

The temperature in pyrolysis has significant role on composition of final products and product yields. When the temperature is increased, the production of solid yield (char) decreases and at the same time there is an increase in gaseous yield (Ly et al., 2016). Due to development of more volatile products, yield of bio-char decreases whereas the carbon content increases with increase in temperature. The quality of the bio-oil is also improved with increase in hydrocarbon content as well as heating value during the pyrolysis process. Increase in temperature from 300 to 500 °C results in decrease of bio-char yield from 45.3 to 24.2% of wt. whereas, increase in aqueous and gaseous product

**Table 1**  
Reaction temperature, bio oil and bio-char yields during the pyrolysis and gasification of algal biomass.

Microalgal strains	Temperature (°C)	Bio-oil yield (%)	Biochar yield (%)/gas yield	References
<i>Chlorella protothecoides</i>	500	17.5	–	(Miao et al., 2004)
<i>Chlorella protothecoides</i>	500	52	–	(Peng et al., 2000)
<i>Chlorella protothecoides</i>	450	57.9	–	(Miao and Wu, 2004)
<i>Chlorella vulgaris</i>	400	72	~22	(Belotti et al., 2014)
<i>Chlorella vulgaris</i>	500	53	31	(Wang et al., 2013)
<i>Chlorella vulgaris</i>	300–900	–	19.3–43.4%	(Yuan et al., 2015)
<i>Chlamydomonas reinhardtii</i>	350	–	44%	(Torri et al., 2011)
<i>Scenedesmus dimorphus</i>	300–600	–	Surface area increased from 1.72 to 123 m <sup>2</sup> /g	(Bordoloi et al., 2016)
<i>Cladophora glomerata</i>	400	–	44	(Norouzi et al., 2016)
<i>Chaetoceros muelleri</i>	500, 20 min	33%	–	(Grierson et al., 2009)
<i>Dunaliella tertiolecta</i>	500, 20 min	24	–	(Grierson et al., 2009)
<i>Nannochloropsis</i> sp.	300–500, 2 h	21–31	–	(Pan et al., 2010)
<i>Spirulina platensis</i>	350–500, 1 h	23–29	–	(Jena and Das, 2011)
<i>Chlorella</i> sp.	300–450, 30 min, Na <sub>2</sub> CO <sub>3</sub>	35–55	–	(Babich et al., 2011)
<i>Chlorella</i> sp.	500	29–36	–	(Campanella and Harold, 2012)
<i>Nannochloropsis</i> sp.	450–550, 30 min	41–59	–	(Borges et al., 2014)
<i>Tetraselmis</i> sp.	500	25.86	~18	(Aysu et al., 2016)
<i>Isochrysis</i> sp.	500	25.49	~25	(Aysu et al., 2016)
<i>Pavlova</i> sp.	500	23.2	~34	(Aysu et al., 2018)
<i>Scenedesmus dimorphus</i>	500	39.6	~27	(Bordoloi et al., 2016)
<i>Isochrysis</i> sp.	475	49.36	–	(Zhao et al., 2015)
Gasification of algal biomass				
<i>Chlorella vulgaris</i>	350, 18 MPa pressure, nickel catalyst	–	Majorly 44–49% CO <sub>2</sub> , and 16–38% CH <sub>4</sub>	(Minowa and Sawayama, 1999)
<i>Nannochloropsis</i> sp.	400–500, 35 MPa	–	Majorly 36% CO <sub>2</sub> , and 37% CH <sub>4</sub>	(Brown et al., 2010)
<i>Phaeodactylum tricornutum</i>	400, 30 MPa, Ru/C catalyst	–	Majorly 40–84% CO <sub>2</sub> , and 34–86% CH <sub>4</sub>	(Haiduc et al., 2009)
<i>Scenedesmus almeriensis</i>	550, 30 min	–	Majorly, ~7.5 mmol/g CO <sub>2</sub> , and 7 mmol/g CH <sub>4</sub>	(Guan et al., 2012)

yield from 13.8 to 20% and 18.9 to 33.5%, respectively (Pan et al., 2010). It is reported that with increase in temperature from 300 to 450 °C, the bio-oil yield increases from 35 to 55% (Babich et al., 2011). When the reaction temperature is increased from 400 to 700 °C, HHV increases from 17.75 to 20.23 MJ/kg (Belotti et al., 2014). Similarly, increase of heating rate directly influences the composition and the final product yield from algal biomass. At lower heating rate, bio-char yield increases. Also, with increase in microwave power from 500 to 750 W, oil-yield increases and reaches to 28.6%, and then it decreases gradually. In contrary, bio-char production decreases when microwave power is increased up to 750 W and after that it remains constant (Du et al., 2011). The enhancement in bio-fuel yield takes place from 74.93% to 87.47% in the presence of 5% of activated carbon as catalysts for microwave assisted power of 2250 W.

### 3.2.2. Residence time/holding time

Holding time or residence time is also another important factor which directly influences the bio-char yield as longer the residence time, higher the bio-char yield. It is one of the deciding parameters to distinguish the nature of pyrolysis process either it is slow or fast. For slow pyrolysis process, the residence or holding time is longer compared to fast pyrolysis process. The char production increases with higher holding time as complete repolymerization of biomass takes place with longer time. Similarly, heating rate also plays an important role on bio-oil or bio-char yield. Longer residence time with low heating rate leads to higher char yield while shorter residence time with high heating rate leads to more oil-yield.

### 3.2.3. Feedstock composition

Feedstock composition is one of the influencing parameters affecting the quality and structure of final product from the process. The carbon yield largely depends upon the presence of carbohydrate content in the algal biomass. From various literatures (Ji et al., 2015; Wang et al., 2013), it is observed that, the final product is having different structural composition as well as physicochemical properties produced from algal biomass compared to lignocellulosic biomass. The bio-char produced from algal biomass through this route is highly enriched in nutrients (Na, Ca, Mg, K and P) and can be used as fertilizer (Wang et al., 2013). The oil-yield of microalgae residues contain higher alkane substances and less aromatics compared to lignocellulose biomass (Ji et al., 2015). Microalgae has higher lipid content compared to macroalgae; thus, it is one of the potential candidates for producing higher oil-yield. So, selection of feedstock is one of the important criteria for yield of various products based on process feasibility and economic constraints.

### 3.2.4. Particle size

Particle size of algal biomass affects the properties of bio-oil and product yield. It is observed that with increase in particle size results in reducing bio-oil yield and increase the bio-char yield. The larger particle size required more heat and energy for activation compared to small particle size biomass. But the smaller particle size biomass creates an increase of cost of handling during the process therefore, processing time is also increased. It is suggested to go for an optimization of biomass particle size which is necessary to improve the product yield. Particle size of 1 mm or less than is preferred for oil-yield whereas, it is more than 2 mm for bio-char production during slow pyrolysis process. As the particle size increases, the distance between surface to centre of the particle increases which results in decrease of heat transfer capability (Kocer et al., 2018). This is due to longer travel distance and increase in heat resistance which further leads to incomplete pyrolysis of the biomass.

### 3.2.5. Carrier gas

Carrier gas and its flow rate provides a better environment to carry forward the pyrolysis process in the reactor. Inert gases such as N<sub>2</sub>, He or Ar are used as carrier gas due to its non-reactive nature. The gas

flow rate depends on the types of pyrolysis used. The presence of carrier gas improves the performance of process significantly without involving in the reaction. Most of the studies used N<sub>2</sub> as a carrier gas (Belotti et al., 2014; Pan et al., 2010; Vardon et al., 2012; Wang et al., 2013). A few attempts on other inert gases such as He (Borges et al., 2014; Campanella and Harold, 2012; Grierson et al., 2009) and Ar (Babich et al., 2011) are applied as carrier gases due to their easily availability, low cost and also, they provide inert atmosphere during the process. The effect of carrier gas flow (N<sub>2</sub>, 10% H<sub>2</sub> or Ar and CO<sub>2</sub>) on microwave assisted pyrolysis (with microwave assisted power of 600 W and 10% of activated carbon as catalyst) was evaluated by Zhang et al. (2016). It was found that the maximum oil-yield was 49.1%, 51.7% and 54.3% for carrier gas flow of N<sub>2</sub>, 10% (H<sub>2</sub>/Ar) and CO<sub>2</sub>, respectively. At carrier gas flow rate of 0.3 L/min, the production of char, liquid and gas yields were in the range of 37.2–32.3, 40.9–37.1 and 21.9–30.6% of wt., respectively. For the same flow rate, HHV estimated was 12.59 and 32.97 MJ/kg for bio char and bio oil, respectively, at a temperature of 350 °C (Agrawal and Chakraborty, 2013).

### 3.2.6. Catalysts

Catalytic mode of pyrolysis improves the quality and yield of final products. As the presence of catalysts affects the product yield, so, special care should be taken while selecting the catalyst for biomass during pyrolysis process. From literature, it is noticed that bio-char yield is improved with the acid catalysts whereas, bio-oil yield is improved with base catalysts (Babich et al., 2011; Campanella and Harold, 2012). There are few attempts have been taken to produce exact amount of required hydrocarbon from the process using catalysts. ZSM-5 zeolites with metal ions (H-, Fe-, Cu- and Ni-) can improve the yield of bio-oil and composition of hydrocarbon. The major catalysts used during catalytic process are Na<sub>2</sub>CO<sub>3</sub> and ZSM-5 zeolites (Babich et al., 2011; Campanella and Harold, 2012; Pan et al., 2010). Bio-oil yields with and without the presence of catalysts were 59 and 57%, respectively, whereas HHV of bio-oil reduced in the presence of catalyst. HHVs of bio-oil produced with and without the presence of catalyst were 26.8 and 32.37 MJ/kg and 27.15 and 42 MJ/kg, respectively, for *Chlorella* sp. and *Nannochloropsis* algal biomass (Borges et al., 2014). Few more attempts have been taken on microwave assisted pyrolysis in the presence of catalysts to increase the bio-oil yields and physicochemical properties (Hu et al., 2012).

All the factors affecting pyrolysis process is having significant influence on final product yield as well as product quality. Reaction temperature and residence time are the deciding parameters to distinguish the nature of pyrolysis process as fast or slow. These factors (heating rate and residence time) are relatively more influential for improving product yield and physicochemical properties. Apart from this, other factors such as particle size, catalysts, carrier gas and biomass composition etc. must be carefully selected to optimize the process efficiency and to enhance the biochar or bio-oil yield further.

## 3.3. Factors affecting gasification process

Gasification method is another thermochemical conversion route which converts algal biomass into bio-fuels. The carbonaceous material in algal biomass is converted into syngas, bio-oils, tar, ash and char as the final output from the process. The studies performed in the gasification process with various algal biomass by different researchers are collected and mentioned in Table 1 with the product output and reaction conditions.

From the Table 1, it is observed that in the gasification process, the operating pressure varies up to 35 MPa (Brown et al., 2010). The reaction time or holding time plays an important role in energy saving and production efficiency. The presence of catalyst such as Ni (Minowa and Sawayama, 1999) or Ru/C (Haiduc et al., 2009) influences the syngas production with product yield. The maximum syngas production such as CO<sub>2</sub> and CH<sub>4</sub> of *Phaeodactylum tricornutum* microalgae in the

presence of Ru/C catalyst are in the range of 40 to 84% and 34 to 86%, respectively (Haiduc et al., 2009). However, for *Chlorella vulgaris*, the productions of CO<sub>2</sub> and CH<sub>4</sub> are in the range of 44 to 49% of wt. and 16 to 38% of wt. respectively (Minowa and Sawayama, 1999). It is observed that the gasification temperature, residence time, microalgal loading rates and types of catalysts used are the major influential factors which affects the process efficiency during gasification process. Conventional and supercritical water gasification (SWG) are the two modes of gasification process as discussed earlier in Section 2. The various aforementioned factors affecting the final fuel composition, product yield such as bio-gases, tar reforming, bio-oil or bio-char and effect on gasifying efficiency and carbon efficiency are explored in detail in this section.

### 3.3.1. Gasification temperature

Increase in gasification temperature significantly enhances H<sub>2</sub> production, but decreases CH<sub>4</sub> and CO<sub>2</sub> yields in the biomass. Therefore, there is a reduction in tar and char production. Higher temperature is one of the most influential parameters to improve the gasification efficiency, hydrogen yield and methanol yield. It is reported that the carbon conversion ratio enhances from 93 to 103% when the gasification temperature is increased from 750 to 1000 °C (Hirano et al., 1998). Higher temperature has a potential to increase the hydrocarbon yield in the biomass but gives a contrary effect on oxygenated compounds such as nitrogen content and phenolic compounds (Li et al., 2020). With excessive increase in temperature, the energy consumption and operating cost become higher, which is not feasible for lower energy applications. Therefore, it is a necessary to evaluate the optimized gasification temperature from the trade-off between gasification efficiency and energy consumption. The optimized temperature, loading rate and residence time estimated were 851 °C, 16.4% of wt., 28.8 min, respectively, for the microalgae of *Chlorella vulgaris* in the presence of tri metal oxide catalyst (ZnO-Ni-CaO) (Raheem et al., 2018). The estimated maximum H<sub>2</sub>, CO, CO<sub>2</sub> and CH<sub>4</sub> gas fractions were 48.95%, 18.27%, 22.64% and 10.12% of vol. for the same optimized condition. At 500 °C, the estimated carbon, hydrogen and oxygen yield were 42, 66 and 76%, respectively (Brown et al., 2010). Similarly, for an optimum temperature of 825 °C, H<sub>2</sub>, CO, CO<sub>2</sub> and CH<sub>4</sub> gas fractions were 30.7%, 24.4%, 27.9% and 19.2% of vol., respectively (Raheem et al., 2017).

### 3.3.2. Equivalence ratio

The increase in equivalence ratio (ER) results in improving temperature, fuel quality as well as conversion efficiency. It is observed that with increase in ER, the gas composition in algal biomass decreases slightly for H<sub>2</sub>, CH<sub>4</sub> and CO but a minor enhancement noticed in CO<sub>2</sub> composition. The enhancement in CO<sub>2</sub> with increase in ER is because of increase in oxygen supply into the gasifier during oxidation process (Yang et al., 2013). There are few studies on ER (0.1–0.35) and to optimize the overall gasification conditions (Raheem et al., 2017). The optimized ER was 0.26 and total gas, bio-char and estimated tar reforming were 77.1, 14.1 and 8.7% of wt. respectively. When ER increases from 0.15 to 0.35, the gas yield increases from 1.14 to 1.93 m<sup>3</sup>/kg whereas there is a decrease in lower heating value (LHV) from 7.09 to 3.26 MJ/m<sup>3</sup> (Vardon et al., 2012).

### 3.3.3. Operating pressure

From most of the studies, it was observed that the conventional gasification occurred at the pressure of 0.1–1 MPa whereas SWG, the pressure was in the range of 22.1 to 36 MPa (Chen et al., 2015a). The carbon gasification rate decreases significantly with increase in pressure. The moderate range of pressure which lies equivalent to supercritical condition pressure (22.1 MPa) gives better gasification condition. There is no significant role on the performance of biomass and product yield, if the pressure increases beyond the supercritical pressure (Haiduc et al., 2009).

### 3.3.4. Holding time/reaction time

Holding time or reaction time is the important parameters required for complete combustion of biomass. Also, it is one the important parameters to increase the process efficiency, product yield and energy yield. When the rate of reaction is constant, the extended reaction time is necessary to complete the reaction. The selection of appropriate reaction time is essential to reduce energy consumption and improving production efficiency.

### 3.3.5. Catalyst loading rate

The catalytic loading also affects the process efficiency. There are numbers of catalysts reported in the literature, they are; ZnO/Ni/CaO (Raheem et al., 2017), KOH, NaOH, Pd/C, Ru/C (Guan et al., 2013; Haiduc et al., 2009), Ru/TiO<sub>2</sub> (Chakinala et al., 2010), Ru/ZrO<sub>2</sub> (Stucki et al., 2009), K<sub>2</sub>CO<sub>3</sub>, Na<sub>2</sub>CO<sub>3</sub> (Caputo et al., 2016) and NaOH/Ni-Al<sub>2</sub>O<sub>3</sub> (Onwudili et al., 2013). These catalysts are used to improve the quality of product yield and efficiency of the process. Ru/C catalyst observed to be one of the most efficient one among the catalysts which increases H<sub>2</sub> concentration significantly. There is a noticeable reduction in gas efficiency with repeatability usage of Ru/C (Guan et al., 2013). Complete gasification of algal biomass (*Chlorella vulgaris*) can be carried out using an excess amount of Ru/TiO<sub>2</sub> catalyst where the gasification efficiency (GE) estimated was 53%. This can be enhanced further to 84% by using nickel-based catalyst for the same gasification conditions (Chakinala et al., 2010). In the presence of catalyst, tar removal efficiency observed to be maximum and it is varied in the range between 80 and 100% (Duman et al., 2014). There is a significant increase in H<sub>2</sub> yield with increase in catalyst loading rate and it is also observed that at 100% loading rate of catalysts of MnO<sub>2</sub>/SiO<sub>2</sub>, the hydrogen sensitivity and gasification efficiency estimated are 41.5 and 28.6%, respectively (Samiee-Zafarghandi et al., 2018). The catalyst structure is more sensitive towards the gasification rate and it affects the composition of gases significantly reported by Tiong and Komiyama (2019).

Among various factors affecting process efficiency and product yield, gasification temperature must be evaluated and optimized from the trade-off between gasification efficiency and energy consumption ratio. Apart from optimized gasification temperature; the other parameters such as reaction time, catalyst, selection of algal biomass and loading rate can significantly improve the gasification process as well as H<sub>2</sub> production.

## 3.4. Factors affecting hydrothermal treatment (HHT)

Hydrothermal treatment (HTT) is another potential mode of bio-energy production from algal biomass. It is further classified into three sub process such as hydrothermal gasification (HTG), hydrothermal liquefaction (HTL) and hydrothermal carbonization (HTC). The major outputs of all the process are in the form of solid (bio-char), liquid (bio-oil or bio-crude) or gaseous (H<sub>2</sub> and CH<sub>4</sub>) products. The studies performed in HTT with various algal biomass by different researchers are mentioned in Table 2 with the product output and reaction conditions.

From Table 2, it is observed that in hydrothermal process, most of the researchers considered the temperature of 300 °C (Reddy et al., 2016; Zhou et al., 2010) or 350 °C (Li and Savage, 2013; Shakya et al., 2015). However, few attempts were made with lower temperature of 230 °C (Hognon et al., 2015). The reaction time or holding time plays an important role in energy saving and product yield. It varies from 5 min to 60 min (Jena and Das, 2011; Yang et al., 2004) whereas, the operating pressure is considered up to 400 bar (Faeth et al., 2013). The maximum bio-oil yield of *Chlorella* microalgae is 94.8% at 300 °C (Biller et al., 2015). For *Botryococcus braunii*, the production of bio-oil yield is 64% of wt. in the presence of 5% Na<sub>2</sub>CO<sub>3</sub> (Dote et al., 1994) catalyst. Similarly, for *Nannochloropsis oceanica*, *S. almeriensis*, *Chlorella* sp., and *Synechocystis* sp., the estimated bio-oil yields were 54% (Caporgno et al., 2016), 62.3% (López Barreiro et al., 2014), 82.9% (Li et al., 2014) and 16.6% (Wagner et al., 2016), respectively. Few attempts

**Table 2**  
Influence of different reaction factors on HTL efficiency of algal biomass.

S. no	Strain	Parameters studied [temperature (°C), reaction time (RT in min), pressure (Psi or bar or MPa)]	Bio-oil yield (%)	Other product yield	Reference
1.	<i>Botryococcus braunii</i>	300, 60 min, 5% Na <sub>2</sub> CO <sub>3</sub>	64	–	(Dote et al., 1994)
2.	<i>Nannochloropsis</i> sp.	300 °C, 30 min RT, 1275 psi	47.5	~22% biochar	(Reddy et al., 2016)
3.	<i>Nannochloropsis</i> sp.	350 °C 1 h,	37	–	(Li and Savage, 2013)
4.	<i>Nannochloropsis</i> sp.	350 °C	43	–	(Brown et al., 2010)
5.	<i>Nannochloropsis oceanica</i>	290 °C	54	–	(Caporgno et al., 2016)
6.	<i>Nannochloropsis</i> sp.	350 °C	48.67	–	(Shakya et al., 2015)
7.	<i>Nannochloropsis</i> sp.	350 °C, 400 bar	23	–	(Faeth et al., 2013)
8.	<i>Nannochloropsis</i> sp.	300 °C, 10 min RT	50	~5%-solid	(Valdez et al., 2012)
9.	<i>Chlorella</i> sp.	300 °C, 30 min RT, 1306 psi	32.5	–	(Reddy et al., 2016)
10.	<i>Chlorella</i>	350 °C	94.8	–	(Billler et al., 2015)
11.	<i>Chlorella</i> sp.	350 °C	27.3	–	(Ross et al., 2010)
12.	<i>Chlorella</i> sp.	220 °C	82.9	–	(Li et al., 2014)
13.	<i>Chlorella pyrenoidosa</i>	280 °C	50	–	(Yu et al., 2014)
14.	<i>C. pyrenoidosa</i>	240 °C, 30 min	31.1	–	(Yu et al., 2014)
15.	<i>C. pyrenoidosa</i>	300 °C, 60 min, 10.7 MPa	72	–	(Yang et al., 2016)
16.	<i>Chlorella pyrenoidosa</i>	280 °C	57.3	–	(Zhang et al., 2014)
17.	<i>Tetraselmis</i> sp. KCTC12236BP	350 °C, 40 min RT	24.65-light 21.41-heavy	9.65%-gas	(Vo et al., 2017)
18.	<i>S. almeriensis</i>	325 °C, 15 min, no catalyst	62.3	5.6%-solid, and 15.7%-gas	(López Barreiro et al., 2014)
19.	<i>Chlamydomonas reinhardtii</i>	230 °C, 1 h RT, 10–20 MPa	71.4	~16%-gas	(Hognon et al., 2015)
20.	<i>Dunaliella tertiolecta</i>	360 °C	25.8	–	(Shuping et al., 2010)
21.	<i>Dunaliella tertiolecta</i>	300 °C, 5 min	43	–	(Minowa and Sawayama, 1999)
22.	<i>Phaeodactylum tricornutum</i>	350 °C, 15 min RT, 28 MPa pressure	38.8	6.1%-solid, 6.5%-gas	(Christensen et al., 2014)
23.	<i>Desmodesmus</i> sp.	375 °C, 5 min	49.4	~24.3%-gas	(Torri et al., 2012)
24.	<i>Desmodesmus</i> sp.	375 °C, 5 min	49	–	(Garcia Alba et al., 2012)
25.	<i>S. platensis</i>	350 °C, 60 min RT, 3000 psi	40.7	6.7%-char ~23%-gases	(Jena and Das, 2011)
26.	<i>Arthrospira platensis</i>	310 °C	~36	–	(Raikova et al., 2016)
27.	<i>Arthrospira platensis</i>	350 °C	35	–	(Lavanya et al., 2016)
28.	<i>Tetraselmis</i> sp.	350 °C	40	–	(Lavanya et al., 2016)
29.	<i>Tetraselmis</i> sp.	350 °C	65	1.6 (H/C)	(Christensen et al., 2014)
30.	<i>Pavlova</i> sp.	350 °C	47.05	–	(Shakya et al., 2015)
31.	<i>Spirulina</i> sp.	340 °C	36.9	–	(Wagner et al., 2016)
32.	<i>Spirulina</i> sp.	260 °C	43.05	–	(Tian et al., 2018)
33.	<i>Spirulina</i> sp.	350 °C, 60 min	61	–	(Matsui et al., 1997)
34.	<i>Synechocystis</i> sp.	340 °C	16.6%	–	(Wagner et al., 2016)
35.	<i>Microcystis viridis</i>	60 min RT, 10–20 MPa	31.6	–	(Yang et al., 2004)
36.	<i>Enteromorpha prolifera</i>	300 °C, 30 min RT, 5 wt% Na <sub>2</sub> CO <sub>3</sub>	23	–	(Zhou et al., 2010)
37.	<i>Cyanidioschyzon merolae</i>	300 °C, 30 min, 120 bar	16.98	Biochar-14.50%, gas-48.48%	(Muppaneni et al., 2017)
38.	<i>Laminaria saccharina</i>	350 °C, 15 min, 1:10 biomass: water ratio	19.3	–	(Anastasakis and Ross, 2011)
39.	<i>Enteromorpha prolifera</i>	290 °C	28.4	–	(Yang et al., 2014)

have been taken to evaluate the bio-char or solid yield and gases through different algal biomass. For *Phaeodactylum tricornutum* algae, the solid and gas yields are 6.1 and 6.5%, respectively (Christensen et al., 2014) whereas, the gas yield of *Desmodesmus* sp. algal biomass is 24.3% (Torri et al., 2012). The biochar and gas yields of *Cyanidioschyzon merolae* algae are 14.5 and 48.48%, respectively (Muppaneni et al., 2017). The various factors affecting the process efficiency are similar to other thermochemical processes as discussed earlier. The major influencing factors such as temperature, holding time, loading rate and catalyst used in various processes are explained in this section. Overall, HTC method is more suitable for modest temperature range of applications, as high temperature and pressure increase the complexity, running cost and also difficulty in handling the process.

### 3.4.1. Reaction temperature

Reaction temperature increases the bio-oil yield but the composition of oxygen and hydrogen content in the bio-oil decreases and carbon content improves further. Improvement of carbon content in the bio-oil enhances HHV (Brown et al., 2010; Garcia Alba et al., 2012; Jena and Das, 2011). It is reported that with increase in temperature from 250 to 350 °C at a loading rate of 1% of wt., HHV of bio-crude increased from 27.9 to 31.7 MJ/kg (Jazrawi et al., 2013). HTG process shows a similar behaviour on the process parameters as the same as gasification process. It is observed that with increase in temperature from 380 to

460 °C, H<sub>2</sub> and CO<sub>2</sub> yield increased from 3.2 to 8.25 mmol/g and 6.2 to 8.22 mmol/g, respectively.

Increase in temperature and residence time have a similar effect on the conversion of H<sub>2</sub>. The estimated gas composition of H<sub>2</sub>, CO, CO<sub>2</sub> and CH<sub>4</sub> were 4.7, 3.3, 40.6, and 46.4% of wt. respectively, and C<sub>1</sub>–C<sub>3</sub> gas yield was 0.133 g/g of dry mass at feed loading rate of 13% of wt. (Haiduc et al., 2009). Increase in temperature increases the ash content whereas, the carbon content decreases. Optimization of reaction temperature, time and loading rate were analysed by Heilmann et al. (2010). It is reported that yield of alga char and carbon recovered at mild range of HTC condition (temperature, time and catalyst loading rate as 200 °C, 3 h and 12.5%, respectively) were 39.4 and 51% of wt., respectively. The combustion of the char obtained from the HTC of *Chlamydomonas reinhardtii* gave a net positive energy balance of 12.01 MJ, while the fresh algae yielded a net negative energy balance of –5.27 MJ (Heilmann et al., 2010). This is another example where hydrothermal process offers a sustainable as well as energy saving platform for the integrated utilization of algae to bio energy, without intensive drying. HHV value of alga char (30.5–31.6 MJ/kg) was more than lignocellulosic char (24.3 MJ/kg) and natural coal (28.6 MJ/kg). The carbon content is enhanced by 50% through HTC process and observed that the reaction temperature, time and particle size are the three major influential parameters affecting the HTC performance (Xu et al., 2013). Overall, the reaction temperature is one of the important factors which plays important role on evaluating the performance of HTT process.



### 3.4.2. Residence time/holding time

Holding time varies from 60 min (López Barreiro et al., 2013) to 120 min (García Alba et al., 2012). With increase in holding time, the gas yield enhances significantly and solid yield remains constant. It also reported that higher reaction temperature with shorter holding time improves the bio-oil yield significantly. So, it is necessary to select appropriate reaction temperature and residence time simultaneously for the process. The optimization procedures need to be adopted to find the correct holding time and reaction temperature. It is also observed that with increase in residence time from 5 to 25 min, the gas yield improved significantly. The time greater than 25 min did not give any impact on gas yield (Safari et al., 2016).

### 3.4.3. Feedstock composition and loading rate

Feedstock composition and loading rate also affect the potential parameters but their significant is less compared to reaction temperature and residence time. The properties of bio-crude oil largely depend on the feedstock composition along with the content of carbohydrates, proteins and lipids (García Alba et al., 2012). With increase in loading rate from 10 to 20%, the bio-oil yield improves from 32.5 to 39.9% of wt. respectively (Jena and Das, 2011). Similarly, when the feed rate is increased from 1 to 10% of wt. at a constant reaction temperature of 300 °C, HHV enhances from 29.6 to 33 MJ/kg (Jazrawi et al., 2013). But, increase in loading rate has contrary effect on the performance of both H<sub>2</sub> and CO<sub>2</sub> yields. Lower biomass feed rate increases the bio-char yield and ash removal.

### 3.4.4. Catalysts

Catalyst affects the performance of the process during liquefaction of algal biomass. Both homogenous and heterogenous catalysts employed in HTL process where Na<sub>2</sub>CO<sub>3</sub> is one of the most commonly used homogenous catalyst. The presence of Na<sub>2</sub>CO<sub>3</sub> as catalyst may increase or decrease the solid residues but it largely depends upon the species of algae (Aravind et al., 2020). The heterogenous catalysts (Co/Mo/Al<sub>2</sub>O<sub>3</sub>, Pt/Al<sub>2</sub>O<sub>3</sub>) improve oil-yield and HHV whereas, oxygen content reduces. It is observed that carbohydrates are converted into bio-oil in the presence of catalysts. Proteins and lipids are converted in to bio-oil without using catalysts. The presence of catalyst during HTL reduces the oxygen content but HHV and bio-oil yield increase (Jazrawi et al., 2013). The yields of CH<sub>4</sub> and CO<sub>2</sub> can be enhanced in hydro-char in the presence of alkali metals (K, Na). Similarly, it reduces CO yield and lighter hydrocarbon composition. The gasification efficiency can be enhanced from 53% to 84% using nickel-based catalyst (Chakinala et al., 2010). It also revealed that higher temperature, longer residence time and low biomass concentration are the important factors for the enhancement of gas yield (Chakinala et al., 2010). The effect of catalysts Pd/C, Ru/C, Zeolites, Ni/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> on *Nannochloropsis* sp. alga using HTL method was analysed by Duan and Savage (2011). All the catalysts lead to a higher oil-yield but the properties of bio-oil are insignificant to the catalyst (Duan and Savage, 2011) because of that the catalysts undergo deoxygenation and hydro-oxygenation reaction during HTL process.

Among various factors affecting hydrothermal process, reaction time or holding time plays relatively more important role in energy saving and product yield. Hydrothermal process observed to be more energy efficient mode of conversion due to the ability of handling wet algal biomass without drying. With increase in residence time, gas yield improves significantly. However, along with residence time, reaction temperature must be selected simultaneously for the optimizing process efficiency. Apart from this, catalyst, feedstock composition and loading rate also affect the overall product yield.

In summary, the thermochemical methods can be used for conversion of algal biomass to produce solid fuels, bio-oils and gas fuels or syngas. Bio-fuels produced through algal biomass can be substituted for fossil fuels due to its feasibility and other similar characteristics.

### 3.5. Perspectives, highlights and challenges on conversion of algal biomass to bio-fuels

Nowadays the production of bio-fuels from algal biomass using thermochemical methods get substantial attention by researchers. There are many studies focussed on improving the process efficiency as well as product yield. It is identified that the bio-fuels have the potential option to replace other non-renewable sources. Though all the studies are in its early stage, the outcomes and challenges of conversion of algal biomass using thermochemical method via torrefaction, pyrolysis, gasification and hydrothermal process are discussed here.

The best suitable technology to treat algal among thermochemical methods (torrefaction, pyrolysis, gasification and hydrothermal) is still debatable. There is lack of studies that have compared all the four-process using same biomass feedstock to get more valuable information. It is worth mentioning that all the four processes have its own significance in terms of its operating parameters (reaction temperature, residence time, pressure etc.) and final products (char, bio-oil and bio-gases) as discussed earlier. Torrefaction, pyrolysis and gasification process are potential options for solid, liquid and gaseous biofuels respectively. Among existing thermochemical methods, HTL (subcritical) and pyrolysis techniques are widely used for transforming the complete algal biomass irrespective of its composition into bio-oil or char products. Moreover, the bio-oil obtained from HTL had a higher energy density and superior fuel properties such as thermal and storage stability, compared to that obtained from pyrolysis. The energy consumption ratio (ECR) value of HTL process was found to be 0.70, indicating that this process was a net energy producer whereas, the pyrolysis process consumed more energy than what could be produced from algal biomass (Jena and Das, 2011). Similarly, Biller et al. (2015) suggested that HTL process is more favourable for wet biomass (having moisture content of 80%) due to lower ECR of 0.4 to 0.6 compared to pyrolysis process (0.9 to 1.2). The process efficiency of the hydrothermal process can be increased further using extraction solvents specifically dichloromethane. Watson et al. (2019) observed a significant improvement in process efficiency regardless of feedstock composition by dichloromethane with the ECR of 0.06 (Watson et al., 2019). However, HTG of microalgae has a number of advantages over HTL, namely the produced fuel is nitrogen-free, allowing the use of high protein microalgae. The organic carbon in the water phase is also much lower than that for HTL, which could increase the carbon gasification efficiency (Biller et al., 2015; Haiduc et al., 2009).

Process conditions such as temperature and holding time plays an important role and their optimization is necessary for improvement of performance and effectiveness of the process. Higher torrefaction temperature and residence/holding time improve the fuel quality but decrease the energy yield. Torrefaction process of algal biomass improves HHV and carbon content in the products so it is a potential option for developing the solid fuels. HHV of bio-oil is more compared to bio-char and bio-gases (Miao et al., 2004). Microwave pyrolysis is the best option to get uniform and controlled heating during the process (Borges et al., 2014; Du et al., 2011). The production of gas can be enhanced using microwave pyrolysis with higher microwave power and heating rate in the presence of catalyst. When the gasification temperature is increased, the production of syngas increases whereas, char and tar yield decrease. Similarly, with increase in particle size, HHV and syngas yield decrease but char and tar yield increase. Catalysts also plays an important role in overall performance improvement. The percentage of yield changes largely depend on species of algae biomass. Use of catalyst in steam gasification process substantially improves H<sub>2</sub> production as well as tar degradation (Duman et al., 2014). In the torrefaction process, higher HHV of biomass is noticed with lower solid yield. Significant focus should be given on improving the process parameters so that a chance of improving the solid yield. There is limited data available on algal-biofuel conversion in specific to torrefaction process. More studies are required in the torrefaction process so that the feasibility and its

potential can be reached to researchers and industries. It creates further confidants to engineers about the solid fuel usage as a potential option for industrial applications.

Low energy efficiency of conventional heating is a challenge in algal-biofuel conversion. Microwave pyrolysis method can overcome this drawback of conventional heating system, still it is facing other issues such as the continuous feeding of biomass, char discharging, etc. Formation of tar during the gasification process is highly undesirable as it has adverse effect on process performance. The tar affects the catalyst of syngas applications and leads to formation of scaling or fouling, corrosion and plugging on the pipelines so, special care needs to be taken to avoid these failures. Ru/C is one of the efficient catalysts used in gasification process, but repeated usage leads to form sulphur which is one of the effective contributors for deactivation of the catalysts (Duman et al., 2014). Apart from temperature and time, other factors such as catalyst types, biomass loading rate, equivalence ratio, particle size, carrier gas and its flow rate, etc. affect the performance of the process and product yield. Special attention should be given for the optimization of process parameters to get the maximum performance of the system and product yield. Aforementioned challenges need to be addressed during algal biomass conversion into bio-fuels using different thermochemical techniques so that it can be a potential and economically viable option for replacement of non-renewable fuels.

#### 4. Conclusions

A comprehensive review has been carried out on thermochemical methods (torrefaction, pyrolysis, gasification and hydrothermal process) and various factors affecting process efficiency and performance parameters. Finally, the highlights and challenges are also listed in this specific area. The following important conclusions were made from this review work.

- Thermochemical methods could be used for conversion of algal biomass to produce bioenergy such as char, bio-oil and syngas.
- Among various thermochemical methods, pyrolysis and hydrothermal processes were widely used and hydrothermal process was most energy efficient route for conversion of wet algal biomass.
- Factors such as reaction temperature, residence time, catalyst, feedstock composition, heating rate, influenced the yield and products of thermochemical process significantly.
- By controlling these factors, the maximum quality and yield of products could be achieved during the thermochemical process.
- The novel insights in torrefaction process are; with increase in reaction temperature, HHV of torrefied biomass increased significantly with increase in carbon yield.
- The torrefied biomass had higher utilization efficiency and could be easier to store and transport compared to its raw biomass.
- Optimum temperature during the slow pyrolysis process was 500 °C and oil-yield decreased beyond this temperature.
- The presence of catalysts affected the final output but it largely depended on the composition of biomass. Presence of catalyst enhanced the char yield during volatilization of biomass.
- Heating rate and residence time were deciding factors for the nature of process as fast or slow. Higher particle size increased the char yield but decreased the bio-oil yield thus, it is necessary to optimize biomass particle size to improve product yield.
- The gasifying agent such as oxygen, air or steam also largely contributed into the bio-char formation. Biomass feed rate optimization was necessary as higher feeding rate decreased the gasification efficiency.
- Low feed rate decreased the syngas production. The yield of H<sub>2</sub>, rate of gasification and gasification rate of carbon were lower in SWG method at low temperatures.
- Steam flow, temperature, reactant concentration and reaction time were the vital process parameters to be optimized for better

gasification efficiency. The selection of materials also had a greater impact on the gasification ability.

- Gas yield improves significantly with increase in temperature during hydrothermal process. The reaction temperature and residence time must be selected simultaneously for optimizing of the process efficiency. Apart from this, catalyst, feedstock composition and loading rate also affect the overall product yield.

#### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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