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On the pyrolysis of different microalgae species in a conical spouted bed reactor: bio-fuel yields and characterization

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Abstract

The aim of this work was to study fast pyrolysis of three microalgae species in a continuous bench-scale conical spouted bed reactor at 500℃. Bio-gas, bio-oil and bio-char yields have been determined and characterized by using GC, GC/MS, elemental analyzer and SEM. Bio-oil was the main product obtained through pyrolysis of microalgae. The non-condensable gaseous stream is made up of mainly hydrogen, carbon monoxide and carbon dioxide, apart from other light hydrocarbons detected in lower concentration, as are methane, ethane, ethylene, propane and propylene. The compounds identified in the bio-oil have been categorized into hydrocarbons, nitrogen containing compounds, ketones, alcohols, acids, lactones, phenols and aldehydes. The nitrogen and carbon contents of the microalgae bio-chars are higher than those for bio-chars derived from other biomasses. Pyrolysis improved the morphology and porous structure of microalgae. Finally, the mechanism involving microalgae pyrolysis has been approached and the main reaction pathways have been proposed.

Keywords: Pyrolysis; Conical spouted bed; Biomass; Microalgae; Bio-fuel; Kinetic pathway

1. Introduction

Renewable energy sources are becoming an alternative to fossil fuels due to the depletion of fossil fuels and their environmental effects, such as global warming, and air and water pollution. Besides, the growth of the world population increases the global energy demand steadily. A practical solution to the mentioned problems is to seek alternative fuels that are green and sustainable. Microalgae have been considered as one of the most promising alternative resources for the production of 3rd generation of bio-fuels due to their high potential for biomass production, efficient CO_2 fixation, high oil content and ease of processing (no lignin in their structure). Besides, they do not compete with productive lands (Azizi et al., 2017).

The heating value of microalgae bio-oil is relatively high, usually in the 27-42 MJ/kg range, which is remarkably higher than those for the bio-oils derived from lignocellulosic biomass (Yang et al., 2019). Furthermore, the carbon and hydrogen contents of the bio-oils obtained from microalgae pyrolysis are in the 51-82 and 7-12 % ranges, respectively, depending on pyrolysis conditions and microalgae nature (Yang et al., 2019), whereas those corresponding to fossil fuels are usually in the 83-87% and 10-14% ranges, respectively. Interestingly, sulfur content of microalgae bio-oil is also low. It should be noted that microalgae contain lipids, proteins and carbohydrates, whereas lignocellulosic biomass is mainly made up of cellulose, hemicellulose and lignin (Gautam and Vinu, 2018; Suganya et al., 2016).

Solid, liquid or gaseous bio-fuels may be obtained from microalgae via two different pathways, i.e., biochemical and thermochemical processes. In the biochemical processes, microorganisms are used to convert the biomass into bio-fuels. In the thermochemical process, biomass is heated under inert or reactive atmosphere and converted into solid, liquid and gaseous bio-fuels.

However, biomass conversion through thermochemical processes is more favorable due to the low conversion, high production cost and lengthy reaction steps of the biochemical methods (Raheem et al., 2015).

The thermochemical routes for the conversion of biomass may be categorized into combustion, gasification, liquefaction and pyrolysis (W. H. Chen et al., 2018). Of all thermochemical conversion processes, pyrolysis (thermal degradation of matter in the absence of oxygen) at a temperature ranging from 400 to 600 ℃ followed by direct condensation of vapors is a promising and cost effective method, which plays a crucial role in biomass conversion (Yildiz et al., 2014). Microalgae pyrolysis performance is greatly influenced by process conditions, especially, heating rate, temperature and residence time (Azizi et al., 2017). Accordingly, reactor design plays a key role in product distribution and their composition. A wide variety of reactor designs have been proposed in the literature, as are slow (fixed beds or autoclave reactors) and fast pyrolysis reactors (fluidized and free fall reactors) (Li et al., 2019). Pyrolysis of *Spirulina plantesis* in a fixed bed reactor showed that temperature in the 400-700℃ range influenced products yields. The highest bio-oil, bio-gas and bio-char yields were obtained at 500, 700 and 400 ℃, respectively. Higher temperatures decreased bio-oil production and increased bio-gas production (Jafarian and Tavasoli, 2018). Pyrolysis of microalgae *Chlorella protothecoides* and *Microcystis aeruginosa* in a fluidized bed reactor led to higher saturated and polar fractions of microalgae bio-oil than those in the bio-oil from wood. Besides, distribution of straight-chain alkanes in the saturated fractions of microalgae bio-oil were similar to those in diesel fuel (Miao et al., 2004). Pyrolysis of the lipid residue extracted from the microalgae *Tribonema minus* in a fixed bed reactor showed that the major compounds in the bio-oil were carbonyls, hydrocarbons and nitrogenous compounds, with a high content of oxygen in their structure. The main

components in the bio-gas were CO_2 and CO, and their contents changed with pyrolysis temperature. Compared to lignocellulosic biomass, the liquid products of microalgae pyrolysis contained more alkane/alkene and less aromatics (Ji et al., 2015). Pyrolysis of *Scenedesmus dimorphus* in a fixed bed reactor showed that the bio-oil yield peaks at the temperature of 500 ℃ and contains n-hexane, ethyl acetate, toluene and methanol (Bordoloi et al., 2015). Pyrolysis of *Scenedesmus sp.* in a spouted-fluidized bed reactor produces bio-oil with an average calorific value of 18.4 MJ/kg. Moreover, the total acid number of this bio-oil was lower than the standard one produced from woody biomass (Harman-Ware et al., 2013). In summary, fixed beds and fluidized beds reactors were commonly used to pyrolyse microalgae(Aboulkas et al., 2017; Adamczyk and Sajdak, 2018). To our knowledge, pyrolysis of microalgae in a conical spouted bed reactor has not been reported in previous literature.

Spouted bed reactors have been applied to study different thermochemical processes, as are torrefaction, gasification, combustion and pyrolysis (Alvarez et al., 2018; Barbarias et al., 2018; Wang et al., 2018). This type of reactor is suitable for handling different kinds of particles, from coarse to fine materials, and even sticky solids, with no agglomeration and segregation problems due to the vigorous solid circulation regime attained (Elordi et al., 2011). Moreover, the particle movement in spouted bed reactors leads to higher heat transfer rates between particles and phases (P K Mollick et al., 2019; Yaman et al., 2019), which makes them especially suitable for the thermochemical conversion of biomass and waste (Perkins et al., 2018). In this study, a conical spouted bed reactor was used for the pyrolysis of different microalgae species. Due to the especial features of microalgae, specifically their low density and tendency to form fines, insertion of a fountain confiner in the conical spouted bed was considered to avoid the elutriation of non-reacted microalgae fine particles (Altzibar et al., 2017). In addition, this device greatly

improves the hydrodynamic performance of the reactor, as it enhances the gas-solid contact in the fountain region and leads to a highly stable bed. It is to note that a remarkable improvement in conversion efficiency was reported when biomass steam gasification was conducted in the mentioned bed provided with fountain confiner (Cortazar et al., 2018).

The aim of this study is to delve into the pyrolysis of the microalgae *Nannochloropsis*, *Tetraselmis* and *Isochrysis galbana* in a conical spouted bed reactor. The experiments were carried out at the temperature of 500 ºC. Product yields (bio-oil, bio-gas and bio-char) were determined and compared with those obtained in other types of reactors. Besides, the pyrolytic products were characterized based on GC and GC-MS and on ultimate and proximate analyses. Finally, a reaction scheme was proposed based on the bio-oil composition obtained from GC/MS analysis.

2. Material and methods

2.1. Feedstock characterization

Three freeze-dried microalgae *Nannochloropsis (NC)*, *Tetraselmis (TS)* and *Isochrysis galbana (IG)* have been used as feedstock. The microalgae were produced at the University of Almeria, Spain. Briefly, they were cultivated in tubular photo-bioreactors operating in continuous mode, with the feed being seawater containing nutrient source. The ultimate and proximate analysis were carried out in a CHN elemental analyzer (LECO CHNS-932) and in a thermobalance (TGA Q500IR), respectively. The higher heating value (HHV) was measured according to the method described elsewhere (Azizi et al., 2018). The results are shown in Table 1.

Table 1

The pyrolysis behavior of the different microalgae samples has been studied in a TGA Q500IR thermobalance. The experiments were carried out with a heating rate of 15 ºC min^{-1} and with a

nitrogen flow rate of 100 ml min^{-1}. As observed in Figure 1, the three evaluated microalgae showed a similar degradation pattern, i.e., pyrolysis was completed when temperature reached 500-550 ºC and the maximum weight loss rate occurs between 295 and 320 ºC. Microalgae pyrolysis starts with moisture evaporation at around 100 ºC, and the main degradation occurs between 200 and 600 ºC. In this stage, all components (carbohydrates, proteins, lipids, and other minor ones) are pyrolysed (Bach and Chen, 2017). It should be noted that the degradation of carbohydrates and proteins overlap (main peak) (Chen et al., 2014), whereas the degradation of lipids appears at higher temperatures and may be associated with the shoulder in the 400-500 ºC range (López-González et al., 2015).

Figure 1

2.2. Pyrolysis plant

Pyrolysis of microalgae was carried out in a bench scale unit with a conical spouted bed reactor made of stainless steel. The development of this reaction unit is based on the wide experience gained in the pyrolysis of different solid wastes, such as tires, plastics and different biomasses (Elordi et al., 2011). The performance of this reactor has been improved with the insertion of a draft tube and a fountain confiner. The draft tube improves the stability of the spouting regime, controls the solid circulation rate and reduces the gas flow rate required for operation (Palash Kumar Mollick et al., 2019). The fountain confiner is crucial for handling fine and low density materials, as it avoids their elutriation prior to full conversion, apart from contributing to bed stability (Altzibar et al., 2017).

The detailed design of this reactor provided with draft tube and fountain confiner is shown in Figure 2. These dimensions were established based in the knowledge acquired in the previous hydrodynamic studies (Altzibar et al., 2017). Thus, the gas inlet diameter is 1 cm and that of the

bottom 2 cm. The total height and that of conical section are 34 cm and 20.5 cm, respectively. The angle of the conical section is 28º (γ/2). The draft tube diameter 1 cm and the height of entrainment zone 2.5 cm. Finally, a fountain confiner with a diameter of 8 cm was welded to the reactor lid, with the total length of this device being 8.2 cm.

Figure 2

The reactor was heated with and electric oven and temperature was monitored with a thermocouple located in the sand bed. Downstream the reactor, a high-efficiency cyclone and a sintered steel filter retain the fines dragged by the gaseous stream. Both devices are located in a convection oven maintained at 300 ºC to avoid the condensation of bio-oil prior to condensation. The condensation system is made up of a double-shell tube condenser cooled by tap water and a steel filter. Finally, the gases leaving the condensation system were filtered by coalescence filters in order to remove bio-oil droplets prior to their analysis in a micro-gas chromatograph (micro-GC). The plant has an original piston feeding system that allows for continuous microalgae feeding without operational problems. Further details about the pyrolysis unit are reported elsewhere(Alvarez et al., 2018).

2.3. Experimental procedure

The pyrolysis experiments were carried out in continues mode by feeding 1 g min^{-1} of microalgae. A bed of 150 g of sand with a particle size of 100-150 μm was used to ensure high heat transfer rates inside the reactor, and therefore operation under isothermal conditions. The nitrogen flow rate was set at 1.5 times the minimum for spouting (3.5 l min^{-1}) to ensure stable spouting and short residence times of the volatiles generated in the reactor. The pyrolysis experiments were carried out 500 ºC, which, as observed in Figure 1, is the minimum temperature for full conversion of microalgae into volatiles. In addition, operating at 500 ºC bio-

oil cracking reactions to produce gaseous products can be attenuated ensuring a high production. In fact this temperature has been usually regarded as the optimum one for bio-oil production from microalgae (Azizi et al., 2018) and more specifically, in the pyrolysis of different biomasses in conical spouted bed reactors (Alvarez et al., 2018; Amutio et al., 2012). When the reactor was heated to the desired temperature, the microalgae were continuously fed into the reactor by the piston feeder. Samples were heated rapidly and the volatiles entrained from the reactor by using nitrogen as carrier gas. The condensable volatiles were trapped in the condenser, which was cooled by tap water, and then passed through the filter to trap the volatiles as much as possible. The non-condensable gas was analyzed in the gas chromatograph and then vented to the atmosphere. After each experiment, the reactor was cooled to the ambient temperature with nitrogen and the char was collected for subsequent analysis.

2.4. Product characterization

The volatile stream leaving the reactor was analyzed on-line in a gas chromatograph (Varian 3900) equipped with a flame ionization detector (FID). The outlet of the reactor to the chromatograph was heated to a temperature of 280 ℃ to avoid condensation of heavy bio-oil compounds. In order to determine correctly the gas and bio-oil yields based on the analysis in the gas chromatograph, cyclohexane was used as external reference because it is not formed in the process. Given that microalgae pyrolysis was carried out in continuous regime, the gaseous product yields may be assessed by comparing their concentration with that of cyclohexane. Thus, a constant flow rate of 0.05 ml min^{-1} was injected into the reactor and analyzed in the GC together with the volatile products formed. Non-condensable gaseous products were analyzed in a micro chromatograph (Varian 4900). It was equipped with three independent analytical modules, namely, Molecular sieve 5, Porapak (PPQ) and Plot Alumina. It is worth noting that all

the runs were repeated at least 3 times under the same experimental conditions to guarantee reproducibility of the results.

The lower heating value (LHV) of the gaseous products was determined according to following equation (Chen et al., 2017a);

$$LHV\left(MJ/m^3\right) = 0.126CO + 0.108H_2 + 0.358CH_4 + 0.665C_nH_m \quad \text{(Eq. 1)}$$

where CO, H_2 and CH_4 are the volume fractions of carbon monoxide, hydrogen and methane in the gaseous stream, respectively. C_nH_m corresponds to any other light hydrocarbon in the gas. The main components of the bio-oil were identified by gas chromatography-mass spectroscopy (Shimadzu QP-2010S). The surface characteristics of the chars were obtained by using a Scanning Electronic Microscope (JEOL JSM-6400). The ultimate, proximate and HHV of the char were determined by the method explained before.

3. Results and discussion

3.1. Product yields

The main products obtained in the pyrolysis may be categorized into gas, liquid and solid. The product yields obtained in the pyrolysis of different microalgae species are shown in Figure 3. As expected, bio-oil is the main product obtained in the fast pyrolysis of the three microalgae species. The pyrolysis product distribution obtained with *NC* is similar to that obtained with *TS*, with bio-oil, bio-gas and bio-char yields being 58%, 13% and 30%, respectively. *IG* showed a different pyrolysis behavior, with bio-oil yield being the highest (66%) and bio-char yield the lowest (21%). However, the gas yield in the pyrolysis of *IG* is similar to the other two microalgae. The higher and lower yields of bio-oil and bio-char obtained from the pyrolysis of *IG* may be conditioned by its higher volatile content compared to *NC* and *TS* which clearly evidences the higher potential for bio-oil production of IG.

In order to evaluate the performance of the conical spouted bed reactor, the bio-oil yields of microalgae have been compared with those obtained in the pyrolysis of microalgae in different reactor configurations. However, direct comparison is really challenging, as product distribution strongly depends on pyrolysis conditions, reactor design and microalgae characteristics (Li et al., 2019). On the one hand, in the slow pyrolysis of microalgae, the sample is heated slowly and the residence time is high (even minutes), which promote the production of a high solid fraction. On the other hand, fast pyrolysis of microalgae leads mainly towards the production of bio-oil (Yang et al., 2019). It should be noted that the bio-oil yields obtained in this study in the pyrolysis of different microalgae are in general higher than those reported in the literature in different technologies, such as fixed reactors, screw kilns, microwave ovens and even fluidized beds (Aboulkas et al., 2017; Du et al., 2011; Miao et al., 2004; Sotoudehniakarani et al., 2019; Yang et al., 2019). Thus, Yuan et al. (Yuan et al., 2015) obtained the highest bio-oil yield of 32.69 wt% from *Chlorella vulgaris* pyrolysis in a fixed bed reactor operating at 500 ºC. Bio-oil production from microalgae *Scendesmus sp*. in a fluidized bed reactor at 440 ºC was of around 52 wt% (Kim et al., 2014). Likewise, the pyrolysis of *Chlorella vulgaris* in a fluidized bed reactor at 500 ºC led to a total bio-oil yield of around 53 wt% (Wang et al., 2013).

The cyclic movement of the particles in the conical spouted bed reactor promotes thermal distribution inside the bed and fast heating rates. Besides, the gas residence time in the bed is particularly low. The aforementioned features reduce secondary reactions in the gas phase, which decrease by-product formation and improve bio-oil production. Although, especially high bio-oil yields are obtained in this study involving microalgae pyrolysis in a conical spouted bed reactor, these values are still lower than those obtained in lignocellulosic biomass pyrolysis in the same type of reactor (Amutio et al., 2015, 2012). This fact is due to the different nature of

lignocellulosic biomass, with higher volatile matter and lower ash content. The water content in the bio-oil is a fact of high relevance for its subsequent use. Thus, the bio-oils from *NC*, *IG* and *TS* contain 26.79%, 24.81% and 24.33%, respectively. The lower water content of microalgae compared to lignocellulosic biomass is probably due to the lower oxygen content of microalgae (W. H. Chen et al., 2018). This is an interesting feature for the downstream utilization of bio-oil, as it leads to higher heating value and lower acid corrosion of equipment. The bio-char yield was 20-30 wt%, which is higher than those obtained from lignocellulosic biomasses, and is explained by the higher ash and fixed carbon contents of microalgae. The gas yield is of around 12 wt% for all the studied microalgae, which is lower than those reported in the literature in different pyrolysis technologies at similar temperatures (Aboulkas et al., 2017; Beneroso et al., 2013; Du et al., 2011; Sotoudehniakarani et al., 2019). Moreover, the gas yields produced from microalgae pyrolysis are comparable to those obtained from lignocellulosic biomasses (of around 10 wt%) in the spouted bed reactor, which remarks the capacity of this reactor for avoiding bio-oil cracking reactions (Amutio et al., 2012). It is to note that this technology was successfully scaled up for biomass pyrolysis. Therefore, a pilot plant with a capacity of 25 kg h^{-1} of biomass continuous feed rate was developed (Fernandez-Akarregi et al., 2013). Thus, the suitable results obtained in bench scale units (Amutio et al., 2012) were confirmed in the pilot plant unit. The promising performance showed by conical spouted bed reactor in microalgae pyrolysis with higher bio-oil yields than other technologies and the reported scalability of this technology clearly remark the industrial relevance of the present results.

Figure 3

3.2. Bio-gas characterization

The non-condensable gaseous stream is made up of mainly hydrogen, carbon monoxide and carbon dioxide with their concentrations being 10-19 vol%, 10-19 vol% and 50-65 vol%, respectively. Other light hydrocarbons, such as methane, ethane, ethylene, propane and propylene, were also detected. Methane is the prevailing light hydrocarbon, whose concentration is the highest (10 vol%) in the pyrolysis of *TS*. These results are consistent with the gas compositions reported in the literature for microalgae pyrolysis under mild conditions (Beneroso et al., 2013; Du et al., 2011; Maliutina et al., 2017).

Microalgae main components are lipids, proteins and carbohydrates. Carbon dioxide is the main gaseous product, which is mainly produced from the cracking of carbonyl and carboxyl groups in carbohydrates and proteins (Chen et al., 2017b). Carbon monoxide is formed in the cracking of ether bonds and carbonyl groups. The formation of hydrogen is related to radical polycondensation from microalgae volatiles. The formation of methane should be attributed to the demethoxylation of algae. The other gaseous products are formed by scission and cyclization reactions of long chain fatty acids in the microalgae (Chen et al., 2017b).

The LHV of the gaseous streams was also determined, with their values being 11.6, 11.64 and 9.45 MJ/m^3 for *NC*, *IG* and *TS*, respectively. These heating values are conditioned by the high CO_2 content, higher than 50 % vol. for all the microalgae studied. It is to note that the quality of these gases may be greatly improved operating at higher temperatures, as they allow increasing H_2 and CH_4 yields and decreasing those of CO and CO_2 (Maddi et al., 2011). The gaseous stream may be used not only as power or heat supplier, but also as feedstock for chemical process, such as Fischer-Tropsch synthesis subsequent to an upgrading process.

Figure 4

3.3. Bio-oil characterization

The concentrations determined by GC/MS analysis for the bio-oil compounds were obtained from the pyrolysis of microalgae species. The identified compounds contain a wide range of organic compounds, and they have been categorized into hydrocarbons (saturated, unsaturated and aromatic hydrocarbons), nitrogenous compounds (NCC) (nitrile, amine, amide, azole, indole and nitrogen heterocyclic compounds (NHC)), ketones, alcohols, acids, lactones, phenols and aldehydes. Figure 5 shows the yields of the families of chemical compounds in the bio-oils derived from the three microalgae. It should be noted that many other compounds not belonging to the mentioned groups have also been obtained, but they have low match factors in the GC/MS. The mass balance has been closed based on the areas of the chromatographic signals (Gautam and Vinu, 2018).

Figure 5

The main compounds produced in the pyrolysis of *NC* were ketones, NCC and hydrocarbons, with their yields being 13.57 %wt, 11.02 %wt and 11.02 %wt, respectively. The yield of alcohols produced in the the pyrolysis of NC is 4.97 %wt. Regarding *TS*, NCC (16.91 %wt), hydrocarbons (16.23 %wt) and alcohols (11.9 %wt) are the main components in the bio-oil. Ketones are also produced in the the pyrolysis of *TS* and their yield is 4.16 %wt. In the case of *IG*, alcohols (28.38 %wt), hydrocarbons (21.12 %wt) and NCC (8.45 %wt) are the main components. Ketones are also produced and their yield is 1.67 %wt. Although the yields of other compounds are rather low, some of them are of interest from the perspective of their specific applications. Thus, a low yield of lactones is present in the pyrolysis of *NC* and *TS* green microalgae.

The compounds obtained in the bio-oil are related to the chemical composition of the original microalgae, i.e., to the relative content of lipids, proteins and carbohydrates. Thus, NCC are

formed by the decomposition of proteins in microalgae, whose structure varies in a wide range depending on the species. Thus, *NC* and *TS* are green microalgae, whereas *IG* is a kind of brown microalga. The content of hydrocarbons in the liquid product is an index of the potential of the biomass as a raw material to produce bio-fuels and bio-components (Adamczyk and Sajdak, 2018), and they are mainly produced by the cracking of lipids. Oxygen is in the bio-oil mainly within oxygen containing organic compounds (acids, ketones, aldehydes, alcohols, furans, phenols, lactones) (Yuan et al., 2015). The formation of most oxygenated compounds is attributed to the thermal decomposition of carbohydrates and lipids in algal biomass (Bordoloi et al., 2015), but phenolic compounds stem from protein thermal decomposition (Maliutina et al., 2017). At temperatures higher than 400℃, carbonyl groups have low thermal stability and undergo decarbonylation reactions leading to ketones, aldehydes and carbon dioxide (Chen et al., 2017b). The presence of oxygen compounds, such as acids, ketones and aldehydes in the bio-oil is responsible for its instability and corrosiveness during transport and storage. Furthermore, the presence of ethers and esters in the bio-oil reduces its heating value (Zainan et al., 2018).

3.4. Bio-char characterization

The ultimate analysis of the bio-chars obtained from the pyrolysis of algal biomass at 500 ºC is shown in Table 2. As observed, the oxygen and hydrogen contents of the bio-char are lower than those of the raw microalgae. This reduction in hydrogen and oxygen content is due to aromatization, decarbonylation, dehydration and decarboxylation reactions (Aboulkas et al., 2017). The nitrogen content of microalgae bio-char is significantly higher than those of other bio-chars (Alvarez et al., 2019, 2018), and is explained by the protein content of microalgae. Furthermore, the higher nitrogen content of this bio-char increases its value as soil amender, but its high ash content is a disadvantage for this application (Sotoudehniakarani et al., 2019). The

carbon content of algal bio-char is relatively high, making it suitable as a renewable solid fuel (Aboulkas et al., 2017).

Table 2

The morphology of raw microalgae and their bio-chars has been studied by using scanning electron microscopy (SEM). There are significant differences between the morphologies of the microalgae and their chars. As observed, the parent biomasses have a relatively smooth surface compared to those of the chars, whose surface is full of holes created during the pyrolysis process due to the release of volatile compounds. As a result, the porosity, and so the surface area, of the parent biomasses is lower than those of the bio-chars. Thus, pyrolysis improves the morphology and porous structure of raw material.

3.5. Possible pyrolysis pathways in the fast pyrolysis of microalgae

Microalgae main components have different pyrolysis pathways, which explains their selective formation. Triglycerides are the main components of lipids. Carbohydrate is a component containing carbon, hydrogen and oxygen atoms, which are connected to each other to form different structures. It is to note that the carbohydrates present in the microalgae are in the form of polysaccharides and oligosaccharides (Yang et al., 2019). Although proteins have complex structures and each microalga species has different types of proteins, their basic units are amino acids, which are connected by peptide bonds. Each amino acid contains amine and carboxyl functional groups along with a side chain, which is specific to each amino acid. Possible pyrolysis pathways responsible for the thermal decomposition of microalgae components during pyrolysis have been proposed.

During pyrolysis, the acyl chains of triglycerides are separated from the glycerol backbone through hydrolyze or cracking process. Such processes result in long chain fatty acids

production. Fatty acids can go further through more reactions including decarboxylation, decarbonylation, fragmentation of glycerin and C-C bond cleavage to form hydrocarbons, acids, esters, alcohols and C_1-C_3 gases (Gautam and Vinu, 2018; Yang et al., 2019). It should be mentioned that although hydrocarbons production is due to pyrolysis of carbohydrate, lipid and protein, production of aliphatic hydrocarbons are mainly attributed to the cracking of lipids.

The reactions occurring during the pyrolysis of proteins are deamination, dehydration, decarboxylation, cyclization and deoxygenation to form nitrogen containing compounds, such as nitriles, amines, amides, hydrocarbons and nitrogen-heterocyclic compounds (Qi et al., 2018). It should be mentioned that the generation of aromatic hydrocarbons is associated with the presence of aromatic amino acids in the microalgae protein (Wang et al., 2013). Thus, the thermal degradation of amino acid chains give way to the formation of different aromatics such as toluene, xylene, and phenols, moreover and nitrogen containing heterocyclic compounds such as indoles are also formed. Furthermore, the formation of olefins could also occur via cracking, deoxygenation, and deamination reactions of protein degradation intermediates (Yang et al., 2019).

Carbohydrate pyrolysis produces oxygen-containing compounds and water, which is the major pyrolysis product (Wang et al., 2017). Primary reactions during pyrolysis of carbohydrates are dehydration, bond cleavage, ring scission, deoxygenation and rearrangement to form cyclic ketones, acids, aldehydes and other hydrocarbons (Yu et al., 2018). For instance, carbohydrates are converted into furans and olefins through dehydration and deoxygenation reactions (Chen et al., 2017b; Qi et al., 2018). Cyclization reactions and Diels–Alder condensation reactions convert olefins into aromatics. It should be pointed out that the extent of the reaction strongly depends on

reaction conditions. Thus, these reaction mechanisms are favored by high temperatures and residence times of pyrolysis volatiles.

Interactions can also occur between microalgae components during pyrolysis. One of these interactions is Maillard reaction, which occurs between the intermediates from carbohydrate and protein pyrolysis. These interactions lead to a large number of products such as heterocyclic compounds containing nitrogen and oxygen, ultra violet absorbing intermediate and dark brown polymeric compounds (Wang et al., 2017). Amino acids and fatty acid react with each other to form protein-fatty acid surfactants and detergents. Lipophilic and hydrophilic group of surfactant are from fatty acid (lipid) and amino acid (protein), respectively. Interactions between carbohydrates and lipids produce alkyl polyglycoside surfactants (Wang et al., 2017). The hydrophilic group is from carbohydrate and the lipophilic group is from lipid. However, almost no biosurfactant nor detergent has been detected in the final bio-oil, which may be due to the high pyrolysis temperature. Biosurfactant such as alkyl polyglycoside can be produced at lower pyrolysis temperatures.

It should be noted that oxygen rich compounds of the microalgae are decomposed during the pyrolysis and oxygen is removed as CO, CO_2 and H_2O (Yu et al., 2018). Cracking and steam reforming of lipids release CO_2, CO, H_2 and CH_4 through decarboxylation, decarbonylation, dehydrogenation and demethylation (Chen et al., 2017b)

3.6. Applications of bio-char, bio-oil and bio-gas

The bio-char has various potential applications, as are those related to solid fuel for bio-energy, carbon sequestration agent, soil amender and absorbent for removal of heavy metals from waste water or pollutants from gaseous streams (Maliutina et al., 2017). The heating value of the gaseous stream is moderate, and may therefore be used for power generation or heat supplying.

Besides, hydrogen and carbon monoxide may be used as feedstock to synthesize hydrocarbons through Fischer-Tropsch process (Chen et al., 2017b). Bio-oil has been considered a promising bio-fuel for generating heat, power and combined heat-power, but it may also be used as an intermediate feedstock for the production of chemicals. The major constituents of bio-oil are hydrocarbons, NCC, phenols, alcohols, acids, ketones and other oxygenated compounds. Among these compounds, hydrocarbons are valuable components to be used as fuel. More specifically, aromatic hydrocarbons may be used as an additive to increase the octane number of industrial chemicals and transport fuels (Bordoloi et al., 2015). Although great efforts have been made for the removal of oxygen and nitrogen containing compounds from the bio-oil (Li et al., 2019), some of them may be a source of valuable chemicals. Thus, NCCs have a great potential for use as platform chemicals in pharmaceutical and polymer industries (Carbas et al., 2017). Some phenols and phenol derivatives can be used as food antioxidant, transportation fuel additives, precursors for chemical products and in resin industry (Negahdar et al., 2016). Oxygenated compounds lead to high corrosiveness, instability and low energy density. Therefore, their content in the bio-oil must be decreased by using catalysts (W. Chen et al., 2018). Moreover, several bio-oil upgrading routes have been proposed in the literature for the production of commercial fuels, the following ones are those with better perspectives for their implantation: i) Catalytic cracking, the use of acid catalysts as zeolites allows for the deoxygenation of bio-oil with the subsequent production of hydrocarbons, usually of olefinic and aromatic nature. ii) Catalytic hydrodeoxygenation /hydrocracking, this strategy is performed under hydrogen pressures and using metallic catalysts. The use hydrogen allows for the production of hydrocarbons from bio-oil, however the high external hydrogen demand of this process represents a major challenge. iii) Electrocatalytic hydrogenation, this novel strategy pursues

stabilization and upgrading of bio-oil to form chemicals and fuels. This process is performed in the presence of catalyst and under milder conditions in relation to conventional hydrodeoxygenation. iv) Catalytic steam reforming, this process is performed at relatively high temperatures (>600 ºC) and steam/bio-oil ratios, the use of metallic catalysts (Ni based are the most common ones) allow for high hydrogen productions. It should be noted that both catalytic cracking and hydrocracking can be performed in refinery units by co-feeding bio-oil mixed with conventional refinery streams. This possibility reinforces the interest of these alternatives as long as already existing units can be used for bio-oil upgrading. Moreover, other less ambitious and simple alternatives for bio-oil pretreatment after an utilization as low grade fuel are esterification and emulsification.

5. Conclusions

Bio-oil was the main product obtained through pyrolysis of three microalgae species. The higher bio-oil yield of *IG* is due to its higher volatile content compared to *NC* and *TS*. Heating value of gaseous products shows that bio-gas may be used as power or heat supplier. Bio-oil constituents were categorized into hydrocarbons, NCC and oxygenated compounds. Formation of NCC may be attributed to the decomposition of protein in microalgae. Hydrocarbons mainly came from the cracking of lipids during the pyrolysis of microalgae. The formation of oxygenated compounds is attributed to the thermal decomposition of carbohydrates and lipids in algal biomass.

Supplementary data

E-supplementary data for this work can be found in e-version of this paper online

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Figure captions

Figure 1. DTG curves of the three microalgae using a heating rate of 15 ºC min^{-1}.

Figure 2. Main dimensions expresses in mm of the spouted bed reactor and its internals (fountain confiner and draft tube).

Figure 3. Product distribution obtained in the pyrolysis of microalgae NC, IG, TS at 500 ºC.

Figure 4. Gaseous product composition obtained in the pyrolysis of NC, IG, TS at 500 ºC.

Figure 5. Main compounds and their relative concentration in the bio-oils produced from the pyrolysis of NC, TS and IG

Table 1. Characteristics of the microalgae used in this study

	NC	***TS***	***IG***
Ultimate analysis (wt.%)[a]			
C	44.45	43.54	48.35
H	6.50	6.76	7.24
N	7.75	7.33	7.60
O[b]	41.30	42.36	36.82
HHV (MJ/kg)	14.25	11.78	16.52
Proximate analysis (wt.%)			
Volatile matter	56.12	55.00	64.02
Fixed carbon	20.35	8.77	10.12
Moisture	2.00	3.36	2.27
Ash	21.51	32.86	23.56

[a] ash free basis

[b] calculated by difference

Table 2. Proximate and ultimate analyses of pyrolysis bio-chars.

	NC	***TS***	***IG***
Ultimate analysis[a]			
C%	72.39	71.78	72.45
H%	4.47	3.66	3.38
N%	11.46	10.53	11.18
O%[b]	11.68	14.03	12.99
HHV (MJ/kg)			
Proximate analysis			
Volatile matter%	3.55	5.98	4.16
Fixed carbon%	21.25	30.44	26.70
Ash%	74.94	62.49	68.83

[a] ash free basis

[b] calculated by difference

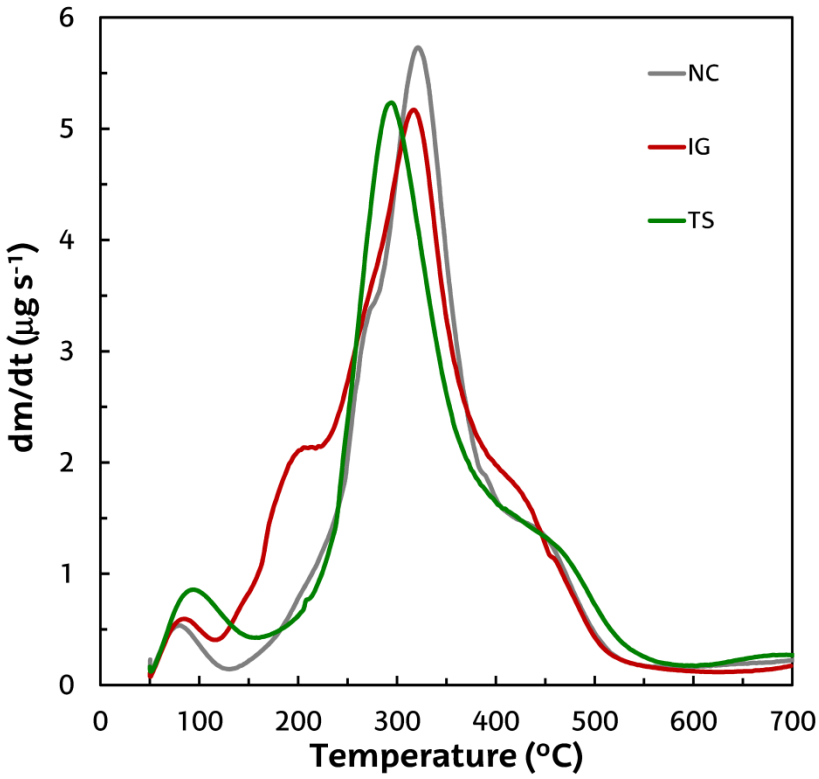
dm/dt (μg s-1)
Temperature (°C)
NC
IG
TS
0
1
2
3
4
5
6
0
100
200
300
400
500
600
700

Figure 1.

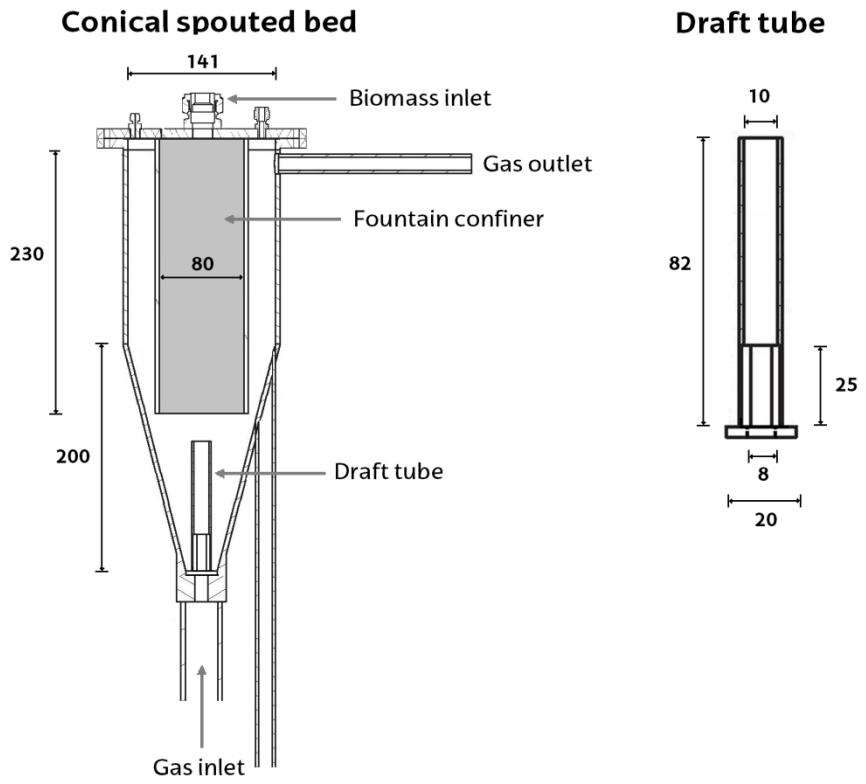
Conical spouted bed
141
Biomass inlet
Gas outlet
Fountain confiner
230
80
200
Draft tube
Gas inlet
Draft tube
10
82
25
8
20

Figure 2.

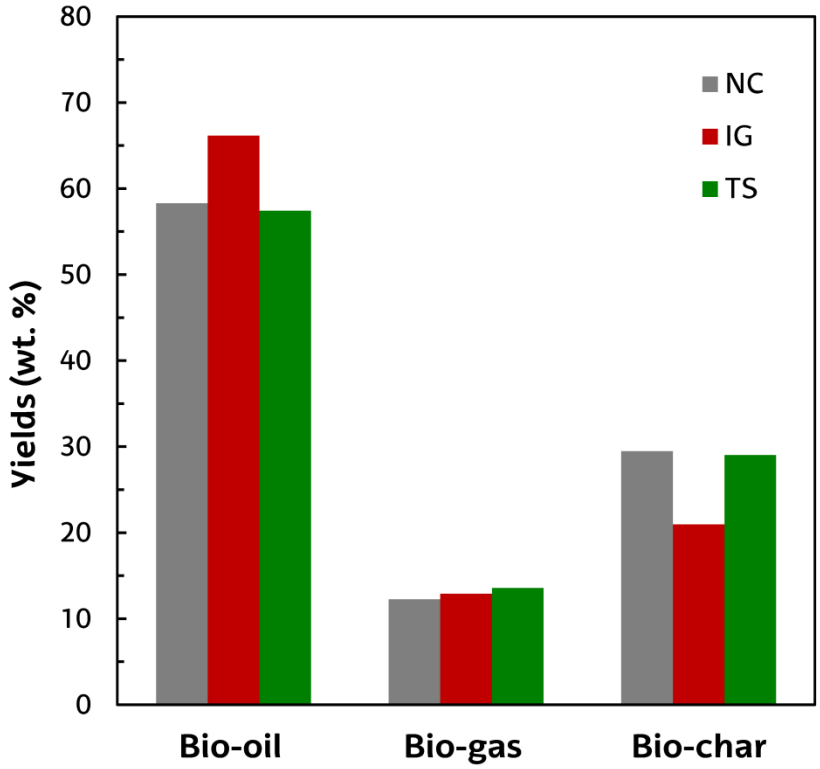
80
70
60
50
40
30
20
10
0
Yields (wt. %)
NC
IG
TS
Bio-oil
Bio-gas
Bio-char

Figure 3.

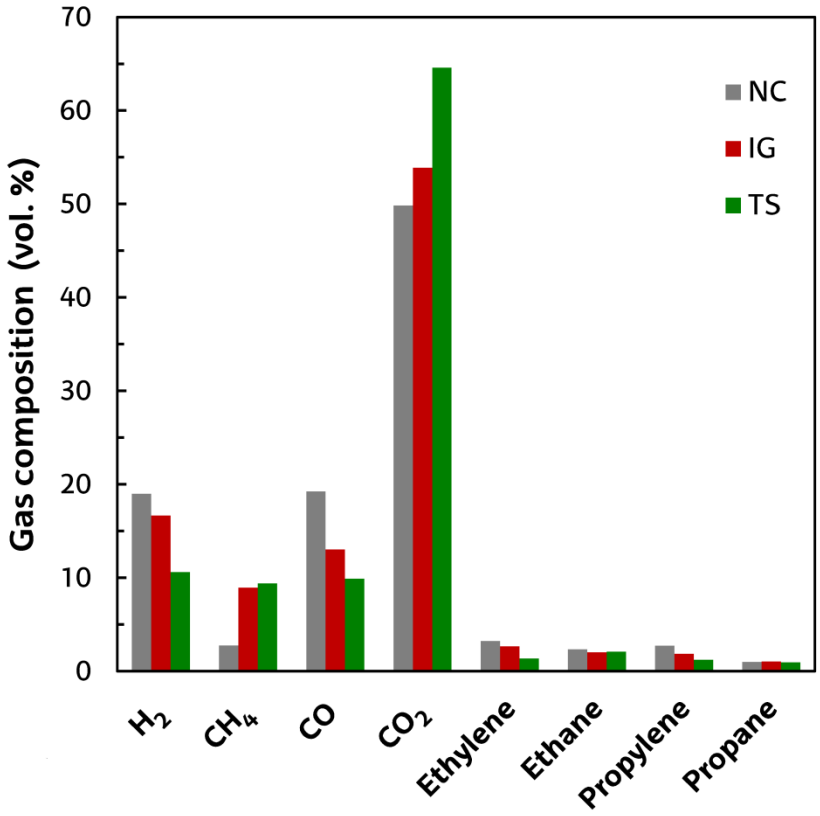
Gas composition (vol. %)
70
60
50
40
30
20
10
0
NC
IG
TS
H2
CH4
CO
CO2
Ethylene
Ethane
Propylene
Propane

Figure 4.

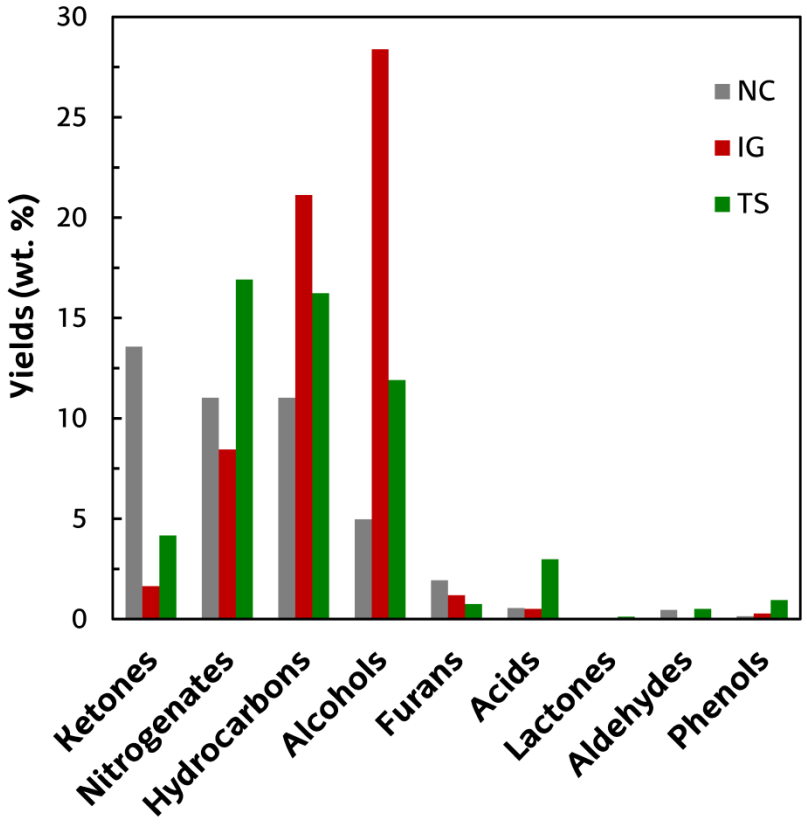
Yields (wt. %)
30
25
20
15
10
5
0
NC
IG
TS
Ketones
Nitrogenates
Hydrocarbons
Alcohols
Furans
Acids
Lactones
Aldehydes
Phenols

Figure 5.