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RESEARCH ARTICLE

Characterization and pyrolysis of *Chlorella vulgaris and Arthrospira platensis:* potential of bio-oil and chemical production by Py-GC/MS analysis

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Abstract Biofuels have been seen as potential sources to meet future energy demand as a renewable and sustainable energy source. Despite the fact that the production technology of first-generation biofuels is consolidated, these biofuels are produced from foods crops such as grains, sugar cane, and vegetable oils competing with food for crop use and agricultural land. In recent years, it was found that microalgae have the potential to provide a viable alternative to fossil fuels as source of biofuels without compromising food supplies or arable land. On this scenario, this paper aims to demonstrate the energetic potential to produce bio-oil and chemicals from microalgae *Chlorella vulgaris* and *Arthrospira platensis*. The potential of these biomasses was evaluated in terms of physical-chemical characterization, thermogravimetric analysis, and analytical pyrolysis interfaced with gas chromatograph (Py-GC/MS). The results show that *C. vulgaris* and *A. platensis* are biomasses with a high heating value (24.60 and 22.43 MJ/kg) and low ash content, showing a high percentage of volatile matter (72.49 and 79.42%). These characteristics confirm their energetic potential for conversion process through pyrolysis, whereby some important aromatic compounds such as toluene, styrene, and phenol were identified as pyrolysis products, which could turn these microalgae a potential for biofuels and bioproduct production through the pyrolysis.

Keywords *Arthrospira platensis* · *Chlorella vulgaris* · Energetic characterization · Biomass · Flash pyrolysis · Bioproducts · Biofuels

Introduction

It is more evident that the utilization of fossil fuel energy reserves is unsustainable due to the emission of pollutant gases related to the greenhouse effect and the emptying of worldwide reserves. Therefore, there are many initiatives that lead to the development of alternative and renewable energy

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resources made of neutral carbon to produce solid, liquid, and gaseous biofuel (Brennan and Owende 2010).

Microalgae have been shown as promising third-generation biofuel and bio product feedstock for partial replacement of fossil fuel and its derivatives due to their high photosynthetic efficiency and higher capacity to produce biomass by area unity and time when compared with other biomasses, such as lignocellulosic and oleaginous crops, not requiring fertile soil or arable land. Furthermore, these microorganisms have high capacity of CO_2 biofixation being a productive biological system for carbon capturing (Milano et al. 2016; Tredici 2010). The production of microalgae does not follow crop regime; thus, it can be carried out daily allowing continuous production processes (Lira et al. 2012). Compared to fossil fuels, biofuel from microalgae is essentially a carbon-neutral process (Prabandono and Amin 2015).

Recently, Chiaramonti et al. (2016) have demonstrated that the production of biofuels from microalgae is technically feasible. However, the cost of algal biomass production for energy is still too high to compete with the cost of fossil fuel production (Kumar et al. 2016). Several studies have demonstrated that cost reductions could be optimized if CO_2, nutrients, and water could be obtained from wastewater (Slade and Bauen 2013). The production of microalgae biomass as a by-product in wastewater treatment increases the sustainability, reduces the cost of cultivation process, and brings environmental benefits.

There are many reports of thermochemical processes from microalgae to produce biofuels, such as pyrolysis (Babich et al. 2011; Chaiwong et al. 2013; Miao et al. 2004; Peng et al. 2001; Miao and Wu 2004), liquefaction (Jena et al. 2011; Barreiro et al. 2013; Leng et al. 2015; Eboibi et al. 2014), and gasification (Mian et al. 2015; Brandenberger et al. 2013; López-González et al. 2014), besides the biodiesel and bioethanol production, but few of them propose an alternative culture medium or low-cost production of microalgae. The microalgae have a great potential for the efficient energy production by various processes. Therefore, its characterization is necessary in order to determinate its energetic use through the most viable process.

Among the conversion processes cited, the pyrolysis has been widely used to produce bio-oil and it consists in the thermal degradation of biomass occurring in the absence of oxygen. In this reaction, the organic material is transformed into gas, a liquid fraction, and a solid residue containing carbon and ash (Demirbas 2007).

Therefore, the present study aims the characterization and analytical pyrolysis (Py-GC/MS) of algae biomasses *Chlorella vulgaris* and *Arthrospira platensis* cultivated in sugarcane vinasse-supplemented medium to evaluate their energetic potential for the production of biofuels and other value-added chemical products.

Materials and methods

Cultivation of biomass

C. vulgaris and *A. platensis* microalgae were cultivated in a bubble column photobioreactor of 5.0 L (L 40 cm × Φ 12 cm and conical section of L 12 cm × Φ 12 cm) with diluted medium (Zarrouk 1966) supplemented with clarified sugar cane vinasse of pH 4.5 and COD 42.500 mg L^{-1}, as additional carbon source, in the proportion of 1:1. The volume of culture medium was 3.0 L with 0.1 g L^{-1} initial inoculum concentration. The aeration was realized by diaphragm bombs with an airflow of 0.02 air volume/mean volume/min (VVM) and illumination by fluorescent lamps providing a light intensity of 25 μmol photons m^2 s^{-1} with a photoperiod of 12-h light/dark, under a constant temperature of 30 °C. Posteriorly, the biomasses obtained from cultivation of *C. vulgaris* and *A. platensis* were harvested by a vacuum filtration system and dried in a stove with forced air circulation (SP-102 model) under a temperature of 80 °C for 3 h. Then, the biomasses were ground in a ball mill, sieved to achieve a 1.18-mm particulate.

Biomass characterization

The biomass proximate analysis was developed in triplicate according to ASTM E871-82 (2006), E1755-01 (2007), and E872-82 (2006) for determination of moisture, ash, and volatile matter, respectively, with fixed carbon calculated by difference. Higher heating value (HHV) was determined by bomb calorimeter PARR 1341 according to ASTM E711-87 (2004), and the apparent density was measured by ASTM E873-82 (2006). The ultimate analysis was performed in triplicate using a Series II CHNS/O Analyzer Perkin Elmer 2400. The oxygen content was calculated by the difference of C, H, N, ash, and moisture. The biomass chemical ash composition was determined using X-ray fluorescence (XRF) by dispersive energy in a Shimadzu EDX-820. Thermogravimetric analysis was developed using a TGA Q 500 balance from TA Instruments, from 25 to 900 °C at 10 °C min^{-1}, using 100 mL min^{-1} of N_2 (99.999%) and 10 mg of each biomass. The FTIR spectrums were obtained in a Fourier Transform Bio-Raid Excalibur Series (model FTS 3000 MX) spectrophotometer, from 4000 to 400 cm^{-1}, using KBr disks. The protein content (Kjeldahl nitrogen; N × 5.95 according to González López et al. 2010) was determined using a digester and distiller Kjeldahl of Tecnal (model TE-036/1), the fatty acid content was quantified by AOCS Official Procedure Am 5-04, and the carbohydrate content was estimated as 100% − lipid − protein − ash − moisture content.

Biomass pyrolysis

Micropyrolysis was performed in a 5200 HP-R CDS Analytical Pyroprobe (Oxford-Pennsylvania, USA) interfaced

with VARIAN 3900 GC-MS gas chromatograph. The experiments were carried out at 600 °C with a heating rate of 10.0 °C/ms, using approximately 1 mg of algae biomass placed between the top and bottom quartz wool in a quartz tube of dimensions 25.38 mm × 1.75 mm ID. The pyrolysis vapors were carried by 50 mL min^{-1} of N_2 (99.999%) to a Tenax trap for desorption at 300 °C, transferred through a transfer line heated at 300 °C, and injected at a GC split mode of 1:30. The products were separated by a ZB-5ms column (60 m × 0.25 mm × 0.1 μm) using 1 mL min^{-1} of He (99.999%) as the carrier gas. The column oven temperature program was 40 °C for 2 min, 40–280 °C at a rate of 10 °C min^{-1}, and 280 °C constant for 14.5 min. MS detection was carried out under electron ionization (EI) conditions in full scan from *m*/*z* 40 to 500. Peak identification was done using the NIST Mass Spectrum Library, considered identified at a similarity above 85%. Semiquantitation was performed based on the relative peak areas.

Results and discussion

The proximate analysis results from Table 1 show moderate volatile matter for both microalgae. *C. vulgaris* showed the lower values for this content despite having a lower ash content. It may be due to its high fixed carbon content.

Table 1 Energetic characterization of dry-based microalgae *Chlorella vulgaris* and *Arthrospira platensis*

Biomass characterization	*Chlorella vulgaris*	*Arthrospira platensis*
Proximate analysis (wt%)		
Moisture	9.43 ± 0.34	8.89 ± 0.27
Ash	4.66 ± 0.48	6.37 ± 0.81
Volatile matter	72.49 ± 0.52	79.42 ± 0.31
Fixed carbon[a]	13.42 ± 0.44	5.32 ± 0.46
Higher heating value (MJ kg^{-1})	24.6	22.43
Bulk density (g cm^{-3})	525.4 ± 1.14	722.5 ± 0.67
Ultimate analysis (wt%)		
Carbon	49.27	46.51
Hydrogen	7.01	6.68
Nitrogen	8.12	10.38
Oxygen[b]	35.59	36.42
O/C	0.72	0.78
H/C	0.14	0.14
Crude proteins (wt%)	50.20	61.70
Lipids (wt%)	3.22	1.15
Carbohydrates (wt%)[c]	41.92	30.78

[a] Calculated by difference: Fixed carbon = 100 − volatile − moisture − ash

[b] Calculated by difference: % O = 100 − C − H − N

[c] Calculated by % Carbohydrates = 100 − lipids − protein − ash − moisture

The ash content of both species was slightly lower than the ash content reported in other studies by Chagas et al. 2016 for *Spirulina* (7.94%) and Gai et al. 2013 for *A. platensis* (9.6%) and *Chlorella pyrenoidosa* (5.7%). The reason for the desirable low ash content is due to its negative effect in pyrolysis. Ash reduces significantly the heating value of biomass since it acts as a catalyst in fast pyrolysis, promoting the formation of gas and char, at the expense of bio-oil yield and can also cause operational problems in reactors (Carpenter et al. 2014; Braga et al. 2014).

The higher heating value (HHV) of the microalgae was higher than some lignocellulosic biomass, such as wood (18.6–21.1 MJ/kg) (Francescato and Antoninini 2008), corn straw (17 ± 0.7 MJ/kg) (Capunitan and Capareda 2012), and elephant grass (15.6 MJ/kg) (Braga et al. 2014). Furthermore, these values are close to the literature, as shown by Babich et al. (2011) where *C. vulgaris* was grown under autotrophic conditions in an open pond under continuous stirring, presenting HHV of 21.20 MJ/kg. Jena et al. (2011) and Anand et al. (2016) pointed out heating values of 20.52 and 20.75 MJ/kg for *A. platensis* provided by Earthrise Nutritionals LLC (Calipatria, CA) and Aqua World, respectively. Heating value and bulk density determinate the energy density, which represent the energetic potential by volume unit of biomasses.

The HHV is associated to higher carbon (C) and lower oxygen (O) content of these species when compared to lignocellulosic biomass such as sorghum (40.79% of C, 53.87% of O, 0.73% of N, and 11.87 MJ/kg), wood sawdust (45.97% of C, 48.97% of O, 0.12% of N, and 18.20 MJ/kg) and pine chips (45.9% of C, 46.03% of O, 1.59% of N, and 19.42 MJ/kg) reported by García et al. (2012). Unlike lignocellulosic biomass, *C. vulgaris* is a blue-green microalgae while *A. platensis* is a cyanobacterium, both of which contain significant protein content; thus, it is expected to have high nitrogen content as shown in Table 1.

Besides requiring light for photosynthesis, a carbon source, and water, the microalgae require inorganic nutrients such as nitrogen, phosphorus, and potassium for their reproduction and synthesis of essential biomolecules including cellular protein (Blair et al. 2014). The conventional nitrogen source is the potassium nitrate, which explains the high concentration of nitrogen in the ultimate analysis results shown in Table 1 and potassium in the *C. vulgaris*' and *A. platensis*' ash chemical composition shown in Table 2. A small amount of iron was observed, which comes from the algae nutrition in the aquatic medium.

The difference between both compositions presented in Tables 1 and 2 is due to the different reproduction conditions, such as nourishment and environmental and also for their different metabolisms, which requires a different amount of substances used in their production of essential components for their reproduction, such as amino acids and proteins (Mezzomo et al. 2010; Wang 2014).

Table 2 Ash composition of *Chlorella vulgaris* and *Spirulina platensis*

Chemical composition (%)	P_2O_5	SO_3	K_2O	CaO	Fe_2O_3	MnO	ZnO
Chlorella vulgaris	39.40	36.80	10.60	9.23	3.67	0.25	0.07
Arthrospira platensis	24.07	24.68	42.71	5.80	2.49	0.14	0.11

The proteins are very important in the chemical composition of the microalgae. They are involved in relevant roles such as growth, repair, and maintenance of the cells, also functioning as cell engines, chemical messengers, and cell activity regulators and to raising the defense against foreign invaders (Solomon et al. 1994). The protein content for *C. vulgaris* and *A. platensis* was 50.2 and 61.7%, respectively (Table 1). The average protein content for a mature *C. vulgaris* is 42–58% of its dry weight (Becker 1994; Seyfabadi et al. 2011), and for *A. platensis*, it corresponds to 45–65% (Jena et al. 2011; Gai et al. 2013; Anand et al. 2016) and varies according to its growth condition.

The species *C. vulgaris* and *A. platensis* cultivated in this study had low lipid content (Table 1), what makes them inadequate for biodiesel production through transesterification of fatty acids, the most applied energy conversion process of microalgae in biofuel studied in the literature (Brennana and Owendea 2010; Demirbas 2011; Rawat et al. 2013). However, its volatile content, high protein, and carbohydrates content are favorable characteristics for pyrolysis process to produce bio-oil and diversified chemicals. The thermogravimetric curves of both microalgae are shown in Fig. 1. According to Marcilla et al. (2009), three main stages occur in the decomposition process of the microalgae *Nannochloropsis* sp. including dehydration (25–180 °C), devolatilization (180–540 °C), and decomposition (540–800 °C). In this study, the main mass loss occurs between 130 and 500 °C and represents the volatile matter present in the biomass *C. vulgaris* and *A. platensis*. The first stage of mass loss known as dehydration occurs between 25 and 130 °C and corresponds to loss of free water and the water loosely bound to biomolecules (Pane et al. 2001). The 130–480 °C range corresponds to devolatilization and involves the decomposition of principal components proteins, lipids, and carbohydrates (Peng et al. 2001; Anand et al. 2016). The percentage of non-volatile matter quantified by TGA refers to the fixed carbon and ash, which corresponds to 18% for *C. vulgaris* and 14% for *A. platensis*, values in accordance with the ones obtained at Table 1.

Despite the similarity in their decomposition temperature range, it is possible to see differences between the TGA curves of both microalgae. At the same heating rate (10 °C.min^{-1}), the *C. vulgaris* degrades slightly before and via multiple steps, as evidenced from two decomposition peaks at 260 and 310 °C, while *A. platensis* showed a significant decomposition peak at 300 °C. Previous studies confirm that mass loss profiles of different microalgae species differ even though the main components are the same (Anand et al. 2016). This can be explained with the difference in structure and composition of both microalgae in this study. While *C. vulgaris* had a protein content of 50.2%, protein content of *A. platensis* was 61.7% (Table 1), having 11% difference.

These microalgae contain high protein content, which are composed of different types of amino acids. Leucine, glutamic acid, aspartic acid, and alanine are the majority of the amino acids in *C. vulgaris*, while for *A. platensis* are arginine, glutamic acid, aspartic acid, and alanine in different proportions (Gai et al. 2013; Kay and Bartin 1991). Therefore, due to the distinct composition of both biomasses, they are supposed to have different thermal decomposition profiles as observed in Fig. 1.

Figure 2 shows the chromatograms of pyrolysis products of biomasses, and according to the results shown in Table 3, the presence of few oxygenated compounds was noted, as opposed to what is observed to pyrolysis of lignocellulosic biomass. The pyrolysis of carbohydrates fraction reveals compounds such as 3-methyl-2-cyclopenten-1-ona, 1-methanol-2-ciclopentane, and 2,5-dimethylfuran (Wang 2014), and the peak area of these compounds corresponds to 29% of the total peak area of *C. vulgaris* and 20% of *A. platensis*. The decomposition of lipids generates compounds of high molecular weight like long chain of fatty acid, aldehydes, alcohols, and saturated and unsaturated linear hydrocarbons (Wang 2014; Maher and Bressler 2007). Fragmentation reaction of different compounds gives lightweight molecules (LMW), such as acetic acid and acetic anhydride, that are represented by C_2–C_4 class.

Among the biomass pyrolysis products shown in Table 3, it is possible to see the presence of interesting monoaromatic hydrocarbons, such as xylene, styrene, and especially toluene, which had the highest peak area (%). It

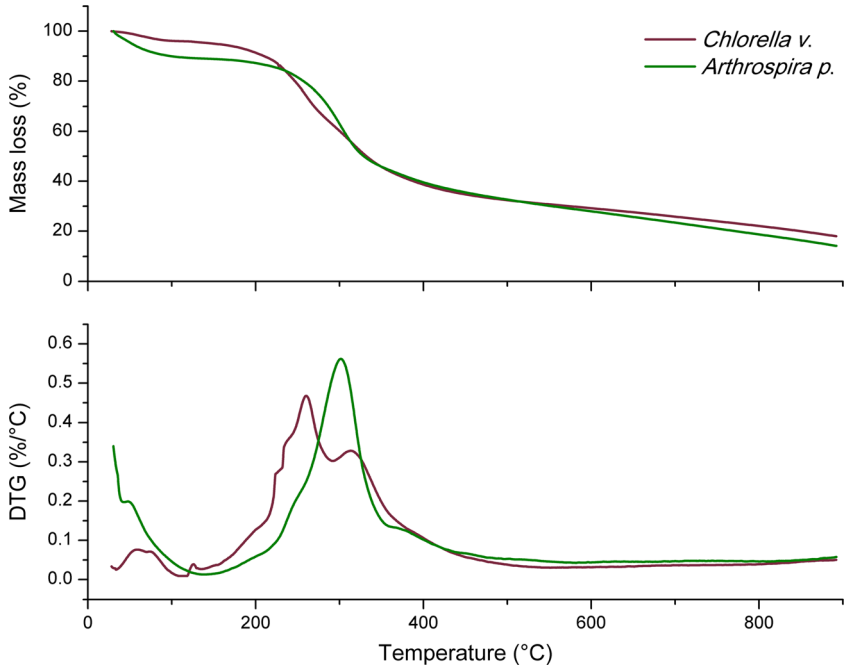

Fig. 1 Thermogravimetric curves (TG/DTG) for *Chlorella vulgaris* and *Arthrospira platensis* biomasses

has been shown that these aromatic hydrocarbons are produced from the proteins (Du et al. 2013; Chagas et al. 2016; Kebelmann et al. 2013). Nevertheless, some aromatic compounds can also be produced from Diels-Alder cyclization of unsaturated lipids (Maher and Bressler 2007), as shown in Fig. 3.

Besides presenting phenolic compounds such as phenol, 2-ethylphenol, 4-methylphenol, 2-methylphenol, and 2,4-

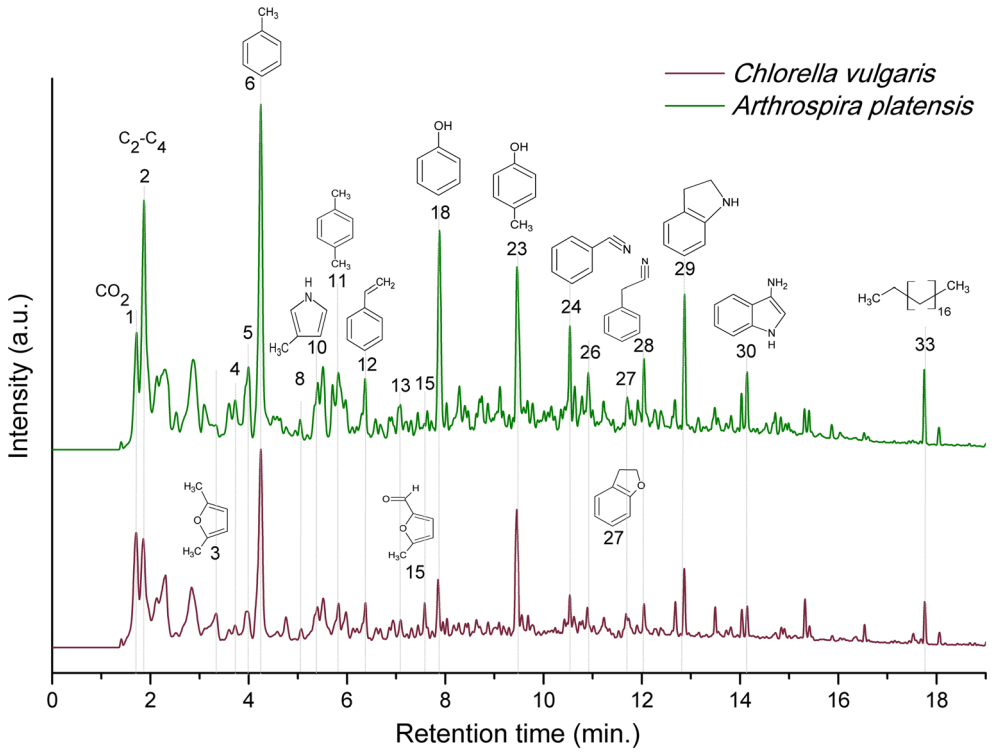

Fig. 2 Chromatograms of pyrolysis products of *Chlorella vulgaris* and *Arthrospira platensis*

Table 3 Pyrolysis products of *Chlorella vulgaris* and *Arthrospira platensis*

	RT	Compound	Peak Area (%)	
			Chlorella v.	*Arthrospira p.*
1	1.4	Carbon dioxide (CO_2)	0.96	0.2
2	1.8	C_2-C_4	40.89	30.01
3	3.3	2,5-Dimethylfuran (C_6H_8O)	3.36	NI
4	3.7	3-Methyl-3-buten-2-one (C_5H_8O)	NI	1.39
5	4.0	1-Methanol-2-cyclopentane ($C_6H_{10}O$)	NI	3.78
6	4.2	Toluene (C_7H_8)	13.94	15.86
7	4.6	1,2-Dichlorocyclopentane ($C_5H_8Cl_2$)	2.33	NI
8	5.0	3-Methylpyridine (C_6H_7N)	0.51	0.57
9	5.1	2-Methylpyrazine ($C_5H_6N_2$)	NI	0.14
10	5.3	3-Methyl-1H-pyrrole (C_5H_7N)	1.11	3.09
11	5.8	Xylene (C_8H_{10})	3.90	3.20
12	6.3	Styrene (C_8H_8)	1.94	2.19
13	7.0	2,5-Dimethylpyridine (C_7H_9N)	0.89	NI
14	7.4	Propylbenzene (C_9H_{12})	0.36	NI
15	7.5	5-Methyl-2-furaldehyde ($C_6H_6O_2$)	1.47	NI
16	7.6	3-Methyl-2-ciclopente-1-one (C_6H_8O)	NI	0.36
17	7.7	1H-Pyrrole, 2-ethyl-4-methyl-($C_7H_{11}N$)	NI	0.31
18	7.8	Phenol (C_6H_6O)	2.13	7.67
19	7.9	Pyrimidinone ($C_5H_6N_2O$)	0.32	NI
20	8.4	2,3,4-Trimethylpyrrole ($C_7H_{11}N$)	0.55	NI
21	9.0	2-Methylphenol (C_7H_8O)	0.26	0.55
22	9.3	3-Pyridinecarbonitrile ($C_6H_4N_2$)	NI	0.32
23	9.4	4-Methylphenol (C_7H_8O)	5.73	6.10
24	10.5	Benzylnitrile (C_8H_7N)	1.02	2.52
25	10.6	2,4-Dimethylphenol ($C_8H_{10}O$)	0.53	1.05
26	10.8	2-Ethylphenol ($C_8H_{10}O$)	0.82	1.16
27	11.7	2,3-Dihydrobenzofuran (C_8H_8O)	1.05	0.92
28	12.1	Benzenepropanenitrile (C_9H_9N)	1.25	1.41
29	12.8	Indole (C_8H_7N)	2.34	3.58
30	14.1	1H-indole, 3-methyl-(C_9H_9N)	0.90	1.54
31	15.4	Tetradecane ($C_{14}H_{30}$)	NI	0.41
32	15.8	Bibenzyl ($C_{14}H_{14}$)	NI	0.35
33	17.7	Nonadecane ($C_{19}H_{40}$)	NI	1.70

RT Retention time, *NI* Not identified

dimethylphenol, the pyrolysis of protein fraction is also responsible for the formation of many nitrogenous compounds: indoles, pyrroles (3-methyl-1H-pyrrol) and nitriles (benzenepropanenitrile) (Wang 2014; Ware 2013). Many of these products are derived from amino acids that composed the original structure of protein. The presence of toluene, phenol, and other aromatic hydrocarbons is associated to the presence of amino acid that contains aromatic rings in its structure, such as tyrosine and phenylalanine in the microalgae proteins (Wang 2014), as shown in Fig. 3. Anand et al. (2016) also identified organic nitrites, nitriles, amines, amides, piperidine, pyrroles, and monoaromatics as pyrolysis products of *A. platensis* at the temperature range 350–800 °C. At higher temperatures, monoaromatic content increased and the formation of nitriles was attributed to the dehydration of amides that are originally present in algae proteins (Anand et al. 2016).

As can be seen in Table 3, most of pyrolysis products are common to the two studied biomasses, but Fig. 4 shows that

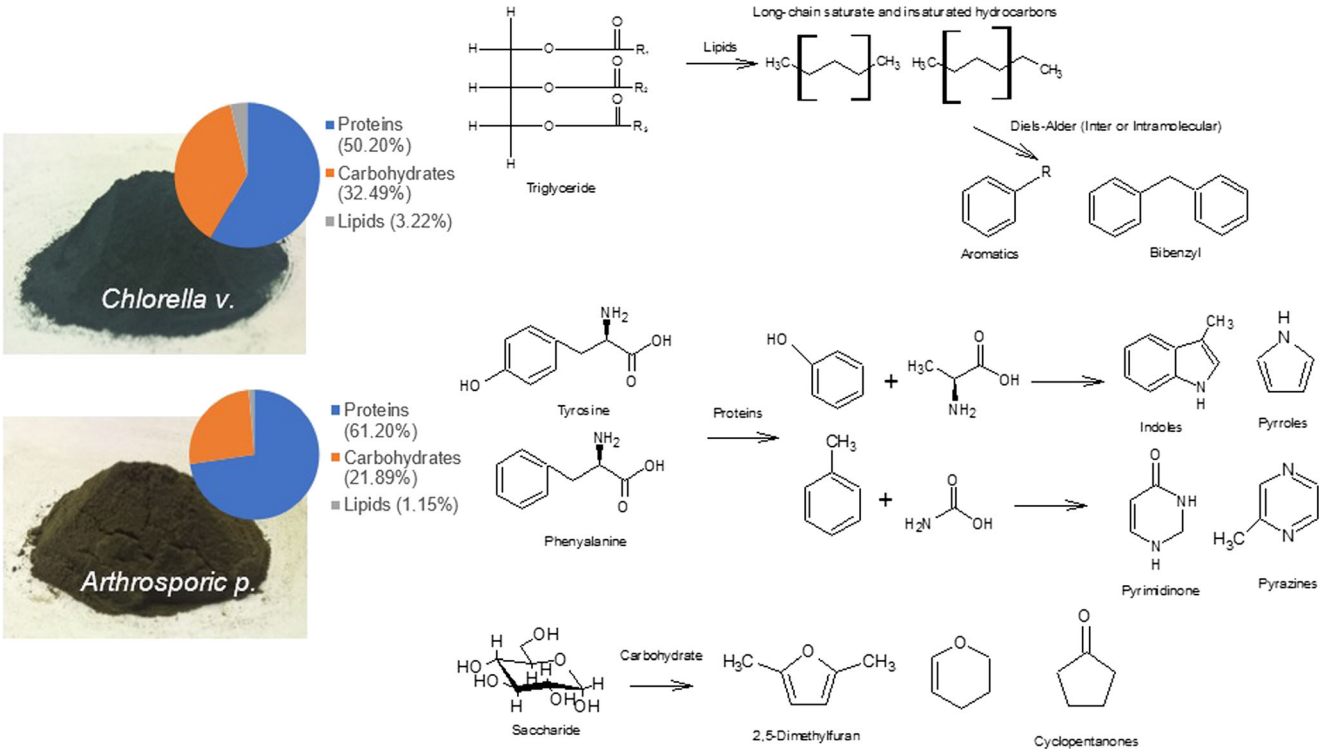

Fig. 3 General proposed pathway of pyrolysis product of *Chlorella vulgaris* and *Arthrospira platensis*

the distributions of these products are different for each. It points out that *A. platensis* has higher amount of aromatics, phenols, and nitrogenates than *C. vulgaris*, what is expected since it has a higher content of proteins (Table 1). On the other hand, the C_2–C_4 content should be highlighted for the *C. vulgaris* and associated to cracking reactions of molecules of higher molecular weight such as carbohydrates, which represents 29.96 wt% of this microalgae and results in furans such as 2,5-dimethylfuran identified between the pyrolysis products of *C. vulgaris*.

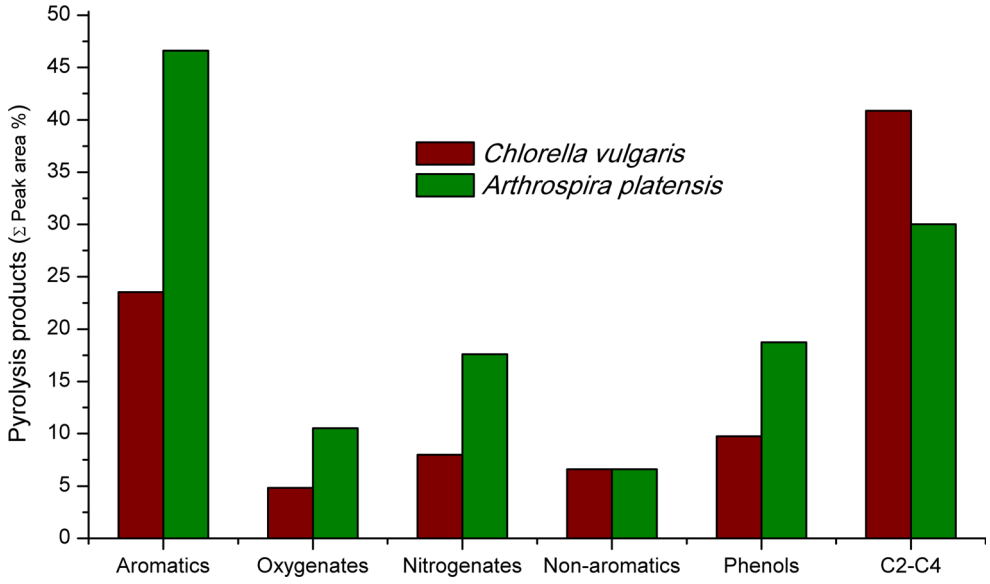

Fig. 4 Distribution of pyrolysis products of *Chlorella vulgaris* and *Arthrospira platensis* by class

Conclusion

C. vulgaris and *A. platensis* were identified as proteinaceous biomass that presented good properties for fast pyrolysis process, including low ash content, high heating value, and high volatile material content that can lead to high yield of bio-oil. High-added-value chemicals were found among the pyrolysis products, such as xylene, styrene, phenol, and toluene. These products could lead to a good-quality bio-oil for biofuel production, but great amounts of nitrogenized compounds were also identified among pyrolysis products, which need to be avoided or removed. Therefore, the great energetic potential of these microalgae makes them an interesting source of bio-oil and even more interesting source for bioproduct production through pyrolysis. Toluene had a significant amount produced, being the major pyrolysis product in both microalgae, what makes them a renewable source to obtain this chemical of great industrial interest.

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