Valorization of *Rhizoclonium* sp. algae via pyrolysis and catalytic pyrolysis

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H I G H L I G H T S

- *Rhizoclonium* sp. algae is used for obtaining bio-oils.
- Pyrolysis of *Rhizoclonium* sp. is carried out in a vertical glass reactor at 400 °C.
- Phytol, a high valuable product, is obtained in the bio-oil.
- The solid catalyst in the reactor increase cracking reactions.

A R T I C L E   I N F O

A B S T R A C T

The valorization of *Rhizoclonium* sp. algae through pyrolysis for obtaining bio-oils is studied in this work. The reaction is carried out at 400 °C, at high contact time. The bio-oil has a practical yield of 35% and is rich in phytol. Besides, it is simpler than the corresponding to lignocellulosic biomass due to the absence of phenolic compounds. This property leads to a bio-oil relatively stable to storage. In addition, heterogeneous catalysts (Al–Fe/MCM-41, SBA-15 and Cu/SBA-15), in contact with algae during pyrolysis, are analyzed. The general trend is that the catalysts decrease the concentration of fatty alcohols and other high molecular weight products, since their mild acidity sites promote degradation reactions. Thus, the amount of light products increases upon the use of the catalysts. Particularly, acetol concentration in the bio-oils obtained from the catalytic pyrolysis with SBA-15 and Cu/SBA-15 is notably high.

1. Introduction

Pyrolysis of biomass has been studied as a promising option for transforming diverse feedstock into bio-oils, which can be employed directly as fuels, upgraded into petroleum replacements or employed as a source of valuable chemicals (Bridgwater, 2012; Duan and Savage, 2011; Elliott, 2007). Traditionally, lignocellulosic waste materials have been utilized for obtaining bio-oils through pyrolysis. These bio-oils are a mixture of a large number of compounds, which show several undesired properties. Although some of such compounds are high valuable chemicals, the separation is difficult. Besides, high concentrations of acidic compounds turn the bio-oil highly corrosive. In addition, phenolic compounds, which are originated in the lignin thermal decomposition, spontaneously re-polymerize forming a separated solid phase (Diebold and Czernik, 1997). Thus, the storage of bio-oils obtained from the pyrolysis of lignocellulosic biomass shows technical difficulties.

The composition of algae (proteins, lipids and carbohydrates) is quite different from the one corresponding to lignocellulosic biomass (cellulose, hemicellulose and lignin). Therefore, the composition of the liquids from the pyrolysis of algae should be different from the classical one corresponding to lignocellulosic material. The absence of lignin would lead to liquids free from phenolic compounds, which are the responsible for polymerization reactions leading to the formation of undesired gums in the bio-oils. Thus, algal bio-oils are more stable than the corresponding to terrestrial biomass (Kim et al., 2013). Besides, the relative high concentration of proteins and lipids in algae would lead to a liquid that could be considered as a source for valuable compounds. It is important to note that lipids are obtained from algae using traditional solvent extraction, which is time consuming and hazardous (Kumari et al., 2011; Roche et al., 2010).

In Argentina, algae are abundant in lagoons, lakes and coastal zones (Esquius and Escalante, 2012). In addition, algae are

cultivated on an industrial scale for biodiesel production (Popovich et al., 2012a,b).

In the last years, the increased agricultural production led to growing levels of nitrate and phosphate into the Pampean shallow lakes in Argentina, causing the eutrophication of water. This phenomenon acts as a trigger for a series of processes that result in changing conditions and eventual replacement of organisms adapted to the new environment (Diovisalvi et al., 2015; Rennella and Quirós, 2006). This fact could be the responsible for the considerable growing of *Rhizoclonium* sp. observed during the months of November and December in a shallow lake located in Puan (SW of Buenos Aires province, Argentina). During these months in this water body, isolated mats of *Rhizoclonium* sp. floats in the lagoon. The massive occurrence of this alga alters nutrient cycling and sediment chemistry since it takes large amounts of nitrogen (Baron et al., 2013; Lagomarsino et al., 2011). The proliferation of algae has triggered several research works, some of them regarding pyrolysis of these materials (Hu et al., 2013; Ross et al., 2008; Yanik et al., 2013; Kim et al., 2013; Plis et al., 2015). However, it is important to note that, as far as our knowledge concern, *Rhizoclonium* sp. has never been studied as a starting biomass for pyrolysis or any other transformation.

The main objective of the present work is to investigate the valorization of *Rhizoclonium* sp. through pyrolysis for obtaining bio-oils. Possible uses of the liquids are evaluated taking into account the compounds present in it, mainly those with a high economical interest. Besides, the influence of solid catalysts on the chemical composition of the liquids is also studied. The major part of the studies regarding catalytic pyrolysis of algae, are mainly focused on obtaining bio-oils in the context of their employment as biofuels. (Suchithra et al., 2012; Aysu and Sanna, 2015; Hu et al., 2013). On the other hand, in the present work the algal bio-oil is considered as a source of valuable chemicals.

The fast pyrolysis of the algae is carried out at 400 °C in a vertical glass reactor at high contact time trying to produce liquids with high yield. Besides, the influence of mesoporous catalysts on the chemical composition of the liquids is also analyzed.

Finally, the properties of bio-oils obtained from *Rhizoclonium* sp. are compared with those corresponding to lignocellulosic biomass (sunflower seed hulls), which is also an abundant biomass in Buenos Aires province, Argentina.

2. Material and methods

Rhizoclonium sp. was extracted in November and December from the Puan shallow lake (8.9 km^2) located in Buenos Aires province, Argentina (37°33′13″S, 62°47′46″W).

The extracted biomass was dried at 50 °C until constant weight and it was milled in particles with sizes in the range of 10–100 μm. The particle size was determined in a Horiba LA-950 laser diffraction equipment.

The fast pyrolysis was carried out in a vertical glass reactor, which was put into a furnace at 400 °C. Approximately 3 g of algae were supported on a porous glass disk fixed at the end of the reactor. The N$_2$ flow (200 ml min^{-1}) was feed from the top creating an inert atmosphere. The vapors downstream were condensed in a water/ice bath. The experimental conditions were selected in order to maximize the yield to liquids. For further details, see (Casoni et al., 2015).

Some pyrolysis experiments were carried out putting approximately 100 mg of three different catalysts (Al–Fe/MCM-41, SBA-15 and Cu/SBA-15) in contact with the biomass. Al–Fe–MCM-41 (with a Si/Me molar ratio of 60 for each metal) was prepared by a classical hydrothermal synthesis as described elsewhere (Casoni et al., 2016). The SBA-15 material was also obtained by

classical hydrothermal synthesis (Meynen et al., 2009) using P123 as tensioactive and tetraorthosilicate (TEOS) as silicium source in acidic medium. The Cu/SBA-15 catalyst presented 10% of cooper, which it was introduced to SBA-15 by incipient wetness impregnation with Cu(NO$_3$)$_2$. The concentration of Fe, Cu and Al in the catalysts was determined by Atomic Absorption Spectroscopy in a Perkin Elmer AAnalyst 700 instrument. X-ray diffraction (XRD) study was carried out in a Philips PW1710 BASED apparatus equipped with a graphite monochromator, operating at 45 kV and 30 mA and employing CuKα1 radiation (15.406 nm); the angle step was 0.035 (2θ) and the counting time was 1 s.

Nitrogen adsorption/desorption isotherm at 77 K was measured for the catalysts in a Quantachrome NOVA 1200e Series instrument.

Before the analysis, all samples were evacuated at 120 °C for 24 h. The specific surface area was calculated following Barrett–Emmett–Teller (BET) method. The pore volumes and pore size distribution were determined by the Barrett–Joyner–Halenda (BJH) approximation from the adsorption branch of the isotherm.

The acidity of the catalysts was measured by potentiometric titration with n-butylamine. The solid was dispersed in 100 ml of acetonitrile and the mixture was stirred for 3 h. Afterwards it was titrated with a 0.1 N solution of butylamine employing an AT500N Automatic Potentiometric Titrator. The total surface acidity was evaluated from the amount of base added to reach the plateau in the titration curve, while the first point of the titration (E_0, mV) was employed for analyzing the acid strength (Covarrubias et al., 2009)

Rhizoclonium sp. alga was characterized by thermo-gravimetric (TG) and differential thermo-gravimetric (DTG) analysis, employing a TA Instruments – SDT Q600. Firstly, the scale was purged with N$_2$ during 20 min to ensure an oxygen free atmosphere. Then 20 mg of the sample were heated at 5, 10 and 20 °C min^{-1}, ranging from room temperature to 800 °C. This equipment was also utilized for performing the proximate analysis of *Rhizoclonium* sp. The conversion, X, calculated by TGA is defined as:

$$X = W_0 - W/W_0 - W_f \tag{1}$$

where W_0 is the initial mass of *Rhizoclonium* sp., W is the pyrolyzed mass and W_f is the mass measured following thermogravimetric analysis. From TGA, at the different heating rates, the differential rate of conversion, dX/dt was calculated. Activation energies values were calculated from Arrhenius equation following the methodology exposed by Kim et al. (2013).

In order to determined ashes, the alga was heated from room temperature to 900 °C under inert gas flow (N$_2$). Afterwards, the inert was switched to O$_2$. The mass obtained following this procedure corresponds to the ashes content of the sample.

The ultimate analysis was performed in a CHNS/O Analyzer Perkin Elmer 2400.

The concentration of Na, K, Ca, Mg, S and P were measured by means of Inductive Coupled Plasma with a Shimadzu simultaneous 9000 equipment following EPA standard 200.7.

The bio-oils from pyrolysis were studied using gas chromatography coupled with mass spectroscopy, employing GC–MS Perkin Elmer CLAURUS 500 chromatograph, equipped with an Elite-5 MS column (60 m, 0.25 mm ID and 0.25 μm df). The applied chromatographic method consisted of an initial temperature of 65 °C hold for 5 min, followed with a ramp of 30 °C/min up to 280 °C hold for 0.83 min.

The identification of chromatographic peaks was achieved according to the NIST MS library with global matches higher than 800, while for the case of majority compounds (acetol and phytol,) the corresponding matches were higher than 900. The quantitative analysis of the bio-oils was determined considering that the peak

area is directly proportional to the concentration of each compound in the sample.

3. Results and discussion

3.1. Characterization of Rhizoclonium sp.

The analysis corresponding to the proximate and the ultimate analysis of *Rhizoclonium* sp. are reported in Table 1, as well as the concentration of metals. For the sake of comparison, the results corresponding to a terrestrial biomass (sunflower seed hulls) are also shown. The results in Table 1 will be discussed in the context of the employment of the algae for producing bio-oils.

The concentration of alkali metals in the algae is much higher in comparison with the concentration corresponding to the lignocellulosic biomass (Table 1). The presence of these elements in the biomass for pyrolysis is a quite significant parameter since it is well known that the alkali metals lead to a lower production of bio-oils and a higher production of char (Ramirez-Corredores, 2013). Besides, high ash contents were measured, which represent a negative characteristic to this algal biomass.

Thermogravimetric analysis (TGA) at different heating rate were performed to obtain an estimation of pyrolysis behavior of *Rhizoclonium* sp. The results are shown in Fig. 1. The profile of algal biomass normally presents three steps. The first one (below 100 °C) is attributed to moisture, while the mass loss at 110 °C is assigned to water in line with the results of Kim et al. (2013). The mass loss between 200 and 270 °C would correspond to decomposition of carbohydrates, while the one below 350 °C indicates the decomposition of the protein fraction (Ross et al., 2008; Bae et al., 2011). The major mass decomposition occurs between 200 and 350 °C, as was observed for other macro algae (Kim et al., 2013; Kim et al., 2012; Li et al., 2011). The mass loss at temperatures higher than 600 °C, would be related with lipids degradation.

The overall activation energy for the degradation of *Rhizoclonium* sp. (see Table 3) are lower than the ones reported for other macroalgae (Kim et al., 2013; Kim and Agblevor, 2007). The activation energy calculated between 20% and 40% of conversion was 178.7 and 235.3 kJ/mol, which would correspond to carbohydrates degradation (see Fig. 1c).

For the sake of comparison, in Fig. 1 TGA/DTA analysis of sunflower seed hulls (taken as a typical lignocellulosic material) is also shown. Apart from the first peak due to moisture, the thermal
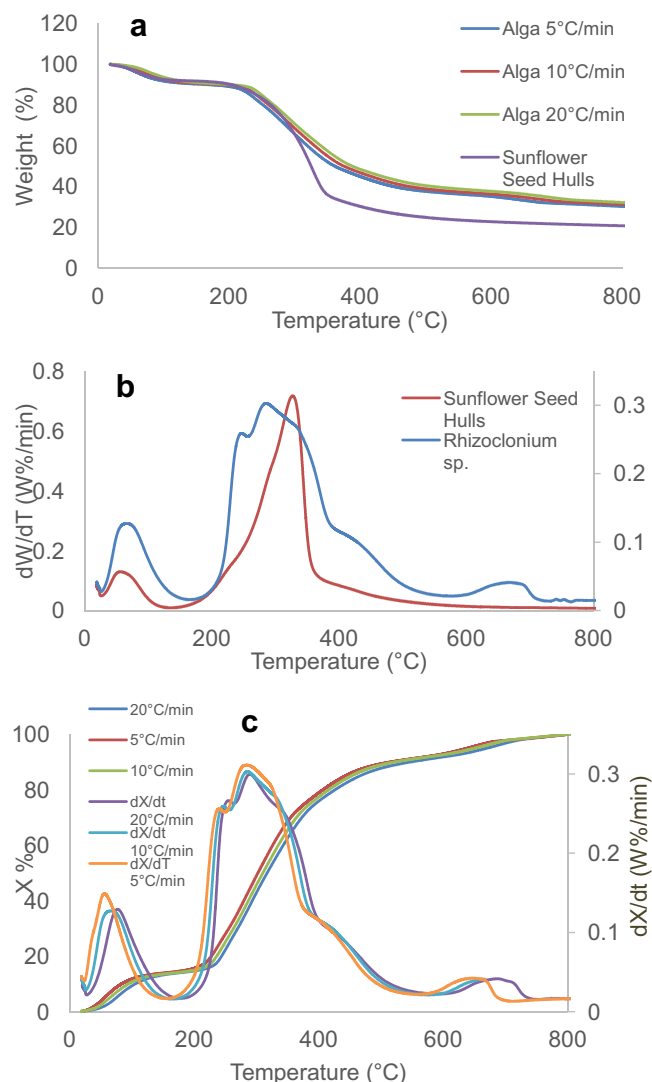

Fig. 1. (a) Weight loss curves for sunflower seed hulls and *Rhizoclonium* sp. at different heating rates; (b) DTA for sunflower seed hulls and *Rhizoclonium* sp. at 10 °C/min and (c) thermogravimetric and differential thermogravimetric curves for *Rhizoclonium* sp. at heating rates of 5 °C/min, 10 °C/min and 20 °C/min.

degradation of algae starts approximately 50 °C before the process corresponding to husks, showing that *Rhizoclonium* sp. is more prone to the thermal attack than the lignocellulosic material. This may happen mainly due to the absence of lignin in the algal biomass. Another difference is the absence of mass loss at high temperatures due to lipids, which are present in low concentration in terrestrial biomass. The mass loss detected by TGA/DTA at 400 °C (the same temperature as the one corresponding to the pyrolysis experiments) is 51.5% and 70% for the algae and for the husks respectively. The lower thermal degradation of alga would be in line with the higher content of refractive alkali metals.

3.2. Bio-oil analysis

The practical yield to bio-oil was approximately 35 wt%, which could be considered as quite high taking into account the presence of alkali metals and the high content of ashes in the algal biomass.

GC–MS analysis was carried out in order to determine the chemical composition of bio-oils. In Table 2, the complex compositions of bio-oils are reported. To simplify the analysis of the compounds of the bio-oil, the following classification was carried out:

Table 1
Characterization of *Rhizoclonium* sp. and sunflower seed hulls.

Analysis	Rhizoclonium sp.	Sunflower seed hulls
Proximate analysis % (dry basis)		
Ash	16.5	2.1
Volatile matter	75.5	79.8
Fixed carbon	8.0	18.1
Moisture	11.2	6.1
Ultimate analysis %		
C	38.1	46.5
H	5.9	6.3
N	4.2	0.7
O [a]	51.8	46.3
Metals (%)		
Na	3.32	0.01
K	1.48	1.04
Mg	0.39	0.19
Ca	1.42	0.32
P	0.35	–
S	1.17	–

[a] Calculated by difference.

Table 2
Properties of the catalyst used in the pyrolysis of *Rhizoclonium* sp.

Catalyst	Wt% of metal	S_{BET} (m²/g)	Pore diam (nm)	Pore volume (cm³/g)	mEq/g
Al–Fe–MCM-41	1.6[a]–2.3[b]	883	4.2	0.83	0.83
SBA-15	–	1323	7.2	1.43	1.25
Cu/SBA-15	9.8	1174	5.6	1.55	1.45

[a] Al (wt%).
[b] Fe (wt%).

Table 3
Calculated kinetic parameters for the pyrolysis of *Rhizoclonium* sp.

X%	Ea (kJ/mol)	Order		
		A (0th)	A (1st)	A (2nd)
5	80.2	3.56E+08	7.12E+07	1.42E+07
10	64.1	1.50E+05	1.50E+04	1.50E+03
20	178.7	6.48E+14	3.24E+13	1.62E+12
30	175.1	4.56E+13	1.52E+12	5.06E+10
40	235.3	3.71E+18	9.27E+16	2.32E+15
50	224.5	4.97E+16	9.94E+14	1.99E+13
60	200.9	6.52E+13	1.09E+12	1.81E+10
70	213.6	7.94E+13	1.13E+12	1.62E+10
80	305.1	2.11E+19	2.64E+17	3.29E+15
90	207.9	5.63E+09	6.26E+07	6.95E+05
95	161.0	1.43E+05	1.51E+03	1.59E+01

nitrogen-containing compounds, furans, low molecular weight acids/ketones/aldehydes (*C* < 4), fatty alcohols, esters, and olefins (Fig. 2). Particular features were observed in the algal bio-oil composition: nitrogen-containing compounds and fatty alcohols in relatively high concentration were detected. Another characteristic is that the liquid from *Rhizoclonium* sp. is free of phenolic compounds. This is an expected result since such compounds are originated in the degradation of lignin, which is totally absent in algae (Ross et al., 2008). It was claimed that phenolic compounds, mainly methoxy-phenols are the responsible for the instability of pyrolytic liquids from terrestrial biomass, since these compounds tend to re-polymerize. In this sense, the algal bio-oil would present a great advantage from a practical point of view, since the storage could be carried out without formation of solid precipitates.

Phytol (3,7,11,15-tetramethyl-2-hexadecen-1-ol) is a highly valuable product, which is mainly used in fragrance industry (McGinty and Letizia, 2010) and in the synthesis of vitamins K1 and E. The concentration of this unsaturated fatty alcohol is quite high and considering the yield to liquid in the pyrolysis of algae under the present experimental conditions, the mass yield to phytol is approximately 10%.

Another aspect to consider is the presence of amines in the bio-oil (dimethyl-amine and trimethyl-amine), which are originated from the degradation of proteins. Therefore, the basic nature of these compounds partially neutralizes the acidity of the bio-oil. The relatively low acidity is another advantageous property. At this point, it is important to consider that the liquids from lignocellulosic materials show highly acidic pH values, thus being highly corrosive (Jacobson et al., 2013). In this sense, the liquids from *Rhizoclonium* sp. would facilitate the storage.

In previous work, the chemical nature of the bio-oils obtained from pyrolysis of a lignocellulosic residue (sunflower seed hulls) has been analyzed (Casoni et al., 2015). The comparison between the bio-oil obtained from the seed hulls and the one obtained from *Rhizoclonium* sp. shows notable differences. The concentration of fatty alcohol, olefins, and amines is null in the former liquid, while these compounds are quite abundant in the algal liquid, as was already commented. On the other hand, a high concentration of phenolic compounds is observed only in the bio-oil from sunflower seed hulls. Thus, the liquid coming from *Rhizoclonium* sp. pyrolysis is less complex than the one obtained from the terrestrial biomass. Another difference between the pyrolytic bio-oils of *Rhizoclonium* sp. and of husks is that the yield corresponding to algae is approximately 35%, while the one of the terrestrial biomass is 34%. The algal bio-oil yield is relatively high in spite of the high concentration of alkali metal.

3.3. Catalytic pyrolysis

In order to modify the chemical composition of the bio-oil obtained from the pyrolysis of *Rhizoclonium* sp., the use of solid catalysts in contact with the algae during pyrolysis was studied. The selected catalysts were mesoporous ones, SBA-15, Cu/SBA-15 and Al–Fe/MCM-41. Mesoporous solids were previously analyzed for carrying out the catalytic pyrolysis of cellulose and it was concluded that the pore dimension of mesoporous systems, as well as
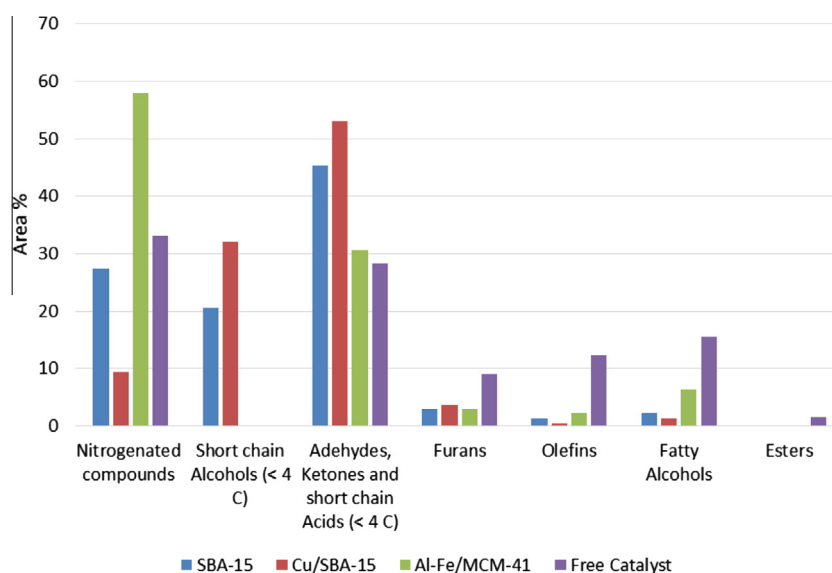

Fig. 2. Products distribution of the bio-oils obtained by pyrolysis and catalytic pyrolysis.

large specific surface areas, promoted high yield to liquid during pyrolysis (Casoni et al., 2016). On the other hand, catalysts with lower pore dimensions (as in the case of microporous solid catalysts) led to a low production of liquid, promoting solid formation (Nieva et al., 2015).

The structure of Cu-SBA-15 and SBA-15 was confirmed by means of XRD analysis: three peaks due to (100), (110), and (200) were detected in the range of $2\theta = 0.5$–$2.5°$. For the case of Al–Fe–MCM-41, an intense peak at 2θ: $2.5°$ was observed, assigned to the diffraction of (100) plane of MCM-41. Other minor peaks at small angles, which are typically observed for the MCM-41 family.

In Table 2, some physicochemical properties of the mesoporous catalysts used in the present work are reported. The three cases present specific surface area higher than 900 m² g⁻¹. Regarding pore volume and pore size, the values are typical of mesoporous systems (Majdaa et al., 2016).

The acid properties of the catalysts were investigated by titration with n-butilamine. This technique determine both, the strength and the concentration of surface acidity of solids. (Covarrubias et al., 2009). All the three catalysts showed mild acidity (which corresponds to Eo in the 0–100 mV range). It can be observed that the concentration of acid sites increases in the following order: Al–Fe–MCM-41 < SBA-15 < Cu-SBA-15 (see Table 2).

The presence of the solid catalysts in the pyrolysis reactor strongly modified the composition of bio-oils from *Rhizclonium* sp. This effect can be clearly observed in Fig. 2 and Table 4, where the percentages of the different products of the bio-oils corresponding to the catalytic pyrolysis are shown. The main effect of all the catalysts was that the concentration of the high molecular weight products (furans, fatty alcohols, olefins, esters) was notably depleted in the bio-oils from catalytic pyrolysis. For instance, the concentration of phytol was 14% in the catalyst free pyrolysis and this value decreased to 1.5% for SBA-15, 1.1% for Cu-SBA-15 and 5.1% for Al–Fe–MCM-41. In the case of olefins (for example 8-heptadecene), the concentration decreased from 13% (catalyst free process) to values lower than 1% for the catalytic pyrolysis.

On the other hand, a marked increase in the concentration of lighter compounds in the bio-oils from catalytic pyrolysis is observed for all the catalytic processes. Thus, the general trend is that the presence of mesoporous catalysts promotes cracking of high molecular weight molecules, increasing the concentration of light compounds. This is clearly observed in Fig. 2, where the rela-
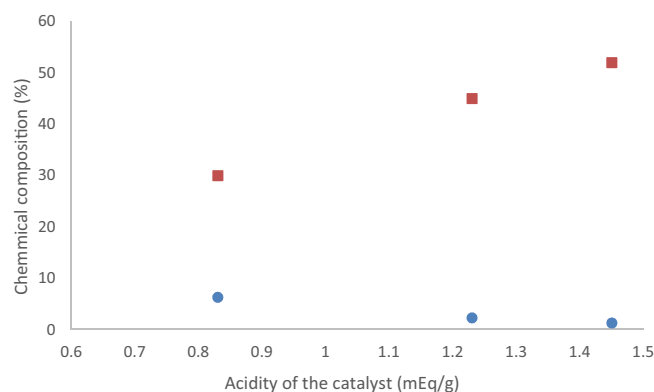

Fig. 3. Dependence of the percentage of the concentration light molecular weight (■) and high molecular weight compounds (●) on the acidity of the mesoporous catalysts.

tive concentration of the different group of compounds is reported for the different pyrolysis. Fatty alcohol, olefins and furans concentration notably diminished upon the use of catalysts, while the one corresponding to aldehydes, ketones and low alcohols increases.

The acidity of the catalysts is a parameter of paramount importance, since acid sites promote a wide variety of reactions. In Fig. 3 the dependence of concentration of light compounds, as well as the one corresponding to heavy ones, on the specific amount of acid sites of the catalysts is shown. The trends in this figure suggest that light compounds (as acetol, for example) are originated in the degradation of large molecules.

It is important to note that the concentration of 1-hydroxy-2-propanone (acetol) is higher in the bio-oils from catalytic pyrolysis. The concentration of this compound is higher than 40% for the bio-oils originated in the pyrolysis using Cu/SBA-15 and SBA-15. Acetol is a high valuable intermediate in the production of polyols, acrolein, and it is employed in the textile and cosmetic industry (Zhu et al., 2013) In this sense, finding an alternative way to obtain acetol is of great technological importance.

Due to the complex nature of bio-oils and the catalytic cracking reactions (involving dehydration, decarboxylation, decarbonylation and rearrangement), the scenario of the catalytic pyrolysis cannot be fully described.

Table 4
Chemical composition (area%) of the bio-oils from *Rhizclonium* sp. with and without catalysts.

Compound	Alga	SBA-15	Cu/SBA-15	Al–Fe/MCM-41
Dimethylamine	4.9	23.5	7.3	23.5
(Aminocarbonyl)amino,oxo-acetic acid	9.5	–	–	–
Trimethylamine	3.4	–	–	14.9
Acetaldehyde	3.2	–	–	–
Acetic acid	8.5	5.1	6.2	13
1-Hydroxy-2-propanone	16.6	40.3	46.9	17.6
2-Propanodiol	–	20.6	32.1	–
2-Hydroxypropanenitrile	–	3.9	2.2	–
Pyrrole	3.2	–	–	5.2
Dimethylformamide	5.1	–	–	3
1-H-imidazole-4-propanamine	2.2	–	–	–
4,5-Dihydro-4,5-dimethyl-1H-Pyrazole	–	–	–	3.6
3-Methyl-1H-pyrrole	–	–	–	4.6
2-Furanmethanol	4.9	3	3.6	2.9
5-Methyl-2-furancarboxaldehyde	4.2	–	–	–
Indolizine	4.8	–	–	–
5H-1-pyrindine	–	–	–	3.1
8-Heptadecene	8.6	–	–	0.4
3,7,11-Trimethyl-1-dodecanol	2.1	0.8	0.2	1.2
3,7,11,15-Tetrametil-2-hexadecen-1-ol	13.4	1.5	1.1	5.1
3,7,11,15-Tetramethyl-2-hexadecene	3.7	1.3	0.4	1.9
14-Methyl-pentadecanoic acid methyl ester	1.7	–	–	–

4. Conclusion

The algal liquids are free of phenolic compounds, which turn them into a material more stable to storage than the classical pyrolytic counterparts corresponding to lignocellulosic materials. In addition, algal bio-oil could be considered as a source of high value chemicals, as for example phytol. The catalytic pyrolysis of *Rhizoclonium* sp., using mesoporous catalysts, leads to strong modification, depleting the concentration of high molecular compounds in the liquid, and increasing the corresponding to light products, some of them, as for example acetol, have great technological importance.

Acknowledgement

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