



Renewable energy sources in Morocco: Comparative study of bio-oils from pyrolysis of lignocellulosic and algal biomass wastes

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Abstract

In the 21st century, new challenges have been thrown up by the globalization process. It is time for a positive economy, which upgrades the countries resources of each territory of the planet. And it is time to an efficient economy that meets needs of the population as much as possible while respecting the environment. Protection of environment is of immediate concern, and this can only be achieved by avoiding the use of chemicals for fuel production. Lignocellulosic and algal biomass wastes are becoming accepted as feedstocks and can be converted into utilizable form of bio-fuel production. Pyrolysis is a thermochemical decomposition process in which biomass is renewed and converted into a volatile matter and carbon rich solid (bio-oil, bio-char and gas products) by heating in the absence of oxygen. Morocco is one of the famous Mediterranean countries known through its industrial activities (production of olive oil, sugar, wood and algae). These activities generate several types of waste which affect the quality of the environment. To act and to remedy these environmental problems, pyrolysis presents an effective solution to minimize these impacts and to convert these wastes to useful products such as bio-oils.

1. Introduction

Most of the scenarios for future energy supply suggest that renewable energy will play significant role in the 21st century [1-3]. Several types of renewable energies are destined to play an important role in energy systems. Lignocellulosic and algal biomasses have great potential by offering annually renewable sources to replace the liquid hydrocarbons [4]. Biomass is an important contributor to the world economy. Today, various forms of biomass energy such as, lignocellulosic biomass and algal biomass are consumed all over the world [5]. These types of biomass provide a clean renewable energy source that could dramatically improve the energy security, environment and economy. Bio-energy does not contribute to climate change through emissions to the atmosphere of CO₂ 'carbon dioxide' or other GHG 'green-house gases' [5, 6].

Conventional biomass is generally divided into two groups: lignocellulosic biomass and algal biomass. Lignocellulosic biomass contains three main components, namely hemicellulose, cellulose and lignin, while the algal biomass is mainly composed of carbohydrates, proteins and lipids [7-10]. The

compositions of biomass determined basically the physicochemical properties of pyrolysis products. Among all technologies connected to renewable energy, used in the past, studied and used in the present, it can be founded thermochemical conversion of biomass [2-4]. Different thermochemical treatment processes include pyrolysis, gasification, combustion and liquefaction. Although pyrolysis is still in the developing stage during existing energy scenario it has received special attention as it can convert biomass directly into liquid (bio-oil), solid (bio-char) and gaseous products by thermal decomposition of biomass in the absence of oxygen, as seen in Figure 1 [7, 8].

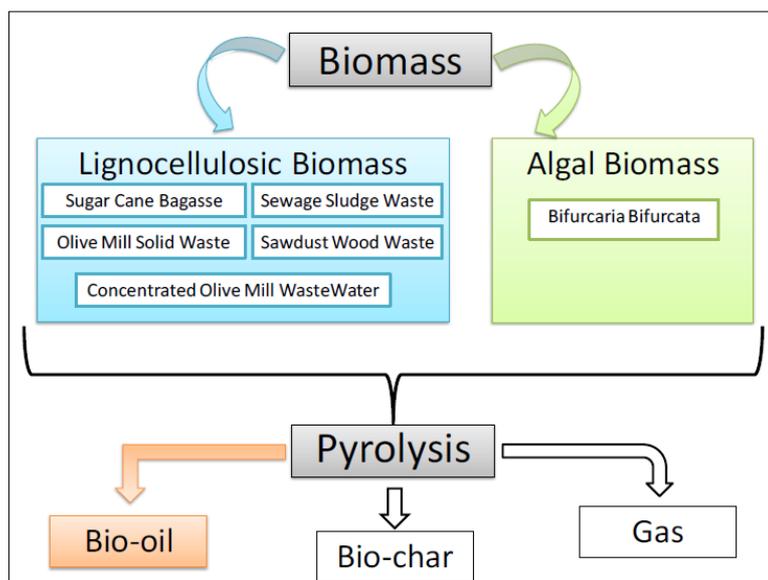


Figure 1: Valuation of lignocellulosic and algal biomass by pyrolysis.

In the last nineteen years, several researches have had the aim to study pyrolysis of several type of biomass such as, lignocellulosic and algal biomasses. As seen in Figure 2, the evolution of published documents has shown an increase between 2000 and 2019. These published documents presented work on pyrolysis of lignocellulosic biomass and algal biomass, which show the importance of pyrolysis and its use in several areas [11-16].

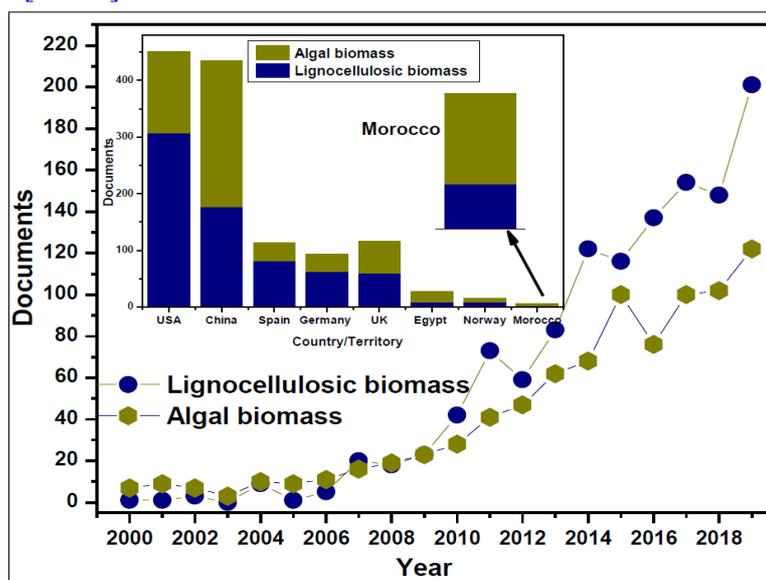


Figure 2: Documents published on lignocellulosic and algal biomasses during 2000-2019 period (keywords: 'lignocellulosic biomass' AND 'algal biomass' AND 'pyrolysis') (Source: Scopus).

Figs. 3 and 4 show that energy, environmental science, chemical engineering and chemistry are domains which use thermochemical treatment and especially pyrolysis of lignocellulosic and algal biomasses. At country level and international scale, the best known countries through their research on pyrolysis of lignocellulosic and algal biomasses are: USA, China, Spain, Germany and UK, as seen in Figure 2. While, nationally in Morocco, it is noticeable that there are little researches on pyrolysis of lignocellulosic and algal biomasses, which represents an advantage for this paper.

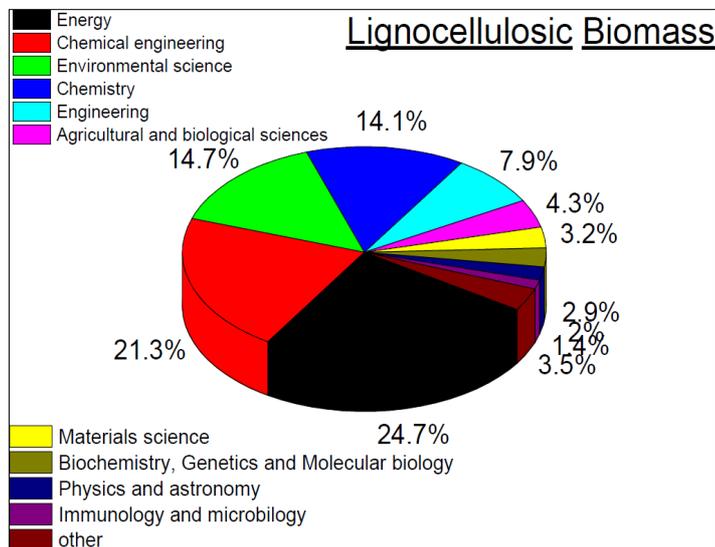


Figure 3: Documents published on lignocellulosic biomass per subject area during 2000-2019 period (keywords: ‘lignocellulosic biomass’ AND ‘pyrolysis’) (Source: Scopus).

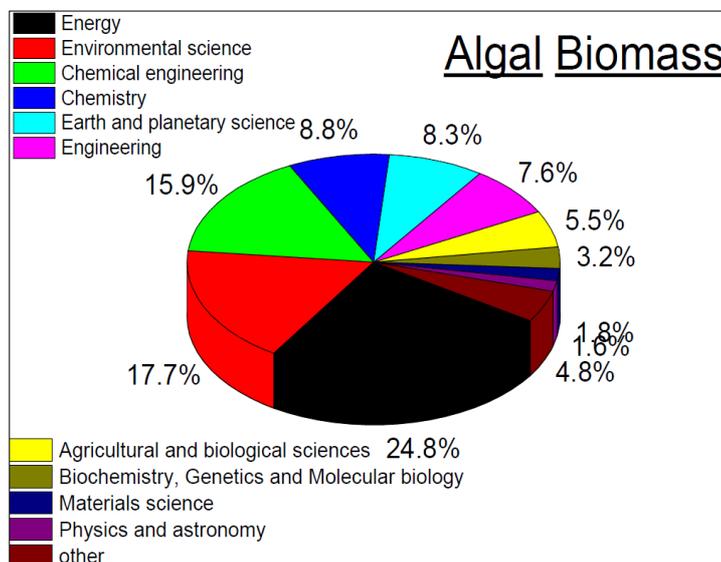


Figure 4: Documents published on algal biomass per subject area during 2000-2019 period (keywords: ‘algal biomass’ AND ‘pyrolysis’) (Source: Scopus).

In this paper, the olive mill solid waste (OMSW), concentrated olive mill wastewater (COMWW), sugar cane bagasse (SCB), sewage sludge waste (SSW), sawdust wood waste (SWW) and bifurcaria bifurcate (BB) were selected as the representative of lignocellulosic and algal biomass, respectively. The pyrolysis experiments were carried out in a stainless steel tubular reactor [2, 4-5, 8-9, 13]. This article describes the potential use of lignocellulosic and algal biomass as sustainable source for renewable fuels such as; bio-oils in Morocco.

2. Samples and pyrolysis procedure

As seen in Figure 5, lignocellulosic biomasses, such as; olive mill solid waste (OMSW), concentrated olive mill wastewater (COMWW), sugar cane bagasse (SCB), sewage sludge waste (SSW) and sawdust wood waste (SWW), and algal biomass such as; bifurcaria bifurcate-brown algae (BB), were collected from different regions of Morocco. Three cities are concerned; Beni-Mellal, Marrakech and Casablanca. These biomass samples were collected, crashed and pyrolyzed in a stainless steel tubular reactor, heated with a furnace tubular type R50/250/12. This compact tubular furnace provided with cupboard of power and integrated regulation of temperature. For the experiments, an amount of lignocellulosic and algal biomasses were placed into the reactor and the experiments were carried out with a series of final temperature and heating rates. The experiments were conducted under nitrogen (N_2) gas with a flow rate of 100 mL/min (Figure 6).

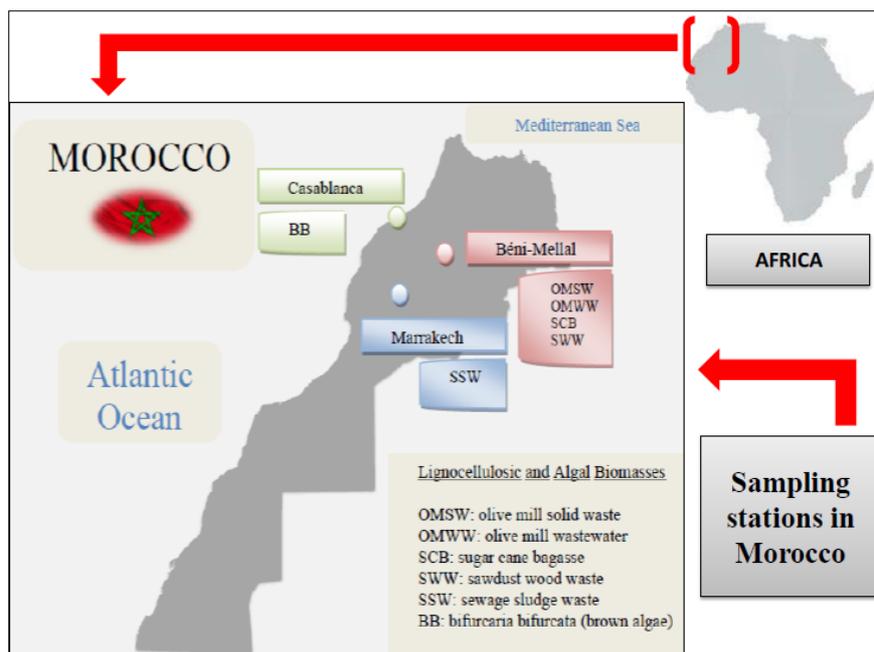


Figure 5: Sampling stations in Morocco.

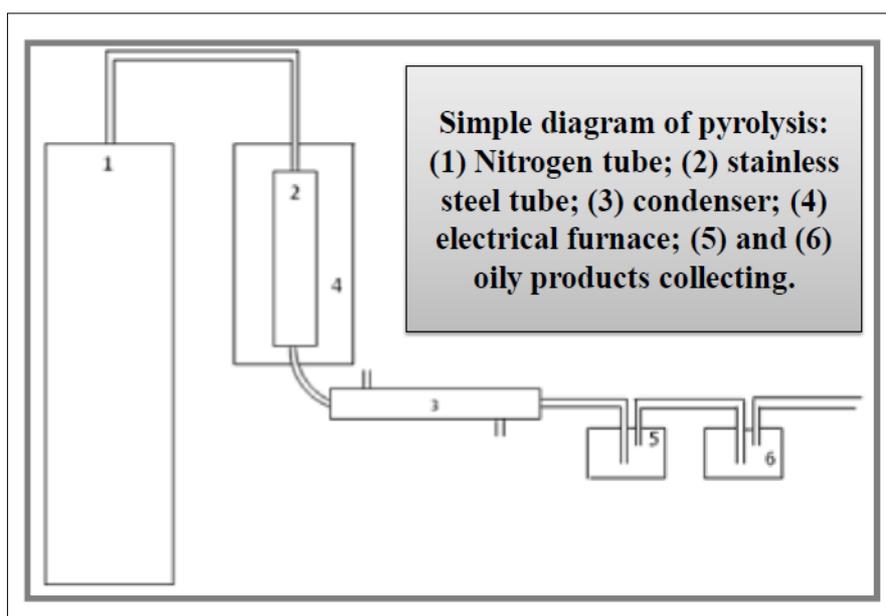


Figure 6: Simple diagram of pyrolysis.

3. Results and discussion

3.1. Characteristics of lignocellulosic and algal biomasses

Figures 7 and 8 show the various characteristics of lignocellulosic and algal biomasses, such as; OMSW, COMWW, SCB, SWW, SSW and BB. Proximate analysis refers four classes of substances such as Moisture (M), Volatile matter (VM), Ash (A) and fixed carbon (FC) content of the sample (wt%). These classes of substances give information about burning and heating properties of substances [11, 17].

From Figure 7, Moisture content in samples ranges from 3.8 wt% to 9.52 wt%. Moisture content is 3.8 wt%, 4.6 wt%, 6.02 wt%, 7.9 wt%, 8.3 wt% and 9.52 wt% for COMWW, SSW, SWW, SCB, OMSW and BB, respectively. From literature, it is known that for pyrolysis process, the moisture content in biomass waste ought to be underneath 10 wt% [17, 18]. SCB, SWW, OMSW and BB have high volatile matter of 78.4 wt%, 75.6 wt%, 73.5 wt% and 70.15 wt%, respectively. COMWW and SSW have low volatile matter of 61.4 wt% and 59.2 wt%. High volatile content biomass samples are desirable for the pyrolysis process since these are more reactive and easily devolatilized [20]. Ash content in biomass represents the inorganic residue leftover after combustion; it is preferable to have low ash content for pyrolysis process. Ash content (residue) in the lignocellulosic biomasses (OMSW, COMWW, SCB, SSW and SWW) and algal biomass (BB) are 4.5 wt%, 25.1 wt%, 2.5 wt%, 7.3 wt%, 27.65 wt% and 11.95 wt%. for OMSW, COMWW, SCB, BB, SSW and SWW, respectively. From literature, ash content varies depending on biomass and material nature. It is 8 wt% for coal, 4 wt% for wheat straw, 4.5 wt% for switchgrass and 6 wt% for barley straw [20-23]. Fixed carbon content in biomass is 13.7 wt% (OMSW), 9.7 wt% (COMWW), 11.20 wt% (SCB), 13.03 wt% (BB), 8.55 wt% (SSW) and 6.87 wt% (SWW) [2, 4, 5, 9, 13, 24].

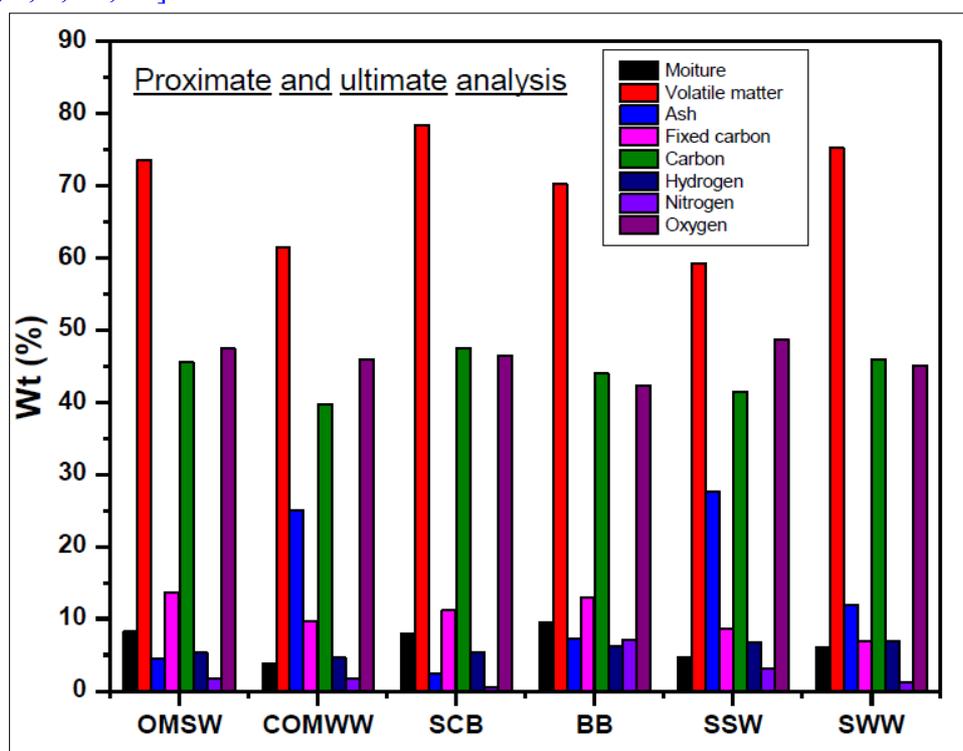


Figure 7: Proximate and ultimate analysis of lignocellulosic and algal biomass.

In all biomasses, the amount of carbon (C) and oxygen (O) is more as compared to nitrogen (N) and hydrogen (H). Low nitrogen and sulfur (S) content in biomass imply that it releases fewer amounts

of SO_x and NO_x during thermochemical conversion processes (pyrolysis). However, higher O content in lignocellulosic and algal biomasses produces oxygenated liquid products during pyrolysis [24-26].

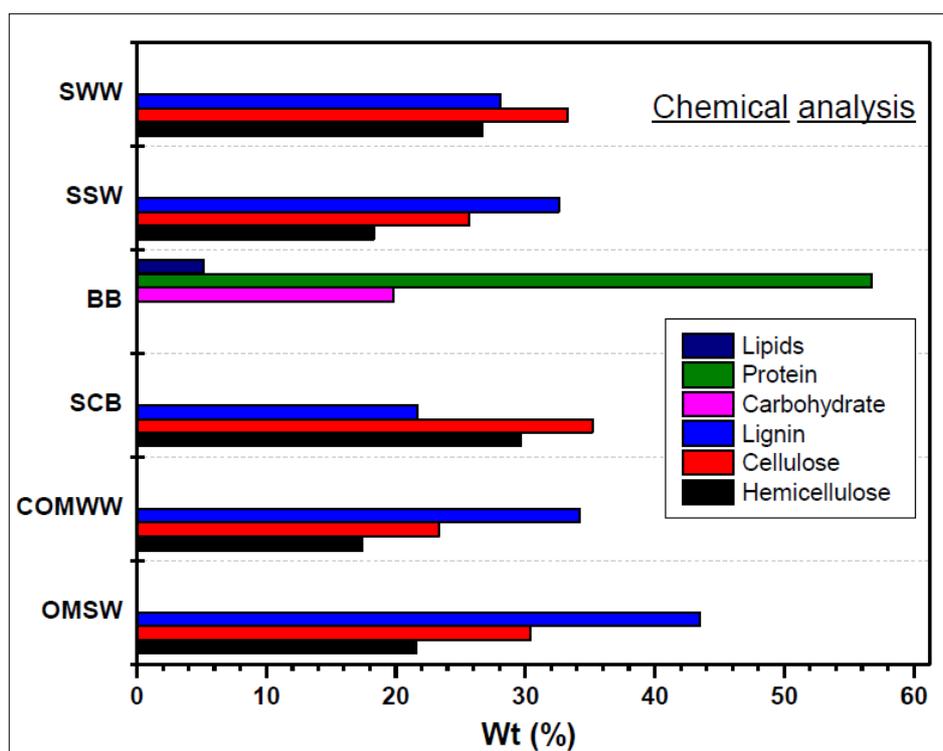


Figure 8: Chemical analysis of lignocellulosic and algal biomass.

Figure 8 presents the chemical analysis of lignocellulosic and algal biomasses. It can be seen that, hemicellulose contents of OMSW, COMWW, SCB, SSW and SWW are 21.6 wt%, 17.4 wt%, 29.68 wt%, 18.3 wt% and 26.7 wt%, respectively. About algal biomass (BB), it does not contain hemicellulose, cellulose and lignin. It contains carbohydrate (19.82 wt%), protein (56.73 wt%) and lipids (5.16 wt%). SCB, SSW and OMSW are the three lignocellulosic biomasses those containing large amounts of cellulose, with 35.20 wt%, 33.25 wt% and 30.4 wt%, respectively. Lignin is founded a lot in OMSW (43.5 wt%), COMWW (34.2 wt%), SSW (32.6 wt%) and SWW (28.1 wt%).

3.2. Yield of bio-oils obtained from pyrolysis and their characteristics

The bio-oil product yields from pyrolysis of OMSW, COMWW, SCB, SSW, SWW and BB at 5°C/min are shown in Figure 9. All yields are given on a dry basis (wt%). The bio-oil yield reached to its maximum at 450 °C for concentrated olive mill wastewater, 600 °C for bifurcaria bifurcata, 550 °C for sugar cane bagasse and 500 °C for olive mill solid waste, sewage sludge waste and sawdust wood waste. The highest bio-oil yields (33.41 wt%, 31.29 wt%, 41.30 wt%, 30.6 wt%, 39.5 wt% and 32.8 wt%) were obtained for OMSW, COMWW, BB, SSW, SSW and SCB, respectively. As can be seen from Figure 10, HHVs for bio-oils obtained are higher than HHVs of lignocellulosic and algal biomasses. Higher heating values in the lignocellulosic biomasses are 16.6 MJ/kg, 11.46 MJ/kg, 17.25 MJ/kg, 15.31 MJ/kg, 10.41 MJ/kg and 18.45 MJ/kg for OMSW, COMWW, SCB, BB, SSW and SWW, respectively. Whereas for HHVs of bio-oil are 22.87 MJ/kg, 25.09 MJ/kg, 30.11 MJ/kg, 28.16 MJ/kg, 27.32 MJ/kg and 27.67 MJ/kg. It is noticed that all values are higher than 22 MJ/kg. These results are consistent with literature, as seen in Table 1. It is known that pyrolysis temperature plays an important role in bio-oil product distribution [24, 26-28].

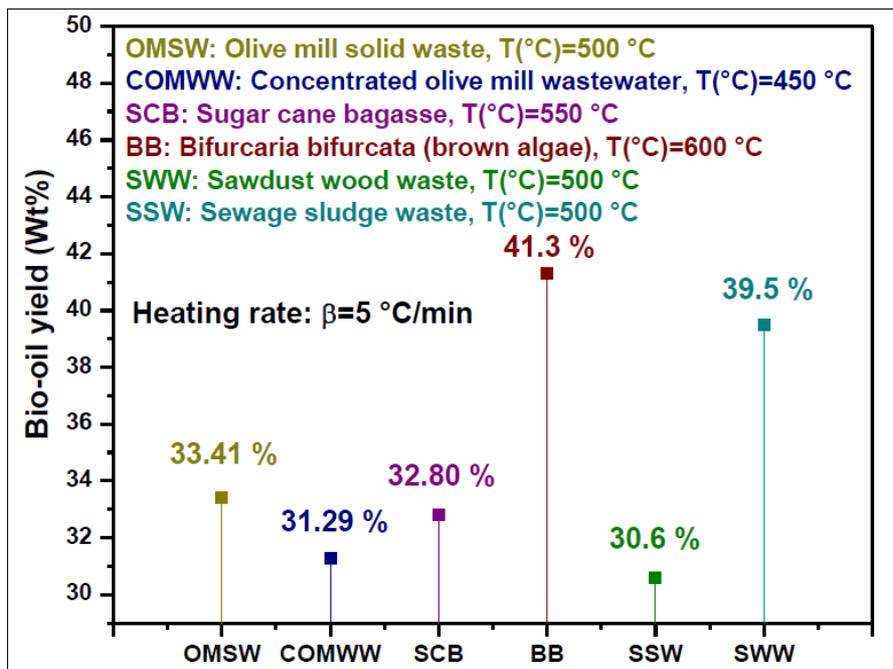


Figure 9: Optimal yield of bio-oil from pyrolysis.

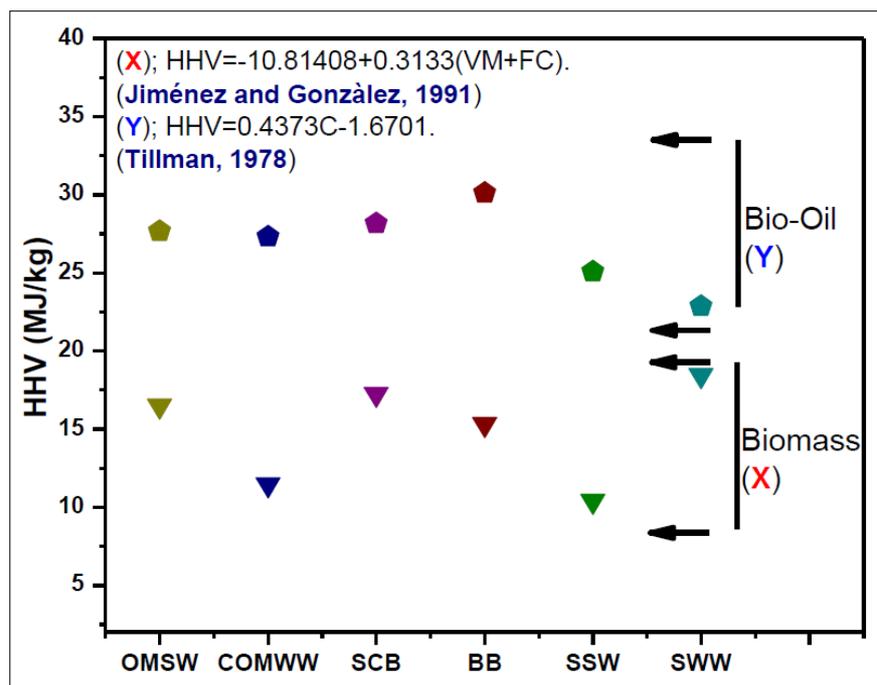


Figure 10: Higher heating value (HHV) of biomass and bio-oil.

From Figures 11 and 12, It can be seen that the percentage of protons contained in bio-oil obtained from pyrolysis of OMSW, COMWW, SCB, BB, SWW and SSW have an aliphatic character and characterized with a higher H/C ratio. H/C ratios for bio-oils produced from lignocellulosic and algal biomass are 1.53, 1.39, 1.7, 1.73, 1.40 and 1.95 for OMSW, COMWW, SCB, BB, SSW and SWW, respectively. Further comparison of H/C ratios of pyrolysis oils with conventional fuels [29-31], indicates that the H/C ratios of the bio-oils obtained are close to those of light and heavy petroleum products, as seen in Table. 2.

Table 1: Comparative study of different type of biomass pyrolysis.

Biomass	Reactor type	Temperature (°C)	Heating rate (°C/min)	Bio-oil yield (%)	HHV of bio-oil (MJ/kg)	Reference
Olive mill solid waste	tubular reactor	500	5	33.41	27.67	Guida et al. (2016) [8]
Concentrated olive mill wastewater	tubular reactor	450	5	31.29	27.32	Guida. (2017) [13]
Sugar cane bagasse	tubular reactor	550	5	32.8	28.16	Guida et al. (2017) [9]
Bifurcaria bifurcata (brown algae)	tubular reactor	600	5	41.3	30.11	Guida et al. (2018) [5]
Sawdust wood waste	tubular reactor	500	5	39.5	25.09	Guida et al. (2019) [4]
Sewage sludge waste	tubular reactor	500	5	30.6	22.87	Guida et al. (2019) [2]
Safflower seed press cake	fixed bed	500	50	36.1	-	Sensoz et al. (2008) [10]
bagasse	fixed bed	500	50	66.1	19.91	Asadullah et al. (2007) [17]
Olive bagasse	fixed bed	500	10	37.7	31.8	Sensoz et al. (2006) [18]
Wood sawdust	semi batch	500	50	44.16	27.82	Kumar varma et al. (2019) [1]
Coconut shell	semi batch	575	20	49.5	19.75	Rout et al. (2016) [3]
Oil palm residues	fixed bed tubular	600	30	34.26	21.92	Yakub et al. (2015) [14]
Jatropha curcas cake	fixed bed tubular	550	5	45	25.91	Majhi et al. (2015) [7]
Paulownia wood	fixed bed reactor	500	50	54	28.6	Yorgun et al. (2015) [11]
Napier grass	Intro. heating	500	100	35.7	-	Lee et al. (2010) [15]

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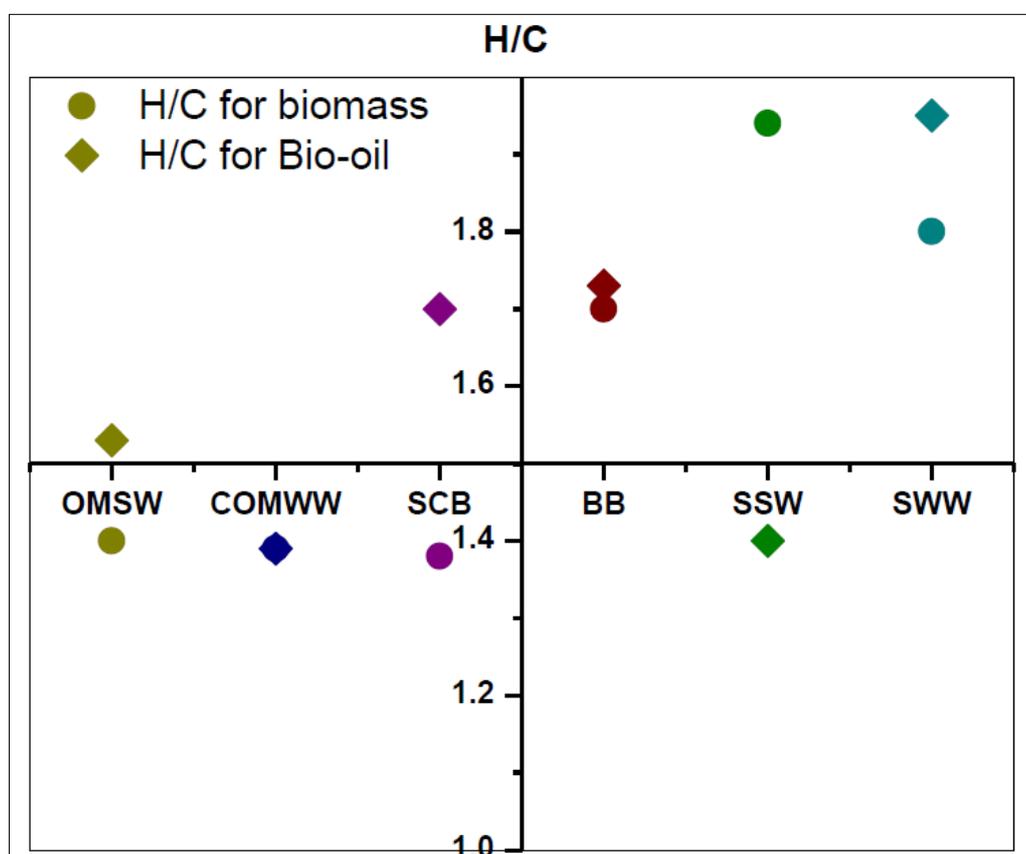


Figure 11: H/C ratio of biomass and bio-oil.

Table 2: General characteristics of various types of fuel.

Type of fuel	Ratio H/C
Natural gas (GNV) stored in the gaseous state under 200 bar	3.5-3.9
LPG-fuel	2.0-2.67
High-octane petrol and regular gasoline	1.7-1.9
Turbine fuel	1.9-2.1
Diesel	1.9-2.1
Heavy fuels	0.8-1.7

Conclusion

In this paper, the lignocellulosic and algal biomass pyrolysis was discussed and showed promising results with a bio-oil yield of 33.41 wt%, 31.29 wt%, 41.3 wt%, 30.6 wt%, 39.5 wt% and 32.8 wt% for OMSW, COMWW, BB, SWW, SSW and SCB, respectively. These results are similar to that of bagasse, wood, olive, jatropha, napier grass and other type of biomasses. The main differences observed in the bio-oil product yields can be partially explained by differences of the biomass nature compositions especially differences with moisture, ash, cellulose, lignin, carbohydrate, proteins, matter volatile, contents of the feedstock.

Morocco is among the countries that have a major biomass deposit and field; this biomass deposit can contribute significantly to the production of energy of different nature, which forces us to give great attention to these renewable resources and their valorization.

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