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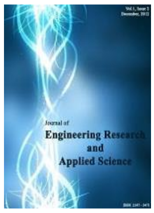

Bio-oil production from microalgae by pyrolysis: A mini-review

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Abstract

Fossil fuel (petroleum, coal, natural gas) reserves have decreased, so it has been necessary to find renewable, sustainable and eco-friendly resources. Biofuels which have been classified as bioethanol, biodiesel, biogas etc. have been obtained from biomass resources. Microalgae as a biomass source can be cultivated in fresh water, brine, sewage or barren lands in a short span of time on a large scale. Its production technology requires the steps which are cultivation, harvesting and drying. After that, the methods such as pyrolysis, transesterification or fermentation can be used for biofuel production from microalgae. Bio-oil production from microalgae have been done by using pyrolysis technique. It has been possible that after upgrading, microalgal bio-oil has been used as biofuel. Upgrading has been necessary because the bio-oil has possessed some undesired properties such as high oxygen content, low high heating value, high viscosity. Thermal cracking with zeolites and co-pyrolysis with several materials have been used to obtain high quality biofuel in one step. Besides that, it has been possible to use bio-oil as a chemical resource because it composes of 100 invaluable compounds in average such as oxygenated ones.

Keywords: microalgae, pyrolysis, bio-oil upgrading, biofuel

1. Introduction

Fossil resources have been in the universe naturally [1]. But, their amount has limited [2]. In addition, environmental problems have occured because of their using in industrial processes [3]. In Figure 1, it was shown that carbon dioxide (CO_2) emmissions which formed due to utilizing of the fossil fuels have increased year by year in the five countries. China and United States have possessed the maximum ratio of total releasing CO_2. Also, Turkey has contributed to the total amount. Due to that reasons, researchers have worked on to find renewable, sustainable and eco-friendly resources nowadays [4].

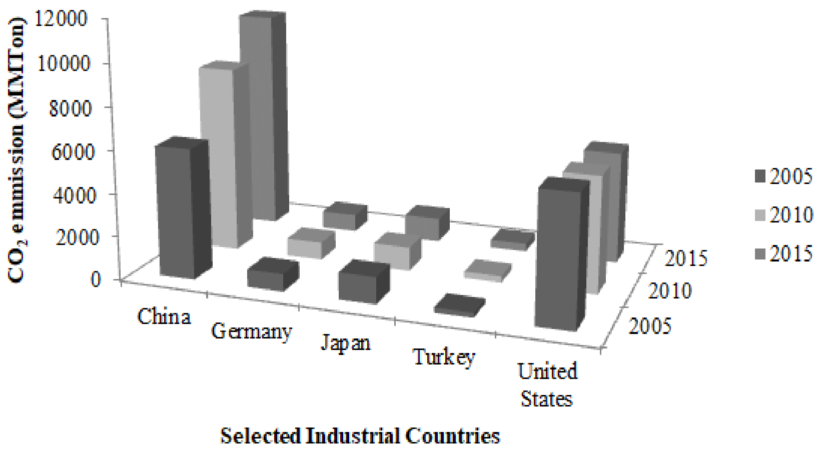

Figure 1: Change in the amount of CO_2 year by year in some industrial countries [5]

Renewable resources have been sun, wind, tide and biomass [6]. Plants, algae and animal waste have formed biomass resources [7]. Biofuel which have been classified as bioethanol, biodiesel, biogas etc.

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have obtained from biomass resources [8]. In Figure 2, it was shown that the amount of biofuel production throughout the World in 2015. Regarding that statistical data, In Turkey that amount which was 136 MmTon has been low between the countries.

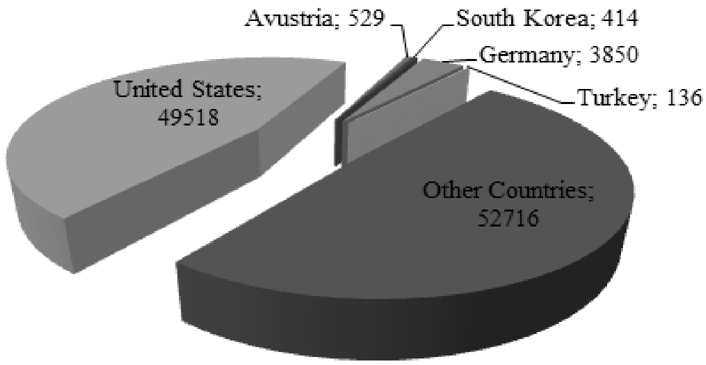

Figure 2: Amount of biofuel production throughout the World (Mmton) in 2015 [9].

Bio-oil production from microalgae which have been known as a type of algae have done by using pyrolysis technique [10], [11]. It has been possible that after upgrading, microalgal bio-oil has been used as biofuel [12]. Upgrading has been necessary because the bio-oil has possessed some undesired properties such as high oxygen content, low high heating value, high viscosity [13]. For upgrading, it had been used hydrogenation under high pressures after pyrolysis [14]. Nowadays it has been tried two routes to upgrade microalgal bio-oil quality directly during pyrolysis. Using that routes, it has been obtained high quality biofuel in one step. The first one has been known as thermal cracking with zeolites [1] while the second one has been known as co-pyrolysis with several materials [15].

In this study, it was aimed to describe biofuel production ways from microalgae. Besides that, it was given place to novel literature knowledge for obtaining high quality biofuel by pyrolysis.

2. Advantages of microalgae as a biomass source

Biomass can be food based such as corn, eggplant, potato, wheat or algae based [16]–[20]. Algae have been classified as macroalgae and microalgae [21]. Brown macroalgae, Red macroalgae, Green macroalgae have been examples of macroalgae species [22]–[24]. *Chlorella*, *Spirulina* and *Dunaliella* have been the most famous species of microalgae [25]–[27].

Microalgae are small-sized algae [21]. They can be grown in fresh water, brine, sewage or barren lands. They are photosynthetic species [28]. It has been known that they were growth in a short span of time on a large scale and they had mostly oil and protein [29]. Especially Spirulina have been used as food supplement because of its high gamma-linolenic acid content [30].

3. Microalgae production technology

Microalgae growth can be done in open pond system or close photobioreactor system. Open pound system can be setted on barren places. Its investment and operation costs are cheap and the system can be operated easily. But it has a desadvantage. Because of the system is open to the air, temperature and pH control is hard. In other words, specific production type is not possible in such system and the system is unstable. Photobioreactor system provides stable conditions. But it requires high investment and operation cost [31], [32].

After their growth, harvesting is applied. Harvesting can be made mainly by following four different ways: Centrifuging, sedimentation, flotation or filtration. Microalgae can be recover from their environment wholly by centrifuging [33], [34]. The process which included cultivation and harvesting of microalgae was shown in Figure 3. In the last step, harvested microlagae are dried [35].

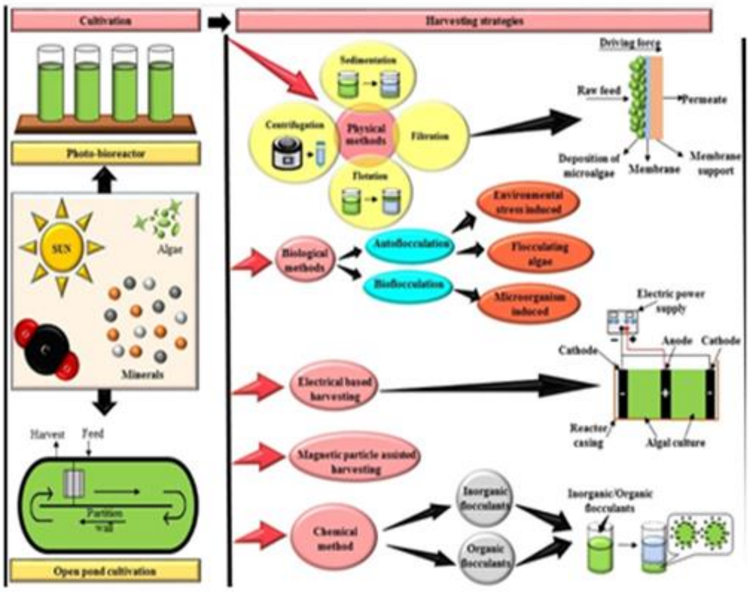

Figure 3: Microalgae production process [33]

4. Biofuel production from microalgae

Biofuel can be producted mainly from microalgae in three different routes. They are thermochemical conversion, biochemical conversion and transesterification [36].

In Biochemical conversion, it can be followed fermantation method. Fermantation covers two steps. In the first step, sucrose inside the microalgae is converted to fructose and glucose. In the second step, glucose is converted to bioethanol and CO_2 on a yeast catalyst. Transesterification is a reaction in which oil inside the microalgae and methanol react to form glyserol and methyl esters (biodiesel) on sodium hydroxide catalyst [37]. Consequently, before transesterification it is necessary to take oil which is inside the microalgae. There are two different choices to oil-extraction. They are cold pressing with chemicals and extraction with supercritical fluids. Cold pressing means that microalgae press with chemical solvent such as benzene, ether, hexane in a mechanical machine. In that method, oil recovery ratio is high. In supercritical extraction, CO_2 is used but that process requires high investment [38].

In Thermochemical Conversion, biofuel from microalgae can be producted in three ways. They are gasification, liquefaction and pyrolysis. Gasification occurs at 800-1000 ˚C on non-catalytic way. CO_2, CH_4 and H_2 are produced by gasification [37]. Liquefaction occurs at around 300 ˚C on catalytic way. The product as bio-oil is obtained [37], [39].

4.1. Microalgae pyrolysis

Pyrolysis is a thermal degradation process which occurs in non-oxygen atmosphere. Pyrolysis is invaluable process to recover chemicals and obtain fuels [40]. It has so many advantages. Solid residue as a pyrolytic product can be a catalyst for another reaction. During operation, flue gas does not form because gas as a pyrolytic product can be gathered and it can be used as fuel. Thanks to pyrolysis, waste ratio in landfills decreases [41].

Microalgae pyrolysis is carried out at 350-700 ˚C under atmospheric pressure [37]. The products are bio-oil, solid residue which has high carbon content and biogas which has non-condensable compounds such as light hydrocarbons, Carbon Monoxide (CO), CO_2 and Hydrogen (H_2) [42]. Bio-oil is a chemical resource that composes of nearly 100 compounds [43]. Especially, it includes oxygenated compounds such as phenols and furfurals are in bio-oil. That compounds occur after degradation of cellulose in microalgae [44].

In conventional pyrolysis which requires slow heating rate and long duration time bio-oil yield is low. That technique is suitable for obtaining solid residue (bio-char) with high yield [45]. Bio-oil yield can be increased by following fast pyrolysis and flash pyrolysis technique [46]. In fast pyrolysis, heating rate and duration time are 1-200 ˚C/s and a few seconds respectively. In flash pyrolysis, heating rate and duration time are 1000 ˚C/s and a second respectively [13].

There have been so many researches about microalgae pyrolysis [43], [47]. For example Chaiwong et al. (2013), carried out pyrolysis of *Spirulina* in a fixed bed reactor at 450-600 °C. They obtained maximum bio-oil yield at 550 °C. GC-MS analysis showed that the main components of bio-oil were heptadecane, toluene, ethylbenzene and indole. Besides that, they found that carbon content of bio-char was the highest one between other microalgae species.

Nowadays bio-oil can be used in diesel engines by mixing with petroleum based oil [49]. But, it is not suitable to use directly in vehicles. That situation arises from physicochemical properties of bio-oil. Because bio-oil has low density and high viscosity, it causes corrosion and accumulation in the engine. Besides that, bio-oil has high oxygen content. Its heating value is low, i.e. Therefore, deoxygenation and hydrogenation processes are applied to bio-oil for upgrading its quality [50]. In Table 1, properties of bio-oil were compared to diesel and gasoline.

Table 1: Comparision of bio-oil properties with conventional fuels [51], [52]

Properties	Bio-oil	Gasoline	Diesel
LHV (MJ/kg)	13-18	43.9	42.6
Density (g/cm^3)	0.0011-0.0013	0.6627-0.7948	0.7802-0.8470
Viscosity (mPa.s)	13-80	0.5-0.7	2.0-7.7

4.2. Microalgae pyrolysis co-pyrolysis of microalgae with several feedstocks

Another way to increase bio-oil quality has been seen as co-pyrolysis. Co-pyrolysis means pyrolysis of two different feedstocks at the same time in a setup. On that way, the synergic effect which causes to react the compounds of microalgae and other material in bio-oil occurs. Consequently, bio-oil can be prospered with compounds which have high energy in case of its burning [53].

There have been so many researches about microalgae co-pyrolysis [54], [55]. C. Chen et al. (2012) carried out co-pyrolysis of *Chronella* and coal. Their purpose was to investigate the effect of microalgae/coal ratio and heating rate on thermal degradation. They made pyrolysis experiments by using TGA. They observed that the mixture (microalgae/coal : 3/7, 5/5, 7/3), pure coal and pure *Chronella* degradeded at 172-600 °C, 320-1000 °C and 168-555 °C respectively. Regarding that result, they determined that degradation temperature of the mixture was near the pure microalgae degradation temperature. Duan et al. (2015) performed co-pyrolysis of microalgae and waste rubber tire (WRT) in the environment of ethanol solvent. They observed that reaction temperature and WRT/Microalgae ratio affected bio-oil yield significally. They obtained maximum bio-oil yield as 65 % wt/wt at 330 °C with 1/4 WRT/Microalgae ratio after 60 min duration time. According to the study, compared to just WRT pyrolysis, existence of ethanol and microalgae in the pyrolysis setup decreased WRT degradation temperature. They found that co-pyrolysis product involved esters, nitrogenous and oxygenated compounds and aliphatic hydrocarbons. Wu et al. (2015) studied on co-pyrolysis of *Dunaliella tertiolecta* sp. Microalgae and polypropylene. According to TGA results, polypropylene addition decreased degradation temperature of microalgae. Besides that, CO_2 amount in biogas fell because of polymer based-small molecules like radicals interacted with pyrolysis product of microalgae. Also, they recorded that particle size of polypropylene affected on feedstock interaction between microalgae and polypropylene significantly.

4.3. Catalytic pyrolysis of microalgae

Catalyst using, especially synthetic zeolites, in pyrolysis is another way to increase bio-oil quality. On that way, it can be obtained bio-oil which has an adequate octane number to be used in the engines [1]. Only desadvantage of catalyst using in pyrolysis has been seen as coking. But it has been known that some metals like Nickel which was impregnated to the zeolite formed less coking compared to other metals [58].

Synthetic zeolites have three dimensional lattice structure. They are compose of silicon and aluminium atoms. They have porous structure. Their pores are molecular size (0.3-2 nm). They are classified with respect to their porous structure such as β-zeolite, Y zeolite, Mordenite, ZSM-5 [59]. ZSM-5 have been preffered to a large extent in microalgae pyrolysis because of its suitable acidity, shape selectivity, its ability to low coke formation and its thermal stability [60], [61].

In the first step of catalytic pyrolysis, microalgae components degradate thermally to produce vapour which is composed of mainly oxygenated compunds (furans, acids, phenolics). Secondly, pyrolysis vapor interacts with the zeolite. Inside the catalyst, that compounds convert to aromatic hydrocarbons such as benzene, toluene and xylene. During that conversion, cracking, deoxygenation, olygomerization, aromatization reactions occur. Oxygen removes with decarbonization, decarboxylation and dehydration reactions. Hence, bio-oil quality increase [62].

There have been so many researches about microalgae catalytic pyrolysis on zeolites (Özçakır & Karaduman, 2019; Abd Rahman et al., 2020; Ma et al., 2020; Xu et al., 2020). Chagas et al. (2016) carried out catalytic pyrolysis of Spirulina with zeolites which had different Si/Al ratios. They recorded that catalyst which had low Si/Al ratio (23) promoted aromatic production in bio-oil. While, catalyst which had high Si/Al ratio promoted aliphatic hydrocarbons, phenolics and nitrogenous compounds in bio-oil. In Figure 4, pyrolysis reaction of Spirulina's protein was given. It is said that aromatics form as a result of protein degradation in Spirulina [66]. Pan et al. (2010) compared catalytic pyrolysis of Nannochloropsis sp. Microalgae on HZSM-5 to whose non-catalytic pyrolysis. They obtained oxygen content of bio-oil as 20% wt/wt and 30% wt/wt for catalytic and non-catalytic pyrolysis respectively. They found heating value of bio-oil as 30 MJ/kg and 25 MJ/kg for catalytic and non-catalytic pyrolysis respectively. In non-catalytic pyrolysis, they determined that bio-oil included long chain hydrocarbons. However in catalytic pyrolysis, they obtained that aromatic hydrocarbons formed in bio-oil instead of long chain hydrocarbons. Both of catalytic and non-catalytic pyrolysis, they found that bio-oil yield was maximum at around 400 °C. Also, they suggested that same amount of catalyst and microalgae were fed to the reactor to obtain maximum bio-oil yield. Thangalazhy-Gopakumar et al. (2012) carried out catalytic pyrolysis of *Chlorella* on HZSM-5 with high catalyst to microalgae ratio (9/1). As a result of their study, they found that bio-oil was composed of 25% wt/wt aromatic hydrocarbons which included mainly banzene, toluen and xylenes (BTX). Du et al. (2013) worked on the same microalgae species pyrolysis on HZSM-5 at 550 °C. As a result of GC-MS analysis of bio-oil, they determined that aromatic content of bio-oil increased with increasing catalyst amount parallelly. They defended that oil and carbonhydrate as well as protein in microalgae strıucture caused formation of aromatic components in bio-oil. Wang & Brown (2013) investigated how reaction temperature and catalyst amount affected on bio-oil for the same algae and the same catalyst. They found that at 700 °C, hydrocarbons, nitrile, pyrrole, phenol, furfural, nitrogenous and oxygenated compounds formed in bio-oil. They determined that by using high catalyst amount (20 fold of microalgae amount) hydrocarbons in bio-oil converted to aromatic hydrocarbons (mainly BTX) wholly. Anand et al. (2016) examined catalytic and non-catalytic pyrolysis of *Spirulina* in quartz reactor under He atmosphere. They carried out non-catalytic pyrolysis at 350-800 ˚C and catalytic pyrolysis at 600 ˚C on ZSM-5, β-zeolite and Y zeolite. They choosed catalyst/ microalgae ratio as 10/1. In non-catalytic pyrolysis, they found that increase in temperature promoted to form low molecular weight hydrocarbons (C10<) and aromatics. They determined that all types of zeolites promoted aromatic formation such as BTX, naphtalane and methyl naphtalane. Lorenzetti et al. (2016) studied on pyrolysis of the same algae on HZSM-5. They recorded that bio-oil was composed of aromatic compounds in high amount.

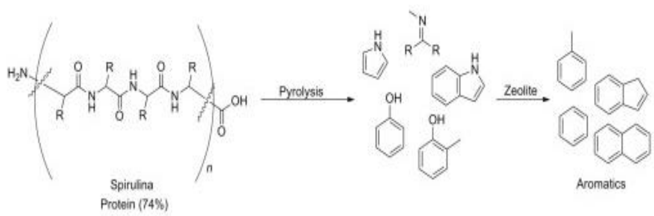

Figure 4: Aromatic compounds formation from *Spirulina* on zeolites [66]

Recently several catalysts except zeolites have been used in microalgae pyrolysis [73], [74]. Chen et al. (2018) worked on catalytic co-pyrolysis of microalgae and bamboo wastes. They used bio-char of bamboo waste as a catalyst. They obtained catalyst by carrying out pyrolysis of bamboo waste under

Argon atmosphere at 600 °C with 30 min duration time. They observed that bio-oil yield decreased to 35% wt/wt in catalytic pyrolysis compared to its non-catalytic pyrolysis. However, they recorded that oxygenated compounds and long chain fatty acids in microalgal bio-oil decreased, aromatic and phenolic compounds increased. Besides that, they observed most oxygen in microalgal bio-oil removed as CO, CO_2 and steam with catalytic co-pyrolysis. Yu et al. (2018) used to oil shale as a catalyst for microalgae pyrolysis. They observed maximum aromatic yield (35% wt/wt) at 600 °C with low amount of oil shale (3% wt oil shale/wt feedstock).

5. Conclusions

Microalgal bio-oil is important for obtaining clean fuels and sustainable chemicals. However, its heating value is low. To upgrade bio-oil, hydrogenation, co-pyrolysis or catalytic pyrolysis methods can be used. Hydrogenation requires high pressures and it follows pyrolysis process. With zeolites, oxygen in bio-oil removes directly as CO_2 and steam during catalytic pyrolysis in one step and its heating value increased. Besides that, the composition of bio-oil can be changed by using different zeolites or the same zeolite with different Si/Al ratios. For example ZSM-5 promotes aromatic components. In addition to, co-pyrolysis of microalgae with polymers are important tor ise bio-oil quality. Because polymers have high hydrogen content, bio-oil heating value increases.

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