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HYDROTHERMAL LIQUEFACTION OF  
SPIRULINA**  
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PRODUCTION OF BIO-OIL VIA CATALYTIC AND  
NON-CATALYTIC HYDROTHERMAL LIQUEFACTION  
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PRODUCTION OF BIO-OIL VIA CATALYTIC AND  
NON-CATALYTIC HYDROTHERMAL LIQUEFACTION  
OF SPIRULINA

By

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## LIST OF ABBREVIATIONS

HTL	Hydrothermal liquefaction
WSP	Water soluble product
sp	Species
RT	Reaction temperature
Rt	Reaction time
EA	Elemental analysis
ER	Energy recovery
UA	Ultimate analysis
HHV	Higher heating value
TGA	Thermogravimetric analysis
FT-IR	Fourier transform infrared
GCMS	Gas chromatography mass spectrometer
SEM	Scanning electron microscopy

## LIST OF SYMBOLS

Symbol	Description	Unit
°C	Degree Celsius	
T	Temperature	°C
t	Time	s, min, hr
s	Second	
min	Minutes	
h	Hour	
%	Percent	
wt. %	Weight percent	
ml	Milli litre	
MJ/kg	Mega joules per kilogram	

# **PENGHASILAN MINYAK BIO MELALUI PENCAIRAN HIDROTHERMA SPIRULINA DENGAN KEHADIRAN MANGKIN DAN TANPA MANGKIN**

## **ABSTRAK**

Pencairan hidroterma telah terbukti sebagai salah satu kaedah yang mampu menghasilkan bahan bakar bio daripada alga secara efektif. Kajian bagi kesan kehadiran mangkin ke atas pencairan hidroterma telah dilaksanakan untuk meningkatkan kuantiti dan kualiti minyak bio yang terhasil. Kajian proses pencairan hidroterma telah dijalankan pada nisbah spirulina kepada air (10 g/100 ml) pada suhu 270 °C. Beberapa faktor (kesan tempoh tindakbalas, kesan jenis mangkin dan kesan dos mangkin) telah diuji bagi menghasilkan kuantiti produk yang tertinggi dengan kualiti yang terbaik. Tempoh tindakbalas telah di ubah dari 0 hingga 40 min dan didapati kuantiti maksimum bagi penghasilan minyak bio adalah pada tempoh masa 20 min (39 %). Jenis mangkin yang berbeza seperti zeolit-HY,  $K_2CO_3$ ,  $Al_2O_3$  dan MgO telah diuji bagi penghasilan minyak bio dan kuantiti tertinggi telah dicapai oleh zeolit-HY (41 %) diikuti dengan  $K_2CO_3$ ,  $Al_2O_3$  dan MgO dengan nilai sebanyak 38.6, 38.1, dan 23.8 %. Kehadiran mangkin zeolite-HY juga didapati mampu meningkatkan kandungan C dan H di sambil mengurangkan nilai N dan O berbanding dengan bahan mentah. Kesan dos mangkin (0.05 g hingga 0.5 g) turut dikaji dan didapati sebanyak 0.1 g mangkin sudah mencukupi untuk menghasilkan kuantiti produk yang tertinggi (49.2 %). Kandungan C dan H dalam produk kajian dengan kehadiran mangkin didapati lebih tinggi daripada kajian tanpa kehadiran mangkin manakala kandungan O, N dan S dalam kajian dengan kehadiran mangkin kurang daripada kajian tanpa mangkin. Mangkin Zeolit-HY berupaya menghasilkan produk yang berkualiti tinggi

dengan kandungan C dan H yang tinggi manakala kandungan O yang rendah berbanding dengan mangkin lain. HHV bagi minyak bio daripada kajian tanpa mangkin (29 MJ/kg) didapati rendah berbanding kajian dengan 0.1 g zeolite-HY (35 MJ/kg). Komponen utama yang didapati dalam kajian dengan kehadiran mangkin dan tanpa mangkin dikategorikan kepada karbonil, asid, hidrokarbon, aromatic, alkohol, dan ketone. Secara keseluruhannya, zeolit-HY mampu digunakan semula sebanyak 4 kali dan hanya sedikit pengurangan dalam kuantiti produk minyak bio yang terhasil.

# **PRODUCTION OF BIO-OIL VIA CATALYTIC AND NON-CATALYTIC HYDROTHERMAL LIQUEFACTION OF SPIRULINA**

## **ABSTRACT**

Hydrothermal liquefaction process has been proven as a promising method to produce bio-oil from microalgae. For the rationale to improve the yield and quality of the bio-oil, the effect of catalytic and non-catalytic hydrothermal liquefaction of spirulina as a feedstock was investigated. The process was performed at a fixed spirulina to water content (10 g/100 ml) at 270 °C in a batch reactor. Various operating parameters (effect of reaction time, effect of catalyst type and effect of catalyst dosage) were investigated for the rationale to attain the highest yield accompanied by the presence of high quality of bio-oil. The effect of reaction time was varied from 0 to 40 min and the highest yield of bio-oil was obtained at 20 min (39 %). Various type of catalysts such as zeolite-HY,  $K_2CO_3$ ,  $Al_2O_3$  and MgO were tested on the production of bio-oil and the highest yield of bio-oil was obtained by zeolite HY (41 %) followed by  $K_2CO_3$ ,  $Al_2O_3$  and MgO with 38.6, 38.1, and 23.8 %, respectively. In fact, the presence of zeolite HY managed to improve the percentage of C and H content while decreasing the N and O values as compared to the feedstock. The effect of catalyst dosage (0.01 to 0.5 g) was then performed and only 0.1 g of catalyst was required to attain the highest yield of bio-oil (49.2 %). The C and H content of the bio-oil obtained from catalytic HTL were found to be higher than those of the blank experiment while the O, N, and S contents of the bio-oil from the catalytic HTL were also lower than those of the blank experiment. Zeolite-HY catalyst managed to produce bio-oil of higher quality as it contain the highest C and H content and lowest in O content among

the tested catalysts. The HHV of bio-oil produced from a blank sample (29 MJ/kg) was relatively lower compared to the value of bio-oil produced in the presence of 0.1 g zeolite catalyst (35 MJ/kg). The main components present in bio-oil produced from catalytic and non-catalytic HTL were categorized into carbonyls, acids, hydrocarbons, aromatics, alcohol, and ketone. Overall, zeolite HY managed to be recycled for 4th time of repetitions and only slight reductions in the yield of bio-oil was observed.

# CHAPTER 1

## INTRODUCTION

### 1.1 Biomass as a Fuel Feedstock

Along with the growth of recent technology, the energy requirement in daily life is also increased. The global energy demand is projected to increase by 50 % or more by the year of 2030 (Maness *et al.*, 2009). However, the consumption of petroleum as an energy sources is currently estimated at an ‘unsustainable’ rate, which is 100 000 times faster than its natural production (Netravali and Chabba, 2003). In order to reduce the dependency on petroleum as fuel sources, many types of renewable energy sources have been introduced such as hydroelectric, wind, biomass, geothermal and solar. The energy consumption for different renewable energy source from year 2007 to 2016 is shown in Figure 1.1.

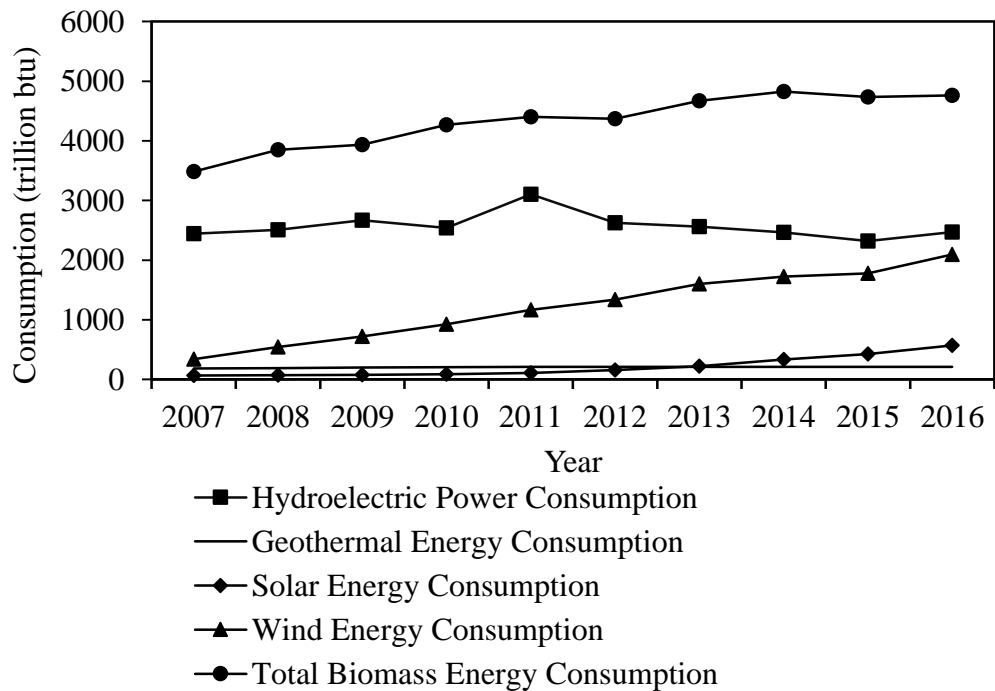


Figure 1.1: Renewable energy consumption by source (EIA, 2018)



It could be seen that, the total biomass energy consumption as a renewable energy was relatively higher for the past ten years as compared to the other types of renewable energy sources such as hydroelectric, wind, geothermal and solar. Thus, biomass is preferable to be studied and explored compared to other sources. Biomass is the collective term used to identify the organic matter generated either in the form of waste such as solid municipal waste or from living plants such as trees, grass, and agricultural crops and residues (Ashter, 2018). Biomass in the form of agricultural and industrial residues can be considered as a potential chemical feedstock and they become popular among new renewable energy sources.

As tabulated in Table 1.1, various types of biomass have been used in the production of bio-oil. It includes micro/macroalgae, food waste, wastewater sludge, and sewage sludge. Biofuels can be divided into first, second and third generation depending upon the sources of feedstock and technological innovation. The first generation biofuels are made from food crop while second generation biofuels are manufactured from agriculture and forest residues as well as non-food crop feedstock such as wood, organic waste, and food waste. Meanwhile, bioethanol and biodiesel manufactured from seaweeds and microalgae, respectively are considered as the third generation biofuels (Sharma *et al.*, 2017).

Table 1.1: Recent research on various types of biomass feedstock used to produce bio-oil.

<b>Biomass feedstock</b>	<b>References</b>
<i>Microcystis viridis</i>	Yang <i>et al.</i> (2004)
<i>Dunaliella tertiolecta</i>	Shuping <i>et al.</i> (2010)
<i>Chlorella vulgaris</i> and <i>Spirulina</i>	Ross <i>et al.</i> (2010)
<i>Laminaria Saccharina</i>	Anastasakis and Ross (2011)
<i>Spirulina platensis</i>	Jena <i>et al.</i> (2012)

Table 1.1: (Continued)

<i>Nannochloropsis</i> sp	Valdez <i>et al.</i> (2012)
<i>Chlorella pyrenoidosa</i>	Zhang <i>et al.</i> (2013)
<i>Nannochloropsis</i> sp	Li and Savage (2013)
<i>Tetraselmis</i> sp.	Eboibi <i>et al.</i> (2014)
Rice Husk	Xigen <i>et al.</i> (2015)
Water hyacinth	Singh <i>et al.</i> (2015)
<i>Ulva fasciata macroalgae</i>	Rojas Perez <i>et al.</i> (2015)
Soy protein concentrate	Luo <i>et al.</i> (2015)
<i>Pavlova</i> ,	Shakya <i>et al.</i> (2015)
<i>Isochrysis</i> and	
<i>Nannochloropsis</i>	
<i>Dunaliella tertiolecta</i>	Chen <i>et al.</i> (2015b)
<i>Scenedesmus almeriensis</i> and	López Barreiro <i>et al.</i> (2016)
<i>Nannochloropsis gaditana</i>	
<i>Nannochloropsis</i>	Saber <i>et al.</i> (2016)
Oil mill wastewater	Hadhoum <i>et al.</i> (2016)
<i>Nannochloropsis</i>	Xu and Savage (2017)
<i>Cyanidioschyzon merolae</i>	Muppaneni <i>et al.</i> (2017)
<i>Dunaliella tertiolecta</i>	Lin <i>et al.</i> (2017)
<i>Dunaliella tertiolecta</i>	Chen <i>et al.</i> (2017)
<i>Cyanophyta</i>	Song <i>et al.</i> (2017)
Waste activated sludge and	Nazari <i>et al.</i> (2017)
Birchwood sawdust	
Rice straw	Younas <i>et al.</i> (2017)
Sewage sludge	Qian <i>et al.</i> (2017)

Among them, considerable attention has been given to wet biomass such as microalgae and cyanobacteria. Spirulina (cyanobacteria) could be one of the alternative feedstock for the production of biofuels. It could be due to the availability of this material (Sumprasit *et al.*, 2017). In Southeast Asia, small factories for the production of spirulina could be found in Thailand, Myanmar and perhaps Vietnam and the Philippines, (Phang, 2010). In Malaysia, cultivation of spirulina was carried out by using raw sago starch wastewater that was collected from a factory in Batu Pahat (Phang *et al.*, 2000). Since the feedstock is easy to be obtained as well as ready

to be cultivated, the long term production of bio-oil should not be the main problems. In fact, biofuels produced from biomass and petroleum liquid fuels have similarities in terms of the energy densities, chemical structure and combustion performances (Guo *et al.*, 2015). Thus, with a proper treating and refining process, fuels derived from biomass could be one of the potential alternatives that could replace the petroleum fuels compared to the other renewable sources.

## **1.2 Conversion of Biomass into Bio-oil**

Conversion of biomass into bio-oil could be performed via biochemical or thermochemical methods (Chen *et al.*, 2015a) (Figure 1.2). Biochemical method is known as the sugar platform that is based on enzymatic hydrolysis and fermentation. In general, the biomass is first converted into sugar which is then be fermented by bacteria, yeasts and other microorganisms into products such as bioethanol (Heydariadzad *et al.*, 2011). For the production of biodiesel, lipid will be extracted from the biomass in the first step before proceeding with the esterification or transesterification process. Meanwhile, thermochemical method is the conversion process conducted at a relatively high degree of temperature (>250 °C) in the absence of presence of catalyst to obtain liquid products from different sources of feedstock (Gollakota *et al.*, 2018). Thermochemical methods could be classified into dry and wet processes. It should be noted that, the choice of process condition is strongly dependent on its feedstock water content. The dry process includes torrefaction, pyrolysis and gasification. While for the wet process, the available methods are hydrothermal carbonization (HTC), hydrothermal liquefaction (HTL) and hydrothermal gasification (HTG).

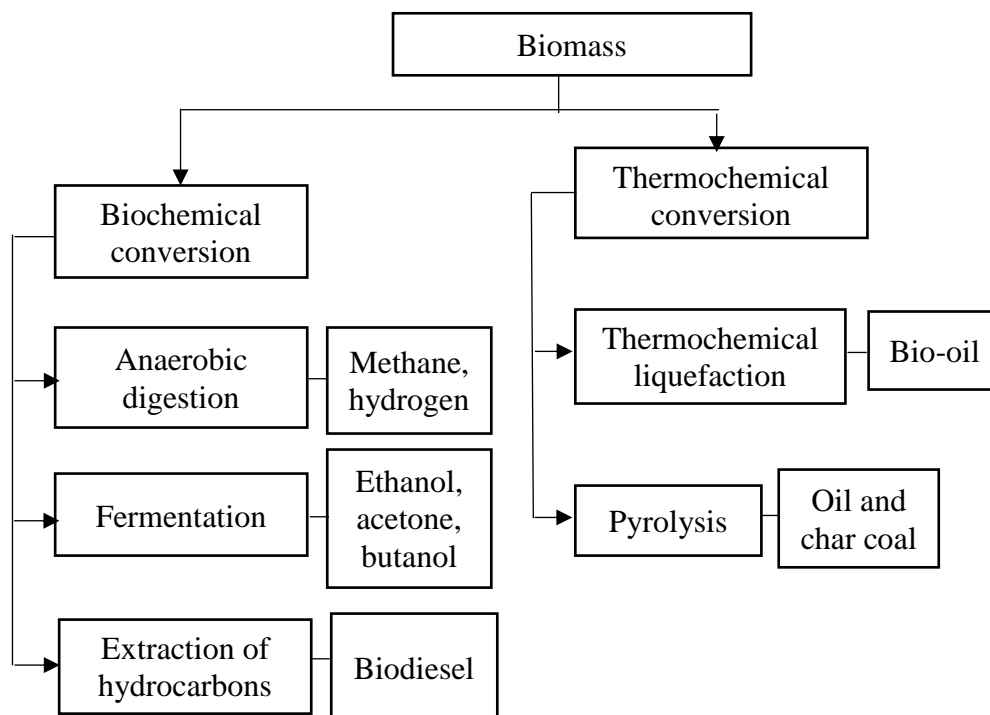


Figure 1.2: Conversion of biomass into biofuels (Chen *et al.*, 2015a).

Table 1.2 outlines the strengths and weaknesses of biochemical and thermochemical methods for the production of biofuels. Among the two methods, thermochemical seems to be the most promising one as the whole feedstock could directly be decomposed and converted into bio-oil without the needs of extracting the lipid content (Song *et al.*, 2017, Guo *et al.*, 2015, Gollakota *et al.*, 2018). Therefore, the available biomass still can be used to produce bio-oil even though they consist of low lipid content. Among the thermochemical methods, only pyrolysis and HTL are mainly focused in the production of bio-oil. Pyrolysis involves the thermal treatment of biomass to produce bio-oil, charcoal and gaseous product at a temperature of 400-700 °C (at atmospheric pressure and in the absence of oxygen). The process is relatively simple as no high-pressure condition is involved.

Table 1.2: Strengths and weaknesses of different techniques to produce biofuels from biomass (Chen *et al.*, 2015a).

Process	Strength	Weakness
Biochemical	<ul style="list-style-type: none"> <li>• No dewatering required</li> <li>• Matured process</li> <li>• High carbohydrates in algae suitable for process.</li> </ul>	<ul style="list-style-type: none"> <li>• High sodium and nitrogen inhibition</li> <li>• Low efficiency in term of yield</li> </ul>
Thermochemical	<ul style="list-style-type: none"> <li>• No caustic chemicals needed</li> <li>• Fast rates of production</li> <li>• No drying required</li> <li>• More effective process</li> </ul>	<ul style="list-style-type: none"> <li>• High energy consumption</li> <li>• High temperature and pressure process</li> <li>• Viscous products</li> </ul>

However, the biomass feedstock needs to be in a dry form before it can be subjected to pyrolysis process. Thus, extra energy is required to dry the biomass at the first stage before it can be converted into bio-oil. Contrary, HTL is a process in which the biomass could be converted into bio-oil in a hot compressed water at a relatively moderate temperature (280-370 °C). As compared to pyrolysis, a relatively lower temperature is required for HTL process to produce bio-oil. Plus, no drying treatment is required as the biomass could be directly used even in a wet form. In fact, higher yield of bio-oil could be achieved and the combustion of crude bio-oil from HTL are much cleaner since the production of sulfur and ash content are relatively low to result in less emission of particulates upon burning (López Barreiro *et al.*, 2013).

### 1.3 Problem Statement

Hydrothermal liquefaction process has been identified as an innovative technique and able to convert aquatic or wet biomass into bio-oil (Sumprasit *et al.*, 2017, Jena *et al.*, 2012). However, there are several limitations in the production of

bio-oil via this process such as low bio-oil yield (which was less than 40 %), high temperature required to conduct the conversion process (~300-350 °C) and long reaction time (40-60 min) are needed to obtain a high yield of bio-oil. In order to tackle those limitations, the temperature of the HTL process was fixed at a relatively mild temperature (270 °C) while the effect of reaction time on the yield of the bio-oil was investigated. This is because, shorter reaction time would cause more water soluble product (WSP) to be produced instead of bio-oil. On the other hand, if the reaction time is too long, the production of gaseous product would be more favorable than bio-oil (Xu and Savage, 2015). Therefore, an appropriate reaction time is deemed to be investigated for the rationale to obtain a maximum amount of oil within short reaction time. Even though HTL of spirulina is reported could produce bio-oil, the presence of the oxygen (O) and nitrogen (N) in the bio-oil are still high. It should be noted that, the presence of high amount of heteroatoms would decrease the quality of the bio-oil. The presence of catalysts have been reported could reduce the O and N content which could further improve the quality of the bio-oil. Therefore, the effect of various type of catalysts such as  $K_2CO_3$ ,  $Al_2O_3$ , zeolite HY and MgO in conjunction with the dosage of the best catalyst was investigated on the yield and product distributions of the bio-oil as well as the reusability and stability of the catalyst.

#### **1.4 Research Objectives**

The objectives of the current study are:

1. To investigate the effect of reaction conditions (reaction time, catalyst types and catalyst dosage) on the yield of bio-oil.
2. To compare the characteristics of bio-oil produced from catalytic and non-catalytic HTL of Spirulina.

## CHAPTER 2

### LITERATURE REVIEW

#### 2.1 Hydrothermal Liquefaction of Spirulina

Hydrothermal liquefaction (HTL) is a thermochemical conversion of biomass into bio-oil at a relatively moderate temperature (280-370 °C) and at a high pressure (10-25 MPa) (López Barreiro *et al.*, 2013). As shown in Figure 2.1, the products of HTL process are commonly classified as oil-phase, water-soluble, gaseous and solid (Guo *et al.*, 2015). The gaseous products consist mainly of hydrogen, nitrogen, carbon monoxide, methane, ethane and carbon dioxide is easily collected after the reaction (Valdez *et al.*, 2012). But in some study, the gaseous products are simply being vented off (Shuping *et al.*, 2010).

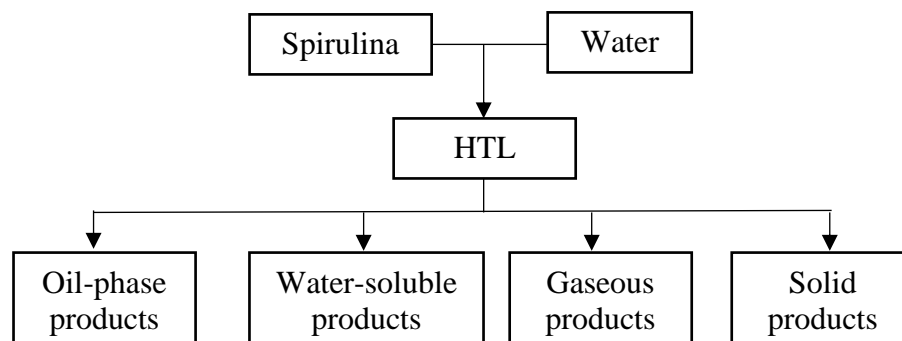


Figure 2.1: Hydrothermal liquefaction products

The mixture of oil-phase, water soluble product (WSP) and solid obtained from HTL of biomass need to be separated after the reaction has completed. Xu and Savage (2014) suggested three different methods to separate the liquid mixture with and without the use of a solvent. The first method is by using a solvent (such as dichloromethane (DCM), acetone and/or diethyl ether) to extract bio-oil directly from

all phase present in reactor before being separated into three phases. The second method is started by removing only aqueous phase from the reactor, proceeded by separating the WSP and bio crude from the aqueous phase and finally extracted the remaining bio crude inside the reactor using a solvent. Meanwhile, the third method did not involve any solvent as the bio-oil would be directly recovered as much as possible from the reactor (Xu and Savage, 2014). Among them, the most common method is by the addition of a solvent into the liquid product obtained just after the HTL reaction completed. This approach has the advantages of producing a relatively higher yield of bio-oil since the bio-oil presence in the water-soluble and solid material could be extracted and recovered in the bio crude fraction (Xu and Savage, 2015). After that, the liquid product was allowed to be settled in a separating funnel to form two layers of oil-phase at the top and water-soluble products at the bottom (depending on the types of the solvent used).

During HTL process, the reaction condition allows the  $H^+$  and  $OH^-$  to dissociate from water to catalyze hydrolysis, acid- and base-catalyzed reactions. Carbohydrates, proteins and lipids contained in the biomass feedstock will undergo isomerization, reforming, depolymerization and repolymerization reactions, before eventually converted to bio-oil containing monoaromatic and single ring heterocyclic compounds (such as benzene, phenol), aliphatic compounds (such as alkanes, alkenes), oxygenated compounds (such as long-chain carboxylic acids, esters, aldehydes and ketones), nitrogenated compounds (such as amides, amines), and polyaromatics (such as naphthalene, indene) (Song *et al.*, 2017, López Barreiro *et al.*, 2013, Chen *et al.*, 2015a). Above the critical point of water, supercritical conditions favor to decarboxylation, cleavage, steam reforming and gasification reactions of



intermediates and lead to higher gas yield (Song *et al.*, 2017). However, low yield and high nitrogen and oxygen content in HTL bio-oil compared to conventional fossil fuels still remain a challenge for refinery before it can be used as transportation fuels (Guo *et al.*, 2015). Therefore, the effect of reaction parameters during the HTL process needs to be investigated for the rationale to obtain higher yield of bio-oil accompanied by a better quality that could be further applied in the industries.

## **2.2 Parameters Affecting the HTL Process**

Various types of reaction conditions have been studied in HTL process such as reaction temperature (Xu *et al.*, 2014, Jena *et al.*, 2011, Ji *et al.*, 2017, Eboibi *et al.*, 2014, Shakya *et al.*, 2015, Xu and Savage, 2017, Biswas *et al.*, 2017), reaction time (Xu *et al.*, 2014, Ji *et al.*, 2017, Jiang and Savage, 2017, Song *et al.*, 2017, Xu and Savage, 2015, Eboibi *et al.*, 2014, Valdez *et al.*, 2012, Anastasakis and Ross, 2011, Jena *et al.*, 2011, Shuping *et al.*, 2010, Yang *et al.*, 2004), feedstock concentration (Xu *et al.*, 2014, Jena *et al.*, 2011, Ji *et al.*, 2017, Eboibi *et al.*, 2014, Xu and Savage, 2015, Xu and Savage, 2017, Faeth and Savage, 2016, Jiang and Savage, 2017), catalyst types (Rojas Perez *et al.*, 2015, Chen *et al.*, 2017, Chen *et al.*, 2015b, Lin *et al.*, 2017, Zhang *et al.*, 2017, Saber *et al.*, 2016, Singh *et al.*, 2015, Patel *et al.*, 2017, Xu and Savage, 2014, Jena *et al.*, 2012, Shakya *et al.*, 2015, Xu and Savage, 2017, Muppaneni *et al.*, 2017, Zhang *et al.*, 2013, Ross *et al.*, 2010) and catalyst dosage (Rojas Perez *et al.*, 2015, Shuping *et al.*, 2010, Li and Savage, 2013). Different operating conditions could positively or negatively affect the yield and quality of the bio-oil produced. In fact, the reaction conditions vary for different kind of feedstock to produce maximum yield of bio-oil (López Barreiro *et al.*, 2013).

### 2.2.1 Reaction Time

Reaction time is one of the critical parameters to be studied in the production of bio-oil and the findings are shown in Table 2.1. Xu and Savage (2015) investigated the effect of reaction time on the production of bio-oil by adopting *Nannochloropsis* as a feedstock. The results demonstrated that an increase in the reaction time from 0 to 60 min had positively enhanced the yield of bio-oil from 38.2 to 40.5 wt. %. In contra, the yield of WSP declined from 6.4 to 3.6 wt. % with respect to the increase in the reaction time. It should be noted that, a decrease in the WSP with time was probably due to the formation of a polar molecule at the initial stage of HTL. The molecules became larger and less polar, which rendered them less soluble in water and increase the bio-oil yield as the reaction time increase.

Another study on the production of bio-oil was carried out by Ji *et al.* (2017) by adopting spirulina as a feedstock. By fixing the reaction temperature at 300 °C and varying the reaction time from 15 to 75 min, the yield of bio-oil sharply rose from 15.08 to 59.5 % at 15 to 45 min, respectively. However, when the reaction time was prolonged to 75 min, the yield was drastically declined to 46.18 %. The reason for reduction of bio-oil yield at higher reaction time was due to further decomposition of the bio-oil into gas and aqueous phase products. A similar trend was observed by Yang *et al.* (2004) as they discovered that the maximum yield of bio-oil obtained was at 30 min. Further increase in the reaction time to 60 min led to the decomposition of the bio-oil and resulted to the decrease in the total oil yield. They assumed that the thermochemical liquefaction of biomass of algae was almost complete within 30 min of reaction.

Table 2.1: Overview of the effect of reaction time on the HTL process

Reaction time	Feedstock	Optimum conditions	Important findings	References
15, 30, 45, 60, and 75 min	<i>Spirulina</i>	RT: 300 °C Rt: 45 min Ethanol content: 50 vol.% S/M ratio: 40/4 ml/g Yield of bio-oil: 59.5 % Catalyst: none	<ul style="list-style-type: none"> <li>The bio-oil yield sharply rose from 15.08 to 59.5 % with respect to the increased in the reaction time from 15 to 45 min.</li> <li>Further prolonged the reaction time to 75 min had gradually declined the yield to 46.18 %.</li> </ul>	Ji <i>et al.</i> (2017)
3 and 60 min	<i>Nannochloropsis sp.</i>	RT: 400 °C Rt: 3 min Algae loading: 15 wt.% Yield of bio-oil: 41.7 % Catalyst: none	<ul style="list-style-type: none"> <li>Longer reaction times (60 min) led to bio-oil with higher Na but lower Fe concentrations.</li> <li>More DCM-soluble Na-containing molecules (perhaps salts of fatty acids) formed at longer time (60 min).</li> </ul>	Jiang and Savage (2017)
15, 30, 45, and 60 min	<i>Cyanophyta</i>	RT: 350 °C Rt: 60 min Algae loading: 25 wt.% Yield of bio-oil: 29.24 % Catalyst: none	<ul style="list-style-type: none"> <li>Total yield of bio-oil initially rose from 25.51 % at 15 min to 29.24 % at 60 min and appeared to approach constant value after 45 min.</li> </ul>	Song <i>et al.</i> (2017)

Table 2.1: (Continued)

10, 30, 45, and 60 min	<i>Nannochloropsis sp. slurry</i>	RT: 350 °C Rt: 60 min Algae loading: 14.1 wt.% Yield of bio-oil: 40.5 % Catalyst: none	<ul style="list-style-type: none"> <li>• The yield of water-soluble bio-oil declined from 6.4 to 3.6 wt.% as time increased,</li> <li>• The yield of water-insoluble bio-oil rose from 38.2 to 40.5 wt.% as time increased from 10 to 60 min</li> </ul>	Xu and Savage (2015)
5, 15, 30, 45 and 60 min	<i>Tetraselmis sp.</i>	RT: 350 °C Rt: 5 min Algae to water ratio: 0.16 Yield of bio-oil: 65 % Catalyst: none	<ul style="list-style-type: none"> <li>• Higher yields of HTL bio-oil from <i>Tetraselmis sp.</i> was obtained using short reaction times at subcritical conditions of 350 °C.</li> </ul>	Eboibi <i>et al.</i> (2014)
10 to 90 min	<i>Nannochloropsis sp.</i>	RT: 300 °C Rt: 20 min Algae loading: 15 wt.% Yield of bio-oil: 50 % Catalyst: none	<ul style="list-style-type: none"> <li>• There were little variation in the bio-oil yield with time at 350 °C.</li> <li>• The yields at 250 and 400 °C were lower than the yields at 300 and 350 °C.</li> <li>• Above the critical point of water, a decrease (38-33 %) in the overall yield of bio-oil at longer times (10- 40 min) was observed.</li> </ul>	Valdez <i>et al.</i> (2012)

Table 2.1: (Continued)

15–120 min	<i>L. Saccharina</i>	RT: 350 °C Rt: 15 min Algae to water ratio: 0.1 Yield of bio-oil: 17.8 % Catalyst: none	<ul style="list-style-type: none"> <li>• 15 min reaction time at 350 °C was sufficient for the seaweed to form oily compounds.</li> <li>• Increase in reaction time caused the decrease in bio-oil yield.</li> </ul>	Anastasakis and Ross (2011)
0, 30, 60, 90 and 120 min	<i>Spirulina platensis</i>	RT: 350 °C Rt: 60 min Algae concentration: 20 % Yield of bio-oil: 39.9 % Catalyst: none	<ul style="list-style-type: none"> <li>• Bio-oil yield increased (39.9 %) with an increase in the reaction time (60 min).</li> <li>• The yield of bio-oil reached its peak at 60 min (39.9 %) and decreased (34-33 %) with further increase in the reaction time (90-120 min).</li> </ul>	Jena <i>et al.</i> (2011)
10, 20, 30, 40, 50, 60 and 90 min.	<i>Dunaliella tertiolecta</i>	RT: 360 °C Rt: 50 min Algae to water ratio:0.1 Catalyst: Na <sub>2</sub> CO <sub>3</sub> Catalyst dosage: 5 wt. % Yield of bio-oil: 25.8 %	<ul style="list-style-type: none"> <li>• The bio-oil yield first increased sharply then remained approximately constant with increasing reaction time beyond 50 min.</li> </ul>	Shuping <i>et al.</i> (2010)

Table 2.1: (Continued)

30 and 60 min	<i>Microcystis viridis</i>	RT: 340 °C Rt: 30 min Catalyst: Na <sub>2</sub> CO <sub>3</sub> Catalyst dosage: 5 wt.% Yield of bio-oil: 33 %	<ul style="list-style-type: none"> <li>The average oil yield was less at 60 min (30 %) reaction time compared to 30 min (33 %).</li> </ul>	Yang <i>et al.</i> (2004)
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\*RT= reaction temperature

\*Rt = reaction time

Previously, Valdez *et al.* (2012) and Jena *et al.* (2011) suggested that the decrease in the bio-oil yield at higher reaction time was attributed to the conversion of the lighter hydrocarbon compounds in the bio-oil into gaseous product. This statement was supported by the increase in the gaseous product from 18.2, 24.8 and 27 % at 60, 90 and 120 min, respectively (Jena *et al.*, 2011). However, a different observation was found by Eboibi *et al.* (2014) in which a high yield of bio-oil (65 %) was successfully attained within just 5 min of reaction by using *Tetraselmis sp* as a feedstock. It could be due to the quick release of the intracellular content of the microalgae that could lead to a sharp decrease in a solid residue and directly increased the yield of bio-oil. Similar results were obtained by Jiang and Savage (2017) where the yield of bio-oil obtained was higher (41.7 %) at a reaction time of 3 min as compared to 60 min (31.7 %).

Additionally, Anastasakis and Ross (2011) found that the optimum reaction time was obtained at 15 min (19.3 %) and a decrease in yield of bio-oil (15-18 %) was observed at a relatively longer reaction time (30-120 min). Meanwhile, Shuping *et al.* (2010) found that the bio-oil yield was increased sharply from 10 min to 50 min and remain unchanged with an increase in the reaction time above 50 min. It could be explained by the competition between the two reactions involved in liquefaction which were hydrolysis and repolymerization. At the initial stage, an increase in the yield of bio-oil was attributed to the decomposition and depolymerization of the biomass to form small compounds. Further prolonged in the reaction time, these compounds could be rearranged through condensation and repolymerization that cause no further significant improvement in the yield of bio-oil.

Based on the previous findings, long reaction time does not guarantee that the yield of the bio-oil could be enhanced. On the other hand, too short of reaction time might be not sufficient for the production of bio-oil. Therefore, an appropriate reaction time must be identified as this factor would affect the yield of the bio-oil produced.

### 2.2.2 Catalyst Type

Although the production of bio-oil has been successfully achieved by direct liquefaction of biomass, the product yield still contains the undesired properties such as high O and N content as well as low calorific values (HHV) (Minowa *et al.*, 1995). Therefore, the effect of adding catalyst during the HTL process has been studied for the rationale to minimize the generation of the undesired properties in the bio-oil as well as to enhance the product yield. As shown in Table 2.2, both homogeneous and heterogeneous catalysts have been used in the hydrothermal liquefaction of biomass. Shakya *et al.* (2015) reported that the addition of  $\text{Na}_2\text{CO}_3$  had successfully increased the carbohydrate conversion at a higher reaction temperature (300 to 350 °C) and helped in increasing the yield of bio-oil for both high carbohydrate containing algae (*Pavlova and Isochrysis*). Catalytic bio-oils yielded a higher percentage of hydrocarbons than non-catalytic bio-oils. Meanwhile, for high protein containing algae (*Nannochloropsis*), an increase in the bio-oil yield (~34 %) compared to non-catalytic reaction (~26 %) was observed at a relatively lower temperature (250 °C). However, further increase in the temperature to 300 °C and 350 °C caused a drastic decrease in the yield of bio-oil (20.6 and 23.8 %, respectively). This observation could be due to a decrease in the activation energy of  $\text{Na}_2\text{CO}_3$  for protein hydrolysis.



Table 2.2: Overview of the effect of catalyst on the HTL process

Catalyst	Feedstock	Optimum Condition	Important findings	References
Na <sub>2</sub> CO <sub>3</sub>	<i>Pavlova</i> , <i>Isochrysis</i> and <i>Nannochloropsis</i>	RT: 350 °C Rt: 60 min Feedstock to water ratio:1/6 Feedstock: <i>Pavlova</i> Catalyst : Na <sub>2</sub> CO <sub>3</sub> Catalyst dosage: 5 wt.% Yield of bio-oil: 47.07 %	<ul style="list-style-type: none"> <li>• The presence of Na<sub>2</sub>CO<sub>3</sub> (alkaline) decreased the total acid number and did not have significant effect on the elemental composition of the bio-oils.</li> <li>• The obtained bio-oil were grouped into different categories such as hydrocarbons (HC), phenolic (Ph), nitrogenated compounds (NC), oxygenates (OC) and organic acids (OA).</li> <li>• The use of catalyst resulted to the presence of few cyclic organic acids like carbamic acid, methyl-3-methylphenylester-, and 1H-Indole-3-propanoic acid.</li> </ul>	Shakya et al.(2015)
Ru/C	<i>Nannochloropsis</i>	RT: 350 °C Rt: 20 min Feedstock loading: 11.4 wt.% Catalyst : 5 wt.% Ru on carbon Catalyst dosage: 10 wt.% Yield of bio-oil: 45 %	<ul style="list-style-type: none"> <li>• The presence of Ru/C increased the yield of water-insoluble bio-oil and decreased the yield of water-soluble bio-oil.</li> <li>• The differences in the yield of water insoluble bio-oil and water soluble bio-oil demonstrated that the presence of Ru/C had no measureable effect on the total yield of bio-oil.</li> <li>• EA results indicate the addition of catalyst decreased the N and O content of total bio-oil.</li> <li>• ER of total bio-oil for HTL with catalyst (70.5 %) was higher compared to without catalyst (67.6 %).</li> </ul>	Xu and Savage (2017)

Table 2.2: (Continued)

<p>CHCOOH, H<sub>2</sub>SO<sub>4</sub>, NaOH and KOH</p>	<p><i>Cyanidioschyzon merolae</i></p>	<p>RT: 300 °C Rt: 30 min feedstock loading: 10 wt.% Catalyst : KOH Catalyst concentration: 0.5 M Yield of bio-oil: 22.67 %</p>	<ul style="list-style-type: none"> <li>• The bio-oil yield increased from 16.98 % without catalyst to 21.23 % with CH<sub>3</sub>COOH, 21.78 % with NaOH and to 22.67 % with KOH and no noticeable increase in the bio-oil yield was observed with H<sub>2</sub>SO<sub>4</sub>.</li> <li>• HHV of bio-oil were not affected by the addition of different types of catalysts and the maximum HHV of 33.76 MJ kg<sup>-1</sup> was obtained when H<sub>2</sub>SO<sub>4</sub> was used as a catalyst.</li> </ul>	<p>Muppaneni et al (2017)</p>
<p>Raney-Ni and HZSM-5 zeolite</p>	<p><i>Chlorella pyrenoidosa</i></p>	<p>RT: 240-300 °C Rt: 30 min feedstock loading: 20g Catalyst loading: 1g Yield of bio-oil: 22.67 %</p>	<ul style="list-style-type: none"> <li>• The presence of catalyst had no significant effect on the yield of bio-oil but it tended to slightly increase the solid residue.</li> <li>• HZSM-5 zeolite slightly increased the HHV of bio-oil (35 MJ kg<sup>-1</sup>) compared to blank (34.61 MJ kg<sup>-1</sup>) while the effects of Raney-Ni were not significant.</li> <li>• ER of bio-oil showed no significant effect for different catalyst (68.15 kJ).</li> <li>• The addition of catalyst had no significant effect on the elemental composition of bio-oil (C-71.5 %, H-9.1 %, N-8.7 %, O-10.7 %).</li> </ul>	<p>Zhang et al (2013)</p>

Table 2.2: (Continued)

<p>Nano-Ni/SiO<sub>2</sub>, Zeolite and Na<sub>2</sub>CO<sub>3</sub></p>	<p><i>Nannochloropsis</i></p>	<p>RT: 250 °C Rt: 60 min feedstock to water ratio:1/15 Catalyst : nano-Ni/SiO<sub>2</sub> Catalyst dosage: 5 wt.% Yield of bio-oil: 30 %</p>	<ul style="list-style-type: none"> <li>• Higher bio-oil yields with the order of nano-Ni/SiO<sub>2</sub> (30 %) &gt; Na<sub>2</sub>CO<sub>3</sub> (24.2 %) &gt; zeolite (24 %) &gt; blank (20.2 %).</li> <li>• The C and H contents of the bio-oil obtained from catalytic HTL (zeolite) (73.37 % and 11.01 %) were higher than those of the blank experiment (70 % and 10 %) but still less than that of the crude oil (87 % and 14 %).</li> <li>• The O, N, and S contents of the bio-oil from the catalytic HTL (zeolite) (12.62 %, 2.99 %, and 0.31 %) were lower than those of the blank experiment (13.80 %, 3.77 %, and 0.42 %) but still higher than crude oil (1.5 %, 2 %, and 6 %).</li> <li>• The ER for catalytic HTL was in the range of 22.45 % to 28.94 % (Na<sub>2</sub>CO<sub>3</sub> and nano-Ni/SiO<sub>2</sub>), which was higher than that of the blank experiment (18.48 %).</li> </ul>	<p>Saber <i>et al.</i> (2016)</p>
<p>Na<sub>2</sub>CO<sub>3</sub>, KOH, CH<sub>3</sub>COOH and HCOOH</p>	<p><i>Chlorella vulgaris</i> and <i>Spirulina</i></p>	<p>RT: 350 °C Rt: 60 min Feedstock: <i>Chlorella</i> Catalyst: CH<sub>3</sub>COOH Catalyst dosage: 27 ml/g feestock Yield of bio-oil: 19.5 %</p>	<ul style="list-style-type: none"> <li>• The yields of bio-oil for <i>Chlorella</i> were higher using the organic acids (CH<sub>3</sub>COOH and HCOOH) (19.5 % and 18 %) compared to using alkali catalyst (Na<sub>2</sub>CO<sub>3</sub> and KOH) (15 % and 16 %).</li> <li>• The bio-oil had an average elemental composition of 74.4 % C, 11.5 % H, 4.7 % N, 0.2 % S and 9.2 % O under alkali conditions.</li> </ul>	<p>Ross <i>et al.</i> (2010)</p>

Table 2.2: (Continued)

<p>SBA-15, Co-SBA-15, NH<sub>2</sub>-Co-SBA-15, SO<sub>3</sub>H-Co-SBA-15 and NH<sub>2</sub>-SO<sub>3</sub>H-Co-SBA-15</p>	<p><i>Dunaliella tertiolecta</i></p>	<p>RT: 260 °C Rt: 30 min Feedstock: <i>Dunaliella tertiolecta</i> Catalyst dosage: 10 wt.% Yield of bio-oil: 18.68 %(blank)</p>	<ul style="list-style-type: none"> <li>• Using organic acids, the bio-oil had an average elemental composition of 70.8 % C, 9.4 % H, 5.3 % N, 0.65 % S and 13.85 % O.</li> <li>• The main compounds identified by GC-MS includes mono-aromatics (toluene, ethyl-benzene and styrene), substituted phenols, N-heterocycles (pyrroles and indole derivatives) and long chain alkanes.</li> <li>• The presence of catalyst decreased the yield of bio-oil. The bio-oil yield were 18.68 wt. %, 17.39 wt. %, 17.77 wt. % and 15.82 wt. % for blank HTL, NH<sub>2</sub>-Co-SBA-15, SO<sub>3</sub>H-Co-SBA-15 and NH<sub>2</sub>-SO<sub>3</sub>H-Co-SBA-15 respectively.</li> <li>• The quality of the bio-oil was greatly improved and the product obtained consisted of more furfural derivative and the amount of the undesired components such as acids and N-containing substances was reduced.</li> <li>• The bio-oil produced by Co-SBA-15 catalyst contained higher C (68.53 wt. %) and lower O (19.75 wt. %) than those of the blank (67.18 wt. % and 22.02 wt. %). However, the remaining samples had lower C contents (63.93-64.28 wt. %) and higher O contents (25.2-25.31 wt. %).</li> </ul>	<p>Lin <i>et al.</i> (2017)</p>
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Table 2.2: (Continued)

Co/CNT, Ni/CNT, and Pt/CNT,	<i>Dunaliella tertiolecta</i>	RT: 320 °C Rt: 30 min feedstock to water ratio:1/10 Catalyst : Co/CNT Catalyst dosage: 10 wt.% Yield of bio-oil: 40.25 %	<ul style="list-style-type: none"> <li>• The introduction of catalyst resulted in the enhancement of conversion (91-95 %) and bio-oil yield (38-40 %) compared to blank sample (90 % and 34 %). However, the bio-oil yields showed no obvious difference over the three different metal catalysts (38-40 %).</li> <li>• TGA results showed that the bio-oil obtained from the Co/CNTs contained smaller molecular weight compounds compared to the non-catalytic, Ni/CNTs or Pt/CNTs catalytic HTL process.</li> <li>• GCMS results showed that the fatty acids and amides were the main components present in the bio-oil produced from non-catalytic reaction.</li> <li>• For the Ni/CNTs and Pt/CNTs, the main compounds present in the bio-oil were: fatty acids &gt;hydrocarbons &gt;N-containing compounds &gt; ketones.</li> </ul>	Chen <i>et al.</i> (2017)
ZrO <sub>2</sub> /SO <sub>4</sub> <sup>2-</sup> , HZSM-5, MgO/MC M-41 and KtB	<i>Dunaliella tertiolecta</i>	RT: 360 °C Rt: 30 min feedstock loading: 4g Catalyst : KtB Catalyst dosage: 10 wt.% Yield of bio-oil: 49.09 %	<ul style="list-style-type: none"> <li>• The trend for conversion and bio-oil yield of the used catalysts were KtB&gt; MgO/MCM-41&gt; Blank&gt; ZrO<sub>2</sub>/SO<sub>4</sub><sup>2-</sup>&gt; HZSM-5</li> <li>• The presence of catalysts managed to reduce the boiling point range and decreased the fixed C content in the bio-oil compared to the blank sample.</li> </ul>	Chen <i>et al.</i> (2015b)

Table 2.2: (Continued)

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- The used of KtB resulted to more complete conversion of carbohydrates which explain better oil yield. For HZSM-5, more ketone compounds existed in the bio-oil.
  - For  $\text{ZrO}_2/\text{SO}_4^{2-}$  and blank HTL products, the organic compounds in the raw material were converted more thoroughly and majority of H, O, and N were effectively transformed as well as the SRs were mainly in the form of fixed carbon.
  - FT-IR result showed that the bio-oil obtained using HZSM-5 and MgO/MCM-41 was more conducive to the formation of the benzene.
  - The KtB as the catalyst has the best energy recovery rate (88.83 %). The highest HHV in product was for the blank experiment ( $35.92 \text{ MJ kg}^{-1}$ ). Lowest HHV for KtB as catalyst ( $32.36 \text{ MJ kg}^{-1}$ ).
  - There were large numbers of ketone, alkene and alkane while very little carboxylic acids existed in HZSM-5 and MgO/MCM-41 systems
  - The carboxylic acid content was very significant when  $\text{ZrO}_2/\text{SO}_4^{2-}$  and KtB were used as the catalyst as well as the blank value.
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Muppaneni *et al.* (2017) compared the performances of acidic ( $\text{CH}_3\text{COOH}$  and  $\text{H}_2\text{SO}_4$ ) and alkaline catalysts ( $\text{NaOH}$  and  $\text{KOH}$ ) for the production of bio-oil from *Cyanidioschyzon merolae*. All the tested catalysts demonstrated an increase in the yield of bio-oil and a decrease in the production of bio char. However,  $\text{H}_2\text{SO}_4$  gave a different observation as the yield of bio-oil was equal to the non-catalytic system (16.98 %). The addition of catalysts was found to give no significant effect on the C content (except  $\text{CH}_3\text{COOH}$ ) but gave an improvement in the H and successfully decreased the N content of the bio-oil.

Effect of various types of homogeneous acid ( $\text{CH}_3\text{COOH}$  and  $\text{HCOOH}$ ) and alkaline ( $\text{Na}_2\text{CO}_3$  and  $\text{KOH}$ ) catalysts on the production of bio-oil were investigated by Ross *et al.* (2010). They concluded that the addition of organic acids had a beneficial effect on the yield of the bio-oil (19.5 % and 18 %) compared to an alkali catalyst (15 % and 16 %). The addition of acid catalysts had a positive effect on the yield of bio-oil as they were either fully decomposed to gaseous products or reacted with the degradation products of microalgae. Although acid catalysts gave a better yield of bio-oil, HHV results indicated that the heat content of the bio-oil for the alkali catalysts (33.4-39.9  $\text{MJ kg}^{-1}$ ) increased with increasing temperature (300-350 °C) and it was higher than the organic acids (33.3-35.1  $\text{MJ kg}^{-1}$ ).

Another research by Chen *et al.* (2015b) found that heterogeneous alkaline catalysts ( $\text{MgO/MCM-41}$  and  $\text{KtB}$ ) produced a higher yield of bio-oil (~37 % and ~49 %) compared to the blank sample (~35 %). Contrary, the presence of heterogeneous acid catalysts ( $\text{ZrO}_2/\text{SO}_4^{2-}$  and  $\text{HZSM-5}$ ) resulted in a decrease in the bio-oil yield (~29 % and ~30 %). In fact, the yield of bio-oil in an acid catalysis system was even lower than