Full Length Article

Quality of bio-oil from catalytic pyrolysis of microalgae *Chlorella vulgaris*

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A B S T R A C T

This study investigates the yield and quality of bio-oil produced from catalytic and non-catalytic pyrolysis of microalgae *Chlorella vulgaris* using Ni supported zeolite (Si/Al = 30) prepared by two different methods, ion exchange (IE) and wet impregnation (WI) to examine the effect of catalyst preparation methods on the bio-oil quality. The experiments were also conducted to investigate the effect of different temperatures (300–600 °C) and catalyst to algae ratio (1:5, 1:2, 1:1 and 2:1) on the yield and quality of bio-oil. The results showed that catalytic pyrolysis using Ni supported zeolites produced high hydrocarbon, less oxygenated and acid compounds compared to non-catalytic pyrolysis. The catalyst preparation method did not affect the yield but had an effect on the bio-oil composition. The results obtained from this study are useful in developing the catalytic pyrolysis process to refine bio-oils for commercial use.

1. Introduction

Fossil fuels such as petroleum, natural gas, and coal are non-renewable resources that are extensively used for transportation and power generation. However, fossil fuel consumption significantly contributes to the emission of greenhouse gasses, particularly CO_2, thus increasing the undesirable effect of global climate change [1,2]. Moreover, studies have revealed that the fossil fuels are depleting, and therefore, it is very important to find sustainable alternative renewable fuel resources. Biomass is a renewable resource for biofuel production. Biomass is considered the fourth largest source of energy in the world and the sources of biomass include wood, residues from agriculture or forestry, the organic component of municipal and industrial wastes as well as oil-rich algae such as microalgae [3].

Microalgae have attracted attention due to several advantages, one of which is the capability to capture CO_2. Another advantage is that microalgae have a faster growth rate and can grow in an aquatic medium avoiding the use of arable land. Moreover, microalgae have no lignin to be removed, unlike woody biomass. There is a growing interest in research on microalgae use as it is capable of producing a variety of products such as food supplements (omega three oil and chlorophyll) and also can be used for the production of biofuels (biodiesel, bio-methane, and bioethanol) [4], along with mitigating CO_2 emissions.

Microalgae biomass can be converted into biofuel via biochemical (fermentation and anaerobic digestion) and thermochemical conversions (combustion, gasification, liquefaction, and pyrolysis). Thermochemical conversion is the relatively new approach for the conversion of algae to bio-oils [5] however, requires more work towards achieving the goal of transportation fuel. Thermochemical conversion such as pyrolysis can be used to convert microalgae biomass into char, gas and liquid product known as bio-oil [6,7]. The research on pyrolysis of microalgae biomass for bio-oil production has been widely carried out [8,9]. The yield and quality of the bio-oil during pyrolysis depends on factors such as temperatures, heating rates and residence time of the biomass in the pyrolysis reactor. Literature studies show that pyrolysis at lower temperatures < 400 °C or low heating rates produce higher levels of char. Lower heating rate and longer residence time also lead to secondary cracking reactions which affect the bio-oil properties. Alternatively, at temperatures > 700 °C pyrolysis produces more gaseous products resulting in low oil yields. The temperature at which high oil yields can be obtained would vary from species to species due to their chemical composition. Hence, it is necessary to optimize the temperature to achieve maximum oil yield. In this work effect of temperature on the yield and quality of the bio-oil was measured in a fixed bed reactor at temperatures of 300–600 °C, where the microalgae were dropped into a fixed bed reactor operated at desired temperature achieving faster-heating rates and more oil yields. The bio-oil produced during pyrolysis of algae has few undesired properties like low heating value, high viscosity, due to the presence of oxygenated compounds and nitrogenated compounds in them and are not miscible with fossil fuels [10]. Therefore, the oils need to be upgraded to meet the standards required for transportation fuel.

Catalytic pyrolysis is considered to be a promising way to upgrade the bio-oil due to the low-pressure requirements [11,12]. Among the

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catalysts, zeolite has shown a significant effect in reducing the oxygenated compounds and increasing the production of aromatic hydrocarbon [8,9,13]. The presence of acid sites in the zeolites can remove undesirable oxygenates and acids and considerably increase the aromatic and phenolic compounds. The acid sites present on the catalyst favor the oligomerization of ethylene and propylene and subsequent cyclization in the pores of the catalyst to produce aromatic compounds [14,15]. The aromatic compounds are formed in the presence of Meso-MFI owing to its high Bronsted acid sites compared to Al-MCM-48 [16]. The high acidity of the catalysts allows cracking large molecules to lower hydrocarbons or effectively produce gas as observed with Meso-MFI catalysts [16]. Other work over microporous zeolites HZSM-5 (Si/Al = 23, 30), HBETA (Si/Al = 25) and HY (Si/Al = 30) showed that catalysts with high acidity, HZSM-5 (SiO_2/Al_2O_3 = 23) showed high selectivity towards aromatic formation [17]. However, the high number of acid sites sometimes can lead to coke formation. Therefore, moderating these acid sites is important in designing a catalyst as it can affect the selectivity of the product formation.

One option to moderate the acid sites in the zeolite is by incorporating transition metal such as nickel (Ni), cobalt (Co), gallium (Ga), palladium (Pd), copper (Cu), iron (Fe), and molybdenum (Mo) to produce a metal-loaded catalyst. Previous studies have shown that the presence of these transition metals can reduce coke formation as well as increase the production of hydrocarbon, and reduce the amount of oxygenated compound found in bio-oil [18,19]. Although several studies have been conducted on pyrolysis of woody biomass using these metal-loaded catalysts [20–24], there are few studies on microalgae using metal loaded catalysts [18,25,26]. The catalysts identified so far are promising but could not meet the standards of transportation fuel through catalytic upgradation. Hence more research in this direction in developing new catalysts and further fine tuning is required. The present work is an effort in this direction.

In this study, Ni supported on the zeolite (Si/Al = 30) catalyst was prepared by ion-exchange (IE) and wet impregnation (WI) methods. The catalyst in this study are represented as Ni (IE) and Ni (WI). Ni is incorporated into zeolite as Ni is able to increase the hydrothermal stability of catalyst and provide an ideal environment for oligomerization of small alkenes which can lead to a greater yield of aromatic production [18]. The microalgae used in this study is *Chlorella vulgaris* (*C. vulgaris*). It is one of the fast-growing green algae with the potential to be used in biofuel production. The pyrolysis experiments were conducted in a fixed bed reactor at different temperatures and different catalyst to algae ratios. The different catalyst to algae ratio are achieved by having a varying amount of catalysts in a fixed bed reactor and allowing the same amount of algae pyrolysis vapors to pass through the catalyst bed instead of mixing the catalyst and algae. The bio-oil produced was collected to determine the yield and its compositions. Information generated from this study will help to provide an insight into the effects of temperatures and catalyst to algae ratios on the liquid products obtained from catalytic pyrolysis of microalgae using Ni (IE and WI).

2. Experimental section

2.1. Cultivation and characterization of microalgae

Microalgae *C. vulgaris* was provided by CSIRO Microalgae Research Centre (Hobart, Australia) and cultivated in Bio Engineering Laboratory, Department of Chemical Engineering, Monash University. The microalgae were cultivated in a medium that consists of nitrate, phosphate, citrate, trace metal and vitamin for 14 days and the microalgae cell was harvested by centrifugation at 3000 rpm for 10 min. The details of the medium preparation and cultivation processes were described in the previous study [27]. The supernatant was removed, and the microalgae were then placed in the Petri dishes before placing in the oven for drying at 60 °C. Microalgae composition such as protein,

Table 1
Characterization of microalgae *C. vulgaris*.

	C. vulgaris
Microalgae composition	
Protein	54.7 ± 2.2
Lipid	25.7 ± 0.8
Carbohydrate	19.2 ± 1.6
Ultimate analysis (%)	
C	43.62 ± 0.58
H	6.99 ± 0.24
N	6.15 ± 0.16
S	6.90 ± 0.06
O[*]	36.34 ± 0.59
Proximate analysis (wt.%)	
Moisture	7.4
Volatile matter	67.4
Fixed carbon	9.4
Ash	15.8

[*] By difference.

carbohydrate and lipid were analyzed using Lowry, Phenol-Sulphuric acid and chemical (Hexane and Isopropanol) methods. The chemical composition of the algae sample was performed in duplicates. The carbon, hydrogen, nitrogen and sulfur contents in *C. vulgaris* were analyzed using an elemental analyzer (Model 2400, Perkin-Elmer, USA) in duplicates, while moisture, volatile matter, fixed carbon and ash content were analyzed using thermogravimetric analyzer (Model STA 449 F3 Jupiter, NETZSCH-Geratebau GmbH, Germany). The details of the analysis were described in the previous study [7,28]. The results for chemical, ultimate and proximate analysis are shown in Table 1.

2.2. Preparation and characterization of catalyst

5% Ni supported on Zeolite-Y (CBV-720, Si/Al = 30) was prepared using wet impregnation (WI) and ion exchange (IE) methods. Zeolite (Si/Al = 30) catalyst was obtained from Zeolyst International, and the catalyst was calcined in the furnace at 550 °C overnight. The preparation of Ni (WI) was as follows: 3.715 g of nickel nitrate, Ni $(NO_3)_2$ was dissolved in 20 ml of distilled water and the solution was then mixed with 14.25 g of zeolite in a beaker. The beaker was placed on the electric stirrer to obtain a homogeneous solution, and the temperature was set at 80 °C. Evaporation of water was allowed for this preparation method, and once the water evaporated in about 2 h, it was placed in the oven for drying at 100 °C for 12 h. The metal-loaded catalyst was crushed into a smaller size and calcined at 500 °C for 5 h.

Similar to the wet impregnation preparation method, 14.25 g of zeolite was added to 3.715 g nickel nitrate, Ni $(NO_3)_2$ solution in 100 ml distilled water. The mixed solution was refluxed at 100 °C with continuous stirring for 9 h. The catalyst solution was filtered using vacuum assisted filter to remove supernatant and any contaminants and dried at 100 °C for 12 h. The metal-loaded catalyst was crushed into a smaller size and calcined at 500 °C for 5 h.

Catalysts prepared from both methods were characterized using Micromeritics Accelerated Surface Area and Porosimetry (ASAP 2020) to determine the surface area, pore size, and pore volume. About 150 mg of sample was loaded into the ASAP sample tube and degassed at 150 °C for 6 h. The tube was then transferred to the analysis port and analyzed for surface area and pore size distribution at −195 °C. Nitrogen was dosed to the sample in controlled increments. After each dose, the pressure was allowed to equilibrate and the quantity adsorbed was recorded. The quantity adsorbed at each pressure defines an adsorption isotherm. With the area covered by each adsorbed gas molecule known, the surface area can be calculated.

Chemisorb 2720 (Micromeritics, USA) was used to analyze the acidity and reduction profile of catalysts by temperature programmed

desorption (TPD) and temperature programmed reduction (TPR) respectively. TPD was conducted to analyze the strength of acid sites presents on the surface of the catalyst. About 100 mg of catalyst sample was pre-treated by heated the catalyst up to 150 °C for 1 h in flowing helium gas (50 ml/min) and was left to cool to room temperature. 10% of ammonia gas in helium gas stream was passed through the sample's to saturate the surface with ammonia and then purged with Helium gas for an hour to remove physisorbed ammonia. The temperature was programmed by increasing linearly with time from ambient to 650 °C at a rate of 10 °C/min and the gasses evolved were detected by thermal conductivity detector (TCD).

TPR is used to measure the reduction profile of metal oxide species present on the catalyst surface and the peak observed indicate the temperature at which reduction of species occur. Similar to TPD, about 100 mg of catalyst sample was pre-treated by heated the catalyst up to 150 °C for 1 h in flowing helium gas (50 ml/min) and cooled to room temperature. Next, a constant flow of 5% H_2/N_2 gas at a flow rate of 50 ml/min was supplied throughout the analysis while the temperature was increased linearly with time from ambient to 650 °C at a rate of 10 °C/min. TCD detected the change in H_2 composition with the reference line during TPR.

2.3. Pyrolysis process

Catalytic and non-catalytic pyrolysis experiments were conducted in a quartz fixed bed reactor. The experiments were carried out at different temperatures (300–600 °C) and different catalyst to algae ratios 5:1, 2:1, 1:1 and 1:2, i.e., a constant weight of algae was dropped with different amounts of catalyst packed between the quartz wool in the reactor. The intention is that only the vapors from algae to interact with different amounts of catalyst preventing the contamination of the catalyst with char and allowing to check the effect on the oil quality. Quartz wool is placed at the center of the reactor (36 mm i.d.) to form a bed, and the reactor was heated to the desired temperature in flowing N_2. Once the temperature is reached, 0.5 g microalgae was dropped into the reactor from the reservoir in flowing N_2 (100 ml/min) for pyrolysis. A flask immersed in ice was used to trap the condensed vapor produced from pyrolysis of algae. The experiment was conducted until no more gasses were evolved from the reactor or maximum 30 min.

A slightly different procedure was adopted for pyrolysis in the presence of a catalyst. The catalysts were packed between the quartz wool plugs in the middle of the reactor. The catalyst was reduced at 400 °C under 5% H_2 (100 ml/min) for 1 h before the experiment to reduce NiO to metallic Ni and to activate the catalyst. After 1 h, the gas was then switched to N_2 flow. The temperature of reduction is determined from the TPR results. The temperature was then set during reactor operation and once reached the microalgae was dropped into the reactor. The vapors from the pyrolysis of microalgae will pass through the quartz wool plug and interact with the catalyst, thus preventing the char interaction with the catalyst. The oil vapors are condensed in the cold trap connected at the bottom of the reactor. The experiment was then conducted for another 30 min. Catalytic and non-catalytic pyrolysis experiments were carried out in duplicate, and the average value is reported in this paper.

2.4. Analysis of pyrolysis products

The bio-oil product obtained from the pyrolysis of microalgae was weighed to determine the yield. The bio-oil was then diluted using dichloromethane with the same concentration (3 g/L) before analyzing with the Gas Chromatography-Mass Spectrometry, GC–MS (PerkinElmer Clarus 600/Clarus 600S). The bio-oil samples were filtered using syringe filters (0.45 μm) to remove any particulates that may be present. Helium was used as the carrier gas at 50 ml/min. The injector temperature was set at 300 °C and the injection size for each sample was 5.0 μL. The initial temperature of the oven was 40 °C, and it

Table 2
BET surface area of the catalyst.

Samples	BET Surface area (m^2/g)	Pore volume (cc/g)	Pore diameter (°A)
Zeolite (Si/Al = 30)	897.96	0.22	53.3
Ni (WI)	656.09	0.19	52.0
Ni (IE)	720.54	0.20	52.5

was kept constant for 2 min before being heated to 300 °C at a ramp rate of 10 °C/min. The final temperature was maintained for 2 min. The National Institute of Standards and Technology (NIST) mass spectral data library was used to identify the major peaks in the chromatogram. The peaks were also integrated using the GC–MS program to determine the relative peak areas.

3. Results and discussion

3.1. Catalyst characterization

Table 2 show the results of BET surface area, pore size distribution and pore volume of Zeolite catalyst and Ni loaded catalysts prepared by both (IE and WI) methods. It is observed that the addition of Ni on the zeolite catalyst results in the reduction of the surface area in the metal loaded catalyst. The decrease in surface area is more in the case of Ni (WI) than Ni (IE), suggesting that nickel is well dispersed on the zeolite surface when prepared by the ion exchange method. During the ion exchange method, the protons on zeolite have been exchanged by Ni cations resulting only the exchange of ions. For Ni (WI), nickel atoms are impregnated on the surface of the zeolite as their hydroxides would form NiO on subsequent calcination in air. These NiO particles block the pores of the support and lead to the reduction of surface area [29]. Fig. 1 shows the nitrogen adsorption-desorption isotherms of Ni (WI) and Ni (IE). Both curves show the Type IV adsorption isotherm indicating that the support retained its mesoporous structure after the introduction of Ni onto zeolite.

Fig. 2(a) shows the TPD profiles of zeolite (Si/Al = 30), Ni (WI) and Ni (IE). It can be observed that there are three main peaks at different temperatures, which indicate desorption of ammonia from the catalyst.
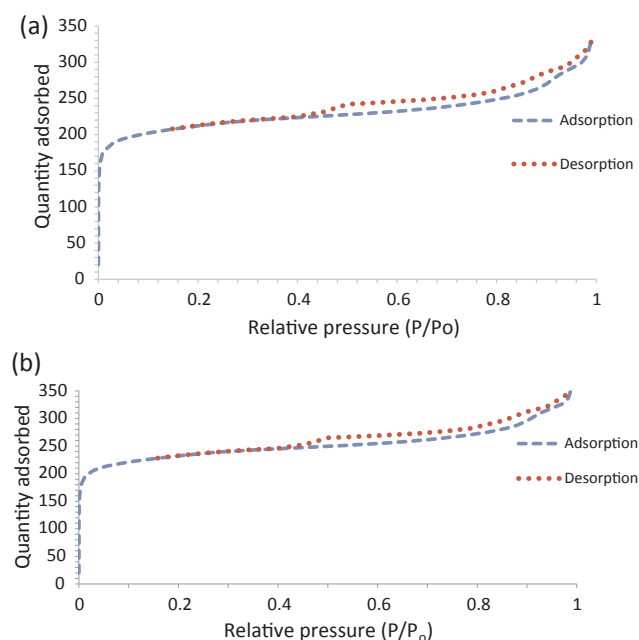

Fig. 1. Nitrogen adsorption isotherm of Ni supported on zeolite prepared by (a) wet impregnation and (b) ion exchange.

a

b

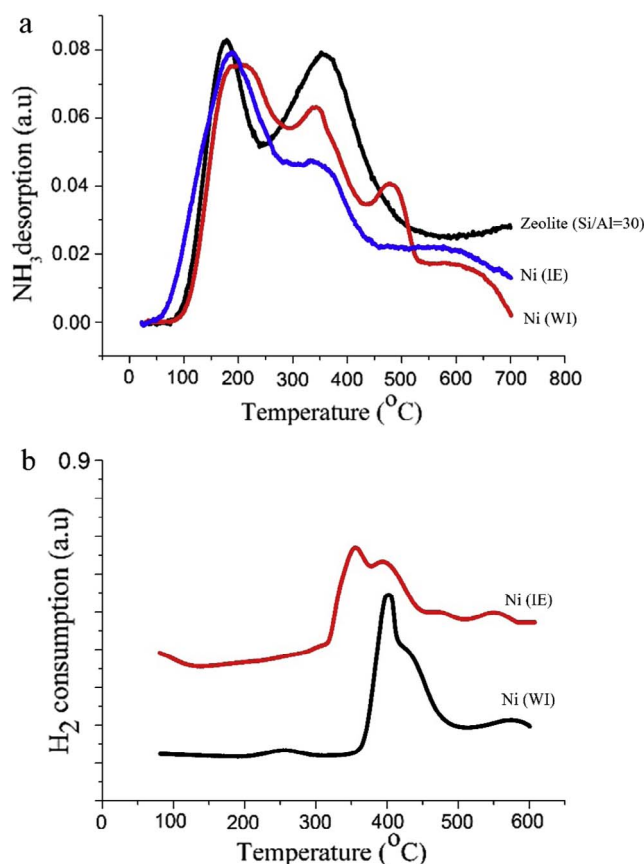**Fig. 2.** (a) TPD and (b) TPR profile of Ni supported on zeolite (Si/Al = 30) prepared from wet impregnation and ion exchange.

The peaks at 140–260 °C, 260–450 °C, and > 450 °C represent weak, moderate and strong acid sites respectively. Zeolite (Si/Al = 30) catalyst shows a higher number of acid sites compared to the metal-loaded catalyst as shown in Fig. 2(a). This indicates that the incorporation of metal to zeolite has reduced the acidity of the zeolite. It can also be observed that Ni (IE) contains less moderate and strong acid sites as compared to Ni (WI). This is due to the exchange of proton (H^+) present in the zeolite by the Ni^{2+} ion, thus resulting in a reduction of the catalyst acidity. In the case of Ni (WI), the nickel is dispersed on the surface of zeolite without replacing the protons, so the acidic protons hydrogen are still intact, imparting higher acidity on Ni(WI) catalysts compared to Ni (IE). Ni (WI) catalysts showed a 3rd peak in the temperature range of 450–500 °C representing strong acid sites. In general strong acid sites are less preferable in catalyst due to its tendency to rapid coke formation which decreases the catalyst activity over time. The effect of Ni addition on the catalytic activity will be discussed in following sections.

Fig. 2(b) shows the TPR profile for Ni (WI) and Ni (IE). The peaks in the TPR profile of Ni (WI) and Ni (IE) represent the reduction of NiO to metallic Ni. The maximum temperature (T_{max}) where reduction of NiO on the wet impregnation catalysts was observed at 400 °C with a shoulder at 450 °C. This peak at 400 °C can be ascribed to the reduction of bulk NiO [30], and the shoulder peak can be attributed to the reduction of NiO present deep inside the pores of the zeolite structure. Ni (IE) catalysts showed multiple peak reduction profile detected at temperature 357 and 401 °C. The low-temperature peak is due to the reduction of well dispersed NiO and the second peak is due to the larger particles size particles. During catalytic pyrolysis experiments, 400 °C is chosen to reduced the NiO particles to metallic Ni before introducing algae into the reactor.
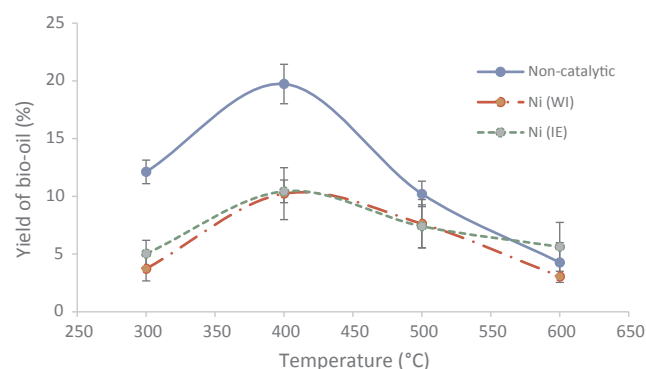

Fig. 3. Yield of bio-oil at different temperatures with catalyst to algae ratio of 2:1 for catalytic pyrolysis.

3.2. Effect of temperature and catalyst to algae catalyst ratio on the yield of bio-oil

Temperature is one of the key parameters that will affect the yield and composition of bio-oil. In this study, the catalytic and non-catalytic pyrolysis experiments were conducted at different temperatures (300, 400, 500 and 600 °C). The ratio of algae to the catalyst in this study was kept at 2:1. Fig. 3 shows the yield of bio-oil obtained from pyrolysis of microalgae *C. vulgaris* at different temperatures. It can be observed that the yield of bio-oil increases with an increasing temperature up to 400 °C. After this temperature, the bio-oil yield dropped significantly which may be attributed to the cracking of the pyrolytic vapors into other gaseous products at a high temperature [31]. Moreover, the yield curves for both non-catalytic and catalytic pyrolysis of microalgae *C. vulgaris* are similar, and the optimum pyrolysis temperature for high yield of bio-oil can be established at 400 °C.

Fig. 3 also shows that non-catalytic pyrolysis produced a high yield of bio-oil compared to catalytic pyrolysis for all temperatures. The yield of bio-oil obtained from non-catalytic pyrolysis is at 19.7% while the yield of bio-oil obtained from catalytic pyrolysis is at 10.2% for Ni (WI) and 10.4% for Ni (IE) at 400 °C. The reason for a lower yield of bio-oil during catalytic pyrolysis is due to the interaction of volatiles from primary pyrolysis with the catalyst surfaces resulting in the further breakdown of the oxygenated functional groups and entrapment of volatiles into the micropores of the catalyst. The volatiles reacts with the acid sites present on the catalyst, and this will promote various secondary reaction such as dehydration, decarbonylation, decarboxylation releasing water and CO_2 increasing hydrocarbon content and lower yields of bio-oil. It can also be observed that the yield of bio-oil produced with different catalyst preparation methods is almost similar except at 600 °C. This indicates the catalyst preparation method in this study did not substantially affect the yield of bio-oil.

Limited studies have reported in the literature the optimum temperature of bio-oil production from microalgae [8,32,33]. The results from these studies showed that the highest yield of bio-oil could be obtained at temperature ranges from 400 to 550 °C. The result obtained from this study are in line with the literature observation [8,32,33]. The minor difference in the optimum temperature is due to the composition of microalgae itself. Diverse types of microalgae contain different inorganic ions due to several types of media used during the cultivation process. The higher metal salt content in microalgae residues could lower the optimal pyrolysis temperature because of its notable catalytic effect. Since the focus of this study is not on the minerals present in the microalgae, the mineral content of microalgae *C. vulgaris* has not been included in this study.

Another parameter that can affect products during catalytic pyrolysis is the ratio of catalyst to algae. Fig. 4 shows the yield of bio-oil at a different catalyst to algae ratios (1:5 (0.25), 1:2 (0.5), 1:1 (1) and 2:1 (2)) using both catalysts; Ni (WI) and Ni (IE). The experiments were
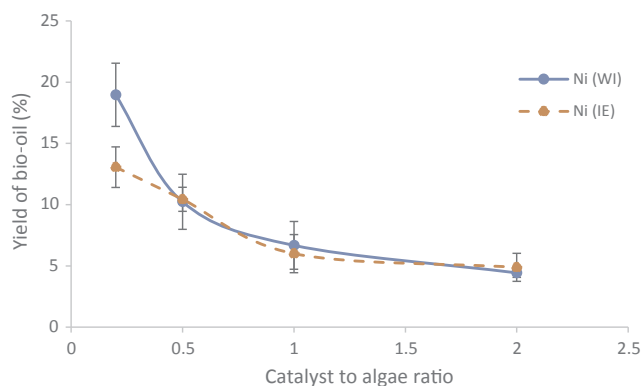
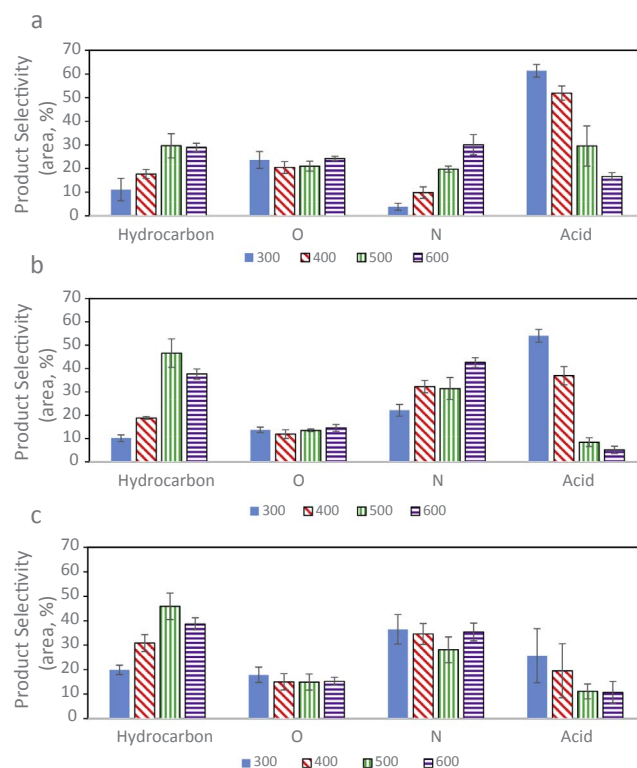Fig. 4. Yield of bio-oil with different catalyst to algae ratios at 400 °C.

Fig. 5. Product selectivity (area, %) of bio-oil compounds produced from (a) non-catalytic pyrolysis (b) catalytic pyrolysis with Ni (WI) and (c) catalytic pyrolysis with Ni (IE) at different temperatures.

conducted based on the optimum temperature (400 °C) obtained from the previous experiment. The yield of bio-oil reduced from 18.97% to 4.43% (Ni (WI)) and 13.06% to 4.88% (Ni (IE)) when the amount of catalyst loaded increased. This is expected because the thickness of the catalyst layer increased, which results in more volatiles trapped inside pores of the catalyst and also lead to secondary reactions with longer residence time producing more gaseous products [8].

The results obtained from this study are similar to Pan et al. [8], where the yield of bio-oil produced from catalytic pyrolysis of *Nannochloropsis* gradually decreased from 25.1 to 20.7 wt% when the catalyst-to-material ratio increased from 0.2/1 to 1/1. Zeng et al. [32] also found that the yield of bio-oil decreased while the amount of gas increased and the amount of char did not vary significantly with an increase in catalyst loading. Although the liquid yields of catalytic pyrolysis are low as compared to direct pyrolysis, the process is commercially attractive as it holds promise for capital cost savings and produces a better quality of bio-oils that are more deoxygenated and chemically stable [34].

3.3. Effect of temperature on the bio-oil composition

The bio-oil obtained from this study was evaluated based on the amount of hydrocarbon, oxygenated and nitrogenous containing compounds as well as acidic compounds. Table 4 shows the list of the compounds that are present in the bio-oil from this study. The hydrocarbons in the oil included both aromatic and aliphatic hydrocarbon. The presence of aromatic hydrocarbons improves the octane value of fuel while aliphatic hydrocarbon is considered high for transportation fuel applications [9,35]. Aliphatic hydrocarbons in this study include alkanes (single bond), alkenes (double bond), cycloalkane and cycloalkene which might be generated from pyrolysis of lipid that is present in microalgae. Aromatic hydrocarbons in this study consist of monocyclic aromatic hydrocarbons (MAHs) and polycyclic aromatic hydrocarbons (PAHs). MAHs in this study include benzene derivatives while PAHs include naphthalene and fluorene. PAHs compounds present in this study can only be detected at a high percentage at high-temperature pyrolysis (600 °C) for both direct and catalytic pyrolysis. PAHs are formed from secondary reactions of derivatives of benzene, which increased with the increase of the temperature [36]. The generation of PAHs at a high temperature (600 °C) in this study is similar to that of other studies [36,37]. PAHs can be found naturally in the environment, and PAHs can also be formed when products like coal, oil, gas and organic materials are incompletely burned. PAHs are a concern as they do not burn easily, and persist in the environment for long periods of time. Therefore, it is recommended to adopt lower temperature pyrolysis to avoid generating the PAHs.

The oxygenated compounds in this study consist of alcohols, aldehydes, ketones, phenols, ethers and esters. The presence of aldehydes and ketones in the bio-oil can result in the instability of the bio-oil

during transport and storage while ethers and esters are undesirable as they can reduce the heating value of bio-oil. Also, the nitrogenous compounds in this study consist of indole, pyrrole, amine, and amide. The existence of these compounds in the bio-oil is due to the degradation of protein in microalgae as it is composed of high protein content (54%). The nitrogenous compounds in the bio-oil can result in potential nitrogen oxide pollution during combustion. Finally, the acids in this study consist of carboxylic acid and fatty acid in the oil. These acid compounds mainly come from the lipid pyrolysis [38]. The existence of acid in the bio-oil can reduce the pH of the bio-oil and make the bio-oil corrosive. From the details above, it can be concluded that a superior quality of bio-oil should have high hydrocarbon compounds, low oxygenated and nitrogenous compounds as well as low acid compounds.

Fig. 5 shows the peak area (%) of bio-oil compounds produced from catalytic and non-catalytic pyrolysis of *Chlorella vulgaris* with temperature. The product quantification in this study is based on the percentages of relative peak areas obtained from the chromatogram. These relative peak areas are then added up according to their associated categories and selectivity of a group of compounds is then realized. It can be observed that the percentage of hydrocarbon increases with the temperature up to 500 °C for both catalytic and non-catalytic pyrolysis beyond which either leveled off or decreased. The decrease in hydrocarbon at higher temperatures is attributed to the secondary cracking and formation of gaseous products. Moreover, catalytic pyrolysis with Ni (IE) and Ni (WI) produced a higher percentage of hydrocarbons compared to non-catalytic pyrolysis. This indicates that the use of the catalyst in this study will increase% hydrocarbon composition in the oil. The hydrocarbon produced from catalytic pyrolysis increases from 29% to 47% when using a catalyst (WI) and 29% to 46% when using a catalyst (IE) at the temperature of 500 °C. Vichaphund et al. [18] also found the percentage of aliphatic and aromatic hydrocarbons increased during catalytic pyrolysis of Jatropha residues with Ni/ZSM-5. The incorporation of metal such as nickel into zeolite shows a bifunctional

Table 3
Comparison of bio-oil composition from pyrolysis and catalytic pyrolysis.

%	400 °C	400 °C (zeolite)	400 °C (IE)	400 °C (WI)	500 °C	500 °C (zeolite)	500 °C (IE)	500 °C (WI)
Aliphatic hydrocarbons	6.98	13.11	26.67	33.62	9.52	16.53	29.46	31.82
Aromatic hydrocarbons	1.55	5.74	10.00	11.21	4.76	7.44	15.18	13.64
Nitrogenous compounds	31.01	29.51	25.83	23.28	33.33	27.27	26.79	29.09
Oxygenous compounds	37.98	33.61	20.83	18.10	31.75	31.40	17.86	16.36
Carboxylic acids	22.48	18.03	16.67	13.79	20.63	17.36	10.71	9.09

Table 4
List of bio-oil compounds that are present in bio-oil.

Groups	Compounds	Formula
Hydrocarbons	Benzene,1-methyl-4-(1propynyl)	$C_{10}H_{10}$
	Cyclopentacycloheptane	$C_{10}H_8$
	Benzene,3-Pentenyl-€	$C_{11}H_{14}$
	1-Phenyl-3-methylpenta-1,2,4-triene	$C_{12}H_{12}$
	6-Tridecene	$C_{13}H_{26}$
	1-Cyclohexylheptene	$C_{13}H_{24}$
	7-Tetradecene	$C_{14}H_{28}$
	Benzocycloheptatriene	$C_{11}H_{10}$
	Naphtalene,1,4-dimethyl	$C_{12}H_{12}$
	Naphtalene1,6,7 trimethyl	$C_{13}H_{14}$
	9H-fluorene, 9-methylene	$C_{14}H_{10}$
	Tridecane, 4-methyl-	$C_{14}H_{30}$
	Octadecane,6-methyl	$C_{19}H_{40}$
	2-methyl-E-7-hexadecane	$C_{17}H_{34}$
	Tetradecane, 2,6,10-trimethyl-	$C_{17}H_{36}$
	Cyclopentane,(2-hexyloctyl)	$C_{19}H_{38}$
	2-Hexadecene, 3,7,11,15-tetramethyl-, [R-[R*,R*-€]]-	$C_{20}H_{40}$
	e,e,1,9,17-Docastriene	$C_{22}H_{40}$
	Benzene,(6-cyclopentyl-3-(3-cyclopentylpropyl) hexyl)	$C_{25}H_{40}$
Oxygenated	Cyclohexanone, 4-hydroxy-	$C_6H_{10}O_2$
	2,3-Anhydro-d-galactosan	$C_6H_8O_4$
	Phenol, 3 methyl	C_7H_8O
	Benzofuran,2,3, dihydro	C_8H_80
	1-Methoxycycloheptatriene	$C_8H_{10}O$
	2-Ethyl-5-propylcyclopentanone	$C_{10}H_{18}O$
	3-(Prop-2-enoyloxy)Dodecane	$C_{15}H_{28}O_2$
	Z,Z-2,5-Pentadecadien-1-ol	$C_{15}H_{28}O$
	Z-10-Tetradecen-1-ol acetate	$C_{16}H_{30}O_2$
	Hexadecen-1-ol,trans9	$C_{16}H_{32}O$
	3-(Prop-2-enoyloxy)tetradecane	$C_{17}H_{32}O_2$
	Z-10-Tetradecen-1-ol acetate	$C_{16}H_{30}O_2$
	Hexadecen-1-ol	$C_{17}H_{34}O$
	2-Methyl-Z,Z-3,13-octadecadienol	$C_{19}H_{36}O$
	5-(Prop-2-enoyloxy)pentadecane	$C_{18}H_{34}O_2$
	5-Nonadecen-1-ol	$C_{19}H_{38}O$
	3,7,11,15-Tetramethyl-2-hexadecen-1-ol	$C_{20}H_{40}O$
Nitrogenous	Hexadecanitrile	$C_{16}H_{31}N$
	2,5-Pyrrolidinedione	$C_4H_5NO_2$
	1-H-Pyrrole,2,5-dihydro-1-nitrose	$C_4H_6N_2O$
	Indole	C_8H_7N
	1-H-Indole,4-methyl	C_9H_9N
	1H-Indole, 5-methyl-	C_9H_9N
	9-Octadecanamide	$C_{18}H_{35}NO$
	8-Methyl-6-nonenamide	$C_{10}H_{19}NO$
Acids	2-Octenoic acid, cis-	$C_8H_{14}O_2$
	n-Hexadecanoic acid	$C_{16}H_{32}O_2$
	Oleic acid	$C_{18}H_{34}O_2$
	1,2-Benzenedicarboxylic acid, bis(2-ethyl)	$C_7H_5N_5O_3$
	Carbamic acid,methyl-3-methylphenyl ester	$C_9H_{11}NO_2$

character which consists of metal and acid sites to promote oligomerization and aromatization. Table 3 shows the comparison of oils formed both in absence and presence of catalyst. In presence of zeolites the ratio of aliphatic to aromatics is 2.3:1. With addition of Ni loading ratio of aliphatic/aromatic increased to 3:1 suggesting the addition of Ni not only enhanced the hydrocarbon content but also enhanced the selectivity of aliphatic component in the oil.

As shown in Fig. 5, there is no specific trend for the oxygenated compounds produced from catalytic and non-catalytic pyrolysis of microalgae *C. vulgaris* in this study with temperature. It can be observed that the oxygenated compounds present in this study are < 30% for both catalytic and non-catalytic pyrolysis of *C. vulgaris*. Moreover, there is a decrease of oxygenated compounds to < 15% and < 18% when using both catalysts, which indicates the occurrence of deoxygenation reaction. The deoxygenation is slightly more in Ni (WI) catalyst than in Ni (IE) catalyst. The presence of more acidic sites in Ni (WI) is attributed to this observation, where Ni atoms are dispersed over the surface without removing the protons from the surface of the catalyst. In Ni (IE) catalyst, the surface protons are exchanges with Ni ions resulting in lower acidity. On the other hand, the% nitrogen composition in the bio-oil linearly increased with temperature in non-catalytic pyrolysis, whereas in catalytic pyrolysis there is no clear trend with temperature but overall the composition of nitrogen compounds increased when compared to non-catalytic pyrolysis. The % increase in nitrogen compounds is more in catalytic pyrolysis compared to non-catalytic pyrolysis. This result is similar to the study of Li et al. [33] in which the relative content of nitrogen compounds increases when the temperature increases. This indicates the Ni loaded zeolite (Si/Al = 30) catalysts are capable of enhancing hydrocarbon concentration and decreasing oxygenated compounds.

Fig. 5(a) shows that acids are the major compound detected in the bio-oil. Non-catalytic pyrolysis produced a high percentage of fatty acids (oleic acid and hexadecanoic acid), and these acids decrease with temperature from 61.4% at 300 °C to 16.7% at 600 °C. A similar trend is observed in Ni-loaded catalysts. Ni (WI), the acid concentration, started at 53.9% and reduced to 5.2% and Ni (IE) the concentration started at 27% and reduced to 11% at temperatures 300 and 600 °C respectively. The results suggest that the presence of catalysts have a positive impact in removing carboxylic functional groups present in the oil samples. Ni (WI) catalysts showed higher impact in reducing the acid functionalities owing to the presence of higher number of acid sites compared to Ni (IE) catalysts. The higher reduction of acid compounds with temperature on Ni (WI) catalysts is due to the presence of strong acid sites active at the operating temperatures of 500–600 °C as observed from Fig. 2(a). Whereas Ni (IE) catalyst are active at low-temperature region at 300–400 °C which showed a reduction in the acid compounds from 61.4% to 27% at 300 °C compared to non-catalytic pyrolysis. However, with an increase in temperature, the impact is less significant. The results suggest the Ni (IE) catalysts are active at lower temperatures 300–400 °C due to the presence of weak and moderate acid sites.

The fatty acids in the bio-oil are < 30% for all temperatures in this study when using Ni (IE), which indicates that Ni (IE) is not only capable of increasing the hydrocarbons but also decreasing the acids in the bio-oil. The presence of Ni supported on zeolite (Si/Al = 30) during catalytic pyrolysis probably converts these fatty acids into hydrocarbons through the decarboxylation reaction, which results in an increase in the concentration of hydrocarbons. On the other hand Ni(WI) showed higher amounts 53 and 42% of fatty acids at 300 and 400 °C which come down to 9 and 6% at 500 and 600 °C. Organic acids which losses their carboxylic functionality by releasing CO_2 also loses oxygen resulted in lower oxygen ratio in the final bio-oil.
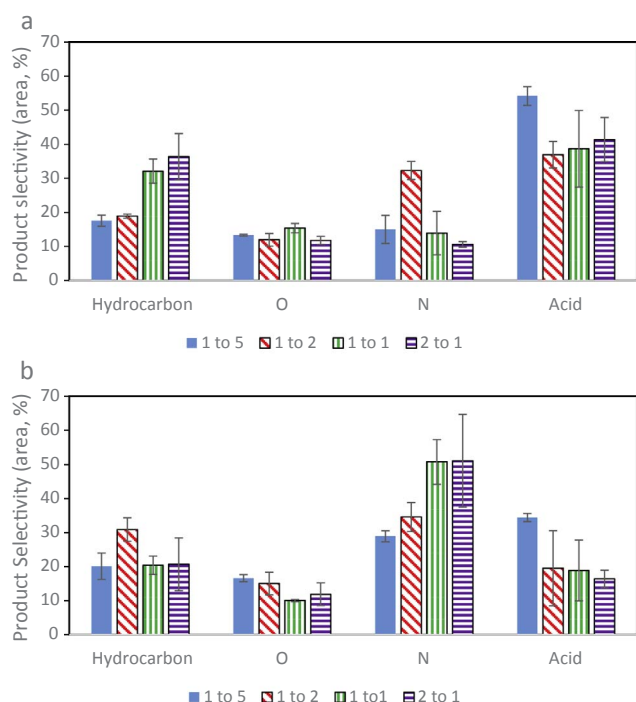
Fig. 6. Product selectivity (area, %) of bio-oil compounds produced from catalytic pyrolysis of *Chlorella vulgaris* with (a) Ni (WI) and (b) Ni (IE) at different catalyst to algae ratios.

Overall, the improved quality of bio-oil in this study was produced at 500 °C for both catalytic and non-catalytic pyrolysis of microalgae *C. vulgaris*. Also, a high percentage of hydrocarbons are produced when using a catalyst with a decrease in oxygenated and organic acid concentration suggesting that the pyrolysis in the presence of Ni loaded zeolite is beneficial in improving the quality of the bio-oil. The percentage of N-containing compounds in this study is higher in the catalytic pyrolysis than in non-catalytic pyrolysis which warrants further investigation.

3.4. Effect of catalyst to algae ratio on the bio-oil composition

This study was conducted at 400 °C based on the highest yield of bio-oil obtained from Section 3.2. Fig. 6 shows the percentage of compounds in the bio-oil using different metal loading techniques and different catalyst to algae ratios (1:5, 1:2, 1:1 and 2:1). The data on Ni (WI) shows that with an increase in catalyst to algae ratio there is an increase in hydrocarbon, a decrease in nitrogenated compounds and only a moderate change in the oxygenate and acid compounds. On the other hand Ni (IE) catalysts showed an increase in hydrocarbon until 2:1 and decrease beyond that and increase in nitrogenated compounds with an increase in catalyst ratio, however, had a positive effect in reducing the oxygenated and acid compounds compared to non-catalytic pyrolysis. The results suggest that of the two catalysts Ni (WI) catalyst in good for improving the hydrocarbon ratio, decrease in nitrogenated compounds in the bio-oil, whereas Ni (IE) catalyst can reduce the oxygenated and acidic compounds in the bio-oil. However, when the temperature is increased to 500 °C in Fig. 5, the acid compound are also decreased for Ni (WI) catalysts along with achieving higher hydrocarbon ratio in the bio-oil.

The catalytic pyrolysis study indicates that Ni loaded zeolite catalysts can enhance the quality of the bio-oil. The catalyst preparation also has an effect on the final quality of the bio-oil produced. In this work Ni, catalysts prepared by wet impregnation showed better quality of oil compared to Ion exchange method. The study also showed that increasing the amount of catalyst during the reaction provide better

contact time for the oil vapors to interact with the catalysts thereby enhancing the hydrocarbon ratio, decreasing the oxygenated and nitrogenated compounds in the bio-oil at 500 °C. Further investigation on the effect of metal loading on the bio-oil quality needs to be done to fine tune the catalysts for the conversion of algae to transportation fuels. The present work did not study the effect of small amounts of H_2 supply in presence of Ni loaded catalyst towards the quality of bio-oil and warrants further investigation.

4. Conclusions

Catalytic pyrolysis of microalgae biomass is a promising thermochemical conversion route for enhancing the quality of bio-oil. The optimal pyrolysis temperature for both catalytic and non-catalytic pyrolysis of *C. vulgaris* appeared to be at 500 °C with high hydrocarbon production and low oxygenated and acid compounds in the oil. Ni (IE and WI) catalysts can produce high hydrocarbons, less oxygenated and less acid compounds compared to direct pyrolysis at 500 °C. This study also shows that the selection of catalyst preparation methods is important as this would dictate the final composition of the bio-oil.

Acknowledgements

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