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

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ABSTRACT

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, biomethane, 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, 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.

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.

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