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Biofuel production from *Nannochloropsis oculata* microalgae in seawater without harvesting and dewatering over alumina-silicate supported nickel catalysts

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ABSTRACT

The aim of this work was to study the production of biofuels from marine *Nannochloropsis oculata* without harvesting and dewatering over the single step sol-gel made alumina-silicate supported nickel catalysts at 80 °C and 1.0 atm. Sulfuric acid, hydrochloric acid, and nitric acid were used in the sol-gel to study the effect of acid type on catalyst activities. The catalyst made using sulfuric acid resulted in 74% microalgae conversion as compared to the catalysts made with other acids. Treatment of this catalyst with ~35 g of NaCl per kg of water at 80 °C and 1.0 atm for 24 h increased microalgae conversion to 91.5% under the same reaction condition and the bio-fuels ranging from mono/polysaccharides, polyols to esters and fatty acids were produced. This study showed that nickel and 25.1 μmol/g of total acidity and acidic strength having 130–380 °C of temperature range was necessary to achieve 91.5% conversion.

1. Introduction

Fossil fuels have been the primary energy sources for more than a century. They have mainly been used for generating electricity and producing transportation fuels. Unfortunately, the adverse impacts of using fossil fuels and their derivatives have resulted in air, water and soil pollutions. Among the pollutions, air pollution and global warming have been found to increase in many countries but especially alarming levels in the developing countries. In addition, geopolitical uncertainties in fossil fuel rich regions have resulted in difficulties in forecasting the future of the world economy. In order to alleviate the effects of geopolitical uncertainties on the economies of the countries around the world and also on the environment and human health, renewable and alternative fuels seem to be plausible candidates. In fact, the European Union declared in the Renewable Energy Directive (2009/29/EC) that biofuels had to be at least 10% in the transport fuel by 2020 (European Union, 2009).

In the production of biofuels, the key challenge has been to find economically viable biomass sources. Among many biomasses, sea water microalgae were shown to be economical and sustainable biomass source since they do not require any agriculture or fresh water in addition to be able to fix carbon dioxide by photosynthesis (Y. Chen et al., 2015; H. Chen et al., 2015). Unfortunately, the most important issue with microalgae has been the cost of harvesting since the weight percentage of the microalgae biomass in water is 3.0–10 wt%; thus, being necessary to increase its concentration to 20 wt% in the production of biofuels. For instance, Batan et al. (2016) reported that the microalgae cultivation, algal oil harvesting, and extraction constituted 96% of the operating cost whereas for the production of biofuels using dry microalgae, dewatering and lipid extraction steps represented ~33% and ~32% of total direct installed capital cost, respectively. In spite of costly harvesting and oil extraction, the use of microalgae in the production of biofuels was reported to be promising because the microalgae had high growth rates (Rittmann, 2008) and they could be harvested more than once a year (Schenk et al., 2008); thus, resulting in a very large amount of microalgae production per hectare per year. Most importantly, seawater or waste water could be used to grow microalgae; hence, eliminating the need of fresh water (Schenk et al., 2008). Besides, the lipid, protein and carbohydrate content could be modified using varying growth conditions (Meher et al., 2006) and atmospheric carbon dioxide or fossil fuel power plants' flue gas could be used as the carbon source in microalgae growth process (Schenk et al., 2008).

There are many studies on the methods of harvesting and also the processes to convert 20 wt% wet or dry microalgae into biodiesel or biofuels. For instance, pyrolysis and hydrothermal liquefaction are the main thermochemical processes used to produce bio-oils and bio-gas from microalgae biomass. Pyrolysis processes were reported to work

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with dry algae at temperatures between 400 and 600 °C under atmospheric pressure while in hydrothermal liquefaction processes, sub or supercritical water condition was required to convert ~20 wt% wet microalgae to crude-oil (Y. Chen et al., 2015; H. Chen et al., 2015). Thus, high temperatures and pressures make these thermochemical processes unviable for large scale continuous production of biofuels. Alternatively, enzymatic and chemical pretreatments were alternative methods to release the carbohydrates from algal cells; for instance, sulfuric acid was used to disrupt the algal cell walls and to hydrolyze carbohydrates to monosaccharide (Harun and Danquah, 2011; Ho et al., 2013). In contrast, the conversion of 3.0–10 wt% microalgae in seawater into biofuels using heterogeneous catalysts under atmospheric pressure and temperatures < 100 °C without harvesting and dewatering would be viable alternative to thermochemical and homogeneous/enzymatic catalytic processes. The cell walls of *Nannochloropsis oculata* (*N. oculata*) was reported to contain carbohydrates and cellulose and a wide range of saturated, monounsaturated and polyunsaturated fatty acids and the highest amount of polysaccharides as total carbohydrate (Arnold et al., 2015; Volkman et al., 1993). Thus, *N. oculata* was used in this study and also to the best of our knowledge, there were no studies on the conversion of 3.0–10% *N. oculata* biomass in seawater without harvesting and dewatering into hydrocarbons and saccharide over heterogeneous catalysts in the literature.

In this study, biofuel production from *Nannochloropsis oculata* in seawater without harvesting and dewatering was studied using the single step sol-gel made alumina-silicate supported nickel catalysts at 80 °C and 1.0 atm.

2. Material and methods

2.1. Catalyst preparation

Alumina-silicate supported nickel catalysts were synthesized using a modified single step sol-gel method developed in this study (Umdu, 2008; Yoldas, 1975). The support oxide of all the catalysts contained 70%Al_2O_3 and 30%SiO_2 and nickel amount was 10%. The following procedure was used. Briefly, tetraethyl-orthosilicate (≥98 purity, Fluka), ethanol (≥99.8% purity, Sigma-Aldrich), and distilled water were mixed with 1.0 M hydrochloric acid (HCl, 36.5–38 wt%, Sigma-Aldrich) at 80 °C for 2.0 h to prepare silica sol while alumina sol was separately prepared by mixing aluminum isopropoxide (≥98% purity, Aldrich), water and an acid, for instance, (H_2SO_4 (≥98 purity, Aldrich) or HCl or HNO_3 (68 wt%, VWR Chemicals)) at 85 °C. After that, two sols were mixed at 85 °C and nickel (II) acetate hydrate (> 99% purity, Alfa Aesar) was added to the mixed sol. Then, the excess solvent was slowly evaporated to obtain the gel. Finally, all the gels, prepared using varying acid types, were dried at 120 °C for 12 h and calcined at 900 °C for 6.0 h. All the calcined catalysts were ground and sieved to 100–200 mesh size prior to being used in the activity and characterizations measurements.

The catalysts were denoted as 10%Ni-70%SiO_2-30%Al_2O_3-Acid; for instance, 10%Ni-70%SiO_2-30%Al_2O_3-H_2SO_4 meant 10%Ni on 70% SiO_2-30%Al_2O_3 prepared using sulfuric acid in the sol-gel method.

2.2. Catalyst activity determination

6.0 wt% *N. oculata* microalgae in seawater, grown in a growth medium and the harvesting time as given in the literature (Durmaz, 2007), was obtained from Dr. Durmaz of Ege University. The direct conversion of 6.0 wt% microalgae to biofuel was carried out in a batch reactor at 80 °C and 1.0 atm for 24 h. 0.25 g of a catalyst was added to 25 ml of 6.0 wt% *N. oculata* in seawater and mixed at a constant stirring speed of 330 rpm to avoid mass transfer limitations. In addition, to better understand the effect of NaCl present in seawater on the activity and product distribution, fresh 10%Ni-70%SiO_2-30%Al_2O_3-H_2SO_4 catalyst was treated with 35 g of NaCl per kg of water at 80 °C and 1.0 atm for 24 h. This treated catalyst was denoted as 10%Ni-70%SiO_2-30%Al_2O_3-H_2SO_4-SW.

The microalgae conversion was calculated using the following equation:

$$\text{Microalgae Conversion (\%)} = \frac{\text{The initial amount of microalgae in seawater} - \text{the final amount of microalgae left on the catalyst}}{\text{The initial amount of microalgae in seawater}} \times 100$$

The initial amount of microalgae (g) in seawater was determined by evaporating water and then microalgae paste was washed with distilled water several times to remove salts and other ions. Finally, washed paste was dried and weighed to find the initial microalgae amount. The final amount of microalgae left on the catalyst was found by first washing the recovered catalyst several times with distilled water to remove salts. Then, it was dried at 50 °C under vacuum for 48 h and weighed at room temperature. After that, the dried recovered catalyst containing microalgae biomass was further dried at 500 °C to burn off the microalgae biomass to determine the amount of the recovered catalyst. Finally, the final amount of microalgae left on the catalyst catalysts at the end of the reaction was calculated by subtracting the amount of catalyst used in the reaction from the amount of recovered catalyst containing microalgae biomass dried at 500 °C. The uncertainty interval in the calculation of the microalgae biomass conversion within 95% confidence was ± 4.5%.

2.3. Product analysis

At the end of 24 h of reaction time, the reaction medium was centrifuged at 4000 rpm for 5.0 min to remove the solid catalyst. Then, the extraction of nonpolar products from the reaction medium was carried out using 2.5 ml of hexane at room temperature for 24 h by stirring at 660 rpm. After that, water-hexane phase separation was achieved in a funnel. The products in hexane phase was analyzed using a gas chromatography–mass spectrometry (GC/MS, Agilent 6890 N/5973 N Network GC/MSD) equipped with DB-5 column. The rest of the products left in water phase was analyzed using a high-performance liquid chromatogram (HPLC, Agilent 1100) equipped with RI detector, and HyperREZ XP Carbohydrate H^+ column (8.0 µm, 300 mm × 7.7 mm). The mobile phase with a 0.4 ml/min flow rate, was pure water and operating temperature was 65 °C. Prior to HPLC analysis, all the water phase samples were filtered.

2.4. Catalyst characterization

Crystalline phases in the catalysts were determined using Philips X'Pert Pro Diffractometer with Ni-filtered CuKα radiation (λ = 0.15406 nm) (operated at 40 kV and 45 mA) in the range of 20–80° 2θ angle. The average crystallite sizes were calculated using the peak broadening of a diffraction peak and Scherrer equation given below.

$$d = \frac{K\,\lambda}{(B\,Cos\theta)}$$

where d was the average crystallite size, K was Scherrer constant (~0.9), λ was the wavelength of the X-ray (λ = 0.15406 nm), B was the peak broadening of a diffraction peak found using the full width at half maximum (given in radian) of the peak and θ was the main diffraction angle of the peak given in degree (Cullity, 1978).

Total specific surface area (BET surface area), the average BET pore size and pore volume were determined using N_2 adsorption isotherm at 77 K using Micromeritics Gemini V. Before the analyses, all the samples were degassed under vacuum (10^{-6} Torr) at 300 °C for 24 h.

The acidity and acidic strength of all the catalysts were measured using ammonia temperature programmed desorption (NH_3-TPD)

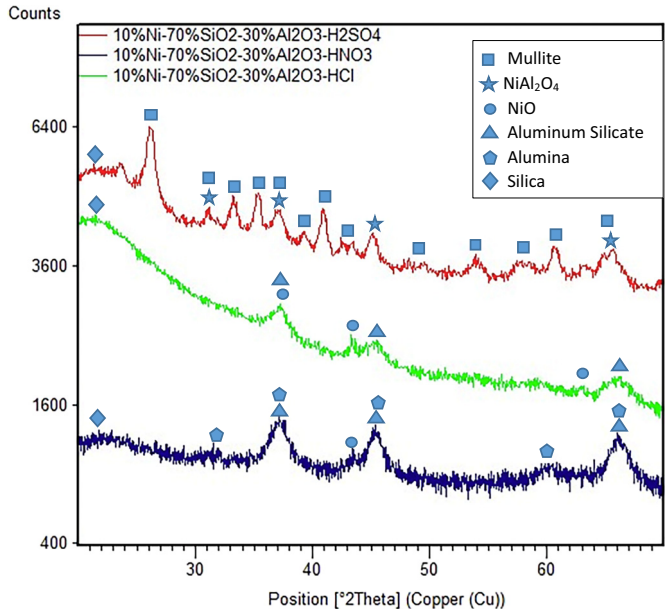

Fig. 1. XRD spectra of all the catalysts.

technique and Micromeritics AutoChem II 2920. The amount of irreversibly adsorbed NH_3 gave the total amount of acidic sites on the catalyst surfaces whereas desorption temperature of NH_3 indicated the strength of the acidic site (Tanabe et al., 1989). In NH_3-TPD, the catalysts were first cleaned at 900 °C for 2.0 h and cooled to room temperature under helium flow. Then, NH_3 adsorption was carried out for 1.0 h at room temperature, which was followed by helium purge at room temperature to remove gas phase and weakly adsorbed NH_3. Desorption was carried out under helium flow while increasing the temperature from room temperature to 900 °C at a heating rate of 10 °C/min.

3. Results and discussion

3.1. Crystalline phases and acidities of the catalysts

The crystalline phases in all the catalysts were identified using 2θ angle of at least 4 diffraction peaks and Powder Diffraction File of International Centre for Diffraction Data (JCPDS-ICDD, 2000). As seen in Fig. 1, the catalyst, prepared with H_2SO_4 acid, contained mullite ($3Al_2O_3$-$2SiO_2$) and nickel aluminate ($NiAl_2O_4$) crystalline phases whereas the catalyst, prepared with HCl acid, contained only aluminum-silicate ($Al_{1.7}Si_{0.15}O_{2.85}$) and nickel oxide (NiO) crystalline phases. In contrast, NiO, aluminum-silicate ($Al_{1.7}Si_{0.15}O_{2.85}$) and alumina crystalline phases were present on the catalyst prepared with HNO_3 acid. In this catalyst, the major diffraction peaks of aluminum-silicate overlapped with that of alumina; thus, making impossible to calculate the crystallite size of aluminum-silicate or alumina. Furthermore, 70%SiO_2-30%Al_2O_3 catalyst prepared with H_2SO_4 without containing nickel did not show any X-ray diffraction peaks, such as the peaks corresponding to alumina or mullite or alumina-silicate crystalline phases, but there was a large broad peak located at ~22° of 2θ corresponding to silica phase (data not shown).

The average crystallite sizes for all the catalysts using the peak broadening of the highest non-interfered peak of the crystalline phase and Scherrer equation were calculated. As seen in Table 1, on the catalysts, made with HCl and HNO_3 acids, the crystallite size of aluminum-silicate phase was 4.0 and 6.0 nm, respectively and on 10% Ni-70% SiO_2-30% Al_2O_3-HCl, NiO crystallite size was ~50 nm while on 10% Ni-70% SiO_2-30% Al_2O_3-HNO_3, it was < 3.0 nm since the largest diffraction peak of NiO, located at 43.3° of 2θ angle, was too small to find the

Table 1
Crystalline phases and crystallite sizes for all the catalysts.

	Crystalline phases and crystallite sizes (nm)				
Catalyst	$NiAl_2O_4$	Mullite	NiO	Al_2O_3	Aluminum silicate
10% Ni-70% SiO_2-30% Al_2O_3-H_2SO_4	11.2	15.9	–	–	–
10% Ni-70% SiO_2-30% Al_2O_3-H_2SO_4-SW	10.9	15.7	–	–	–
10% Ni-70% SiO_2-30% Al_2O_3-HCl	–	–	49.9	–	4
10% Ni-70% SiO_2-30% Al_2O_3-HNO_3	–	–	< 3	6	–

Table 2
Acidity/acidic strength and BET surface areas for all the catalysts.

Catalysts	BET surface area (m^2/g)	Acidity (μmole NH_3/g of catalyst)	Maximum desorption peak temperatures (°C)
10%Ni-70%SiO_2-30%Al_2O_3-H_2SO_4	130	16.96	134 181 376 622 733
10%Ni-70%SiO_2-30%Al_2O_3-HCl	309	85.98	151
10%Ni-70%SiO_2-30%Al_2O_3-HNO_3	325	62.63	147
10%Ni-70%SiO_2-30%Al_2O_3-H_2SO_4-SW	97	25.14	130 183 300 387

crystallite size (Cullity, 1978). On NaCl treated catalyst made with H_2SO_4 acid, $NiAl_2O_4$ crystallite size was found to be ~11 nm and mullite crystallite size was ~16 nm. This indicated that the treatment of 10% Ni-70% SiO_2-30% Al_2O_3-H_2SO_4 with NaCl did not result in a new crystalline phase formation or a change in the crystallite sizes within the detection limits of the wide-angle XRD used in this study.

As seen in Table 2, 86 μmol/g of the highest total acidity was observed on the catalyst prepared with HCl acid whereas 17 μmol/g of the lowest total acidity was found on the catalyst prepared with H_2SO_4 acid. It was difficult to make a sound comparison between acidity results obtained in this study and similar heterogeneous catalysts reported in the literature since the sol-gel preparation method and the calcination temperature were different. For instance, Agliullin et al. (2014) reported that 75 wt% SiO_2-15 wt%Al_2O_3 catalyst without nickel, made with a sol-gel method and calcined at 650 °C for 5.0 h, had a 405 μmol/g of total acidity. This indicated that 900 °C of the calcination temperature used in this study resulted in a much less acidity than 650 °C of the calcination temperature used to prepare catalysts reported by Agliullin et al. (2014).

The acidic strengths, i.e. the maximum NH_3 desorption peak temperature, of all the catalysts, were given in Table 2. On 10% Ni-70% SiO_2-30% Al_2O_3-HCl and 10% Ni-70% SiO_2-30% Al_2O_3-HNO_3 catalysts, there was only one maximum desorption peak temperature, located at ~147–150 °C. Agliullin et al. (2014) reported an arbitrarily assigned acidic strength scale for NH_3 desorption temperatures; for instance, weak acidic strengths and strong acidic strengths were assigned to the temperatures ranging from 100° to 350 °C and the temperatures ranging from 350° to 550 °C, respectively. Based on their acidic strength scale, a strong acidic strength in this study was assigned to the acid sites having the desorption temperatures > 550 °C which was observed on 10% Ni-70% SiO_2-30% Al_2O_3-H_2SO_4 whereas 10% Ni-70% SiO_2-30% Al_2O_3 made with HCl and HNO_3 acids had weak acidic strengths since NH_3

desorption temperatures was < 350 °C. Interestingly, the high desorption peak temperatures, such as 620° and 730 °C observed on 10% Ni-70% SiO_2-30% Al_2O_3-H_2SO_4 disappeared after this catalyst was treated with NaCl, -i.e. 10% Ni-70% SiO_2-30% Al_2O_3-H_2SO_4-SW- which had only desorption temperatures ranging from 130 to 385 °C as seen in Table 2.

The BET surface areas of 10% Ni-70% SiO_2-30% Al_2O_3-HCl and 10% Ni-70% SiO_2-30% Al_2O_3-HNO_3 catalysts were a factor of ~2.5 higher than the surface areas of 10% Ni-70% SiO_2-30% Al_2O_3-H_2SO_4 and 10% Ni-70% SiO_2-30% Al_2O_3-H_2SO_4-SW. It was found that treatment of 10% Ni-70% SiO_2-30% Al_2O_3-H_2SO_4 with NaCl resulted in ~25% of the decrease in the BET surface area, as given in Table 2.

3.2. The effect of acids used in the preparation of 10% Ni-70% SiO_2-30% Al_2O_3 on the conversion of microalgae

The most important challenge in converting microalgae to biofuels without harvesting and dewatering was the low amount of microalgae biomass, e.g. 6.0 wt% of microalgae biomass, in seawater and also the presence of a very large amount of NaCl, 35 g of NaCl per kg of seawater.

As seen in Fig. 2, 36.5% of the microalgae conversion was observed on 10% Ni-70% SiO_2-30% Al_2O_3-HCl while 54.4% conversion was observed on 10% Ni-70% SiO_2-30% Al_2O_3-HNO_3. In contrast, the microalgae conversion increased to 74% on 10%Ni-70%SiO_2-30%Al_2O_3-H_2SO_4. Most importantly, 10%Ni-70%SiO_2-30%Al_2O_3-H_2SO_4-SW gave 91.5% of the highest microalgae conversion. Besides, there was no microalgae conversion in the absence of a catalyst in the reactor and also, no conversion on 30%SiO_2-70%Al_2O_3 catalyst prepared with H_2SO_4 (i.e. without containing nickel) under the same reaction condition within the experimental uncertainty of ± 4.5%. In this study, it was the first time that a heterogeneous catalyst was shown to convert microalgae in seawater to biofuels without harvesting and dewatering at 80 °C and 1.0 atm. In fact, there are no studies on the conversion of microalgae to biofuels without harvesting and dewatering using heterogeneous catalysts under atmospheric pressure and low temperatures, such as 80 °C, in the literature. In contrast, there are many studies on the conversion of microalgae to sugars and organic acids using homogeneous catalysts, such as dilute sulfuric acid, hydrochloric acid, and enzymes. For instance, Park et al. (2016) reported the conversion of *C. vulgaris* to the reducing sugars, such as glucose and galactose, using hydrochloric acid, sulfuric acid, nitric acid, peracetic acid, and phosphoric acid with acid concentrations ranging from 1.0 to 4.0% (w/w) at 121 °C of the reaction temperature. Park et al. (2016) showed that 8.0–11% (w/w) of the highest microalgae conversions to glucose and galactose were achieved by using hydrochloric acid in the same acid concentration range. Similarly, Choi et al. (2015) investigated the hydrolysis of *Golenkinia* sp. using sulfuric acid and the cellulose enzyme Cellic CTec2 and found that the sugar extraction yield to glucose in the enzymatic hydrolysis of *Golenkinia* sp. at 50 °C and pH 4.8 was 19.2% after 72 h whereas 2.0% sulfuric acid showed a 72.6% yield to glucose in 120 min at 120 °C. In addition, Choi et al. (2015) reported that the hydrothermal acid hydrolysis at 150 °C for 15 min followed by enzymatic hydrolysis for 48 h resulted in a 75.4% of the total sugar extraction yield. Beside of using homogeneous acidic and enzymatic hydrolyses in the literature, a high temperature and pressure hydrothermal liquefaction of microalgae to bio-oils (usually occurring above 300 °C in an autoclave reactor) were reported using heterogeneous catalysts, such as HZSM-5 or KOH, in the literature. In all the hydrothermal liquefaction studies in the literature, microalgae paste or dried microalgae were used to produce bio-oils. This meant that harvesting and dewatering had to first be done to obtain the paste or dried microalgae. For example, Xu et al. (2014) reported that at 300 °C in an autoclave reactor, 49.9% of bio-oil yield was obtained using *Chlorella pyrenoidosa* over Ce/HZSM-5 in comparison to 34% of bio-oil yield found over HZSM-5 and also in the absence of a catalyst. Similarly, Duan and Savage (2011) showed that over Pd/C catalyst, 57% of *Nannochloropsis* sp. microalga paste was converted into the crude bio-oil at 350 °C in an autoclave in 60 min whereas ~35% of the crude bio-oil yield was observed in the absence of the catalyst in the autoclave under the same reaction condition. In addition, Y. Chen et al. (2015) and H. Chen et al. (2015) studied the hydrothermal liquefaction of *D. tertiolecta* over ZrO_2/SO_4^{2-} and HZSM-5 solid acid catalysts and also the solid base catalysts, such as MgO/MCM-41 and Potassium tert-butoxide (KtB), at 360 °C. They observed 94.8% of the microalgae conversion and 49.1% of the bio-oil yield on KtB while lower

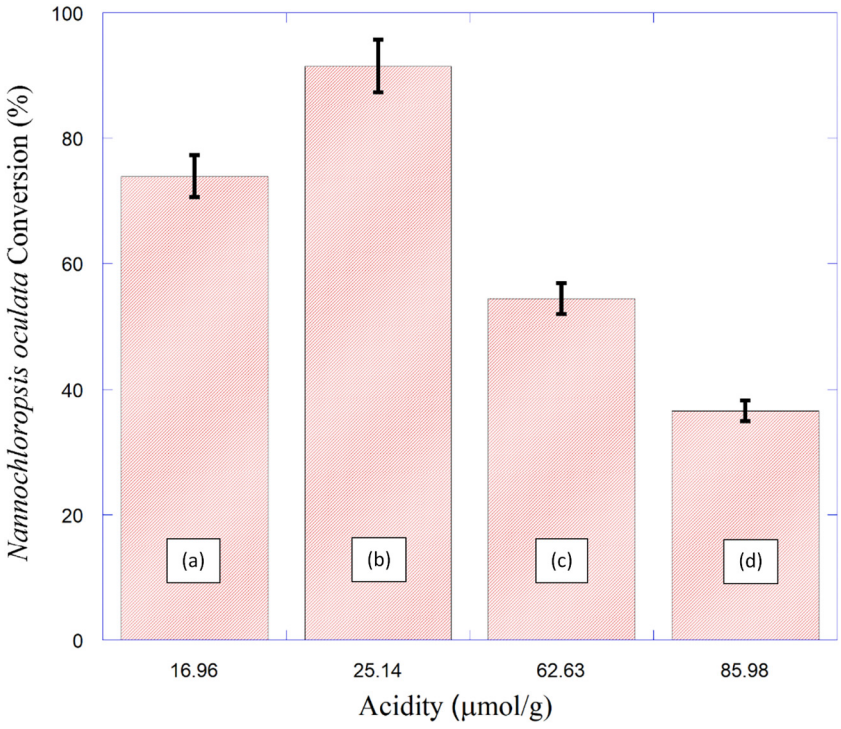

Fig. 2. *Nannochloropsis oculata* conversion (%) vs. acidity (μmol/g) (a) 10% Ni-70% SiO_2-30% Al_2O_3-H_2SO_4, (b) 10% Ni-70% SiO_2-30% Al_2O_3-H_2SO_4-SW, (c) 10% Ni-70% SiO_2-30% Al_2O_3-HNO_3, (d) 10% Ni-70% SiO_2-30% Al_2O_3-HCl. Reaction conditions: 80 °C for 24 h under atmospheric pressure, 0.25 g of a catalyst in 25 ml of 6.0 wt% *N. oculata* in seawater.

conversions and bio-oil yields were found on all the acid catalysts. They concluded a microalgae conversion and a bio-oil yield trend of KtB > MgO/MCM-41 > no catalyst > ZrO_2/SO_4^{2-} > HZSM-5.

Most importantly, in all the studies in the literature, microalgae were first harvested, dewatered and dried. After that, the paste or dried microalgae were mixed with deionized water before being used in the hydrothermal liquefaction reaction carried out using homogeneous or heterogeneous catalysts. In fact, dewatering and drying was reported to be the major operational cost drawback in the production of bio-oils or bio-fuels using microalgae (Batan et al., 2016). Also, the hydrothermal liquefaction required high temperatures, such as 300–360 °C, and high autoclave pressures. However, in this study, *N. oculata* was not harvested and not dewatered prior to the reaction study. Alumina-silicate supported nickel catalysts prepared in this study showed better or comparable conversions under high salinity, low temperature and pressure than the studies reported in the literature. In the studies on enzymatic and homogeneous acid hydrolysis, a major drawback is that enzymes and homogeneous acids cannot be recovered at the end of the hydrolysis reaction. However, heterogeneous catalysts could be easily recovered the reaction and be used multiple times. Indeed, in this study, alumina-silicate supported nickel catalysts were recovered and reused at least twice under the same reaction conditions without losing catalyst activities. In contrast, the reusability tests of the solid catalysts used in the hydrothermal liquefaction studies in the literature were not investigated. This was one of the major issues in hydrothermal liquefaction studies since the leaching of active components of the catalysts occurring under the hydrothermal conditions could result in the loss of activity.

As seen in Table 3, alumina-silicate supported nickel catalyst used in this study converted the microalgae to a variety of esters, triglycerides, monosaccharide, polyols and alkanes. The analysis of the aqueous phase showed that glucose, arabinose and glycerol were the main products on all the catalysts but glucose and glycerol (i.e. no production of arabinose) were observed on 10%Ni-70%SiO_2-30%Al_2O_3-H_2SO_4-SW. The absence of arabinose meant that arabinose could be dehydrated to furfural as reported by Hongsiri et al. (2015). In fact, there were some unidentifiable compounds in the aqueous phase in this study. Thus, those unidentified compounds may be phospholipids or carbohydrates, such as furfural. In addition, it was plausible to observe glycerol because the hydrolysis of triglycerides yielded glycerol, carbohydrates, such as glucose, esters and fatty acids (Ozdogru, 2017). The analysis of the hexane phase showed the presence of fatty acids and their esters, such as hexadecanoic acid (Palmitic acid) and 9-octadecanoic acid, methyl ester; thus, confirming the hydrolysis of triglycerides. Besides, the product distribution found using alumina-silicate supported nickel catalysts prepared in this study was in parallel with the product distribution, such as esters and fatty acids, found using homogeneous catalysts, such as sulfuric acid and hydrochloric acid, and also the solid catalysts used in the hydrothermal liquefaction studies reported in the literature (Choi et al., 2014; Park et al., 2014; Duan and Savage, 2011). Moreover, this was the first time that in this study, 6.0 wt% microalgae in seawater was converted to saccharides, esters, hydrocarbons and fatty acids without harvesting and dewatering at atmospheric pressure and 80 °C; thus, eliminating the costly harvesting/dewatering steps necessary in traditional processes or high pressure/temperature liquefaction processes to produce biofuels from microalgae (Xu et al., 2014; Duan and Savage, 2011; Y. Chen et al., 2015; H. Chen et al. (2015)).

3.3. The relation between physical-chemical properties and the microalgae conversion

Hydrolyses of saccharides, peptides and triglycerides were reported to occur faster using an acid catalyst than using a base catalyst (Umdu, 2012; Ozdogru, 2017). To better understand the correlation between acidity/acidic strengths of the catalysts and the conversion, the observed conversion was plotted as a function of the catalyst acidity (Thomas and Thomas, 1997). *N. oculata* conversion as a function of the catalyst acidity as seen in Fig. 2 indicated that the conversions above 70% occurred on the catalysts having 15–25 μmol/g of the total acidity whereas the lower conversions were found when the total acidity was higher than 60 μmol/g. For instance, the maximum *N. oculata* conversion occurred on 10% Ni-70% SiO_2-30% Al_2O_3-H_2SO_4-SW having 25.1 μmol/g of total acidity and the lowest *N. oculata* conversion was obtained on 10% Ni-70% SiO_2-30% Al_2O_3-HCl having the highest total acidity of 86 μmol/g. The results of this study indicated that a low total acidity was required for a high microalgae conversion but the effect of acidic strength, i.e. the maximum desorption peak temperature of NH_3, on the microalgae conversion had to be considered, too. Indeed, as seen

Table 3
Product distribution.

Catalysts	Products in aqueous phase	Products in hexane phase	Peak area (%)
10%Ni-70%SiO_2-30%Al_2O_3-H_2SO_4	Glucose (69 mg/L)	$C_9H_{10}O$, Benzaldehyde 2,5-dimethyl-	33.3
	Arabinose (71 mg/L)	$C_{14}H_{30}$ (Tetradecane)	4.6
	Glycerol (97 mg/L)	$C_{12}H_{26}O$ (1-Dodecanol)	9.1
		$C_{10}H_{12}Cl_2O$ (2,6-dichloro-4-(1,1-dimethylethyl)phenol)	12.5
		$C_{16}H_{34}$ (hexadecane)	7.2
		$C_{19}H_{38}O_2$ (Isopropylpamitate)	14.3
		$C_{21}H_{42}O_2$ (Isopropylstearate)	19.0
10%Ni-70%SiO_2-30%Al_2O_3-HCl	Glucose (88 mg/L)	C_9H_{12} (Benzene,1,3,5-trimethyl)	81.4
	Arabinose (58 mg/L)	$C_{19}H_{36}O_2$ (9-Octadecanoic Acid, Methyl Ester)	18.6
	Glycerol(95 mg/L)		
10%Ni-70%SiO_2-30%Al_2O_3-HNO_3	Glucose (145 mg/L)	C_9H_{12} (Benzene,1,3,5-trimethyl)	30.1
	Arabinose (36 mg/L)	$C_{14}H_{30}$ (Tetradecane)	5.5
	Glycerol (81 mg/L)	$C_{16}H_{34}$ (Hexadecane)	13.3
		$C_{20}H_{42}$ (Eicosane)	10.2
		$C_{18}H_{38}$ (Octadecane)	12.7
		$C_{18}H_{36}O_2$ (Hexadecanoic acid, ethyl ester)	16.5
		$C_{20}H_{40}O_2$ (Octadecanoic acid, ethyl ester)	11.8
10%Ni-70%SiO_2-30%Al_2O_3-H_2SO_4-SW	Glucose (86 mg/L)	C_9H_{12} (Benzene,1,3,5-trimethyl)	10.4
	Glycerol (103 mg/L)	$C_{10}H_{22}$ (Hexane,2,2,3,3-tetramethyl)	3.4
		$C_{20}H_{42}$ (Eicosane)	4.1
		$C_{16}H_{32}O_2$ (Hexadecanoic acid)	12.4
		$C_{18}H_{36}O_2$ (Hexadecanoic acid, ethyl ester)	11.4
		$C_{15}H_{28}O_2$ (Dodecylacyrlate)	11.7
		$C_{20}H_{39}ClO_2$ (3-Chloropropionic acid, heptadecyl ester)	22.6
		$C_{30}H_{50}$ (Squalene)	24.0

in Table 3, 10% Ni-70% SiO_2-30% Al_2O_3-H_2SO_4 had a wide acidic strength distribution range of 130–730 °C but the acidic strengths at 600–730 °C which was observed on the untreated catalyst disappeared and shifted to a low range of 130–380 °C on NaCl treated 10% Ni-70% SiO_2-30% Al_2O_3-H_2SO_4 catalyst. These results indicated that a high microalgae conversion was obtained on the catalysts having low acidity and 130–380 °C of an acidic strength distribution. Besides, the total acidity on 70% SiO_2-30% Al_2O_3-H_2SO_4 (i.e. without containing nickel) was found to be 19.5 μmol/g and an acidic strength distribution was centered at 165 °C (data not shown). This was close to the acidity and the acidic strength of the NaCl treated 10% Ni-70% SiO_2-30% Al_2O_3-H_2SO_4 catalyst but the microalgae conversion on 70% SiO_2-30% Al_2O_3-H_2SO_4 without containing nickel was zero. Thus, this study showed that not only the acidity/acidic strength distribution but also the presence of nickel was necessary to obtain high microalgae conversions.

The reusability of 10% Ni-70% SiO_2-30% Al_2O_3-H_2SO_4 catalyst and the effects of possible poisons coming from the microalgal biomass, such as phospholipids, on the microalgae biomass conversion were checked in this study since the highest conversion was observed on 10% Ni-70% SiO_2-30% Al_2O_3-H_2SO_4 catalyst. At the end of 24 h reaction time, without removing the catalyst from the reactor, a fresh amount of microalgae mixture was added to the reactor and then the reactor was kept at 80 °C and 1.0 atm for additional 24 h. Then, the liquid phase was analyzed to determine the microalgae biomass conversion and the product distribution. After 48 h of the reaction time, it was found that the microalgae conversion improved, which proved that there was no coke formation or any adverse effects of possible poisons and NaCl on the catalyst activity.

4. Conclusions

This study showed that 70% SiO_2-30%Al_2O_3 supported 10%Ni catalyst, prepared with the sol-gel method and sulfuric acid, converted 74% of *N. oculata* microalgae in seawater to bio-fuels without harvesting and dewatering at 80 °C and 1.0 atm. The treatment of this catalyst with ~35 g of NaCl per kg of water at 80 °C and 1.0 atm for 24 h increased the conversion to 91.5%. Nickel presence and 25.1 μmol/g of total acidity and 130–380 °C of acidic strength range was necessary to achieve 91.5% of the microalgae conversion at 80 °C and 1.0 atm.

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Declaration of interest

None.

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