Pyrolysis of Isochrysis Microalgae with Metal Oxide Catalysts for Bio-Oil Production

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Abstract: Pyrolysis of Isochrysis microalga was carried out in a fixed-bed reactor without and with metal oxide catalysts (CeO_2, TiO_2, Al_2O_3) for the first time at the temperatures of 450, 500 and 550 °C with a constant heating rate of 40 °C/min. The pyrolytic conditions including catalyst and temperature were studied in terms of their effects on the yields of pyrolytic products and quality. The amounts of bio-char, bio-oil, and gaseous products were calculated. The composition of the produced bio-oils was determined by Elemental analysis (EA), Fourier transform infrared spectroscopy (FT-IR), proton nuclear magnetic resonance (^{1}H NMR) and Gas chromatography/mass spectrometry (GC–MS) techniques. As a result of the pyrolysis experiments, it is shown that there have been significant effects of both catalyst and temperature on the conversion of Isochrysis microalgae into solid, liquid (bio-oil) and gas products. The highest bio-oil yield (24.30 %) including aqueous phase was obtained in the presence of TiO_2 (50%) as catalyst at 500 °C. 98 different compounds were identified by GC-MS in bio-oils obtained at 500 °C. According to ^{1}H NMR analysis, bio-oils contained ~60-64% aliphatic and ~17-19% aromatic structural units. EA showed that the bio-oils contained ~66-69% C and having 31-34 MJ/kg higher heating values.

Keywords: Energy; microalgae; isochrysis; pyrolysis; catalyst.

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INTRODUCTION

In recent years, petroleum and crude oil prices have been highly flexible due to the increasing energy demand. Researchers have sought to produce renewable, alternative and sustainable fuels to meet this increasing energy demand and to stabilize prices. Biomass is a promising candidate in this regard as it is renewable, carbon-neutral, and highly productive [1]. However, biomass feedstocks should have some advantages such as being cheap, easily available, abundant, fast growing, not in competition with food industry, and with minimum by products and waste [2]. Algae, the microorganisms grow fastly in water, are considered as potential feedstocks for production of bio-fuels. Recently, algae have already attacted much attention [3,4]. There are different processes of bio-fuel production from algal biomass which include supercritical water gasification, bio-diesel production by solvent extraction, bio-gas production by anaerobic digestion and bio-oil production by pyrolysis. Algae are considered as promising feedstocks for the following reasons: (i) high yield per area, (ii) high growth rate (up to 20 g dry algae per m^2 per day) (iii) high efficiency in CO_2 capture and solar energy conversion, (iv) no competition with agricultural food. Algae can grow in open water such as sea water and ponds or in photobioreactors on non-arable areas. However, only a few microalgal species are currently cultivated in an industrial manner [5].

Algae contain mainly three components: carbohydrates, proteins, and lipids. Microalgae are suitable feedstocks for biodiesel production as some species may contain up to 80% of lipid content [6]. A great number of studies have been performed for commercialization of microalgae-based biodiesel production [7,8]. However, at present, commercialization of biodiesel from microalgae is still highly expensive [9,10]. Currently, biodiesel from algae is produced by lipid extaction using organic solvents, such as hexane, or by pressing of dry algae and this is followed by transesterification in methanol or ethanol in the presence of basic catalysts [11-13]. In biodiesel production, only one part (lipid) of organic content of algae is utilized for biofuel production. From an economic point of view, biofuel production from microalgae requires utilization of the complete biomass as efficiently as possible. Solid residues derived from algae processing contain minerals up to 10% and these can be fed back to the growth cycle as a soil amendment product [14]. However, the rest 60% of microalgae is considered as waste, and this process is neither attractive nor economical [2]. Therefore, all components need to be used completely based on the microalgae biorefinery concept to develop economically feasible processes for microalgae biofuels. Thermochemical processes can be used to utilize all organic contents of algal biomass completely for biofuel production [15].

There are various biomass conversion processes that can yield high quality liquid bio-fuels and value-added products. Pyrolysis is a processing technique that is applied to achieve

degradation of biomass thermally in inert atmosphere which produces solid, liquid and gases. The produced liquids, called bio-oil are used in direct combustion for energy generation, or can be upgraded into transportation fuels and/or biochemicals [16]. Algal biomass can be converted into bio-fuels through different methods such as thermochemical liquefaction, transesterification, and pyrolysis. Pyrolysis is more economical than organic solvent extraction or thermal-acid conversion methods and transesterification methods for conversion of algal biomass into bio-fuels since pyrolytic process is more efficient than other methods. Among the three products obtained from pyrolysis, bio-oil is the most important one while bio-char and gases have various uses as well. Bio-oil can be used as fuel for heat and power or as feedstock for chemical industry and is considered to be a very promising bio-fuel [17].

The conversion of biomass species to renewable bio-fuels and development of catalysts have received great attention because of negative environmental impacts fossil fuels exploitation. As biomass is considered as CO_2-neutral, its usage as a renewable energy source helps reducing the dependence on fossil fuels and the greenhouse effect [18]. Microalgal species such as *Chlorella, Nannochloropsis* and *Tetraselmis* have received growing interest recently due to their high oil content, high mass productivity, and the ability to grow in a wide range of conditions (climates and lands). High quality bio-oils can be produced from non-catalytic and catalytic pyrolysis of algae that have been widely studied as an alternative. In a previous study, Gopakumar *et al*. (2012) performed the catalytic pyrolysis of green algae (*Chlorella vulgaris*) using H^+ZSM-5 catalyst for hydrocarbon production. The results showed that a bio-oil yield of 52.7 wt% was obtained which contained aromatic and alkane compounds [19]. In another study performed by Chaiwong *et al*., bio-char and bio-oil have been produced at temperatures between 450 and 600 °C in slow pyrolysis of Spirulina sp. without catalyst. The components found in bio-oil were identified by GC-MS which showed saturated functional carbons in the range of heavy naphtha, kerosene, and diesel oil [20]. Campanella and Harold (2012) carried out the non-catalytic and catalytic (ZSM-5 catalysts) pyrolysis of microalgae to produce organic liquid fuel precursor. They observed that using catalyst has resulted in the formation of highest yields of desired fraction (hydrocarbons) whereas the highest bio-oil yield was obtained without catalyst. It was found that HZSM-5 catalyst has increased the hydrocarbon fraction yield significantly (from 21% to 43%) in the organic phase [21].

The chemical composition of lignocellulosic biomasses (feedstocks) such as wood are very different from microalgae. Lignocellulosic biomasses including wood are made up of hemicelluloses, cellulose, and lignin whereas microalgae are composed of mainly proteins and carbohydrates in addition to lipids and do not contain lignin. Therefore, microalgae pyrolysis bio-oils have different compounds than lignocellulosic biomass pyrolysis bio-oils. Microalgae pyrolysis bio-oils are mainly composed of linear hydrocarbons, nitrogen containing compounds which come from the decomposition of lipids, and proteins respectively along with some

amount of oxygenated compounds from carbohydrates' pyrolysis. In principle, improved properties of microalgal bio-oils such as low tar formation and high heating value are resulted from these differences between lignocellulosic and algal feedstocks. In addition, bio-char obtained from microalgae pyrolysis can be used in agriculture due to its high nitrogen content. However, there have been a small number of studies on the pyrolytic characteristics of algae so far [22]. As the selection of process conditions, catalysts, product yields, and quality are affected by the heterogeneous compositions of the different feedstocks, effective catalysts for lignocellulosic biomass conversion may not be suitable for conversion of marine (algal) feedstocks. There is lack of works available in the literature on the behavior of Isochrysis algal pyrolysis with metal oxide catalysts. Accordingly, the purpose of this study was to investigate the effects of ceria, titania, and alumina catalysts on microalgae conversion yields and products selectivity and to investigate the possibility of producing biofuels. In this work, catalytic pyrolysis of Isochrysis was performed in a fixed-bed tubular reactor at temperatures of 450 °C, 500 °C and 550 °C with a constant heating rate of 40 °C/min under N_2 atmosphere. Firstly, the amounts of all pyrolytic products (solid, liquid, gas) were determined which revealed the catalysts and temperature effects on the yields of products. Secondly, various techniques (EA, FT-IR, ^{1}H NMR) were used to analyze the pyrolytic products.

MATERIALS AND METHODS

Feedstock

Microalgal sample, isochrysis, was provided from Reed Mariculture. Chemical composition (protein, lipid, and carbohydrate) of microalgae was also provided from Reed Mariculture. The cells of microalgal sample were dried in an oven at 45 °C, and pulverized to a particle size of 80 mesh and then stored in a desiccator for further use.

Proximate and ultimate analysis

The proximate analyses were conducted according to ASTM standards (D2016, D1102-84, E872-82,). C, N and H were determined using LECO CHNS-932 analyzer, while O content was obtained by the difference. Higher heating values (HHV) of samples were obtained using the Dulong's Formula as given below.

HHV (MJ/kg) = 33.86 x C + 144.4 x (H-O/8) + 9.428 x S where C, H, O, and S are the mass fractions obtained from ultimate analysis.

Fourier transform infrared spectroscopy (FT-IR)

FT-IR analysis of bio-oils was performed using Perkin Elmer Spectrometer system to detect the characteristic peaks and their functional groups.

Proton nuclear magnetic resonance (^{1}H NMR)

Agilent 400-MR NMR Spectrometer operating at 400 MHz was used for the ^{1}H NMR analysis of *Isochrysis* bio-oils. The bio-oils were dissolved in $CDCl_3$ using 1:1 ratio by volume in 5 mm NMR tubes and TMS (tetramethylsilane) was used as the internal standard.

Gas chromatography–Mass spectrometry (GC–MS) analysis

An Agilent GC-MS 7890A/5975C series (column: HP 235–INNOWAX; transfer line at 270 °C, ion source at 250 °C and electron energy of 70 eV) was used for the GC-MS analysis of the bio-oils [28]. The bio-oil components were identified using mass spectral libraries (PMW_Tox3.l, Wiley7n.1 and NIST05a.L).

Pyrolytic experiments

The pyrolytic experiments of *Isochrysis* were performed using a fixed-bed reactor. The set-up was previously descibed [23]. The catalytic and non-catalytic algal pyrolysis experiments were performed at temperatures of 450 °C, 500 °C and 550 °C under N_2 atmosphere. The heating rate was 40 °C/min and the nitrogen flow rate was 100 mL/min. The reactor was kept constant at the final temperature for 60 min. The bio-oils were recovered in three Dreshel bottles. The remaining solid was recorded as bio-char yield (subtracting the catalyst weight). The gaseous products were not collected and calculated by difference (subtraction of total solid and liquid yields from the amount of initial feedstock).

The distribution of the parent algal material energy in the pyrolytic products was based on the pyrolytic material balance and HHV of bio-oils and bio-chars.

RESULTS AND DISCUSSION

Feedstock characterization

Table 1 shows the results of ultimate and proximate analysis and chemical composition of Isochrysis. The alga contains relatively high amount of proteins (44%) and carbohydrates (25%), and low lipids (19%). The high protein content of Isochrysis is in good agreement with other microalgal species reported in literature such as *Chlorella vulgaris* and *Scenedesmus almeriensis* [24]. Accordingly, the nitrogen content was high (6.63%) because of the protein component. Ultimate analysis shows that Isochrysis has relatively high amount of carbon (41.23%). This is good in terms of suitability for biofuel production. The proximate analysis shows that Isochrysis has 53.52% volatile matter, 18.14% ash and 22.78% fixed carbon, relatively high when compared to given values in literature [25].

Table 1 Main characteristics of Isochrysis.

Components	
Moisture (%)	5.56
Proximate analysis[a] (%)	
Ash	18.14
Volatile matter	53.52
Fixed carbon	22.78
Ultimate analysis[b](%)	
Carbon	41.23
Hydrogen	5.74
Nitrogen	6.63
Oxygen[c]	46.40
H/C molar ratio	1.67
O/C molar ratio	0.84
Empirical formula	$CH_{1.67}N_{0.14}O_{0.84}$
Higher Heating Value (MJkg^{-1})	
Dulong's formula	13.86
Chemical composition (%)	
Protein	44
Lipid	19
Carbohydrate	25

[a]Weight percentage (dry basis). [b] Weight percentage (daf). [c]By difference.

Effect of temperature on product distibution

Table 2 presents the conversion (total volatiles) and product distribution of pyrolysis of Isochrysis with (50%) and without catalyst. Heating rate of 40 °C/min and N_2 flow rate of 100 mL/min was used in the pyrolysis of Isochrysis. According to Table 1, temperature increase in 50 °C increments resulted in sharp increases in both conversion (total volatiles) and the gas yields, while the bio-char (solid) yields were decreased in all runs. For example, when temperature was increased from 450 to 500 °C, the conversion (total volatile) was increased from 62.14% to 66.04% in the non-catalytic runs and from 65.17% to 68.92% in the catalytic runs with CeO_2.

The gas yields were constantly increased with temperature (slightly at 500 °C, sharply at 550 °C). This was because the highest bio-oil yields were attained at 500 °C. The highest liquid (bio-oil) yield of 24.30% was achieved with TiO_2 at 500 °C. The bio-oil yields did not increase in a monotonic trend with temperature. A slight increase was observed in bio-oil yields at 500 °C, but a decrease again at 550 °C. This was due to the secondary cracking reactions of pyrolysis vapors which occured at high temperature [26]. Bio-char (solid) yields were decreased constantly with temperature because of the primary decomposition of Isochrysis components as well as the secondary decomposition of char residues. As the temperature of pyrolysis was increased from 450 to 550 °C, bio-char yields were decreased from 37.86% to 30.76% without catalyst and from 36.47% to 31.80% with alumina. Similar results were obtained for pyrolysis of not only algal biomass but also lignocellulosic biomass. Paddy husk

pyrolysis was studied recently using a drop-type pyrolyzer. The pyrolytic experiments were carried out at temperatures between 350 and 600 °C. The results showed that bio-oil yields were first increased and then decreased at 600 °C. The gas yields were increased, while bio-char yields were decreased with the incremental of pyrolysis temperature [27].

Table 2 The conversion[a] and product distribution of Isochrysis pyrolysis.

Temperature (°C)	Conversion (%)	Solid (%)	Liquid (%)	Gas (%)
No catalyst				
450 °C	62.14	37.86	16.82	45.32
500 °C	66.04	33.96	20.13	45.91
550 °C	69.24	30.76	18.07	51.17
CeO_2				
450 °C	65.17	34.83	20.82	44.35
500 °C	68.92	31.08	22.97	45.95
550 °C	71.52	28.48	19.91	51.61
TiO_2				
450 °C	66.82	33.18	22.41	44.41
500 °C	70.47	29.53	24.30	46.17
550 °C	73.61	26.39	21.10	52.51
Al_2O_3				
450 °C	63.53	36.47	19.36	44.17
500 °C	65.66	34.34	22.10	43.56
550 °C	68.20	31.80	20.03	48.17

[a]Mass fraction percentage of feedstock (daf)

Effect of catalysts on product distribution

Biomass can be converted into solid, liquid, and gaseous fuels by liquefaction and pyrolysis processes. However, bio-oils produced from thermal degradation of both lignocellulosic and algal biomass have generally a low quality as they are highly acidic with oxygenated compounds and have low higher heating values. For this reason, catalysts were applied in liquefaction and pyrolytic processes in biomass conversion to valuable chemical and bio-fuels. The studies reported in literature showed that most of the catalysts were effective in these processes [28]. The main aim of catalytic biomass pyrolysis is to decrease the amount of oxygen containing compounds in bio-oils generated from biomass pyrolysis. Generally, algal biomass contains 35–45% of oxygen.

Oxygen in biomass can be removed by two major deoxygenation reactions. These are decarboxylation and dehydration reactions in which oxygen is removed in the forms of carbon dioxide and water, respectively. The long chain carboxylic acids in biomass are cracked thermally during decarboxylation reaction which reduces the chain size and releases carbon dioxide. If an effective catalyst is used, it can enhance deoxygenation and improve the bio-oils' quality. The function of using a catalyst in biomass pyrolysis is to speed up deoxygenation including decaboxylation, dehydration, and decarbonylation which result in the production of

desired compounds such as hydrocarbons. Some amount of the hydrogen and carbon in feedstock are converted to water, hydrogen gas, and carbon monoxide during pyrolysis as well [29]. In recent years, many types of catalysts including Ni and Mg-based have been utilized in pyrolysis and gasification studies.

As for the present study, we see that catalysts had different effects on the yields of products and quality. Almost all used catalysts had positive effects and increased the total amounts of volatiles (conversions) with temperature increase when compared to runs without catalyst except alumina at 500 and 550 °C. Titania was the most effective catalyst in terms of conversion. The highest conversion of 73.61% was obtained with titania in the catalytic runs at 550 °C. The least effective one was alumina with the lowest conversion of 63.53% obtained at 450 °C in the catalytic runs. On the other hand, effects of catalysts on liquid yields were different from the effects of conversion. All catalysts increased the liquid yields compared to non-catalytic runs, with titania being the most effective. The solid (bio-char) yields obtained with and without catalyst were found to be decreasing with increasing the pyrolysis temperature and the lowest yield of 26.39% was obtained in the presence of titania at 550 °C. As for the gas yields, the effect of catalysts differed from each other. The highest gas yields 51.61% and 52.51% were obtained with ceria and titania at 550 °C respectively while the lowest yield (43.56 %) was obtained in the presence of alumina at 500 °C.

In terms of energy recovery, Figure 1a shows that most of the starting microalgal energy was recovered in the bio-oils. Titania and ceria were the most effective catalysts, which maintained 59.96% and 54.69 % of the starting energy in the bio-oils, repectively, while alumina was the least effective one and maintained only 50.12% of the starting energy. Figure 1b shows the nitrogen distribution in the products of catalytic and non-catalytic pyrolysis of Isochrysis at 500 °C. Bio-oil obtained without catalyst contained about 23.16 wt % of the nitrogen, while 18.28 wt % remained in the solid bio-char and 58.54 wt % went into the gas products. From a fuel quality point of view, nitrogen in bio-oil is detrimental. The use of catalyst did not have a significant effect on the nitrogen content in the bio-oils. Titania was the most effective catalyst in removing nitrogen from feedstock and released the most of nitrogen (59.22%) as uncondensable gases, while keeping only 15.81% in bio-char.

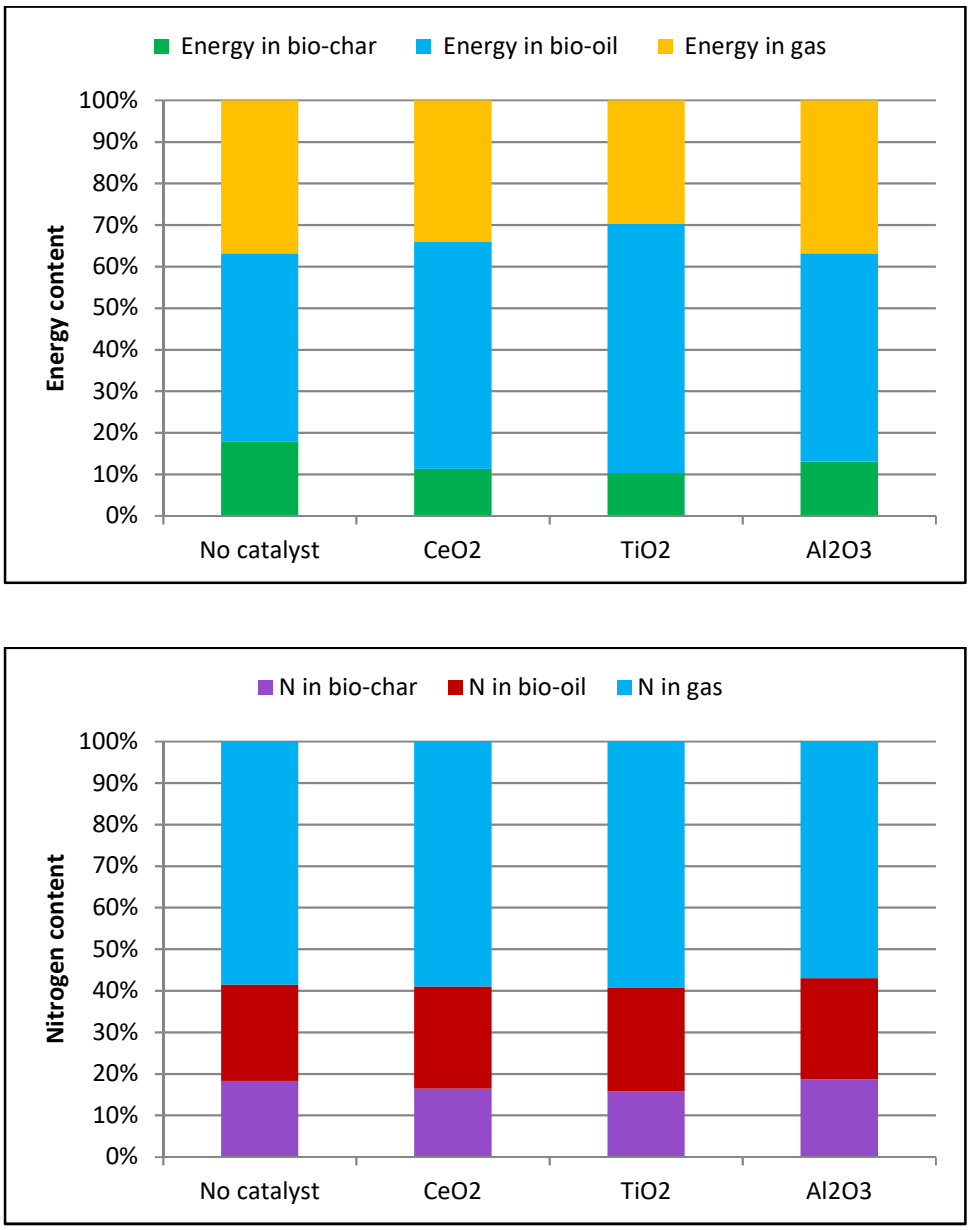

Figure 1. Energy and nitrogen contents of bio-oils obtained at 500 °C top: energy bottom: nitrogen.

EA, FT-IR, ^{1}H NMR and GC–MS analysis

The results of elemental (ultimate) analysis of bio-chars and bio-oils are given in Table 3. The elemental analysis of bio-chars obtained from Isochrysis pyrolysis showed their lower calorific values (4-7 MJ/kg) compared to that of feedstock (13.86 MJ/kg). This is because most of the starting microalgal energy was maintained in the bio-oils. Due to their low energy content, bio-chars may be utilized as soil amendment as they contain high ash and nitrogen (~3%) contents.

Table 3 The results of elemental analysis of Isochrysis bio-chars.

Elemental analysis [a] (Bio-chars)	No catalyst	CeO_2	TiO_2	Al_2O_3
Carbon	37.25	38.91	38.63	39.41
Hydrogen	1.31	1.40	1.36	1.37
Nitrogen	3.57	3.50	3.55	3.61
Oxygen[b]	57.87	56.19	56.46	55.61
H/C molar ratio	0.42	0.43	0.42	0.42
O/C molar ratio	1.16	1.08	1.09	1.06
HHV (MJ kg^{-1})	7.31	5.04	4.84	5.27
Elemental analysis (Bio-oils)				
Carbon	66.70	68.34	69.74	67.33
Hydrogen	8.14	8.82	9.14	8.15
Nitrogen	7.63	7.10	6.81	7.30
Oxygen[b]	17.53	15.74	14.31	17.22
H/C molar ratio	1.46	1.55	1.57	1.45
O/C molar ratio	0.19	0.17	0.15	0.19
HHV (MJ kg^{-1})	31.14	33.00	34.20	31.43

[a] Weight percentage (daf). [b]By difference.

When we look at the HHVs and elemental analysis of bio-oils from Isochrysis, we see that all catalysts increased C and H content in bio-oils and consequently enhanced their energy content. The most effective catalysts in improving bio-oil energy content were ceria and titania which increased the HHVs of bio-oils up to 33.00 and 34.20 MJ/kg, respectively, compared to non-catalytic run (31.14 MJ/kg). The decreasing amount of oxygen in bio-oils was due to the deoxygenation reactions which removed the oxygen in the form of carbon monoxide and/or carbon dioxide. The high nitrogen contents of bio-oils were obviously originated from proteins and chlorophyll present in Isochrysis. The pyrolysis bio-oil from Isochrysis had higher carbon and hydrogen content but lower oxygen content than the bio-oils from pyrolysis of lignocellulosic biomass, which makes it more suitable for fuel use.

GC-MS analysis of bio-oils produced at 500 °C was carried out in order to determine the main chemical compounds. The total ion chromatograms of bio-oils obtained at 500 °C are given in the Supplementary data (Figure S1,a-d). The list of the compounds identified by GC-MS in (Figure S1, a-d) is given in Table 4.

The presence of the metal oxide catalysts affected the distribution and number of the identified chemicals. The complete identification and quantification of all chemical compounds is not possible by GC-MS as the pyrolysis bio-oils have complex nature and may contain compounds with very high boiling points which can not pass through the GC column. Yet, elemental and FT-IR analysis of bio-oils were consistent and confirm the presence of compounds given in Table 4. As seen in Table 4, bio-oils from Isochrysis were composed of a mixture of different functionalities such as aliphatics, monoaromatics, oxygenates, nitrogenates and polycyclic compounds. As seen in Table 4, catalysts have formed aliphatics such as alkanes and alkenes.

Aliphatics (alkanes and alkenes) were mainly generated during the depolymerization of algal saturated and unsaturated fatty acids. Some examples are "Hexadecane", "Undecane", "Heptane, 2,4-dimethyl", "1,4-Pentadiene" and "2-Undecene". Aliphatics are valuable compounds which increase the high heating values of bio-oils. The nitrogen containing compounds in bio-oils, such as nitriles, amines, amides, pyrroles, and pyridines were assumed to be derived from protein degradation in algal cells. Oxygenated compounds, identified in pyrolysis bio-oils are represented with a wide range of compounds which include carboxylic acids, alcohols, esters, aldehydes, ethers and ketones. The main monoaromatics were phenol, phenol substitutes and benzene, which were produced from algal components thermal cracking, metal oxide promoted cracking, dehydration, decarbonylation, and decarboxylation reactions. A small number of phenolics were formed due to composition of microalga which has no lignin in its structure. The produced bio-oils had the carbon and hydrogen contents which are close to the conventional fossil fuels, however the oxygen and nitrogen contents are still high than desired amounts. The undesired NOx compounds are formed during combustion if nitrogen is found in bio-fuels. Therefore, the oxygen and nitrogen should be removed from bio-oils or lowered to a certain degree first if intented to be used as a transportation fuel. Hydrodenitrogenation and hydrodeoxygenation are the two main upgrading processes to lower the nitrogen and oxygen content in the bio-oils.

Table 4 Main chemical compounds present in bio-oils.

No	**Compound**	**Relative abundance (% area)**			
		No catalyst	**CeO_2**	**TiO_2**	**Al_2O_3**
1	2-Pentanone, 4-hydroxy-4-methyl-	75.80	–	–	–
2	3-Octanol	–	48.15	57.73	61.76
3	Aziridine, 1-(1-propenyl)-, (Z)-	–	–	–	1.09
4	Undecane	–	–	–	11.79
5	Heptane, 2,4-dimethyl-	–	–	4.14	–
6	Hexadecane	–	–	15.65	–
7	Methanamine, N,N-dimethyl-	–	0.27	–	–
8	Azetidine	–	0.88	0.56	–
9	Bicyclo[2.2.1]heptane-2-carbonitrile, 2-methyl-, exo-	–	0.30	–	–
10	(1S,3R,4R)-3-(Hydroxymethyl)-2-methyl-2-	–	–	1.09	–
11	1-Methyl-3-butenyl 3-methyl-3-hydroxybutyl ether	–	–	1.20	–
12	Ethenamine, N-methylene-	–	–	–	0.42
13	Dodecane	–	5.74	–	–
14	2(3H)-Furanone-3,3,4-d3, dihydro-4-D-	–	1.06	–	–
15	1-Octanol, 2-butyl-	–	20.08	–	2.67
16	2-Propynamide	–	0.36	–	–
17	Oxalic acid, isobutyl nonyl ester	–	5.04	–	–
18	Propiolonitrile	–	0.87	–	–
19	Decane	–	6.84	–	–
20	1,3-Butadiene, 2,3-dimethyl-	–	0.26	–	–
21	1,5-Hexadien-3-yne, 2-methyl-	–	0.25	–	–
22	Azetidine-D1	–	0.44	–	–
23	Methane, isocyanato-	–	0.26	–	–
24	Furan, 2,5-dihydro-	–	0.69	–	–

25	Ethene, methoxy-	0.39	–	–	0.38
26	Cyclopropane, 1,2-dimethyl-, trans-	–	–	–	0.81
27	Dodecane, 1,1-difluoro-	–	–	–	4.08
28	Oxalic acid, cyclobutyldecyl ester	8.90	–	–	–
29	2-Propenamide	1.04	–	–	0.47
30	2-Octanol formate	–	–	–	0.69
31	Dodecanal	–	1.78	–	–
32	1,3-Pentadiene, (e)-	–	1.21	–	–
33	3-Pentenenitrile, 2-oxo-	–	0.29	0.30	–
34	Bicyclo[4.3.1]dec-1(9)-ene oxide	–	–	3.33	–
35	1-Propanethiol, 2,2-dimethyl-	–	–	0.66	–
36	2-Oxaadamantan-6-ol	–	–	0.32	–
37	2-Propynenitrile	–	–	0.30	–
38	Pyridine, 2,3,4,5-tetrahydro-	–	–	0.87	–
39	2,4-Decadien-1-ol, (e,e)-	–	–	0.38	–
40	Trans-2-ethyl-3,3,5-trimethylcyclopentanone	–	0.25	–	–
41	Cyclopentanone, 2-methyl-3-(1-oxopropyl)-, trans-	–	–	0.33	–
42	Acetamide, 2-fluoro-	–	–	0.54	–
43	2-Butenedinitrile, (E)-	–	–	0.31	–
44	4-Isopropyl-5-methylhexa-2,4-dien-1-ol	–	–	0.50	–
45	1,5-Hexadiyne	–	–	0.36	–
46	3,7-Diazabicyclo[3.3.1]nonane, 9,9-dimethyl-	–	–	0.42	0.48
47	3-Furazancarboxamide, 4-(1-aziridinyl)-	–	–	–	0.53
48	2(1H)-Naphthalenone, octahydro-, trans-	–	–	0.50	–
49	9,9-Dimethyl-3,7-diazabicyclo[3.3.1]nonane	–	–	0.37	–
50	Pyridine, 2-methoxy-5-nitro-	–	–	0.58	0.51
51	Furazan-3-carbohydrazide, 4-methyl–N2-	–	–	0.41	–
52	2-Propenoic Acid, 3-(1-cyclopenten-1-yl)-, methyl	–	–	–	0.45
53	1H-Indene-2,5(3H,4H)-dione, tetrahydro-, cis-	–	–	–	0.38
54	1-Phenyl-3-hydroxy-2-fluoropropene-1	–	–	–	0.58
55	Phenol, 4-(aminomethyl)-2-methoxy-	–	–	0.39	–
56	Phenol, 3-methyl-2-nitro-	–	–	–	0.52
57	(2H) Benzene	–	0.24	–	–
58	1H-1,2,4-Triazole	–	0.35	–	–
59	Butane, 2-chloro-2-methyl-	–	0.66	–	–
60	1-Propanethiol	–	0.30	–	–
61	1-Dodecanol, 2-Methyl-, (S)-	3.16	–	–	–
62	1,3-Propylenimine	0.45	–	–	–
63	1H-Pyrrole	0.43	–	–	–
64	2,3-Dihydrofuran	1.27	–	–	–
65	8-Nonynoic acid	0.39	–	–	–
66	Acetonitrile, amino-	0.46	0.25	–	–
67	3-Pentanethiol	–	0.29	–	–
68	2-Propenenitrile, 2-methyl-	–	0.34	–	–
69	2-Azetidinecarboxylic acid, 1-nitroso-	–	0.27	–	–
70	2-Pentadecanone	–	2.23	–	–
71	N-Nitroso-methyl-D3-ethylamine	0.38	–	–	–
72	1,5-Pentanediol, 3-methyl-	1.10	–	–	1.78
73	1,4-Pentadiene	–	–	–	1.60
74	Acetonitrile, hydroxy-	–	–	–	0.50
75	Trimethylamine	–	–	–	2.28
76	1-Propanol, 2-methyl-	–	–	–	0.36
77	Carbon disulfide	–	–	–	0.42
78	2-Propenal	–	–	–	0.32

79	3,8,11-Trioxatetracyclo[4.4.1.0(2,4).0(7,9)]undecane, (1.alpha.,2.beta.,4.beta.,6.alpha.,7.beta.,9.beta.)-	0.48	–	–	–
80	Methyl vinyl ketone	0.57	–	–	–
81	3-Cyclohexen-1-one, 4-(1,5-dimethyl-4-hexenyl)-,	0.47	–	–	–
82	Propanenitrile	0.42	–	0.31	0.32
83	Dichloroacetic acid, 4-methylpentyl ester	–	–	3.46	–
84	Dodecane, 1,2-epoxy-	–	–	4.97	–
85	2-Undecene, (E)-	0.63	–	–	–
86	3-Butenenitrile	0.39	–	–	0.59
87	1-Heptadecanol	–	–	–	1.21
88	Cyclohexanone, 2,6-diethyl-	–	–	–	0.46
89	1-Heptyn-3-ol	–	–	–	0.71
90	Aziridine, 1-(1-propenyl)-, (E)-	–	–	–	0.31
91	[1R-(1Alpha.,5.alpha.,6.beta.)-6-N-propyl-3-azabicyclo[3.1.0]hexan-2-one	–	–	–	0.33
92	2-Cyclohexene-1-thione, 3,6,6-trimethyl-	–	–	–	0.59
93	(Z)-Cis-9,10-Epoxyheptadec-6-ene	–	–	–	0.61
94	2-Ethyl-3,3,5-methylcyclopentane	0.40	–	–	–
95	Pyridine-2,6-D2, 3-methyl-	0.54	–	–	–
96	2,3-Difluoro-2-(trifluoromethyl)-2H-azirine	0.81	–	–	–
97	2-Heptenal, 2-propyl-	0.66	–	–	–
98	3-Cyclopropylidene-1-propyne	0.85	–	–	–

FT-IR spectra of bio-oils obtained from pyrolysis of Isochrysis at 500 °C are given in Figure 2,a-d. FT-IR spectra, which represent the functional groups of bio-oils are consistent and confirm the presence of various types of compounds given in Table 4. The vibrations between 3000 and 3100 cm^{-1} are the characteristics of O–H groups, which indicate the presence of phenolics and alcohols. The sharp C–H and =C-H stretching vibrations between 2900 and 3000 cm^{-1} indicate the presence of aliphatics such as alkanes. The typical carbonyl group (C=O) streching vibrations at about 1700 cm^{-1} indicate the presence of aldehydes, ketones or carboxylic acids in bio-oils. Presence of alcohols and esters can be confirmed by C–H bending vibrations between 900 and 1350 cm^{-1} and C–O stretching vibrations between 1000 and 1350 cm^{-1} in bio-oils. Aromatic compounds are confirmed by the aromatic C=C stretching vibrations between 1350 and 1500 cm^{-1}.

Proton NMR spectra of the bio-oils obtained without and with metal oxide catalysts are given in Figure 3, a-d, while the integrations of selected regions of the spectra versus specific chemical shift ranges are presented in Table 5. NMR analysis is a powerful tool and of great importance, as it provides a complete overview of the chemical functionalities present in the bio-oils [30]. NMRs, which give an overview of the chemical functionalities present in the bio-oils, show that metal oxide catalysts altered the functionalities distribution. The aliphatic proton region of the metal oxide catalysts oils (0.0 to 1.5 ppm) was the most abundant. Among metal oxide catalysts, TiO_2 had the highest percentage of aliphatic protons (45.21% of all), while Al_2O_3 had the lowest (38.07% of all). The next integrated region from 1.5 to 3.0 ppm (aliphatic protons bonded to C=C double bond (aromatic or olefinic) or H two bonds away from a heteroatom)

did show slight differences between bio-oils obtained without and with catalyst, with CeO_2 having the lowest amount (19.43%) of protons in in this region. The region of the spectra (3.0-4.4 ppm) that characterises the aliphatic alcohol/ether protons, or methylene groups joining two aromatic rings were less in presence of metal oxide catalysts than without catalyst (9.54%). This sharp decrease in alcohols is mainly ascribed to the cracking of phytol, with TiO_2 being the most effective catalyst. The protons in the carbohydrates/aromatic ether (4.4-6.0 ppm) region were found to be in small amounts (~6-8 %) in all bio-oils, with lower levels in the presence of almost all metal oxide catalysts except Al_2O_3. These results are in accordance with the elemental (Table 3) and GC-MS (Table 4) analyses of bio-oils, which show lower oxygen contents when the catalysts were used. The aromatic region of the spectra (6.0-9.5 ppm) contain ~17-19 % of the protons in the bio-oils and the highest value of 19.44% was obtained without catalyst. Al_2O_3 produced the highest amount (18.57%) of aromatics while CeO_2 had the lowest (16.98%). This region represents hydrogen atoms both in benzenoid aromatic compounds and in heteroaromatics which contain oxygen and nitrogen such as furan and pyridine (Table 4). Negligible amount (~2 %) of aldehydes and carboxylic acids (9.0-10.1 ppm) were detected in bio-oils. The proton NMR results show that high percentages of the aliphatic structural units exist in the bio-oils obtained from pyrolysis of *Isochrysis*.

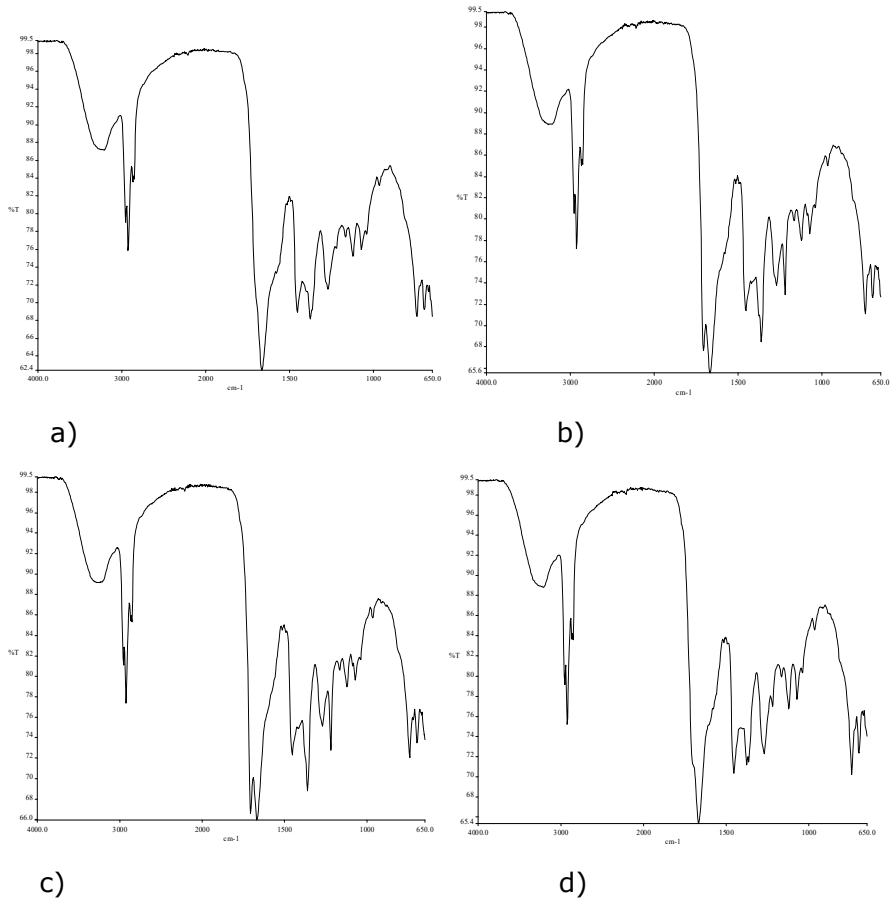

Figure 2 FT-IR spectra of bio-oils obtained at 500 °C a) without catalyst b) with ceria c) with titania d) with alumina.

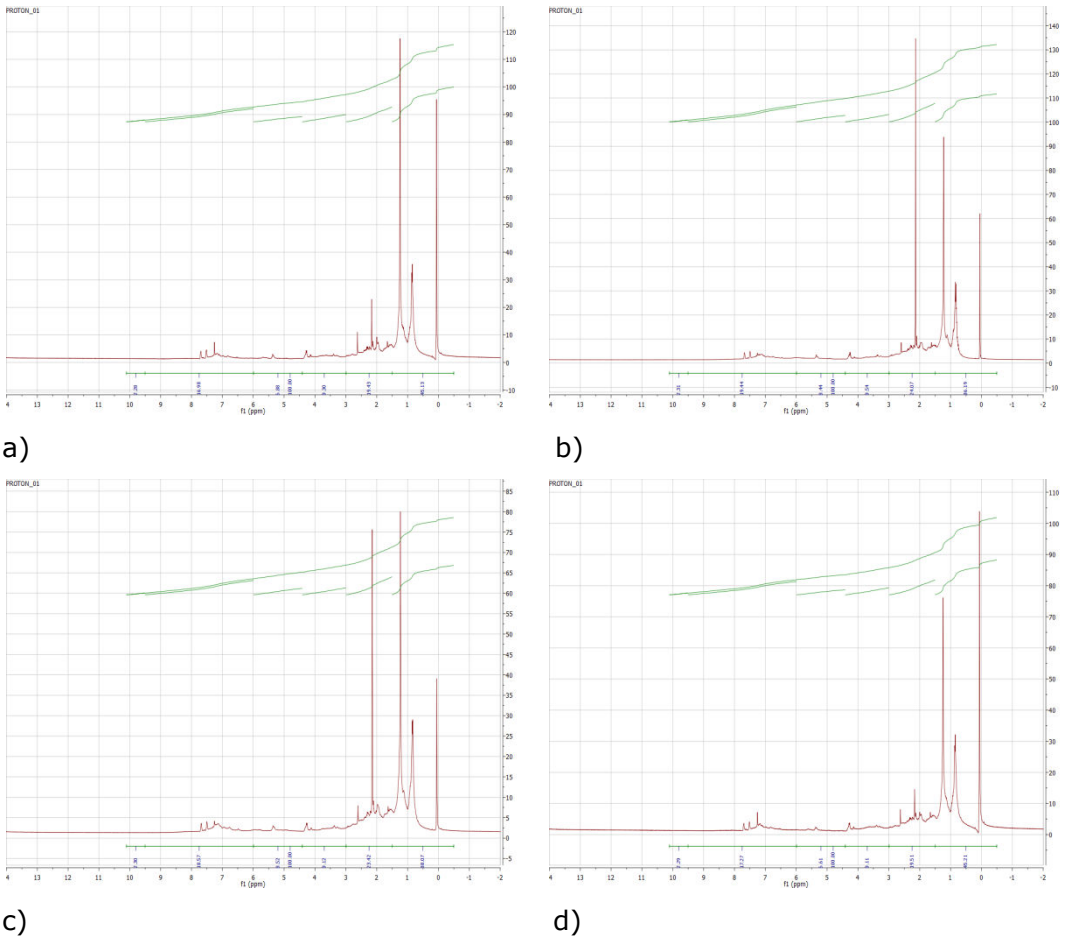

Figure 3 H^1-NMR spectra of bio-oils obtained at 500 °C a) without catalyst b) with ceria c) with titania d) with alumina.

Table 5 ^1H NMR Integrations of *Isochrysis* bio-oils obtained at 500 °C versus specific chemical shift ranges.

Chemical shift region (ppm)	**Proton assignment**	**Hydrogen content (% of all hydrogen)**			
		No catalyst	**TiO_2**	**CeO_2**	**Al_2O_3**
0.0 – 1.5	Alkanes	36.19	45.21	45.13	38.07
1.5 – 3.0	Aliphatics α-to heteroatom or unsaturation	24.07	19.51	19.43	23.42
3.0 – 4.4	Alcohols, methylene-dibenzene	9.54	9.11	9.30	9.12
4.4 – 6.0	Methoxy, carbohydrates	8.44	6.61	6.88	8.52
6.0 – 9.5	(Hetero-) aromatics	19.44	17.27	16.98	18.57
9.5 – 10.1	Aldehydes	2.31	2.29	2.28	2.30

CONCLUSION

In this study, an algal biomass (Isochrysis microalgae) was evaluated as feedstock for the catalytic (ceria, titania and alumina) production of bio-oils. The highest conversion of 73.61% and liquid (bio-oil) yield of 24.30% were obtained with titania at 550 and 500 °C respectively. The produced bio-oils were analyzed and characterized by EA, FT-IR, ^1H NMR and GC-MS which

indicated that temperature and catalyst have effected the product distribution. HHVs of bio-oils obtained in the presence of catalysts were higher than those obtained without. All bio-oils obtained with catalysts have suffered strong deoxygenation, with O level decreased from 46.40% in the starting feedstock to 14-17%. Elemental analysis showed that the bio-oils contained ~66-69% C and having 31-34 MJ/kg higher heating values. ^{1}H NMR analysis showed that all catalysts favoured the formation of aliphatics and lowered oxygen content of bio-oils. GC-MS analysis indicate that the bio-oils were enriched in alcohols, ketones and aliphatics.

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Türkçe Öz ve Anahtar Kelimeler

Biyoyağ Üretimi için Isochrysis Mikroalginin Metal Oksit Katalizörleri ile Pirolizi

Tevfik Aysu[1]*

Öz: Isochryris mikroalginin pirolizi sabit yataklı bir reaktörde katalizörsüz ve metal oksit katalizörleri (CeO_2, TiO_2, Al_2O_3) ile ilk defa 450, 500 ve 550 °C sıcaklıklarda 40 °C/dak ısıtma hızı kullanılarak gerçekleştirilmiştir. Sıcaklık ve katalizör gibi piroliz parametrelerinin ürün verimleri üzerine etkileri incelenmiştir. Elde edilen katı, sıvı (biyoyağ) ve gaz ürünlerin miktarları hesaplanmıştır. Piroliz sonucu üretilen biyoyağların içerikleri elementel analiz (EA), Fourier Dönüşümlü Kızılötesi Spektroskopisi (FT-IR), proton nükleer manyetik rezonans (^{1}H NMR) ve Gaz Kromatografisi-Kütle Spektrometresi (GC-MS) teknikleri ile belirlenmiştir. Sonuçlardan, sıcaklık ve katalizörün Isochrysis mikroalginin katı, sıvı ve gaz ürünlere dönüşümü üzerine önemli etkilerinin olduğu görülmüştür. Sıvı faz dâhil en yüksek biyoyağ verimi %24.30 olarak TiO_2 (50%) katalizörü varlığında 500 °C sıcaklıkta elde edilmiştir. GC-MS analizi sonucu 500 °C'de elde edilen biyoyağlarda 98 farklı bileşiğin bulunduğu belirlenmiştir. ^{1}H NMR analizi biyoyağların ~60-64 % alifatik ve ~17-19 % aromatik yapısal birimlerden oluştuğunu göstermiştir. Elementel analiz sonuçlarına göre biyoyağların ~66-69 % karbon içerdiği ve 31-34 MJ kg^{-1} arasında ısıl değere sahip oldukları tespit edilmiştir.

Anahtar Kelimeler: Enerji; mikroalg; piroliz; *isochrysis*; katalizör.

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