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Ceria promoted deoxygenation and denitrogenation of *Thalassiosira weissflogi* and its model compounds by catalytic in-situ pyrolysis

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ABSTRACT

Pyrolysis of microcrystalline cellulose, egg white powder, palm-jojoba oils mixtures *Thalassiosira weissflogi* model compounds was performed with CeO_2 at 500°C, to evaluate its catalytic upgrading mechanism. Light organics, aromatics and aliphatics were originated from carbohydrates, proteins and lipids, respectively. Dehydration and decarboxylation were the main reactions involved in the algae and model compounds deoxygenation, while nitrogen was removed as NH_3 and HCN. CeO_2 increased decarbonylation reactions compared to in absence of catalyst, with production of ketones. The results showed that the catalysts had a significant effect on the pyrolysis products composition of *Thalassiosira weissflogi*. CeO_2, $NiCeAl_2O_3$ and $MgCe/Al_2O_3$ catalysts increased the aliphatics and decreased the oxygen content in bio-oils to 6-7 wt% of the algae starting O_2 content. Ceria catalysts were also able to consistently reduce the N-content in the bio-oil to 20-38% of that in the parent material, with $NiCe/Al_2O_3$ being the most effective.

Keywords: Catalytic pyrolysis, Bio-oil, *Thalassiosira weissflogi*, Model compound, Ceria.

1. Introduction

Fossil fuels currently provide the majority of our energy and chemical needs. However, fossil fuels are limited, unsustainable and have a negative impact on the environment. Biomass has attracted worldwide attention as renewable source for fossil fuels replacement. Algae or microalgae represent a promising alternative renewable source since they can be cultivated on non-arable land and recycle nutrients from waste water and flue-gas, and thus providing additional environmental benefits.The potential of microalgae as feedstock has already been investigated (Vardon et al., 2015; Costanzo et al., 2015).Compared to lignocellulosic biomass, microalgae have high photosynthetic efficiency, high productivity, high lipid (up to 80%) content and do not compete with food crops (Maguyon et al., 2013). In recent years, high-lipid microalgae species have received increasing attention for biodiesel production. However, the extraction of oil from algae has higher costs compared to vegetable oils, due to the intrinsic different algae physico-chemical properties, such as cell size and cell wall chemistry. Furthermore, algae biodiesel has certain disadvantages, such as a high cloud point and low energy content that limit its wider usage (Gerpen JV, 2005). Another problem with algal biodiesel is that only the lipid portion of algae is utilized and the rest (carbohydrates and proteins) is considered as waste in terms of fuel use (Na et al., 2012). For low-lipid microalgae, thermochemical conversion processes such pyrolysis for conversion of all components is more suitable to produce bio-fuels or valuable chemicals (Vardon et al., 2015; Wang et al., 2013). Among thermochemical processes, pyrolysis has received growing attention in conversion of whole microalgae due to its relatively low cost and flexibility. Pyrolysis bio-oil can be used as feedstock for value-added chemicals such as resins, adhesives and phenols or can be used as liquid fuel (Abdullah et al., 2008; Trinh et al., 2013). Although microalgae to biodiesel has been studied extensively, microalgae catalytic pyrolysis has received less attention, with studies mainly focusing on the effect of the process variables

using acid zeolites, which tend to favour dehydration reactions and formation of aromatics products (Gopakumar et al., 2012).Microalgae have a very different chemical composition from wood and other lignocellulosic feedstocks. Hence, bio-oil produced from pyrolysis of microalgae contains a variety of different compounds, such as oxygenates, linear hydrocarbons and nitrogenous species resulting from pyrolysis of lipids and proteins, respectively. In principle, these differences from lignocellulosic feedstocks may lead to improved properties in the resulting bio-oil, such as higher heating values and reduced tar formation. Since microalgae contain carbohydrate, protein, and lipid as their main components, they devolatilize relatively at lower temperatures than lignocellulosic biomass materials (Peng et al., 2001). Furthermore, the bio-oil produced from microalgae is generally more stable due to lower O/C ratio, less acidic and has higher HHV compared to lignocellulosic bio-oil (Fisk at al., 2009). However, to date, there have been a limited number of studies on the pyrolytic characteristics of algae and their components. Since the heterogeneous composition of the different bio-feedstock affects the selection of the catalysts, process conditions and products yield and quality, catalysts that are effective in converting lignocellulosic biomass may not perform well with marine biomasses. For example, alumina supported Ni-based catalysts have been used in pyrolysis–gasification of freshwater algae to produce H_2 rich gases. Ni-based catalyst activated the cracking and reforming of biomass volatiles and tars released during pyrolysis at low temperatures (Díaz-Rey et al., 2014). Most of the previous studies on catalytic conversion of biomass (lignocellulosic and algal) have been primarily focused on the effects of process variables on the quality and quantity of bio-oil. Few reports on pyrolysis mechanism of biomass components have been reported (Du et al., 2013; Gai et al., 2015; Wang et al., 2014). Therefore, there are significant knowledge gaps on catalytic upgrading mechanisms using different catalysts that can favour the removal of O_2 from in-situ biomass decarboxylation and may selectively favour desired products.

In our previous study (Aysu and Sanna, 2015), we have evaluated the influence of ceria based alumina and zirconia supported catalysts on pyrolysis product yields and bio-oil properties of relatively high lipid containing alga, *Nannochloropsis*. However, there is no comparative study regarding the effect of ceria based catalysts on pyrolyis of low lipid algae such as Thalassiosira weissflogi and a lack of studies on the effect of ceria catalysts on microalgae model compounds pyrolysis. Therefore, the objectives of this study were: (i) to evaluate the effect of temperature and alumina supported ceria catalysts on product yields and the distribution of pyrolytic products using ^{1}H-NMR, EA, TGA and GC-MS, (ii) to evaluate the mechanisms involved in the in-situ catalytic upgrading of the algae major components (proteins, fatty acids and carbohydrates), by conducting pyrolysis of model compounds using gas analysis and GC-MS.

2. Materials and Methods

2.1 Feedstock pre-treatment

The microalgae sample, *Thalassiosira weissflogi* was obtained from Varicon Aqua Solutions in liquid form. The algae cells were dried in an oven at 50 °C, pulverized to a particle size between 80 and 140 meshes (105-174 μm) and stored in a desiccator for further use. Micro-crystalline cellulose, dried egg whites (mixture of albumins, mucoproteins and globulins) and fatty acids (mixture of 70% palm oil (rich in C16:1) and 30% jojoba oil (rich in C20:1 and C22-2)) were used as model compounds of carbohydrates, proteins and lipids, respectively.

2.2. Catalyst preparation and characterization

Commercial ceria (CeO_2) nanopowder was purchased from Sigma-Aldrich. Ceria containing catalysts (Ce/Al_2O_3, $NiCe/Al_2O_3$, $MgCe/Al_2O_3$) were prepared by incipient wet impregnation method with $Ce(NO_3)_3x6H_2O$, $Mg(NO_3)_2x6H_2O$, $Ni(NO_3)_2x6H_2O$ as precursors using alumina support. The preparation method has been previously described (Aysu and Sanna, 2015). The Ce/Al_2O_3 catalyst preparation was carried out by stirring cerium (III) nitrate

solution and alumina support at 300 rpm for 3 h at 80 °C. Then, the mixture was dried at 110 °C for 24 h. The dried $Ce(NO_3)_2/Al_2O_3$ was calcined in air at 600 °C for 3 h to obtain a theoretical 5% Ce/Al_2O_3 and to achieve well dispersion (Ying et al., 2012). The Ce-Ni/Al_2O_3 catalyst was prepared by wet impregnating alumina with the cerium (III) nitrate solution and nickel (III) nitrate solution. The other catalysts were prepared using the same impregnation/calcination method described above. The surface area, pore volume and average pore size of the prepared catalysts were analyzed by N_2 adsorption method at -195.8 °C using Micromeritics Gemini VII instrument. The catalyst samples were outgassed overnight at 180 °C. The surface area and pore size distribution of the samples were calculated by using the standard Brunauer–Emmett–Teller (BET) equation andthe Barrett–Joyner–Halenda (BJH) method, respectively. The crystalline phases of the catalysts were identified by powder X-ray diffraction using Bruker D8 Advance powder diffractometer, operating with Ge-monochromated Cu *K*α1 radiation (wavelength=1.5406 Å, 40 kV, 30 mA) and a LynxEye linear detector in reflectance mode. Data were collected over the angular range 5°-85° degrees in two-theta under atmospheric pressure.

2.3. Feedstock and products analyses

2.3.1. Proximate and ultimate analysis

The moisture content and proximate analysis (volatile matter and ash content) of the dried *Thalassiosira weissflogi*, bio-oils and bio-chars were determined according to ASTM standarts (D2016, E872-82, D1102-84). The carbon, hydrogen and nitrogen contents of dried *Thalassiosira weissflogi* and model compounds bio-oils and bio-chars were determined using Exeter Analytical CE440 analyzer and the oxygen content was calculated by difference. Higher heating values (HHV) of samples were calculated by using Dulong's Formula as shown in Eq. (1), based on the elemental composition.

$$HHV\ (MJ/kg) = 0.3383*C + 1.422 * (H-O/8) \quad (1)$$

where C, H, and O represent the weight percentages of carbon, hydrogen, and oxygen, respectively (Aysu, 2015).

2.3.2. ^{1}H NMR analysis

The ^{1}H NMR analyses of *Thalassiosira weissflogi* and model compounds bio-oils were performed using Bruker Avance III operatingat 400 MHz. The samples were prepared in $CDCl_3$ with the ratio of 1:1 by volume in 5 mm NMR tube and using TMS (tetramethylsilane) as the internal standard.

2.3.3. TGA analysis

Thermogravimetric analysis was carried out using a TA Q500 thermogravimetric analyzer. TG-pyrolysis using N_2 as carrier gas was used to determine the moisture content, volatile matter and fixed carbon and to compare/comfirm with the results obtained by ASTM standarts. TG-combustion using air as carrier gas was used to determine the ash content. The samples, weighing approximately 10 mg, were heated from 25 to 800 °C with a constant heating rate of 20°C/min under N_2 and then the temperature was decreased to 600°C to determine the fixed carbon and ash contents under air atmosphere. The loss of weight between 25 and 105 °C was used to calculate the moisture content of the samples. The volatile content of the raw material was determined from the weight loss between 105 and 600°C as primary volatiles and 600 and 800 °C as secondary volatiles. The ash content of the sample was determined from the amount of solid remaining at the end of the combustion step. Fixed carbon was calculated by subtracting the ash content from the solids remaining at the end of run. The volatile contents of the bio-oils were determined from the weight loss between 25 and 105°C as light volatiles, and 105 and 600°C as heavy volatiles.

2.3.4. GC-MS and gas analysis

Agilent GC-MS 7890A/5975C series (Agilent Technologies, Santa Clara, CA) was used for the semi-quantitative GC-MS analysis of produced bio-oils. The column was an HP 235–

INNOWAX with 60 m length, 0,250 mm inner diameter, 0.25 μm film having temperature limits between 40 ^{o}C to 300 ^{o}C. GC and the injector temperatures were the same during analysis. Helium was used as the carrier gas at a flow rate of 1.7 ml/min. 1 μL samples was injected with a split ratio of 1:20. The GC oven temperature program was as follows: start at 40 °C; hold for 10 min, raise from 40 °C to 200 °C at a heating rate of 5 °C/min; hold for 15 min, raise to 240 °C at a heating rate of 10 °C/min; hold for 15 min, raise to 260 °C at a heating rate of 10 °C/min; hold at the final temperature for 10 min.The end of column was directly introduced into the ion source of a mass selective detector of Agilent 5975C series with operating conditions of transfer line at 270 °C, ion source at 250 °C and electron energy of 70 eV. Identification of bio-oil components was done using mass spectral libraries (PMW_Tox3.l, Wiley7n.1 and NIST05a.L). During pyrolysis of *Thalassiosira weissflogi* and model compounds, the produced gases were collected in a gas bag and analyzed by a MKS Cirrus Mass Spectrometer.

2.3.5. Coke analysis

The amount of coke deposited on each catalyst was determined by the weight change during combustion using a thermogravimetric analyzer (TGA Q500). The burning of coke was carried out. 30 mg of sample in the alumina crucible were heated from 25°Cto the final temperature of 900°C at a rate of 10°C/min under a 70 mL/ min air atmosphere.

2.4. Pyrolysis experiments

The pyrolysis experiments of *Thalassiosira weissflogi* and its model compounds were performed using a fixed-bed reactor (Aysu and Sanna, 2015). The biomass sample was dried at 110°C overnight before pyrolysis runs. N_2 gas was fed at a flow rate of 15 ml/min for 10 min to remove the air in the reactor before pyrolysis. In a typical run, 3g dried *Thalassiosira weissflogi* powder or dried *Thalassiosira weissflogi*/catalyst (1:1) mixture or model compound/catalyst (1:1) mixture was placed in to the reactor in a ceramic container. Then, the

reactor was closed tightly and N_2 gas flow through. An external electric furnace was used to heat the reactor during which the temperature was controlled by a temperature controller. The algae pyrolysis experiments were performed at temperatures of 400, 500 and 600^{o}C at a constant heating rate of 100 ^{o}C/min, with and without catalyst. The model compounds pyrolysis tests were carried out only without catalyst and in presence of CeO_2. The reactor was kept constant at the final temperature for 60 min. The oil-condensation system was made of 3 Dreschel bottles maintained at 0^{o}C using a ice-water bath. The gaseous products were not collected and vented out. The condensed bio-oils were recovered using acetone. The reactor was also washed with 100 ml of acetone to account for oil condensed between the heated reagion and the condensation set-up. Carryover of char into the condensation system was not noticed in any of the run, so that the bio-char recovered from the reactor represented the totality of it. Then the solvent was evaporated at 40^{o}C and 11 kPa using a rotary evaporator to recover the oil which was recorded as bio-oil yield. When the reactor was cooled to room temperature, the remaining solid left behind was taken out, weighed and recorded as bio-char yield (subtracting the catalyst weight). The pyrolysis experiments without catalysts (400°C and 500°C) and in presence of CeO_2 (500°C) and Ce/Al_2O_3 (500°C) were carried out in triplicate to evaluate the standart deviations (STD) (Table S1). STD on bio-char and bio-oil yileds were between 0.17 and 1.96. Average values were reported. The total volatiles (liquid+gas yield) of *Thalassiosira weissflogi* in pyrolysis was calculated by subtraction of amount of solid (bio-char) left behind in the reactor. The amount of gaseous products was calculated by subtraction of solid and liquid yields from the amount of initial raw material (3 g). The following equations were used to calculate the total volatiles and product distribution (yields) of pyrolysis experiments:

$$\text{Total volatiles (\%)} = \frac{(W_{Biomass,db} - W_{Solid,db})}{W_{biomass,db}} \text{x}100 \quad (1)$$

$$\text{Liquid yield (wt \%)} = \frac{(W_{Liquid})}{W_{Biomass,db}} \text{ x100} \quad (2)$$

$$\text{Solid yield (wt \%)} = \frac{(W_{Solid,db})}{W_{Biomass,db}} \text{ x100} \quad (3)$$

Gas yield (wt %) = 100% – liquid yield (wt %) –solid yield (wt %) (4)

where $W_{Biomass, db}$ and $W_{Solid, db}$ are the weights of initial algal biomass and remaining solid (bio-char) respectively on dry basis. The distribution of the parent algal material energy in the pyrolysis products was calculated considering the energy content of the different materials (microalgae, bio-oil, bio-char, bio-gas (by difference) and the pyrolysis material balance. Firstly, the product yields (%) of bio-char and bio-oil were determined by weighting the material collected into the condensation trap (bio-oil) and that left into the reactor (bio-char). Then, the gas yield was calculated by difference. The energy content of each product (bio-char and bio-oil) was calculated by multiplying the HHVs to the wt% of the products recovered. The energy content of bio-gas was calculated by subtracting the energy content of the bio-char and bio-oil from the starting energy content of the raw material (microalgae).

3. Results and discussion

3.1. Raw material and catalysts characterization

Thalassiosira weissflogi (Table S.2) contains relatively high amount of proteins (43%) and low lipids (5%) and carbohydrates (12%). The *Thalassiosira weissflogi* low lipid content renders this alga not ideal for biodiesel production, but suitable for pyrolysis. The high protein content is in good agreement with literature and consistent with other algal species studied for production of biofuels such as Nannochloropsis and Dunaliella (Brown et al., 2010; Kim et al., 2015). Accordingly, the nitrogen content was high (4.64 wt%) due to high protein content. Ultimate analysis shows that *Thalassiosira weissflogi* has relatively high carbon content (38.84 wt%) on dry basis which makes it a suitable feedstock for biofuel production, while the proximate analysis shows high ash content (40 wt%). Thermogravimetric and DTG analysis of *Thalassiosira weissflogi* (Fig. 1) was performed to determine its thermal behaviour.

Overall, the pyrolysis curves can be divided into three stages: dehydration, devolatilization, and decomposition of the carbonaceous matter. There were seven main decomposition steps of which, the two at T<130°C corresponds to dehydration and short chain fatty acids decomposition. The four decomposition events between 200 and 500°C are related to algae compounds devolatilization and the final decompositin event at T >650°C corresponds to the decomposition of char formed in the previous steps. As indicated by TGA analysis, the decomposition stages between 200 and 500°C involved cellulose (375°C), proteins (220 and 300°C) and lipids (460°C) volatilisation. The latter event may also involve proteins decomposition. The high amount of solid residue left behind (51 %) after 800 °C represents fixed carbon and inorganic materials (ash) in the parent material. The TGA shows that the initial decomposition temperature and the maximum weight loss rate of *Thalassiosira weissflogi* were lower than those of lignocellulosic biomass (Yuan at al., 2015; Maddi et al., 2011). For lignocellulosic biomass, the primary classes of thermally degradable biopolymers are hemicelluloses, cellulose and lignin. Hemicelluloses, cellulose and lignin decompose in the temperature range of 220–315 °C, 315–400 °C and from 200 to 900°C, respectively (Yang et al., 2007). The main reason for the shifting at lower temperature of the microalgae devolatilisation is attributed to the absence of lignin, which results in a complete volatilisation of *Thalassiosira weissflogi* at 500 °C. Extractives, triglycerides and hexane soluble components in microalgae are less thermal resistant than lignin present in lignocellulosic biomass (Sanchez-Silva et al., 2012).

The total pore volume, specific surface area (BET) and average pore diameter of Al_2O_3 support were 0.129 cm^3/g, 75.39 m^2/g, and 37.44 Å, respectively. Addition of metal oxide to Al_2O_3 influenced the catalyst properties. Surface area and pore volume were decreased, while pore size was increased slightly. Surface areas of Ce/Al_2O_3, $NiCe/Al_2O_3$, and $MgCe/Al_2O_3$ were found to be 55.1, 60.2, and 49.6 m^2/g, respectively (Aysu and Sanna, 2015). The X-ray

diffraction patterns of the prepared catalysts with Al_2O_3 support are shown in the Supplementary data (Fig. S1-a,b,c). XRD diffraction patterns confirm the formation of the metal oxides (CeO_2, NiO, MgO) with exact matches. XRD patterns of Ce/Al_2O_3catalyst (Fig. S1-a,b,c) exhibit peaks (2θ scale) at 28.5°, 33.10°, 47.60°, 56.39°, 59.13°, 69.51° and 79.10° attributed to the cubic cerium (IV) oxide crystal phase. XRD patterns of Ni-Ce/Al_2O_3 (Fig. S1-b) show peaks that match the cubic nickel (II) oxide at 2θ scale = 37.20°,43.18°, 62.90°, 75.22°, and 79.40°. Mg-Ce/Al_2O_3 (Fig. S1-c) catalyst shows peaks for cubic magnesium oxide (MgO) crystal at 2θ scale=37.00°, 43.00°, 62.30°, and 78.50°. These results were consistent with those previously reported in literature (Qiao et al., 2009; Hernández-Enríquez et al., 2012; Aysu and Sanna, 2015).

3.2. Effect of temperature on product distribution

The total volatiles and distribution of products obtained by pyrolysis of *Thalassiosira weissflogi* at different temperatures with (1:1 ratio) and without catalyst are given in Table S.3. High char yields are probably due to the slow heating rate used (100°C/min) during pyrolysis (Kersten et al., 2005). The total volatiles and the gas yields were increased generally, while the bio-char yields decreased in all experiments. The highest liquid yield of 25.8% was achived with CeO_2 at 500 ^oC. The effect of temperature on changing the products yields was limited, probably due to the use of a batch reactor operating with slow heating rates. Ni-Ce on alumina support had a positive effect on cracking and minimising char at 400 and 500 °C, while mainly boosted gas formation at 600 ^oC, compared to the other tested catalysts. Therefore, NiCe-Alumina actively promoted secondary cracking reactions of char (Rover et al., 2014; Li et al., 2012). This trend is in agreement with our previous study on *Nannochloropsis* catalytic pyrolysis, where Ni-Ce/Al_2O_3 resulted in good deoxygenation effect at 500 °C (Aysu and Sanna, 2015).

3.3. Effect of catalysts on product distribution

The catalysts used in this study exhibited a negligible effect on product yields (Table S.3). However, the use of ceria catalysts affected the quality of the products from the microalgae and model compounds as discussed in the following sections. The highest total volatiles (85.8%) were obtained with $NiCe/Al_2O_3$ at 600°C. This can be related to the secondary cracking of tars in presence of Ni on alumina support and to the larger surface areas and pore volumes of $NiCe/Al_2O_3$ compared to the other doped catalysts (Díaz-Rey et al., 2014). CeO_2 based catalysts catalyse ketonisation and aldol condensation of carbonyl compounds in pyrolysis vapour with rejection of the oxygen of carboxylic acid as CO_2 and water, due to their facile reduction/oxidation and acid–base properties (Alonso et al., 2010).

In terms of energy recovery, most of the starting microalgae energy was recovered in the bio-oils as can be seen in Fig. 2. CeO_2 and $NiCe/Al_2O_3$ were the most effective catalysts, which maintained 82.8% (daf) and 76.0% (daf) of the starting energy in the bio-oils repectively. This indicates that deoxygenation of *Thalassiosira weissflogi* in presence of CeO_2 and Ce/Ni-alumina is very effective compared to deoxygenation of other microalgae under the same conditions (Aysu and Sanna, 2015).

Fig. 3 shows the nitrogen distribution in the products of catalytic and non-catalytic pyrolysis of *Thalassiosira weissflogi* at 500°C. Bio-oil obtained without catalyst contained about 41.5 wt% of the nitrogen, while 11.5 wt% remained in the solid bio-char and 47.0 wt% went into the gas products. From a fuel quality point of view, nitrogen in bio-oil is detrimental. The use of Ce-catalysts lowered the nitrogen content in the bio-oils. $MgCe/Al_2O_3$ was most effective catalyst in removing nitrogen from bio-oil (19.4%) and released the most of nitrogen (69.7%) as uncondensable gases, while keeping only 10.9% in bio-char.Also, Ce/Al_2O_3 (24.2%) and $NiCe/Al_2O_3$ (27.8%) wereable to consistently reduce the N content in bio-oils, compared to without catalyst. These N removal data are comparable with those obtained by pre-treating microalgae (e.g. Nannochloropsis) with low temperature hydrothermal liquefaction (225°C,

15 min) and then subjecting the solid residue to hydro-thermal liquefaction (350°C, 60 min) (Costanzo et al., 2015). Moreover, previous work showed that nitrogen sent to gas phase can be recycled in a loop process to fed microalgae and boost their growth (Wang et al., 2013; Jena, 2011).

TGA of the spent (coked) catalysts was carried out in pure air to evaluate the amount of coke formed on catalysts. Figs. S.2-S.5 show the TGA curves of the coked catalysts. Initial mass loss between 25 and 100 °C was associated to release of absorbed water. The second mass loss between 100 and 600°C was associated to decomposition of the char, while the third (final) mass loss between 600 and 900 °C was associated to coke combustion. $NiCe/Al_2O_3$ had the lowest amount of coke (5.2%) while $MgCe/Al_2O_3$ had the highest (7.5%). This is in agreement with the pyrolysis mass balance (Table S.3), which shows their catalytic activities in terms of high total volatiles. Oxygen affinity of Ce improved the activity of Ni/Al_2O_3 catalyst in terms of coke suppression. Adsorbed O species in presence of Ce and Ni, due to lattice O and redox properties of Ce forms gas species such as CO_2 and CO instead of coke deposition (Oemar et al., 2014). Fig. 4-d also suggests that CeO_2 oxygen affinity can promote oxidation of coke with formation of CO.

3.4. Characterization of bio-chars and bio-oils by EA, TGA, ^{1}H NMR and GC–MS analysis.

The elemental analysis of bio-chars obtained from *Thalassiosira weissflogi* pyrolysis (Table S.4) showed their lower calorific values (5-9 MJ/kg) compared to that of raw material (11 MJ/kg). This is because most of the starting microalgae 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. The EA (daf) of the bio-char indicates that the C content is lower than typical bio-chars and richer in O. High O content can be related to low-temperature pyrolysis, which produces biochar enriched in volatile-matter composition with relatively high O content. Low C content is attributed to the high ash content (~ 80%) in the

Thalassiosira W. derived bio-chars. Typically, microalgae ash is rich in Si, which can favours the formation of the Si–C bonds, thereby increasing the number of aromatic components and recalcitrance of the bio-chars as a result of temperatures (Jindo et al, 2014). A previous study reported that the presence of silicon in rise husk biochar obtained at 500 °C formed a dense carbon structure with Si-encapsulated carbon; in contrast, in the bio-chars prepared at the temperature of 700 °C, the silicon component was physically distanced from the carbon structure (Guo and Chen, 2014).

The HHVs and elemental analysis of bio-oils from *Thalassiosira weissflogi* are given in Table 1. 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 CeO_2 and $MgCe/Al_2O_3$ which increased the HHVs of bio-oils up to 35.37 and 36.37 MJ/kg, respectively, compared to non-catalytic run (32.85 MJ/kg). High nitrogen contents of bio-oils, which comes from chlorophyll and proteins in *Thalassiosira weissflogi* was somehow reduced in both bio-char and bio-oil and preferentially send to gas phase when the catalysts were used. Bio-oil from *Thalassiosira weissflogi* had lower oxygen content than bio-oils from pyrolysis of lignocellulosic biomass, which makes it more suitable for fuel use. CeO_2 was the most effective catalyst in reducing O_2 content (12.28%) in bio-oil compared to in absence of catalysts (15.81%). When considering the elemental analysis of bio-oils obtained from pyrolysis of the microalgae model compounds with CeO_2 (Table 2), it can be noticed that CeO_2 increased the C content of fatty acids bio-oil and H content for all the model compounds, while it decreased N content in protein derived bio-oil and O content in fatty acids and cellulose bio-oils. In contrast, the O content was slightly increased in bio-oil derived from protein pyrolysis.

The proximate analysis of *Thalassiosira weissflogi* and model compounds bio-oils were determined by TGA (Tables S.5 and S.6). Most of the bio-oils mainly contain volatiles with

negligible amount of fixed carbon (except cellulose bio-oils) and ash, which is important in terms of bio-fuels production.

The integration of the ^{1}HNMR spectra of the *Thalassiosira weissflogi* and model compounds bio-oils obtained without and with catalysts are presented in Tables 3 and 4, respectively.As seen in Table 3, there were clear differences in the overall chemical composition of the *Thalassiosira weissflogi* bio-oils from different catalysts. The region (0 to 1.6 ppm) representing aliphatic proton was the most populated for the bio-oils indicating their higher aliphatic content. Almost all catalyts have increased the aliphatics products and decreased the total oxygenates compared to non-catalytic run. Bio-oils obtained in the presence of CeO_2 and $NiCe/Al_2O_3$ contained the highest percentage of aliphatic protons (~59 and ~62 % of all). The regions (1.6 to 2.2 ppm and 2.2 to 3.0 ppm) which represent protonson aliphatic carbon atoms bonded to a C=C double bond (olefinic or aromatic) or two bonds away from a heteroatom (O or N) were abundant in the bio-oil obtained with CeO_2 and $MgCe/Al_2O_3$. The protons in the region (4.2-6.4 ppm) that represents aromatic ether (such as methoxyphenols) and carbohydrate-like molecules were in small amounts (~1-6%) in all bio-oils. This is consistent with the low O content in bio-oils from EA (Table 1). The distribution of the protons in the aromatics and N/O heteroaromatics regions (6.4-6.8and 6.8-8 ppm) indicate that CeO_2 did not affect aromatics production compared to the run in absence of catalyst, while $NiCe/Al_2O_3$ increased the aromatics. Aldehydes and carboxylic acids (8-10 ppm) were not detected in all bio-oils. When we look at the ^{1}H NMR results of model compounds (Table 4), we see that CeO_2 reduced the total oxygenates and increased aliphatics products in cellulose and protein pyrolysis. Proteins also produced aromatics. Instead, Ce-catalysts did not affect fatty acids pyrolysis, where both non-catalytic and catalytic bio-oils were rich in aliphatics.

GC-MS analysis of the *Thalassiosira weissflogi* and its model compounds bio-oils produced at 500^{o}C was carried out in order to determine the main products.While NMR is able to give a picture of the whole bio-oil composition, the GC-MS technique is limited to the identification of the components with boiling point up to 270°C, which corresponds to the highest temperature used in the GC-MS analysis. The list of the main functionalities identified by GC-MS- from pyrolysis of *Thalassiosira weissflogi* is given in Table 5 (Identified compounds are listed in Table S.7). Represented chemical functionalities are consistent with those detected by ^{1}H NMR. While major compounds were found in all bio-oils, catalysts affected both their number and distribution. Owing to complex nature of pyrolysis bio-oils and bio-oil TGAs, about 80% of the bio-oils compounds were identified by GC-MS, which consistently confirmed the EA, TGA and NMR data. Bio-oils produced from pyrolysis of *Thalassiosira weissflogi* are complex mixture of organic compounds with different molecular structures and molecular weights. These compounds can be divided into several functional groups: aliphatics, monoaromatics, oxygenated compounds, nitrogen containing compounds and their derivatives. As confirmed by proton NMR, majority of the compounds were aliphatics (alkanes and alkenes), which were mainly generated from the conversion of saturated and unsaturated fatty acids in algal cells and protein branches. Bio-oils contained relatively high levels of long-chain alkanes which contribute to the good combustion property. The nitrogen containing compounds in bio-oils, such as indole, nitriles, amines, and amides derived from protein degradation in algal cells. Large amount of ketones were formed from partial decarboxylation and decarbonylation reactions. The main aromatics were phenol, phenol substitutes and benzenes. Phenolics were formed in relatively low amount than other compounds as algae contain no lignin in their structure. The carbon and hydrogen contents of obtained bio-oils were close to conventional fossil fuels but the content of oxygen and nitrogen were still high. Combustion of nitrogen in fuels forms undesirable NOx compounds.

3.5. Pyrolysis mechanism

The ^{1}H NMR analysis (Tables 3 and 4) of *Thalassiosira weissflogi* and model compounds indicate that ceria increased the aliphatics products and decreased oxygenates throught deoxygenation. This trend was supported by EA (Table 2), where carbon and hydrogen content increased and oxygen decreased more in presence of ceria. Also, the elemental analysis and mass balance calculations show that nitrogen decreased in *Thalassiosira weissflogi* and protein bio-oils indicating nitrogen removal in presence of ceria.

To establish the deoxygenation pathways and to find the production pathways of the major compounds in algal bio-oils, gas analysis (MS) of *Thalassiosira weissflogi* and its model compounds (cellulose, egg white powder and palm-jojoba oils mixture) was performed. The GC-MS analysis of the oils was also carried out and correlated to the gas analysis (MS) and ^{1}H NMR analysis to study the pyrolysis reaction mechanism.

Gas (MS) analysis (Fig. 4, a-d) clearly indicates that dehydration and decarboxylation were the main reactions involved in the algae and model compounds deoxygenation in absence of catalyst, while CeO_2 also promoted decarbonylation (Fig. 4-d). Nitrogen was removed as ammonia gas (NH_3) and hydrogen cyanide (HCN). Oxygen from cellulose was eliminated as CO_2 and H_2O. Ceria (CeO_2) increased the dehydration and decarbonylation compared to in absence of catalyst (Fig. 4-a). CeO_2 based catalysts have been investigated for their capacity to catalise ketonisation and aldol condensation of carbonyl compounds in pyrolysis vapour with the oxygen of carboxylic acid is rejected as CO_2 and water. CeO_2 is highly active for this purpose and tolerant to water. The catalytic activity of ceria based materials is due to their facile reduction/oxidation and acid–base properties (Alonso et al., 2010).

GC-MS analysis of cellulose bio-oils (Table 6 and Table S.7) shows levoglucosan (90.4%) as main product, while cellulose was partially re-arranged to smaller compounds in presence of CeO_2 such as isopropyl acetate, 2 (3H)-furanone,2-hydroxy-gamma-butyrolactone and

cyclopentanone. The GC analysis of bio-oil from fatty acids (Fig. 4-b) clearly shows that decarboxylation reactions were enhanced by CeO_2. This is supported by GC-MS results (Table 6 and Table S.8), where less amount of carboxylic acids (from fatty acids) such as palmitic, linoleic and capric acid were detected in presence of ceria. Decarboxylation led to paraffinic compounds, both linear and cyclic and favoured the production of ketones (2-Heptadecanone, 3-Tetradecanone, 2-Nonadecanone). Ceria promoted the decarbonylation and decarboxylation of model protein (egg white powder) and *Thalassiosira weissflogi* during pyrolyis (Fig. 4-c, 4-d). Removal of nitrogen compounds from proteins was favoured in presence of CeO_2 as NH_3 and HCN. Pyrolysis of proteins (Table 6 and Table S.8) produced aromatic compounds such as indole, pyrroles, skatole, phenyl ethanol and phenol. CeO_2 also showed high selectivity towards ketones. Large amount of ketones were formed from the partial decarboxylation and decarbonylation of *Thalassiosira* microalga (57% by GC-MS) and its fatty acids and proteins compounds. CeO_2 showed better cracking because of acid sites and reduced the total amount of aldehydes, which are undesirable due to their poor thermal stability.

4. Conclusion

The catalytic pyrolysis of *Thalassiosira weissflogi* and its three major components in presence of ceria catalysts was studied. Light oxygenates, aromatics and aliphatics were originated from carbohydrates, proteins and lipids components, respectively. Dehydration and decarboxylation were the main reactions involved in deoxygenation, while nitrogen was removed as NH_3 and HCN. CeO_2 increased decarbonylation reactions compared to in absence of catalyst, with production of ketones. Ceria catalysts were able to consistently reduce the N-content in bio-oil to 20-38% of that in the parent material and reduce the formation of coke due to its excellent redox properties and coke oxidation by decarbonylation.

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Figures Captions

Figure 1. Thermogravimetric profile of *Thalassiosira weissflogi* and its derivative analysis.

Figure 2. Energy (daf) distribution in the pyrolysis products.

Figure 3. Nitrogen (N) distribution in the pyrolysis products.

Figure 4. Gas analysis in absence and presence of CeO_2 from the pyrolysis of (a) cellulose, (b) fatty acids, (c) proteins and (d) *Thalassiosira weissflogi*.

Table 1 The results of elemental analysis of the *Thalassiosira weissflogi* bio-oils obtained at 500 ^{o}C.

Elemental analysis [a]	No catalyst	CeO_2	Ce/Al_2O_3	$NiCe/Al_2O_3$	$MgCe/Al_2O_3$
Carbon	67.59	71.46	71.07	70.25	71.47
Hydrogen	8.90	9.30	9.34	9.42	10.21
Nitrogen	7.70	6.96	5.20	5.35	4.24
Oxygen[b]	15.81	12.28	14.39	14.98	14.08
H/C molar ratio	1.58	1.56	1.57	1.60	1.71
O/C molar ratio	0.17	0.12	0.15	0.16	0.14
HHV (MJ/kg)	32.85	35.37	34.92	34.65	36.37

[a] Weight percentage on dry and ash free basis. [b] By difference

Table 2 Elemental analysis, H/C and O/C molar ratios and HHV of model compounds bio-oils obtained at 500 ^{o}C.

Elemental analysis [a]	Cellulose	Cellulose + CeO_2	Egg white powder	Egg white powder+ CeO_2	Palm-jojoba	Palm-jojoba+ CeO_2
Carbon	46.13	46.52	58.20	57.99	74.70	78.52
Hydrogen	5.80	6.39	7.82	7.91	12.28	12.87
Nitrogen	-	-	11.97	10.97	-	-
Oxygen[b]	48.07	47.09	22.01	23.13	13.02	8.61
H/C molar ratio	1.50	1.64	1.61	1.63	1.97	1.96
O/C molar ratio	0.78	0.75	0.28	0.30	0.13	0.08
HHV (MJ/kg)	15.30	16.46	27.00	26.86	40.64	43.58

[a] Weight percentage on dry and ash free basis. [b] By difference

Table 3 ^{1}H NMR Integrations of Thalassiosira weissflogii bio-oils formed at 500 °C versus specific chemical shift ranges. nd: not detected.

Chemical shift region (ppm)	Type of protons	Hydrogen content (% of all hydrogen)				
		No catalyst	CeO_2	Ce/Al_2O_3	$NiCe/Al_2O_3$	$MgCe/Al_2O_3$
0.0 – 1.6	-C**H**$_3$, -C**H**$_2$-	44.77	59.22	54.91	65.44	56.78
1.6 – 2.2	-C**H**$_2$-, aliphatic O**H**	17.05	15.20	14.04	8.35	14.68
2.2 – 3.0	C**H**$_3$OC-, C**H**$_3$-Ar, -C**H**$_2$Ar	19.38	11.47	10.99	4.86	11.85
3.0 – 4.2	C**H**$_3$O-, -C**H**$_2$O-, =C**H**O	8.17	4.88	7.81	4.01	4.90
4.2 – 6.4	=C**H**O, ArO**H**, **H**C=C	3.10	1.38	3.99	5.74	6.15
6.4 – 6.8	**H**C=C (nonconjugated)	0.29	0.73	1.03	1.72	0.68
6.8 – 8.0	Ar**H**, **H**C=C (conjugated)	7.30	7.28	7.20	9.89	4.95
8.0 – 10.0	-C**H**O, -COO**H**, downfield	nd	nd	nd	nd	nd

Table 4 ^{1}H NMR Integrations of Thalassiosira weissflogii and model compounds bio-oils formed at 500 °C versus specific chemical shift ranges.

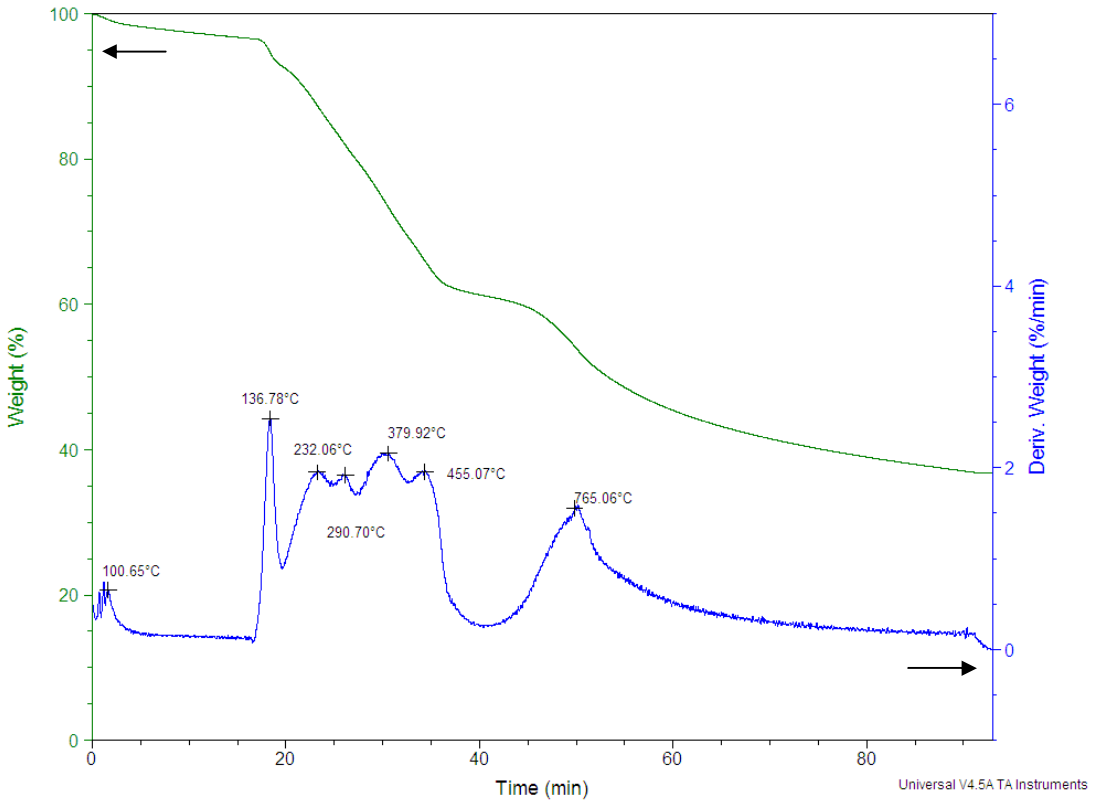
Chemical shift region (ppm)	Type of protons	Hydrogen content (% of all hydrogen)							
		No catalyst	CeO_2	Cellulose	Cellulose + CeO_2	Egg white powder	Egg white powder + CeO_2	Palm-jojoba	Palm-jojoba + CeO_2
0.0 – 1.6	-C**H**$_3$, -C**H**$_2$-	44.77	59.22	5.25	9.19	40.44	46.06	81.78	80.97
1.6 – 2.2	-C**H**$_2$-, aliphatic O**H**	17.05	15.20	6.13	9.31	14.17	12.84	8.86	8.68
2.2 – 3.0	C**H**$_3$OC-, C**H**$_3$-Ar, -C**H**$_2$Ar	19.38	11.47	7.03	8.24	17.89	19.90	4.38	4.55
3.0 – 4.2	C**H**$_3$O-, -C**H**$_2$O-, =C**H**O	8.17	4.88	43.8	43.73	11.59	8.86	0.35	0.90
4.2 – 6.4	=C**H**O, ArO**H**, **H**C=C	3.10	1.38	32.5	25.03	6.45	3.07	4.18	4.48
6.4 – 6.8	**H**C=C (nonconjugated)	0.29	0.73	1.04	0.93	1.46	0.85	0.02	0.02
6.8 – 8.0	Ar**H**, **H**C=C (conjugated)	7.30	7.28	2.65	2.22	7.99	8.43	0.47	0.40
8.0 –	-C**H**O, -COO**H**, downfield	0.00	0.00	1.50	1.35	0.00	0.00	0.00	0.00

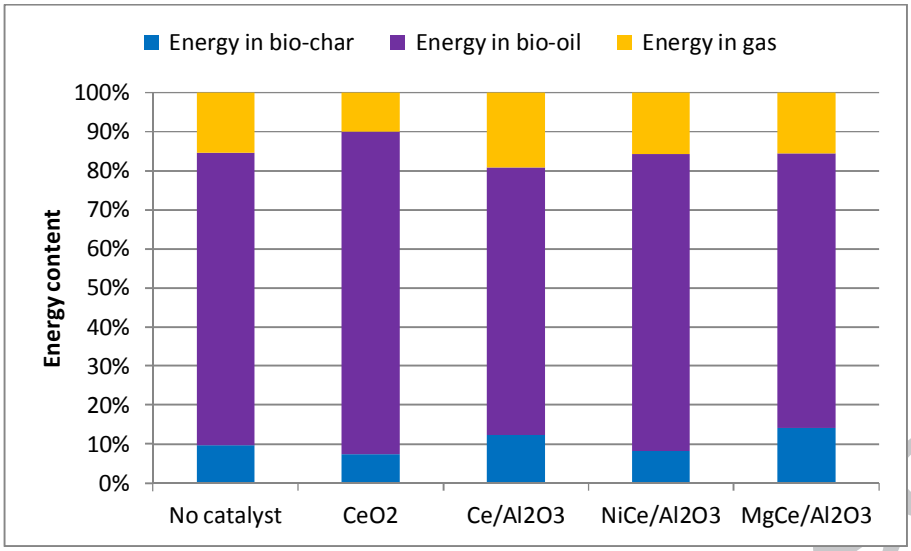
Table 5 GC–MS analysis of bio-oil products of Thalassiosira weissflogii pyrolysis.

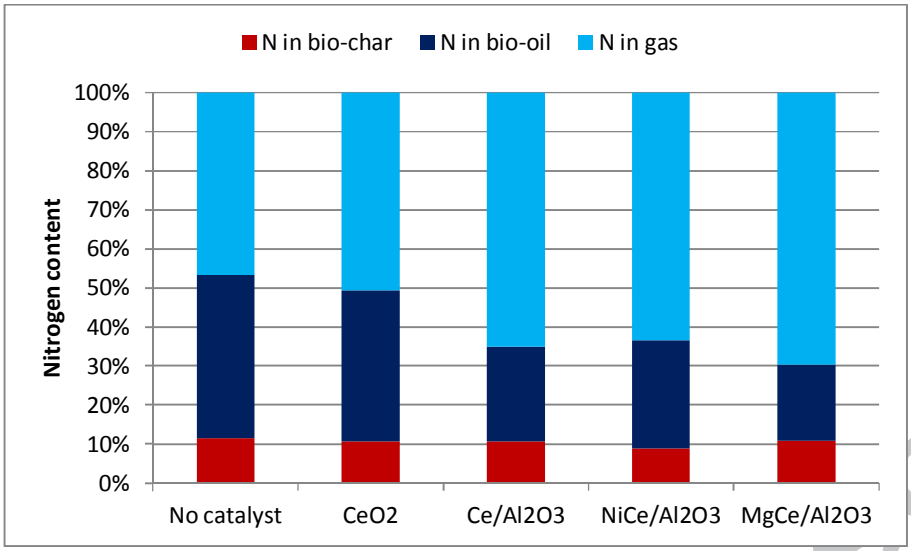
Compounds	**Relative abundance (% area)**				
	No catalyst	***CeO_2***	***Ce/Al_2O_3***	***$Ni\text{-}Ce/Al_2O_3$***	***$Mg\text{-}Ce/Al_2O_3$***
Monoaromatics	5.16	6.38	5.41	7.72	1.05
Aliphatics	27.76	12.10	28.52	49.20	69.70
Alcohols	16.10	4.22	6.53	0	1.1
Aldehydes	7.52	0.22	0	0	0
Ketones	14.57	57.36	18.81	20.26	18.82
Carboxylic acids	0	0	2.86	0	0.88
Esters	0	1.25	0	0	0.69
Ethers	0.54	5.94	11.79	0	0
Nitrogen compounds	12.99	8.11	20.91	15.04	7.68
Total	84.64	95.58	94.83	92.22	99.92

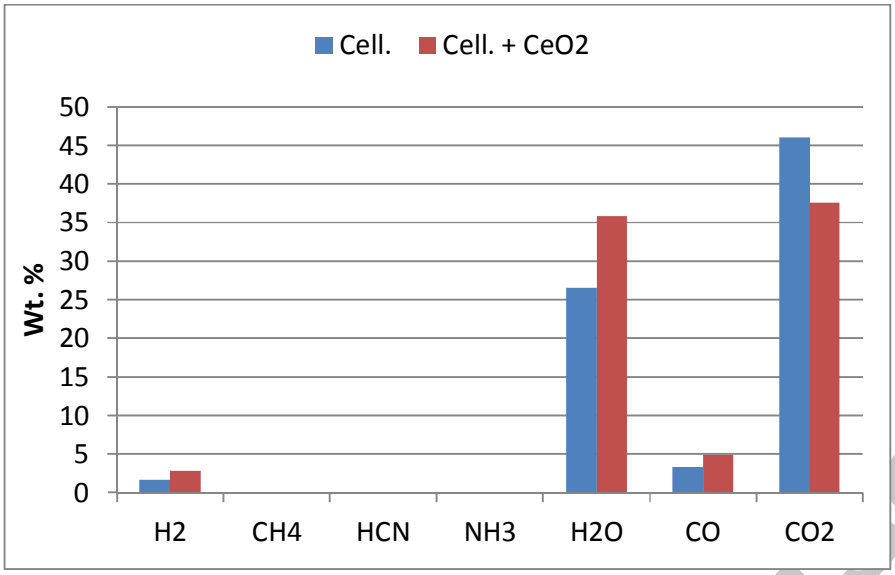
Table 6 GC–MS analysis of bio-oil products of Thalassiosira weissflogii and model compounds pyrolysis.

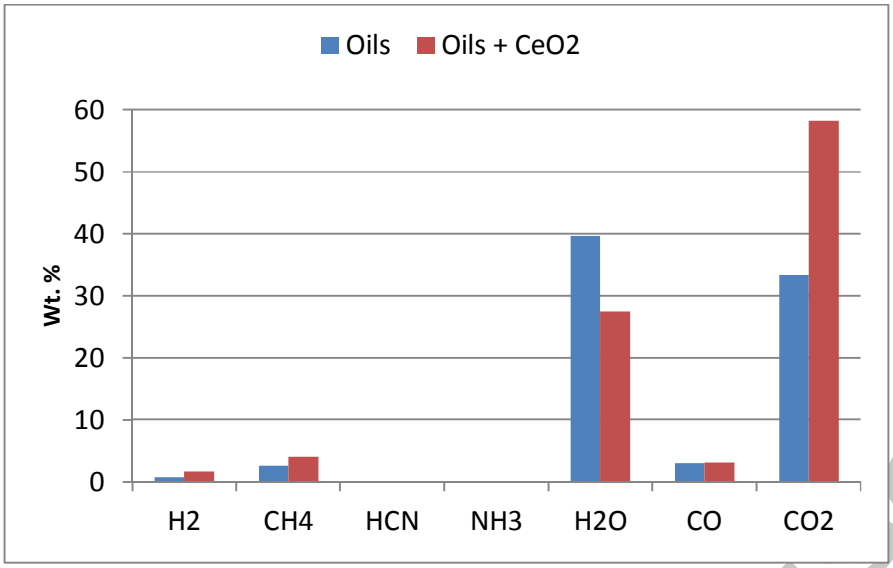
Compounds	**Relative abundance (% area)**							
	No catalyst	**CeO_2**	**Cellulose**	**Cellulose+ CeO_2**	**Palm-jojoba**	**Palm-jojoba+ CeO_2**	**Egg white powder**	**Egg white powder + CeO_2**
Monoaromatics	5.16	6.38	0	0	0	0	12.40	8.34
Aliphatics	27.76	12.10	0	0.55	28.56	36.87	0	5.89
Sugars	0	0	94.67	88.61	0	0	0	0
Alcohols	16.10	4.22	0	2.14	0	0	10.97	8.36
Aldehydes	7.52	0.22	0.30	0.25	0	0	0	0
Ketones	14.57	57.36	5.03	5.92	0.70	13.05	2.35	7.41
Carboxylic acids	0	0	0	0	70.67	49.44	0	0
Esters	0	1.25	0	2.53	0	0.52	2.64	0
Ethers	0.54	5.94	0	0	0	0	0	0
Nitrogen	12.99	8.11	0	0	0	0	44.33	35.34
Total	84.64	95.58	100	100	99.93	99.88	72.69	65.34

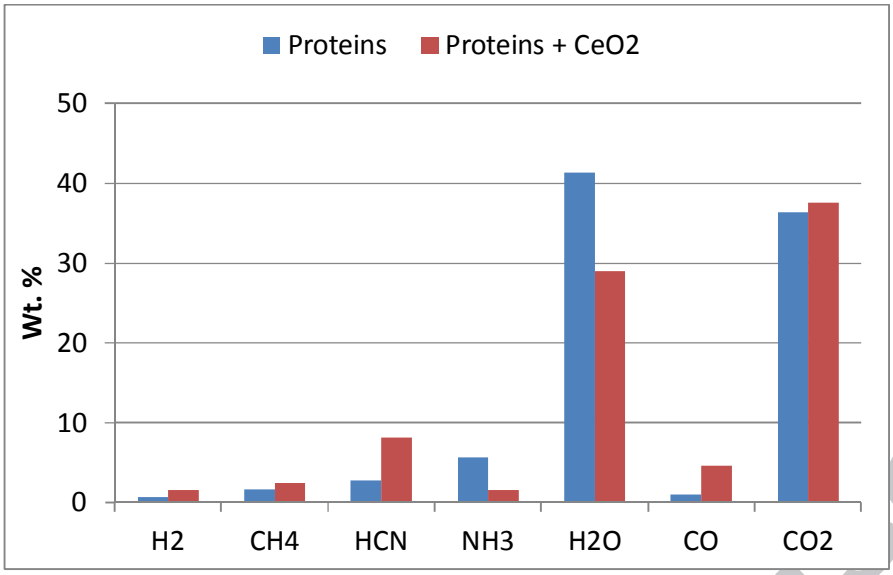


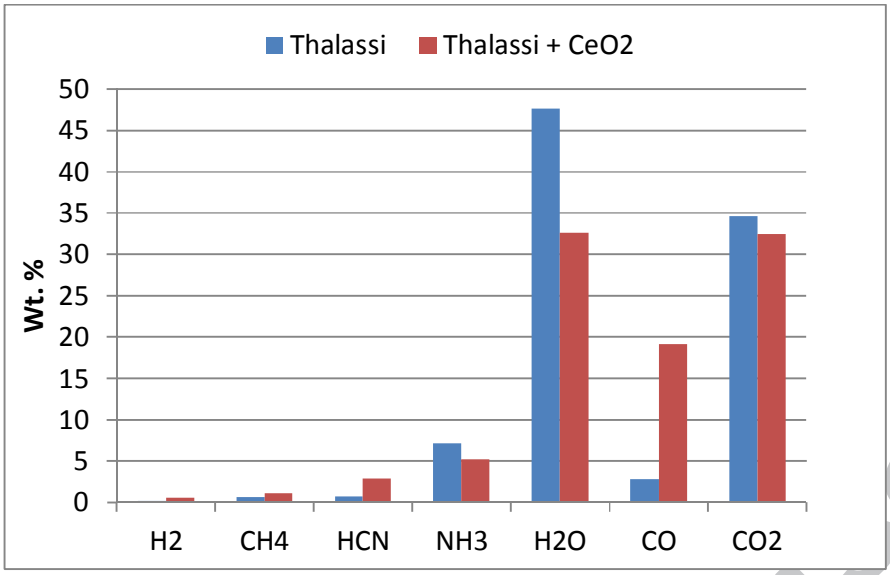












Highlights

- *Thalassiosira weissflogi* and its model compounds were pyrolysed over ceria catalysts
- The highest liquid yield (25.8%) was obtained in presence of CeO_2 at 500^{o}C
- Ceria catalysts increased aliphatics and decreased oxygenate compounds
- Dehydration and decarboxylation were the main deoxygenation reactions
- Ceria catalysts consistently reduced N-content in bio-oil