



Catalytic Hydrothermal Liquefaction of Microalgae using Fe-MCM 41 Catalyst in Presence of Carbon Monoxide

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Among the various types of biomass, microalgae have a potential to become a significant energy source for the production of third generation biofuel. The hydrothermal liquefaction is the direct biomass-to-liquid conversion route carried out in the hot compressed water with or without the presence of a catalyst. In this study, the process pressure and temperature is reduced, but at a lower temperature, bio-oil yield is not high enough to make hydrothermal liquefaction an economical technique. Thus, Fe-MCM 41 catalyst was used to increase the bio-oil yield at low temperatures (250 °C). This catalyst increased the total bio-oil yield from 42.7 to 61.28 % in hydrothermal liquefaction of *Chlorella pyrenoidosa*. The bio-oil yield (%) of oil 1, 2 & 3 were 24.72, 17.08 & 19.48, respectively obtained at 250 °C by using catalyst. Moreover, use of catalyst also resulted in the decrease in oxygen and nitrogen contents of bio-oil and consequently increases in its heating value.

Keywords: Bio-oil, Hydrothermal liquefaction, Fe-catalyst, *Chlorella pyrenoidosa*, Catalytic conversion.

INTRODUCTION

Microalgae plays a key role as a feedstock for bio-oil production and also have drawn a great attention from both research and industrial point of view [1]. Microalgae for biofuel production have several advantages over other types of biomass, including fast growth rate, wastewater treatment, higher lipid content and ability to sequester carbon dioxide from flue gas. Moreover, drying of biomass can increase the production cost of biofuel. In this interact, hydrothermal liquefaction (HTL) has been observed as a stimulating conversion method for biofuels production from microalgae which is carried out without the need of drying the biomass [2,3]. The bio-oil obtained from hydrothermal liquefaction process is known as the alternative for petroleum to produce transportation fuels and extraction of valuable chemicals in the industry [4].

Hydrothermal liquefaction is one of the main processes for bio-oil production in which the reaction of biomass in water at elevated temperature (200-370 °C) and high pressure (2-20 MPa) with or without using a catalyst is done [5]. Hydrothermal

liquefaction does not require dewatering and drying steps and therefore, it is suitable for processing aquatic biomass and this reduces the cost of production of bio-oil. But hydrothermal liquefaction require more expensive and elaborated safety systems with trained manpower [6]. The characteristics of bio-oil can be improved by two methods: one approach is catalytic hydrothermal processing with homogeneous catalysts such as alkali catalysts or organic acids [7-9]; whereas another is heterogeneous catalysts such as alkalis, and metal salts, zeolite or supported metal catalysts [10,11]. Use of catalysts in hydrothermal liquefaction process can increase the bio-oil yield of microalgae [7-9]. Biller *et al.* [10] confirmed heterogeneous catalysts in hydrothermal liquefaction process (Co/Mo, Ni/Al and Pt/Al) and concluded that the heterogeneous catalysts results in the higher heating value and the level of de-oxygenation, with improved bio-oil yields. Heterogeneous catalysts attained also significant in de-nitrogenation levels in bio-oil [11].

MCM-41 was used in catalytic hydrothermal liquefaction (HTL) of *Dunaliella tertiolecta* for the production of bio-oil [12]. Moreover, Fe₂O₃/MCM-41 magnetic catalyst was synthe-

sized in a facile, reproducible route and used for hydrothermal liquefaction of microalgae along with deoxygenation upgrading of derived bio-oil in absence of hydrogen [13]. Metal-substituted MCM-41 has highest possibility for oil with less oxygen and nitrogen content compared to other catalyst. Moreover, carbon monoxide (CO) is a better process gas for catalytic hydrothermal liquefaction, whereas H₂ is found to be better process gas for non-catalytic hydrothermal liquefaction [14]. Different catalysts were used for hydrothermal liquefaction of *Chlorella pyrenoidosa* as reviewed in Table-1.

TABLE-1
BIO-OIL YIELD FROM DIFFERENT REACTIONS

Temp. (°C)	Time (min)	Yield (%)	Catalyst	Ref.
280	120	39.4	No cat	[15]
240-280	30	52.0	NaOH	[16]
300	20	50.0	Ce/HZSM	[17]

EXPERIMENTAL

Microalgae: The microalgae species *Chlorella pyrenoidosa* was purchased from National Collection of Industrial Microorganisms (NCIM), National Chemical Laboratory (NCL) Pune, India. *Chlorella pyrenoidosa* was selected in this research because of its high lipid content, high growth rate, and the ability to grow in fresh water as well as in wastewater. *Chlorella pyrenoidosa* was one of the best oil producer microalgae, with the total lipid content of 51 % of dry biomass [18]. The proximate and ultimate analysis of *Chlorella pyrenoidosa* is listed in Table-2. The proximate analysis was carried out by the ASTM D3172-13 and Ultimate analysis (CHNSO) was determined by a Flash 2000 CHNS/O Organic Elemental Analyser (Thermo Scientific). Higher heating value (HHV) of microalgae, solid residue and bio-oil was calculated by using Dulong's formula (eqn. 1) [19].

$$\text{HHV (MJ/kg)} = 0.338C + 1.428\left(H - \frac{O}{8}\right) + 0.95S \quad (1)$$

TABLE-2
CHARACTERISTICS OF MICROALGAE *Chlorella pyrenoidosa*

Weight % (on air dried basis)					
Moisture content	Volatile matter	Ash content	Fixed carbon		
3.1	80.5	3.7	12.7		
Elemental composition (on dry basis) in wt %					
Carbon	Hydrogen	Nitrogen	Sulphur	Oxygen	HHV (MJ/Kg)
51.91	11.18	8.79	0	27.52	37.53

Catalyst: Fe-MCM 41 was employed as a catalyst in this research. MCM-41 is a favourable catalyst support in liquid phase reactions because of its well-defined mesoporous structure in combination with a high surface area [14,20]. The introduction of microporous catalysts like MCM-22, HZSM-22, HZSM-5, H beta and SAPO-11 with high hydrothermal stability improve the bio-oil quality as well as accelerate the rate of hydrothermal reaction. Fe-MCM-41 was synthesized and characterized by FT-IR spectrometer.

Sodium meta-silicate (28.42 g) was dissolved in 50 mL of distilled water taken in a polypropylene bottle and stirred

for 30 min. Then 0.202 g of ferric nitrate (initial gel Si/Fe ratio = 198) which were dissolved in 10 mL distilled water, were added dropwise to the mixture and kept for stirring for 1 h. Sulphuric acid (80 mL, 2N) were added drop wise to maintain the pH of the solution around 10-11 kept for 2 h stirring which becomes the solution into gel form. Further, 6.728 g of cetyltrimethyl ammonium bromide dissolved in 20 mL distilled water were added drop wise to gel and kept for 2 h stirring. Then the solution was transferred into autoclave and kept at 150 °C for 48 h in hot air oven. After 48 h, the autoclave was allowed to cool naturally. The solution was filtered and washed with distilled water till the pH becomes 10. The samples were dried at 110 °C for 4 h in hot air oven. The calcination process was done at 550 °C for 6 h.

FT-IR spectra were recorded in air at room temperature on a Perkin Elmer MB104 spectrometer in KBr pellets. The FT-IR spectrum (Fig. 1) of MCM-41 shows the stretching vibrating absorption peaks of O-H band in the surfaced hydroxyl consists of a band of terminal silanol groups and in the planar water is seen at 3440 cm⁻¹. The symmetry and asymmetry flexural vibrating peaks of Si-O-Si at 1,180, 812 and 464 cm⁻¹, respectively, are related to the framework of silicon [21].

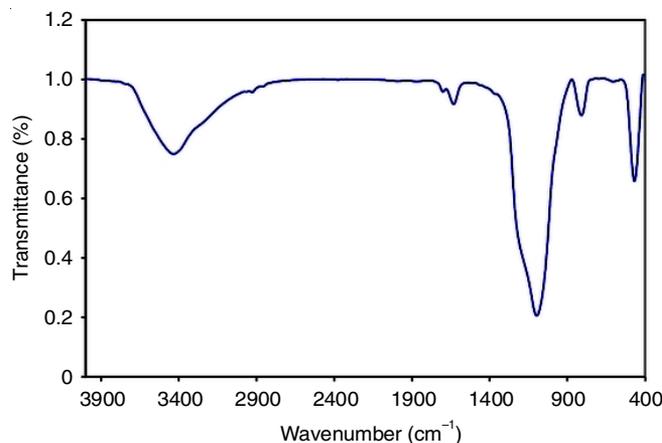


Fig. 1. FTIR spectra of Fe-MCM-41

Hydrothermal liquefaction reactor: The hydrothermal liquefaction was carried out in a micro reactor of 100 mL stainless steel high temperature pressure reactor (BR 100 Berghof) with a magnetic stirrer. The flow diagram of the reactor with tubing and high pressure gas regulator is shown in Fig. 2. The reactor was heated by an external electrical furnace and the temperature was measured by a thermocouple and controlled within ± 10 °C.

Experimental procedure: The hydrothermal liquefaction experiment was carried out in reactor of a volume of 100 mL stainless steel high temperature pressure reactor. Earlier to the reaction, 70 % of volume of reactor was filled with a microalgae-water mixture (mass ratio 1:10) and 1 g of catalyst. Thereafter, the reactor was flushed with nitrogen to eliminate the air present inside. Following this, reactor was loaded with an initial pressure of 45 bar of carbon monoxide to ensure that enough pressure was provided to the system to maintain water in a liquid state throughout the heating process and the reaction. The reactor were then tightly closed and placed in a magnetic stirrer with heating

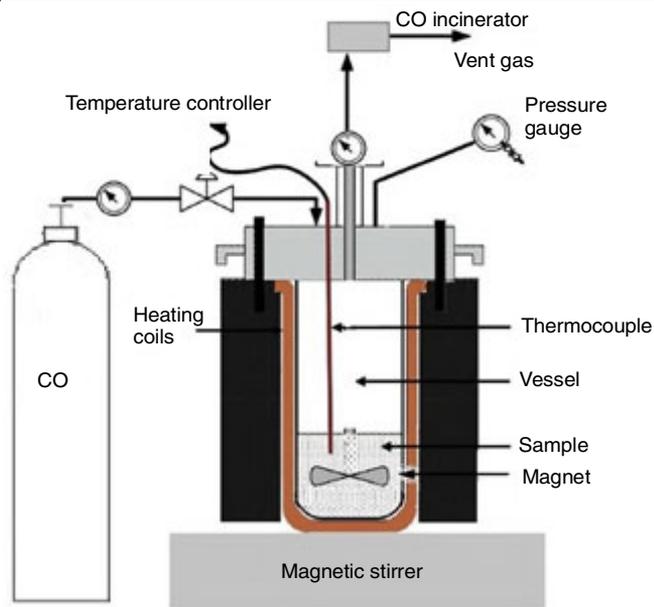


Fig. 2. Flow diagram of high temperature pressure reactor

coils connected with temperature controller, which allowed an easy control of the temperature. Reactants were agitated by magnetic stirring at 1400 rpm. The reaction was carried out at 250 °C and pressure of 90 bars during 0.5 h. The reaction time started once the content inside the reactor attained the desired 250 °C (measured by a thermocouple). The preceding heating took around 25 min, which corresponded to a heating rate of 10 °C min⁻¹. This experiment was carried out twice to assess the reproducibility of the data.

After 0.5 h, the reactor was kept for cooling to room temperature. Once the reactor was cooled to room temperature, carbon monoxide was removed from the reactor with the help of vent pipe through CO incinerator. The remaining hydrothermal liquefaction products (biocrude oil, aqueous phase and solid residue) were thereafter recovered from the interior of the reactor.

The product mixture and aqueous slurry was separated into oil 1 (ether extract), oil 2 (ethyl acetate extract), oil 3 (acetone extract of solid) and residue, by following the procedure reported by Karagoz *et al.* [22]. As the present study involves water insoluble catalyst unlike Karagoz *et al.* [22], residue included the spent catalyst and hence the residue was burnt at 500 °C for 30 min to get the ash content and then yield of solid residue (SR) was obtained by subtracting the ash content from the residue. The % yields of bio-oils, % conversion, % yield of solid residue and % biomass conversion to bio-oil, were calculated as per the following equations:

$$\text{Yield of oil 1 (\%)} = \frac{\text{Weight of oil 1}}{\text{Mass of dried microalgae (g)}} \times 100 \quad (2)$$

$$\text{Yield of oil 2 (\%)} = \frac{\text{Weight of oil 2}}{\text{Mass of dried microalgae (g)}} \times 100 \quad (3)$$

$$\text{Yield of oil 3 (\%)} = \frac{\text{Weight of oil 3}}{\text{Mass of dried microalgae (g)}} \times 100 \quad (4)$$

$$\text{Yield of oil SR (\%)} = \frac{\text{Weight of oil SR}}{\text{Mass of dried microalgae (g)}} \times 100 \quad (5)$$

$$\text{Yield of total oil (\%)} = \frac{\text{Weight of oil (1 + 2 + 3)}}{\text{Mass of dried microalgae (g)}} \times 100 \quad (6)$$

$$\text{Conversion (\%)} = 100 - \% \text{ Yield of SR} \quad (7)$$

Catalyst recovery: After the hydrothermal liquefaction process, it is necessary to recover the catalyst especially if the catalyst is costly. In this work, recovery of Fe-MCM41 catalyst from the solid residue was conducted. Solid residue is one of the products in hydrothermal liquefaction process of the microalgae. Since this hydrothermal liquefaction experiment is conducted at low temperatures, there is a possibility that the solid residue still contains hydrocarbons. After extracting oil 3 from solid residue, the solid residue was burnt for the process of catalyst recovery. After burning the solid residue, solid catalysts were retained, catalyst particles can be separated and recovered from the ash.

The reaction runs were performed in duplicates for with and without catalyst to ensure the repeatability of the results. The maximum deviation between the yields of products obtained in the duplicate runs was within 3 %, and the values reported are the average of these.

RESULTS AND DISCUSSION

Bio-oil yield: The bio-oil yield is basically the mass of bio-oil divided by the mass of dried algae (eqn. 2). Fig. 3 shows the bio-oil yields oil 1, oil 2 and oil 3 at 250 °C with Fe-MCM 41 catalyst as well as the blank experiment where no catalyst was applied. For blank experiment, bio-oil yields of oil 1, oil 2 and oil 3 were 16.8, 11.3 and 14.6 %, respectively. The yield of oil 1 was found to be more as compare to oil 3 and oil 2. The same trend was found in the catalytic experiment where a bio-oil yield of oil 1 was more as compare to oil 3 and oil 2 as shown in Fig. 3. For the catalytic experiment, bio-oil yields of oil 1, oil 2 and oil 3 were 24.72, 17.08 and 19.48 %, respectively.

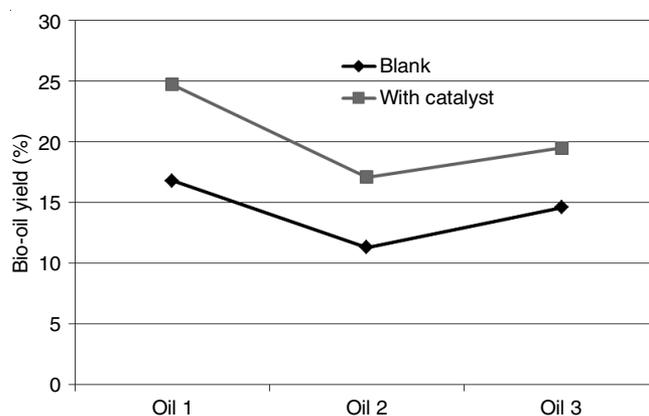


Fig. 3. Bio-oil yields with and without catalyst

Previous works on the hydrothermal liquefaction of *Chlorella pyrenoidosa* have shown that the catalysts can generally increase the bio-oil yield as summarized in Table-1. However, the bio-oil yield in the catalytic experiment was found to be more than that of the blank or non-catalytic experiment at 250 °C [10].

Elemental composition and high heating value of bio-oils: The ultimate analysis, atomic ratios and high heating value of bio-oil produced at 250 °C without using catalyst and with

TABLE-3
ELEMENTAL COMPOSITION AND HIGH HEATING VALUE OF THE BIO-OIL (WITH AND WITHOUT CATALYST)

Bio-oil	Without catalyst						With catalyst (Fe-MCM 41)					
	Weight of bio-oil (g)	Elemental composition (%)				HHV (MJ/Kg)	Weight of bio-oil (g)	Elemental composition (%)				HHV (MJ/Kg)
		N	C	H	O			N	C	H	O	
Oil 1	0.4050	1.30	55.30	25.03	18.37	51.20	0.618	0.41	62.71	27.59	9.29	58.99
Oil 2	0.3110	2.31	51.90	23.02	22.77	46.39	0.427	0.74	61.23	26.25	11.78	56.13
Oil 3	0.3515	1.22	48.31	27.05	23.42	50.81	0.487	0.59	57.43	29.32	12.66	59.07

catalyst (Fe-MCM 41) are listed in Table-3. The carbon and hydrogen content of all three bio-oils from catalytic hydrothermal liquefaction were more than those of the reaction without catalyst. The oxygen and nitrogen contents of bio-oil from the catalytic hydrothermal liquefaction were less than reaction without catalyst or blank experiment [23,24]. The heating value of the bio-oil was in the range of 56.13 to 59.07 MJ/Kg which was higher than that of the blank experiment (46.39 to 51.20 MJ/Kg) as a result of a lower oxygen content.

Percentage conversion: From the hydrothermal liquefaction of *Chlorella pyrenoidosa*, the total yield of bio-oil was found to be 1.07 g in blank reaction and 1.53 g in reaction with catalyst. The production of oil 2 was low in both the reactions as compared to oil 1 from run 3. The remaining portion of oil products (oil 3) was obtained from the acetone extraction of the solid residue. The weight of solid residue of 1.25 g in blank reaction and 0.79 g in reaction with catalyst was obtained. This is due to the increase in bio-oils yield with the influence of catalyst [22]. The solid residue was calcination at 550 °C for 6 h for the recovery of catalyst. In this reaction, 55 % of the catalyst was recovered from solid residue. The decrease of percentage yield of solid residue was achieved from 50 % in blank to 31.6 % with catalyst at 250 °C for 0.5 h. This increased the percentage conversion from 50 % to 68.4 % with the used of Fe-MCM 41 catalyst [25].

Conclusion

In this article, the catalytic hydrothermal liquefaction of *Chlorella pyrenoidosa* was carried out at 250 °C. Fe-MCM 41 catalyst was used to investigate its effects on the bio-oil yield and its composition. The major result of this work was higher bio-oil yields and biomass conversion to bio-oil with less percentage of oxygen. The bio-oil yield was found to be increased by adding Fe-MCM 41 catalyst *Chlorella pyrenoidosa*. Fe-MCM 41 catalyst was also recovered from the solid residue. The trend of bio-oil yield was found to be oil 1 > oil 3 > oil 2. This trend of bio-oil yield was same in both hydrothermal liquefaction of *Chlorella pyrenoidosa* with Fe-MCM 41 catalyst and without catalyst. The highest total bio-oil yield of 61.28 % was obtained at 250 °C by using Fe-MCM 41 catalyst, whereas total bio-oil yield of 42.7 % was obtained at 250 °C without catalyst.

For the catalytic experiment, oxygen and nitrogen contents of bio-oil for all types of oil were less than that of without catalyst experiment. The heating value was higher for all bio-oil produced by the catalytic hydrothermal liquefaction. The output of this research represent that using Fe-MCM-41 catalyst can increase the bio-oil yield at low temperatures by decreasing

its oxygen and nitrogen contents which makes the possibility for commercialization of hydrothermal liquefaction at low temperature and pressure.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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