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ORIGINAL ARTICLE

Holistic utilization of *Chlorella pyrenoidosa* microalgae for extraction of renewable fuels and value-added biochar through in situ transesterification and pyrolysis reaction process

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Abstract

Present study deals with a holistic approach to bioenergy production from a single-celled green algae *Chlorella pyrenoidosa* aiming to valorise all biomass components. In the first phase, the microalgae biomass was used to produce biodiesel in a microwave-assisted biodiesel reactor by in situ transesterification process. The biomass residue left after biodiesel production was pyrolyzed in a fixed bed pyrolysis reactor at various isothermal temperatures (400, 450, 500, 550, and 600°C) in second phase. The pyrolysis reaction results revealed that the highest bio-oil yield was 35.33 wt% along with 51.23 wt% biochar and 13.44 wt% pyrolysis gas at 500 °C. FTIR and GC–MS analyses of bio-oil confirm the existence of hydrocarbons as well as oxygenated chemicals like esters, phenols, and acid derivatives. Furthermore, the fuel properties of bio-oil as well as biodiesel e.g. viscosity, density, calorific value, flash point, and pour point were determined using standard procedures (ASTM D6751–02, EN–14214, and IS) and confirmed to be appropriate for stationary engine application. On the other hand, the biochar characterisation showed that it holds good potential for usage as a biocoal in industrial boilers/power plants or cooking stoves. Hence, this study demonstrates the utilization of *Chlorella pyrenoidosa* microalgae for production of eco-friendly renewable fuels as well as a wide range of value-added co-products with a zero-waste biorefinery approach.

Keywords *Chlorella pyrenoidosa* · Biodiesel · Pyrolysis · Bio-oil · Biochar · Pyrolysis gases

1 Introduction

Today's era of industrialization, urbanization, and modernization led to the exploitation of fossil fuels to a greater extent. Fossil fuels are not sustainable, and they can lead to financial insecurity as well as environmental and ecological issues. The combustion of fossil fuels resulted in the release of greenhouse gases (GHG), which has adverse effects on the environment and leads to global warming [1, 2]. In recent years, a major research focus was to develop renewable sources of energy to overcome problems like overexploitation of fossil fuels, air and water pollution, global warming, and acid rains [3, 4]. According to the 2021 report on renewables' global status, renewable energy accounts for 19.3% of worldwide energy demand and makes a significant contribution to GHG emission reduction [5]. Among the several renewable energy sources, biofuels showed a great potential to reduce carbon emissions as well as to meet the current demands of energy [6–8]. Recently, microalgae-based biofuels are gaining more interest, as they are a natural bioresource pool that produces lipids, carbohydrates, proteins, and value-added biominerals depending upon culture conditions. In addition, microalgae can be grown throughout the year while terrestrial plants are seasonal crops and can be harvested once annually [9–11].

Highlights

- Renewable fuels were generated from microalgae by transesterification and pyrolysis pathways.
- In situ transesterification of CP resulted in 19.84% biodiesel yield.
- Pyrolysis of CPMR yields 35.33 wt%, 51.23 wt% biochar, and 13.44 wt% syngas at 500 °C.
- One hundred kilograms of CP biomass can be converted into 15.47 kg biodiesel, 29.67 kg bio-oil, and 43.03 kg biochar.
- Blends of diesel, biodiesel, and bio-oil showed good potential for CI engine application.

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Microalgae being rich in lipids, carbohydrates, and proteins can be converted into biofuels such as biodiesel/bioethanol (biochemical route) or syngas/bio-oil (thermochemical route) and other valuable products such as polyunsaturated fatty acid (PUFA) protein and vitamins [2, 12–14]. In recent decades, a number of investigations have been conducted on biodiesel production from microalgae [15–20]. However, the microalgae biodiesel production process faces many challenges such as high production cost and time consumption [21, 22]. These challenges can be addressed through microwave-assisted in situ transesterification that takes place simultaneously [22]. Microalgae have a rigid cell wall and do not allow releasing of lipids from the cell easily. The employment of microwave-assisted technology in the biodiesel synthesis process may achieve significant improvements in terms of reaction time and product yield, allowing for full utilization of the oil in biomass [9, 23, 24]. Microwave heating, unlike traditional heating methods, transfers the energy to reactants directly from the inside to the outside, resulting in strong microwave hot spots. As a result, the activation energy necessary for the transition state of biodiesel production is overcome, and the reaction rate process is accelerated [10, 24, 25]. Hence, this research deals with the microwave-assisted in situ transesterification technology used to combine oil extraction and biodiesel production, which not only broke the cell wall to release lipids, but also strengthened the transesterification process to improve the reaction rate, reducing the production process cost and time. On the other hand, the biodiesel-extracted microalgae biomass (de-oil cake) is also an excellent feedstock for further energy recovery [26, 27] which can be reused as a hydrogen-rich feedstock for bio-oil and syngas production [28, 29] via pyrolysis or biogas production via anaerobic digestion [30, 31] and play a big role in the establishment of economic biorefinery. Nonetheless, the defatted microalgae leftovers, which are mostly made up of protein and carbohydrates, have considerable biofuel potential that has yet to be fully explored. Recent reports showed that the pyrolysis of lipid-extracted microalgae de-oiled cake could be a good choice for solid, liquid, and gaseous biofuels production to improve biodiesel economics [28, 32]. Hence, aiming to improve the economics of microalgae biodiesel production, holistic use of whole biomass is necessary. For example, despite the excellent results potential of *Chlorella pyrenoidos*a as oleaginous microalgae [33], to the best of our knowledge, there is no study available examining its application in the recommended cascade process. Therefore, to fill this gap in the literature, this study focuses to develop a process for the holistic conversion *C. pyrenoidosa* microalgae biomass (CPM) to a range of green fuels, by converting the lipids to biodiesel and subsequent using the microalgae de-oiled cake to generate additional liquid, and gaseous fuels via pyrolysis. The main aim of this study was to extract the maximum amount of energy from microalgae biomass through a zero-waste production approach. In addition, fuel properties of ternary blends of diesel, biodiesel, and bio-oil were also examined for diesel engine application. The results of this research could help in the establishment of an integrated low-cost biorefinery strategy for sustainable fuel production.

2 Material and methods

2.1 Raw materials

In the present study, the green algae was cultivated outdoors in a 20L plastic bottle type photo-bioreactor using BG-11 and fertilizer nutrient media [24]. To harvest microalgae biomass, alum was used as a flocculation agent (Sharma, Sahoo et al. 2016)and followed by filtration through a muslin cloth. Harvested biomass was washed with distilled water 4–5 times to remove any contamination. After that, it was dried in a hot air oven at 60 °C for 24 h. The dried biomass was used to produce biodiesel through in situ microwave transesterification.

2.2 *Production of biodiesel through* in situ *transesterification*

The experiment was performed by using a three-neck flask (250 ml) equipped with a reflux condenser in a microwave reactor (Ragatech, Pune, India) capable of controlling temperature and power functions. To conduct the experiment, 5 g of dried microalgae biomass was added to a premixed homogenous solution of methanol, hexane, and potassium hydroxide in the three-neck flask and mixed with a magnetic stirrer under constant speed. The mixture was then subjected to fixed microwave irradiation. Experiments were conducted using the following conditions: temperature, 50–65 °C; catalyst concentration (KOH), 1–5% (w/w_{biomass}); microwave radiation, 400–800 W; and algae to methanol ratio (w/v), 1:2–1:10. The amount of co-solvent (hexane) was fixed at 100 ml in each experiment. After completion of the reaction, the liquid phase (organic phase) is separated from the solid algae biomass phase through vacuum filtration and the residual algae biomass was washed several times using hexane and saturated NaCl solution. The organic phase was separated using a centrifuge. Afterward, the organic phase (biodiesel + hexane) underwent vacuum distillation and pure biodiesel was collected in a borosilicate bottle [2, 9, 34]. All the experiments were repeated three times. All data were expressed as mean ± standard deviation (SD). After each experiment, the microwave reactor was cooled down to normal conditions. Biodiesel conversion yield was determined by dividing the weight of obtained FAME (fatty acid methyl ester) by the weight of total lipid in the microalgae sample.

To analyse the total FAME in microalgae biomass, lipids were extracted from *C. pyrenoidosa* cells by using chloroform:methanol:water (1:2:0.8; *v/v/v*) and microwave treatment method [24]. The yield of extracted lipid was 16.38 wt%. The extracted lipids were transesterified with 10 ml of methanol and 300 µl sulphuric acid in a microwave reactor for 10 min. After completion of the reaction, biodiesel was mixed with slightly hot water and n-hexane. The mixture was vortexed and centrifuged at 5000 rpm for 5 min. The hexane layer was carefully separated and collected in a borosilicate bottle. The process is repeated 4–5 times. Now, hexane is removed from biodiesel using the distillation method and collected in a vial [24]. FAME conversion and yield was calculated with the help of Eqs. 1 and 2 [35].

$$\mathbf{FAME_s\,Yield(Biodiesel\ Yield)} = \frac{\mathbf{Total\ weight\ of\ FAME_s\ (g)}}{\mathbf{Total\ weight\ of\ biomass\ (g)}} \times 100 \tag{1}$$

$$\mathbf{FAME_s\,Conversion(Biodiesel\ Conversion)} = \frac{\mathbf{Total\ weight\ of\ FAME_s\ (g)}}{\mathbf{Total\ weight\ of\ algaelipid\ (g)}} \times 100 \tag{2}$$

A gas chromatograph (Nucon 5700 series) with a flame ionisation detector (FID) and a capillary column (EOX column) with dimensions of 30 m length, 0.25 mm ID, and 0.25 m stationary phase was used to determine the FAME content of microalgae biodiesel. Hydrogen and pure nitrogen (99.999%) were used as fuel and carrier gas respectively. The following conditions were used to run GC: the oven was preheated to 160 °C for 2 min, then increased to 240 °C at a rate of 4 °C/min for 40 min. The injector was set to 240 °C, and the FID detector was set to 240 °C. Supelco 37 component FAME mixture was used as standard (Sigma-Aldrich, USA). Fuel properties of *C. pyrenoidosa* microalgae biodiesel were analysed according to the ASTM standard methods [24].

2.3 Pyrolysis of microalgae de-oiled cake for biofuel production

C. pyrenoidosa microalgae residue (CPMR) obtained after in situ transesterification was washed many times with distilled water and dried under sunlight for 2 days prior to pyrolysis trials. The pyrolysis experiments were conducted in a stainless steel fixed bed reactor having dimensions of 45 cm in length and 6 cm in internal diameter. To collect the volatiles released from the pyrolysis reaction and make them condense, the reactor was equipped with condensers in series with water cooling jackets.

The pyrolysis experiments were performed at different temperatures (400, 450, 500, 550, and 600 °C) with a heating rate of 10 °C min^{-1}. *C. pyrenoidosa* residue microalgae biomass (50 g) was fed into the pyrolysis reactor, in which nitrogen was purged to make an inert atmosphere. The product yield of bio-oil and biochar was determined on a weight basis while pyrolysis gases yield was computed by difference from 100 wt%. Each experiment was carried out twice and the average values reported here are within the standard deviation of ± 1.0%. The production methodology of CP microalgae biomass to biofuels is shown in Fig. 1.

2.4 Microalgae and product analysis

2.4.1 Proximate and ultimate analysis

The moisture content, volatile matter, and ash content of solid CPMR and biochar were determined using the ASTM D3172-07a method, whereas fixed carbon was computed using the difference from 100 wt% [36, 37]. The element composition of CPMR biomass and bioproducts was determined with a Thermo Flash 2000 CHNS/O elemental analyser calibrated with 2,5-bis(5-tert-butyl-benzoxazol-2-yl) thiophene (BBOT) as a standard.

2.4.2 Thermogravimetric analysis (TGA) analysis

TGA analysis of CPM, CPMR biomass, and reaction products was performed using an EXSTAR TG/DTA 6300 thermogravimetric analyser in an inert atmosphere (nitrogen) with a temperature range of ambient temperature to 950 °C with a 10 °C min^{-1} heating rate.

2.4.3 Fourier transform infrared (FTIR) analysis

FTIR spectrometer (PerkinElmer, Waltham, MA, USA) was used for FTIR analysis of CPM, CPMR, and bio-oil in the frequency range of 400–4000 cm^{-1} with the resolution of 8 cm^{-1} using potassium bromide (KBr) pellet method.

2.4.4 Gas chromatography–mass spectrometry (GC–MS) analysis

To analyse the chemical composition of bio-oil, a GC–MS (PerkinElmer) equipped with a DB-5 MS column (30 m in length and 0.25 mm in diameter) and a FID detector was used. During the analysis, the oven temperature was kept at 75 °C for 5 min, then increased to 300 °C at a rate of 10 °C min^{-1} and held for 25 min. At a flow rate of 1.5 ml min^{-1}, helium was used as the carrier gas. The mass spectrometer functioned at 240 °C with a 200 °C ion

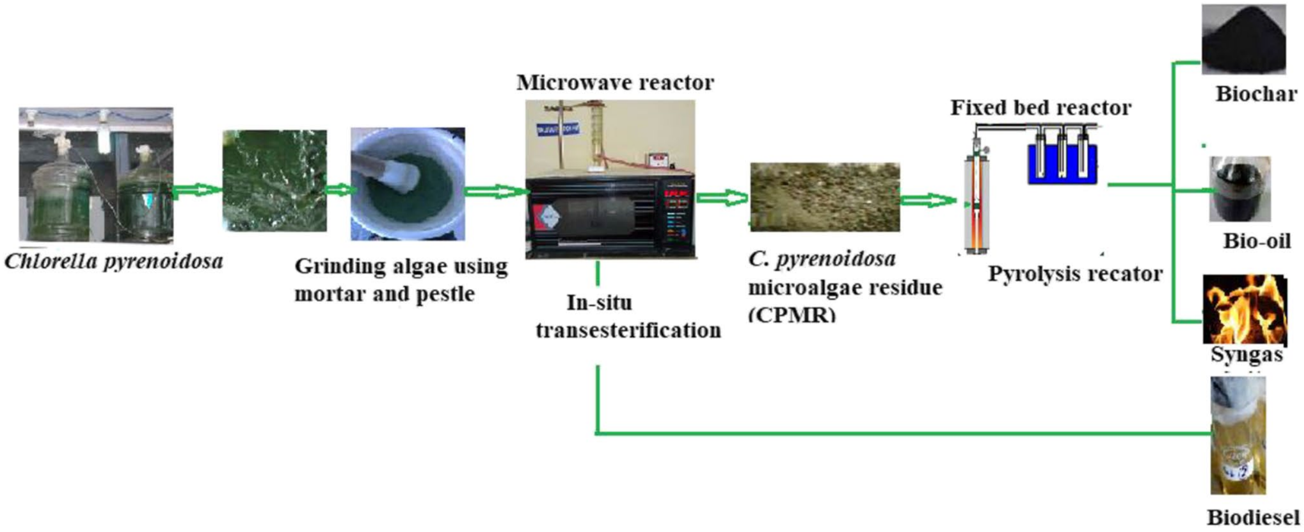

Fig. 1 Production of renewable fuels from microalgae *Chlorella pyrenoidosa*

source with a range of 40–1000 m/*z*. The compounds were identified with the help of the NIST 11 library.

2.4.5 Gas analysis of pyrolysis gases

A NUCON 5700-series gas chromatography (Nucon Engineers, Mumbai, India) fitted with a thermal conductivity detector was used to analyse the non-condensable gases (pyrolysis gases). To separate the gases for analysis, a Porapak Q column (0.32 cm in diameter and 24.37 cm in length) and a molecular sieve 5A, 60/80 mesh (0.32 cm in diameter and 24.37 cm in length), were employed in series. Argon was employed as a carrier gas. The oven and detector temperatures were kept at 60 °C and 90 °C, respectively, throughout the analysis. A typical gas mixture of pyrolysis gases (CO, CO_2, CH_4, N_2, and H_2) was used to calibrate the GC.

3 Results and discussion

3.1 *Process optimisation of* in situ *biodiesel production from C. pyrenoidosa microalgae biomass*

The in situ transesterification of *C. pyrenoidosa* microalgae biomass was carried out using methanol as solvent, hexane as co-solvent, and KOH as a catalyst in a microwave reactor under different reaction conditions. The effects of reaction temperature, algae to methanol ratio, catalyst concentration, time, and microwave radiation on biodiesel conversion yield are shown in Fig. 2. As shown in Fig. 2a, when the temperatures is increased from 50 to 65 °C keeping other parameters constant (catalyst 1%, algae to methanol 1:2, microwave radiation 500 W, and reaction time 3 min), the biodiesel yield was increased from 57.3 to 70.3%. This may be due to the reason that higher temperature supports both lipid extraction and transesterification reactions. High temperatures can cause the creation of microzones known as “hot spots”, which can accelerate the rate of chemical reactions. On the other hand, microwaves increased the extractive properties of methanol by increasing the temperature and thermal effect, allowing more lipids in the biomass to be extracted via diffusive extraction, while the extended microwave effect caused the oils to be forced out of the cell walls and into the solvent mixture via disruptive extraction. Therefore, with increasing temperature, biodiesel conversion yield also increases [24, 38]. Furthermore, raising the reaction temperature above the boiling point of the solvents causes a high number of bubbles to develop, which inhibits the reaction at the three-phase interface of oil, methanol, and catalyst. In addition, when the biomass to methanol ratio increased from 1:2 to 1:6 (*w/v*), the biodiesel was found to be increased from 71.45 to 74.85% whereas a further increase in the algae to methanol ratio had only a detrimental effect (Fig. 2b). Lower algal biomass-to-methanol ratios are ineffectual in shifting the equilibrium transesterification reaction to the product side to achieve maximum conversion [3, 8]. With increasing dry algae to methanol ratios, the influence of methanol concentration on the fatty acid methyl ester yield is significant. Methanol serves as both a solvent for extracting algal /lipids and a reactant for transesterification of esters, and higher algae to methanol ratio leads to more lipid extraction and transesterification simultaneously. Further increasing of algae to methanol ratio resulted in lower FAME yield. This could be due to an excess of methanol in the process, which prevents the alkyl ester and glycerol from being separated by increasing the glycerol

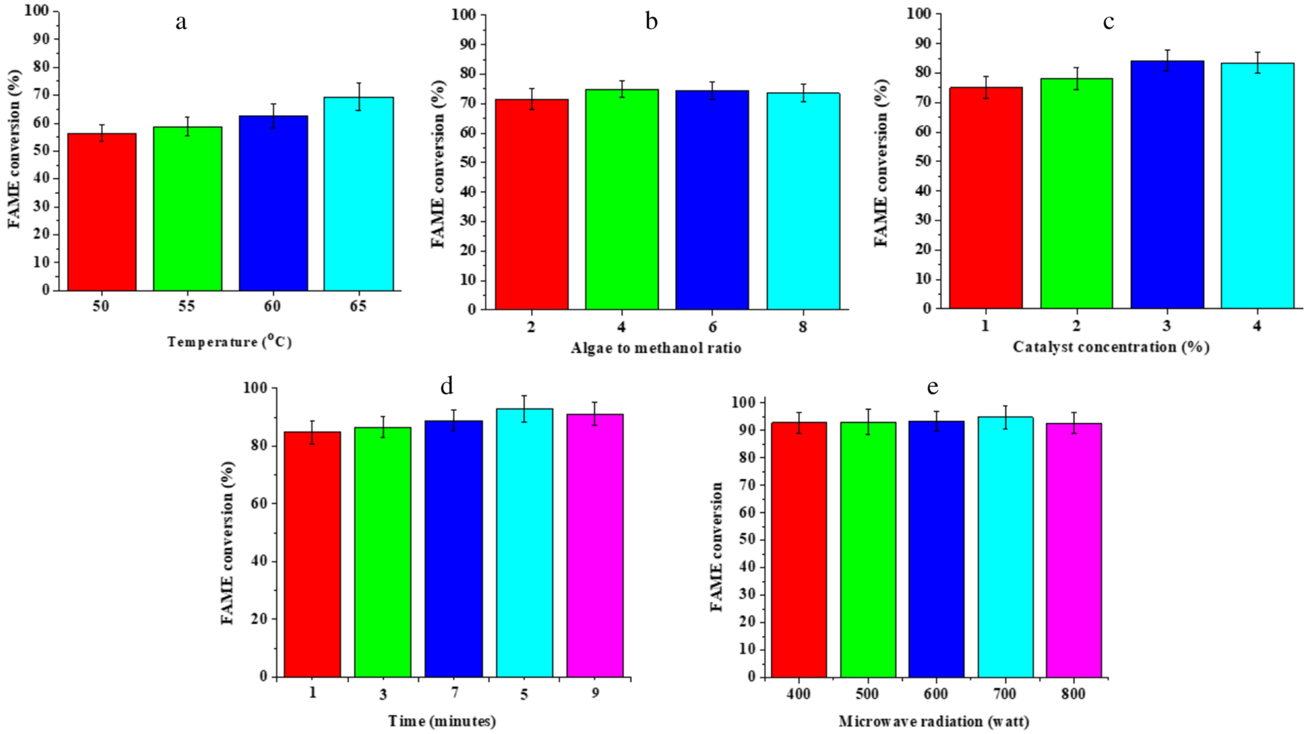

Fig. 2 Effect of different parameters on biodiesel conversion through in situ transesterification, **a** effect of temperature, **b** effect of algae to methanol ratio, **c** effect of catalyst concentration, **d** effect of microwave radiation, **e** effect of time duration

solubility. As a result, some diluted glycerol remains in the alkyl ester phase, causing apparent alkyl ester final product loss due to soap formation. [25].

The concentration of catalysts plays a key role when optimizing the biodiesel production process. As shown in Fig. 2c, CPM biodiesel conversion yield improved from 75.05 to 84.25% by increasing the catalyst concentration from 1 to 3 wt% while keeping other parameters constant (temperature 65 °C, algae to lipid ratio 1:4 time 3 min, and microwave radiation 500 W). However, as the concentration of catalyst further increased to 5%, the biodiesel yield and conversion efficiency slightly reduced. The excessive amount of KOH catalyst employed in the transesterification reaction would result in significant ion collisions due to the abundance of free ions in the mixture, thus reducing the activation energy needed by the oil to increase the rate of reaction and, as a result, lowering biodiesel yield. Furthermore, using an excessive amount of KOH catalyst causes soap to form (saponification reaction), complicating the process of separating biodiesel from soap and excess glycerol during the purification process and lowering biodiesel yield [39]. Reaction time is also an important factor when optimizing biodiesel production yield. As shown in Fig. 2d, biodiesel yield increased with time and was found maximum (92.8%) at 7 min. Furthermore, the yield of biodiesel was found to be lower when the reaction was carried out for a longer time (greater than 7 min). This could be because transesterification is a reversible reaction; therefore, a lengthy reaction time results in a backward reaction, lowering biodiesel yield, while a short reaction time results in an incomplete reaction, lowering biodiesel output [24, 25]. Finally, as the microwave radiation was amplified from 400 to 700 W, the conversion of lipids to biodiesel had an increasing trend and reached up to 94.5% at 700 W, whereas a further increase to 800 W slightly decreased the yield (Fig. 2e). The quick reorientation of the dipole moment of methanol took place at elevated microwave power, which destroys the two-tier structure of the interface of methanol and lipid extracted from the dry algae. As a result, the dielectric constant and polarity of the methanol are reduced allowing it to solvate lipids to form a single phase and produce a higher algal biodiesel yield. When the microwave radiation increased from 700 to 800 W at 65 °C, the methanol got heat speedily resulting in some amount vaporisation. The resulting methanol vaporises and lessens the amount available for the reaction process. Hence, biodiesel yield falls [9, 24, 25].

At the reaction conditions ($T = 65°$; algae to methanol ratio = 1:4; catalyst concentration = 3%; time = 7 min; and microwave radiations = 700 W), the maximum biodiesel conversion efficiency was 94.5% while the maximum biodiesel yield with respect to biomass (dry wt) was observed as 15.48 wt%.

FAME composition of produced biodiesel is shown in Table 1 which revealed that CPM biodiesel has 41.89%

Table 1 Fatty acid composition of biodiesel

Fatty acid	Fatty acid composition		
	C. pyrenoidosa (this study)	*C. pyrenoidosa* [40]	*Chlorella* sps. [41]
C14.0	1.94	0.25	0.92
C16.0	32.86	32.52	22.50
C16:1	5.97	5.74	23.31
C16:2	-z	0.73	1.95
C17	-	0.36	-
C18.0	6.23	4.51	2.18
C18.1	3.84	-	45.36
C18.2	22.73	19.42	1.14
C18.3	25.15	36.34	-
C20	1.96	-	2.64
Saturated fatty acids	41.89	27.36	28.24
Mono unsaturated fatty acids	9.80	5.74	68.67
Polyunsaturated fatty acids	47.88	56.5	3.09

saturated fatty acids, 9.80% monounsaturated fatty acids, and 47.88% of polyunsaturated fatty acids. Higher compositions of polyunsaturated fatty acids indicate that biodiesel has poor oxidation stability and good cold flow properties. As shown in Table 1, palmitic acid (32.86%), palmitoleic acid (5.97%), stearic acid (6.23%), linoleic acid (22.73%), and linoelaidic acid methyl esters (25.15%) were the main constituents of CPM biodiesel. In addition, CPM biodiesel also had a small quantity of myristic acid and arachidic acid methyl esters. The results of CPM biodiesel are in line with other studies [40, 41].

3.2 Pyrolysis of de-oiled C. pyrenoidosa microalgae

3.2.1 Characterisation of de-oiled C. pyrenoidosa microalgae

The proximate and ultimate analysis of CPMR biomass is depicted in Table 2. The ultimate analysis revealed that the moisture content in CPMR was 8.9 wt%. The volatile content of CPMR was determined to be 73.3 wt% that makes it a suitable candidate for pyrolysis or combustible source. In this study, the ash content of CPMR biomass was 4.90% which was lower than in other studies i.e. *Haematococcus pluvialis* residue (28.48%), *D. tertiolecta* residue (8.40%), *Chlorella vulgaris* residue (8.72%), and *Chlorella* sps. residue (43.00%) (Table 2). Similarly, the fixed carbon of CPMR biomass was observed higher (12.70%) compared to *Haematococcus pluvialis* residue (4.08%). *D. tertiolecta* residue (11.80%) while lower than *Chlorella vulgaris* residue (15.27%). The lower amount of ash content and fixed carbon in CPMR biomass pose an advantage for the pyrolysis process.

The ultimate analysis of CPMR biomass revealed that it included 64.84% C, 5.85% H, 2.83% N, 0.78% S, and 25.7% O (w/w). The molar ratio of H/C and O/C was 1.08 and 0.28 respectively. On the basis of elemental composition, the empirical formula of CPMR was derived as $CH_{1.08}N_{0.03}S_{0.004}O_{0.28}$. CPMR biomass showed a slightly lower molar ratio of hydrogen and oxygen than other microalgae biomass [42, 43]. The H/O molar ratio in biomass generally affects its heating value. The higher will be the molar ratio of H/O, the higher will be heating value. The higher heating value of CPMR biomass was analysed to be 18.63 MJ kg^{-1} which was lower than *C. vulgaris* (21.07 MJ kg^{-1}) but higher than *Chlorella* spp.

Table 2 Proximate and ultimate analysis of *Chlorella pyrenoidosa* microalgae residual biomass compared to other microalgae de-oiled residual biomass

Properties		CPMR (wt%)	*Haematococcus pluvialis* residue [43]	*D. tertiolecta* residue [45]	*C. vulgaris* residue [44]	*Chlorela* spp. residue [42]
Proximate analysis (wt%)	Moisture content	8.90 ± 1.3	36.55	9.80	4.39	7.00
	Volatile matter	73.30 ± 2.5	29.89	87.10	76.01	47.00
	Fixed carbon	12.70 ± 0.75	4.08	11.80	15.27	10.00
	Ash content	4.90 ± 1	29.48	8.40	8.72	43.00
Ultimate analysis (wt%)	Carbon	64.84	23.31	42.9	49.34	30.20
	Hydrogen	5.85	3.53	7.09	7.53	10.20
	Nitrogen	2.83	0.20	5.45	10.72	5.60
	Sulfur	0.78	0.18	0.87	–	1.70
	Oxygen (by difference)	25.70	6.75	43.69	32.41	52.30
	H/C molar ratio	1.08	-	1.98	1.83	4.05
	O/C molar ratio	0.28	-	0.76	0.49	1.29
Heating value (MJ kg^{-1})		18.63	23	16.86	21.7	15.49

(15.49 MJ kg^{-1}) and *Dunaliella tertiolecta (D. tertiolect)* (16.86 MJ kg^{-1}) residue biomass [42–44].

3.2.2 TGA analysis of C. pyrenoidosa microalgae and C. pyrenoidosa microalgae residual biomass

TGA analysis of CPMR biomass with respect to temperature is shown in Fig. 3. It was observed that the thermal degradation of the biomass started at a temperature of 200–250 °C, at which stage 15–20% weight loss was observed, under inert nitrogen conditions. At 500 °C, about 97.7% of mass degradation was observed for CP microalgae biomass, and after that, thermal degradation became stable. While in the case of CPMR, the maximum mass degradation was about 70 at 500 °C. In addition, it was also found that the thermal decomposition of biomass undergoes three stages with respect to temperature (i) from room temperature to 200 °C, (ii) from 200 to 500 °C, and (iii) from 500 °C onwards.

Microalgae are generally composed of carbohydrates, proteins, and lipids that degrade at different temperature ranges, with a minor reaction peak at < 150 °C, water, 250–380 °C for carbohydrates and proteins while the third peak represents lipids presence. As most of the lipids are already extracted, therefore, the mass loss of around 490 °C is very low for CPMR. The maximum mass loss rate (DTG$_{max}$) was observed at 323 °C. The TGA analysis of this algal biomass i.e. CP and CPMR was consistent with TGA of other microalgae biomass and lipid-extracted biomass residue [42, 46, 47]. Therefore, based on the TGA/DTG analysis, it was confirmed that the pyrolytic zone of CPMR was in the range of temperature of 200 to 500 °C.

On the other hand, the analysis of TGA and proximate and ultimate analysis data also confirmed that CPMR biomass would be the suitable feedstock for pyrolysis.

3.2.3 Product distribution of C. pyrenoidosa microalgae residual biomass pyrolysis

The product distribution of CPMR biomass pyrolysis at different temperatures is presented in Fig. 4. The yield of bio-oil was 21.66%, 28.33%, 35.33%, 32.66%, and 31.67% wt% at the pyrolysis temperature of 400, 450, 500, 550, and 600 °C respectively. All the experiments were performed at a heating rate of 10 °C min^{-1}. The biochar yield was observed to be maximum (64.33% *w/w*) at 400 °C and found to decrease with increasing pyrolysis temperature. On the other hand, non-condensable pyrolysis gases quantity increased with rising in temperature and detected 22.83% wt% as maximum yield at 600 °C temperature. At lower temperatures of 400–450 °C, carbonisation reaction are dominating which results in lower bio-oil yield due to lower volatile matter evaporation [47]. As the temperature increases from 450 to 500 °C, the rate of evaporation of volatile matter is also increasing which leads to a higher liquid fraction (bio-oil) yield [48]. A further increase in temperature to 600 °C results in a break-down of volatile matters into non-condensable gases. In addition, the unstable intermediate compounds are also cracked in smaller hydrocarbon molecules which may be hydrocarbon gaseous molecules. This may lead to lower bio-oil yield but higher produced gas at a higher temperature [49].

Similarly, Casazza et al. [47] carried out fast pyrolysis of lipid-extracted *A. platensis* biomass (APLE) at 450 °C for 1 h and obtained a maximum bio-oil yield (39.7%) along with 33.9% biochar and 28.1% gas [50]. Francavilla et al. [28] carried out fast pyrolysis of *Dunaliella tertiolecta lipid–extracted residue* in the temperature range 450–750 °C, with a heating rate 50 °C/s at atmospheric pressure in He and achieved a maximum yield of bio-oil (45.13%), biochar

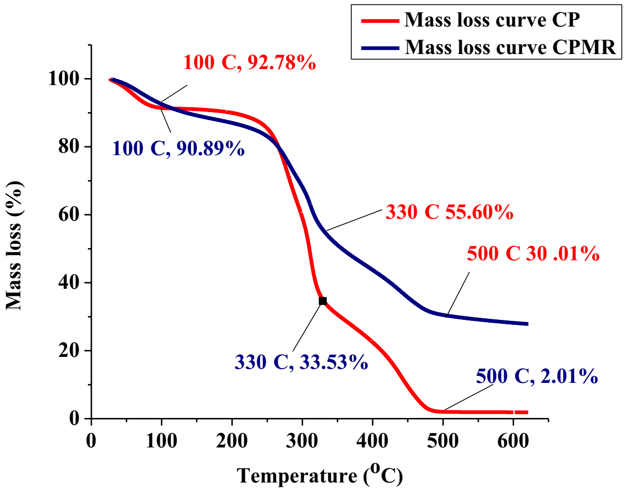

Fig. 3 TGA analysis of *Chlorella pyrenoidosa* microalgae and *Chlorella pyrenoidosa* microalgae residual biomass

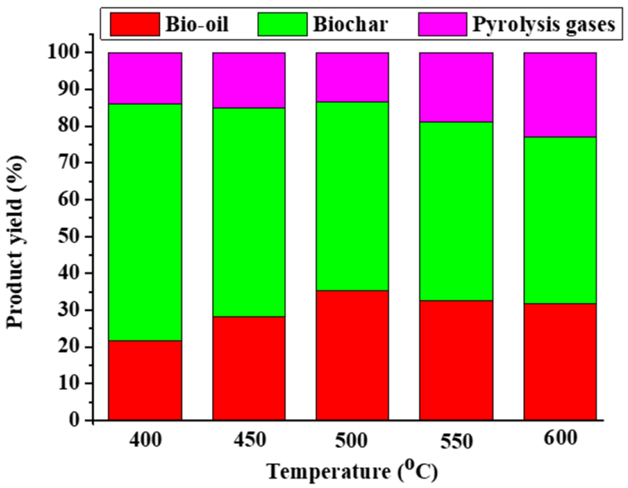

Fig. 4 Product yield of pyrolysis of *Chlorella pyrenoidosa* microalgae residual biomass

(29.34), and pyrolysis gas (25.53%). Gong et al. [43] carried out pyrolysis of *Haematococcus pluvialis* microalgae biomass and lipid-extracted biomass at 400–800 °C with a heating rate of 20 °C and obtained a maximum bio-oil yield of 20.07% and 14.67% respectively [43] which is lower than the bio-oil yield obtained in the current study. The yield of the pyrolysis products CPM depends generally on biochemical composition, type of reactors, heating rate, and temperature as well as the catalyst [48, 49, 51].

3.3 Characterisation of pyrolysis products

3.3.1 Characterisation of bio-oil produced from C. pyrenoidosa microalgae residual biomass by GC–MS and FTIR

GC–MS and FTIR analysis were used to examine the chemical composition of bio-oil produced from CPMR at 500 °C. Tables 3 and 4 show the results of the FTIR and GC–MS study of CPMR bio-oil. According to the literature, the primary groups of organic compounds that make up the content of pyrolyzed bio-oil include aliphatic, heterocyclic, mono-aromatics, polyaromatics, oxygenates, and nitrogenates [48, 49]. The existence of hydrocarbon, esters, and aromatics in the bio-oil certifies its potential as a fuel candidate for an internal combustion diesel fuel. The concentration of nitrogenates compounds in bio-oil was 2.3% while oxygenates were observed at 13.22%. The presence of some hydrocarbons made it more valuable in terms of liquid transportation fuel. In addition, the carbon compounds were in the range of C5 to C17 and indicate its feasibility as both gasoline and diesel fuels by upgrading with suitable catalytic reactions.

FTIR analysis of bio-oil is shown in Fig. 5 and Table 3. The results revealed that a broad spectrum was obtained between 3600 and 3200 cm^{-1} which corresponds to O–H stretching and indicates the presence of moisture, phenol, and alcohols. C-H stretching at 2925 and 2851 cm^{-1} confirms the presence of the alkane group while C-O stretching at 1708 cm^{-1} confirms the presence of aldehyde and ketones groups in bio-oil. The existence of alkenes and aromatics was shown by demonstrating C = C stretching vibration at 1647 cm^{-1}. Furthermore, the $C \equiv C$ deformation vibrations at 1437 cm^{-1} represented the presence of alkyne. Besides, O–H bending vibrations at 1365 cm^{-1} indicate the presence of alcohols and phenols. Besides that, the subsistence of C = O stretching and deformation implies the ether and esters group in the range of 1300–950 cm^{-1}.

3.3.2 Fuel characteristics of bio-oil

The fuel properties of bio-oil derived from pyrolysis of CPMR biomass are compared with lingo-cellulosic biomass, other microalgae bio-oil, CPM biodiesel, and diesel in Table 5. All the physicochemical properties i.e. calorific value, density, weight% of elements (C, H, N, O, and S), flash point, viscosity, pH, and pour point were analysed using standard methods. The calorific value of a fuel is one of the most important properties which highly influence engine performance and power generation. The calorific value of CPMR biomass bio-oil, CPM biodiesel, and diesel fuel was analysed using an oxygen bomb calorimeter and found to be 21.89 MJ kg^{-1} and 36.23 MJ kg^{-1} in comparison to diesel (43.65 MJ kg^{-1}). In addition, the calorific value of CPMR biomass bio-oil was also found to be comparable with other pyrolysed bio-oils such as from lignocellulosic biomass (rice husk and Jatropha seeds) and *Nannochloropsis* sp. microalgae bio-oil (Table 5). It is assumed that the calorific value of bio-oil was lower than biodiesel and diesel hydrocarbons due to the presence of more oxygen and nitrogenous compounds [52, 53]. The flash point of the bio-oil was found to be higher (72 °C) than conventional diesel (56 °C) but lower than Jatropha seed-based bio-oil (132 °C). According to the literature, a higher flash point of a fuel is advantageous as it results in easier handling, transportation, and storage [2]. The pH of the bio-oil was found to be 2.1 which may be due to the presence of some organic acids. Before using it in engines, it is necessary to upgrade bio-oil [48]. When bio-oil was blended with diesel and microalgae biodiesel, the pH of blends lies between 5.1 and 6.1 which was closer to

Table 3 FTIR analysis of bio-oil produced from pyrolysis of *Chlorella pyrenoidosa* microalgae residual biomass

Wavelength	Functional group	Remark
Between 3600 and 3200 cm^{-1}	Moisture, phenol	O–H stretching
2925 cm^{-1}, 2851 cm^{-1}	Alkane	-C-H stretch, CH_3, CH_2 & CH (strong)
1708 cm^{-1}	Aldehyde, ketone	C-O stretching
1647 cm^{-1}	Alkene aeromatics	C = C stretching
1437 cm^{-1}	Alkyne	$C \equiv C$ stretching
1365 cm^{-1}	Alcohols and phenols	O–H bending
1300–950 cm^{-1}	Ether and esters group	C = O stretching and deformation
Below 1000 cm^{-1}	Alkane, alkene	= C-H bending and fingerprint region

Table 4 GC–MS analysis of bio-oil produced by pyrolysis of *Chlorella pyrenoidosa* microalgae residual biomass

S. no	Molecule name	Molecule formula	Molecular weight	Retention time
1	Toluene	C_7H_8	92	3.55
2	Pyrrole	C_5H_7N	67.09	4.23
3	Cycloheptane	C_7H_{14}	98	6.57
4	Cyclooctane	C_8H_{16}	112	9.34
5	Cyclopentane, propyl-	C_8H_{16}	112	12.22
6	Cyclopentane, butyl-	C_9H_{18}	126	15.90
7	4-methyl-1H-indole	C_9H_9N	131.17	18.78
8	Cyclodecane	$C_{10}H_{20}$	140	22.75
9	Formic acid, heptyl ester	$C_8H_{16}O_2$	144	27.05
10	Cyclopentane, hexyl-	$C_{11}H_{22}$	154	3031
11	1-Decanol	$C_{10}H_{22}O$	158	33.04
12	1-Decanethiol	$C_{10}H_{22}S$	174	35.45
13	Formic acid, octyl ester	$C_9H_{18}O_2$	158	37.66
14	1-Tetradecanol	$C_{14}H_{30}O$	214	38.18
15	Phenol, 2-methoxy-4-(2-propenyl)-, acetate	$C_{12}H_{14}O_3$	206.23	39.75
16	Cyclohexanecarboxylic acid, heptyl ester	$C_{14}H_{26}O_2$	226	42.26
17	Cyclohexanecarboxylic acid, nonyl ester	$C_{16}H_{30}O_2$	254	43.96
18	Isoheptadecanol	$C_{17}H_{36}O$	256	44.08
19	*n*-Hexadecanoic acid	$C_{16}H_{32}O_2$	256.4	45.51
20	9,12-Octadecadienoic acid (Z, Z)	$C_{18}H_{32}O_2$	280.4455	48.23
21	Octadecanoic acid, ethyl ester	$C_{20}H_{40}O$	312.58	50.54

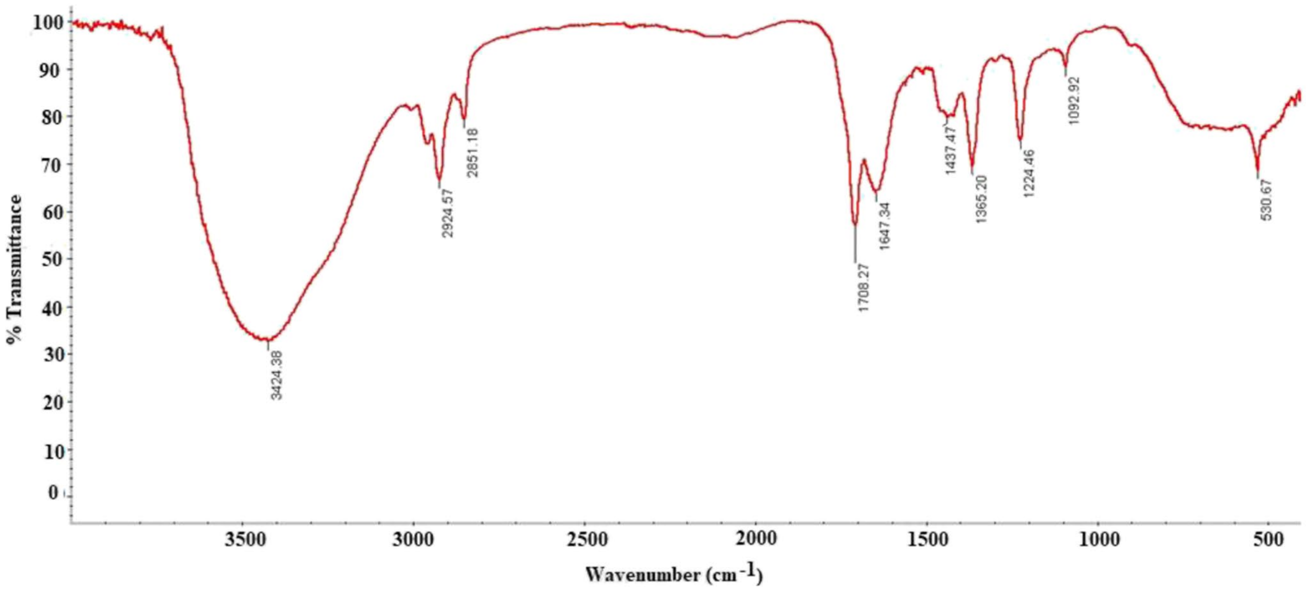

Fig. 5 FTIR analysis of bio-oil produced from pyrolysis of *Chlorella pyrenoidosa* microalgae residual biomass

neutral pH as compared to crude bio-oil, and hence, blends were considered more suitable for engine applications.

At 40 °C, the viscosity of bio-oil was found to be much greater (20.13 cP) than that of diesel fuel (2.81 cP) and CPM biodiesel (6.69 cP). Furthermore, as compared to ordinary diesel fuel (821 kg m^{-3}) and CPM biodiesel (889 kg m^{-3}), the density of CPMR bio-oil was 998 kg m^{-3}. Higher fuel viscosity and density result in

Table 5 Fuel characterisation of *Chlorella pyrenoidosa* microalgae biodiesel and *Chlorella pyrenoidosa* microalgae residual biomass bio-oil compared to other bio-oils

Properties	Diesel	CPM biodiesel	CPMR bio-oil	90% D + 5% CPM-BD + 5% CPMR -BO(Hossain and Davies 2013)	80%D + 10% CPM-BD + 10% CPMR -BO (Chintala, Kumar et al. 2017)	80%D + 15% CPM-BD + 5% CPMR -BO
Calorific value (MJ kg^{-1})	43.65	36.23	21.89	41.74	38.60	40.84
Flash point (°C)	56.0	127	72	73	96	89
Density (kg m^{-3})	821	889	998	0.832	841	838
Viscosity at 40 °C (cP)	2.3	6.69	20.13	7.12	10.62	8.93
Pour point (°C)	−1	−2	6.7	3.4	6.4	3.9
pH	6.4	6.3	2.1	6.1	5.1	6.0
Water content (wt%)	0.005	0.008	9.5	0.01	0.18	0.16
C (% of dry biomass)	-	-	60.9	-	-	-
H (% of dry biomass)	-	-	7.6	-	-	-
N (% of dry biomass)	-	-	6.4	-	-	-
S (% of dry biomass)	-	-	0.77	-	-	-
O* (% of dry biomass)*	-	-	24.33	-	-	-

*by difference.

poor atomization and incomplete combustion, resulting in poor engine performance and higher emissions [2, 54]. Therefore, it is avoided direct application of bio-oil in engines and needs further modifications. To address the problem of higher viscosity and density, it is either blended with diesel in a certain ratio or modified by some chemical reaction in presence of a catalyst. The moisture content in CPMR bio-oil was 9.5% and can be reduced using a centrifuge or using some absorbent. The elemental analysis of CPMR bio-oil is shown in Table 5. The results show that bio-oil has a significant amount of carbon and hydrogen substance (60.9% and 7.6%) with some content of oxygen (24.33%) and nitrogen (6.4%). The presence of oxygen in a fuel promotes complete combustion, which improves engine performance and reduces pollutants. However, a high oxygen concentration lowers a fuel's calorific value and diminishes engine performance.

3.3.3 Biochar characterisation of C. pyrenoidosa microalgae residual biomass

CPMR biochar was characterised in terms of proximate and ultimate analysis. Table 6 shows the proximate analysis of biochar made from CPMR biomass. The volatile matter of CPMR biomass was found to have decreased from 73.3 to 31.62%, whereas fixed carbon increased from 12.7 to 54.3%, indicating efficient carbonisation. When compared to CPMR biomass, CPMR biochar had a greater ash concentration of 12.18%. This increment in ash content may be due to leftover minerals [55]. The ultimate analysis of CPMR biochar is compared with other biochar obtained from biomass (Table 6). The ultimate analysis of biochar results in 74.65% C, 4.12% H_2, 2.84% N_2, 0.67% S, and 17.72% oxygen which are similar to the elemental composition of other biomass as reported by other researchers [48, 55, 56]. In addition, the calorific value of CPMR biochar was 17.15 MJ kg^{-1} and was found to be comparable with other feedstock biochar such as *Chlorella vulgaris,* Jatropha de-oiled cake, and Mahua biochars (Table 6). Due to its good calorific value, it can be used in power industries or boilers as solid fuels.

3.3.4 Analysis of non-condensable pyrolysis gases

The composition of non-condensable pyrolysis gases is shown in Fig. 6. The results revealed that hydrogen (H_2), methane (CH_4), carbon monoxide (CO) and carbon dioxide (CO_2), and gas were the main components. As shown in Fig. 6, carbon dioxide was the major gas present in non-condensable pyrolysis gases, amounting to 23.6%. This may be due to the thermal degradation of C–O and –COOH groups, as well as the effect of the water–gas shift reaction [36, 57]. In addition, hydrogen and methane gas shared 7.5% and 5.6% non-condensable pyrolysis gases composition. Moreover, small quantities of C_2-C_3 hydrocarbons were also observed in traces. These results are in line with other studies performed with lipid-extracted biomass [32, 58, 59]. The existence of hydrogen, methane, and carbon monoxide confirms that non-condensable pyrolysis gases have good potential as a fuel candidate in SI engines.

Table 6 Characterisation of biochar derived by pyrolysis of *Chlorella pyrenoidosa* microalgae residual biomass compared to biochars from other sources of biomass

Characteristics		CPMR biomass biochar (present study)	*Chlorella vulgaris* FSP-E biochar [55]	Jatropha seed biochar [48] Chintala, Kumar et al. 2017)	Mahua biochar [56] (Pradhan, Singh et al. 2016)
Proximate analysis (wt%)	Moisture content	1.90 ± 0.5	3.81	2.30	5.14
	Volatile content	31.62 ± 3	17.40	36.40	36.17
	Fixed carbon	54.30 ± 3	65.34	48.50	50.03
	Ash content	12.18 ± 0.5	13.45	12.80	8.66
Ultimate analysis (wt%)	C	74.65	61.32	71.14	78.12
	H	4.12	3.55	3.89	4.12
	N	2.84	9.76	4.55	2.81
	S	0.67	0.02	0.17	0.16
	O*	17.12	11.92	20.07	14.84
Higher heating value (MJ kg^{-1})		17.15	23.42	16.15	26.05

*by difference.

3.4 Sustainability of integrated transesterification-pyrolysis process and implication for cleaner production of renewable fuels

This study explores the production of different green fuels from *C. pyrenoidosa* biomass by transesterification of microbial lipids and pyrolysis of the residual de-oiled biomass via a biorefinery concept. Specifically, we produced four different types of green fuels: biodiesel (through in situ transesterification of CPM biomass) and bio-oil, non-condensable pyrolysis gases, and biochar (by pyrolysis of CPMR biomass). On the basis of the above experiments, it can be predicted that about 100 kg of *C. pyrenoidosa* microalgae (CPM) biomass can be resulted in the production of 15.47 kg of biodiesel, 29.67 kg of bio-oil, and 43.03 kg of biochar using these optimised experimental conditions. As shown in Table 5, the fuel properties of biodiesel were similar to commercial diesel and found under ASTM standards. Therefore, it can be utilized as an alternative to diesel in CI engines/power plants or industry boilers. The bio-oil was the product of pyrolysis process and has both positive and negative aspects to use as a fuel candidate. It is composed of different hydrocarbon, ester, and oxygenate compounds. The flash point of bio-oil is comparable with diesel and biodiesel. Moreover, the caloric value of bio-oil was observed to be 21.89 MJ kg^{-1} which makes it suitable as a fuel candidate for different applications such as power industries, furnace, burner, hot water generators, hot air generators, and thermic fluid heater systems for heating applications. On the downside, it showed poor density, viscosity, and acidic value which made it unfit for engine applications. However, these properties could be improved by different oil upgrading techniques [60, 61]. Two blends of diesel, CP-BD, and CPMR bio-oil (D90% + 5% CP-BD + 5% CPMR-BO and D80% + 10% CP-BD + 10% CPMR-BO) and their phyisco-chemical properties were compared with diesel biodiesel and bio-oil, they showed good potential for engine application also [2, 52]. Many researchers have shown that it has good potential to run CI engines with some modifications [52, 60, 61]. The non-condensable pyrolysis gases were the mixture of different combustible gases such as hydrogen, methane, carbon monoxide, ethane, and ethylene with good heating value. These gases can be used as a heat source to run biodiesel or pyrolysis reactor for minimizing external heating load which also

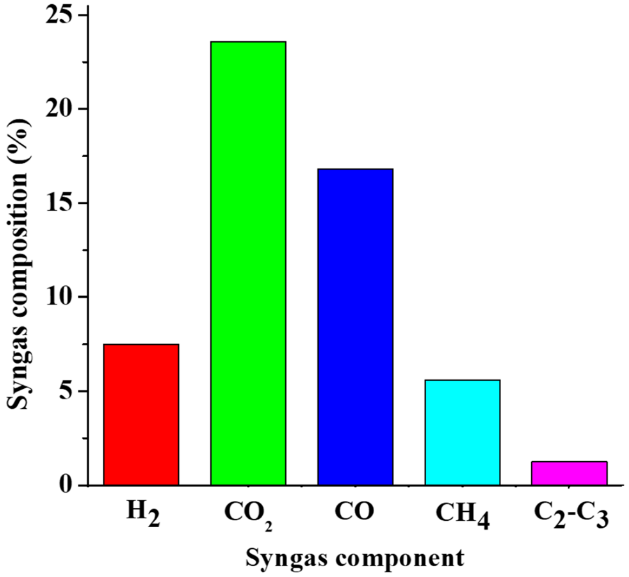

Fig. 6 Composition of non-condensable pyrolysis gases' composition

helps to improve the economics of the whole process reaction. In addition, it can be utilized in SI engines to replace natural gas. CPMR biochar also has a good calorific value (17.15 MJ kg^{-1}) and has shown good potential to use as a solid fuel in power industries/ boilers [62]. In addition to the above, biochar can be upgraded to activated carbon which has broad application in the removal of metal ions, pesticides and herbicides, dyes, and phenols from wastewater and chemical industries [63, 64].

4 Conclusion

This study demonstrates the production of a range of renewable fuels from *C. pyrenoidosa* biomass through a cascade transesterification of lipids and pyrolysis of de-oiled cake via a biorefinery concept. CPM biomass has been transesterified under different reaction conditions through in situ process. Furthermore, the biomass left over after biodiesel extraction (CPMR) was pyrolysed in a fixed bed reactor to optimise the reaction products such as bio-oil, non-condensable pyrolysis gases, and biochar. Based on physical and chemical properties, both bio-oil and biodiesel showed good potential for diesel engines. Additionally, the presence of combustible gases, such as hydrogen, methane, and carbon monoxide, in non-condensable pyrolysis gases has demonstrated its possibility as a SI engine fuel. Biochar was also characterised and found to have an excellent H/C and O/C ratio, as well as a calorific value of 17.15 MJ kg^{-1}, indicating that it might be utilized as a solid fuel in power plants, or converted to activated carbon for use in wastewater treatment technologies. However, utilization of the suitable catalyst, reactor, and lifecycle analysis should be explored to study the potential of this integrated technology for the production of renewable fuels. Furthermore, this study may be beneficial to establish and design a robust microalgal biorefinery for the production of biofuels.

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Author contribution Amit Kumar Sharma: conceptualization; methodology; data curation; writing—original draft preparation. Pankaj Kumar Sharma: project administration, resources, supervision. Praveen Kumar Ghodke: methodology, software, investigation. Arivalagan Pugazhendhi, writing-reviewing and editing, Leonidas Matsakas: supervision, reviewing, and editing. Alok Kumar Patel: software; writing—reviewing and editing,

Declarations

Conflict of interest The authors declare no competing interests.

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