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Short Communication

Rapid alkali catalyzed transesterification of microalgae lipids to biodiesel using simultaneous cooling and microwave heating and its optimization

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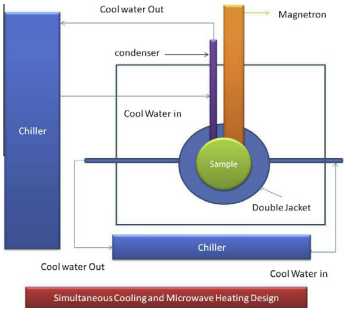
HIGHLIGHTS

- Transesterification of lipid using simultaneous cooling and microwave heating (SCHW).
- Conventional and microwave heating transesterification were controls for comparison.
- The yields from SCMH were higher (83.33%) compared to control methods.
- SCMH optimum settings; 50 °C, 800 W, 16 h reaction, cooling at 15 °C; 0 H_20 content.
- SCHW produces lower carbon components (<19 C) and has good CN and IV properties.

GRAPHICAL ABSTRACT



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ABSTRACT

Biodiesel with improved yield was produced from microalgae biomass under simultaneous cooling and microwave heating (SCMH). *Nannochloropsis* sp. and *Tetraselmis* sp. which were known to contain higher lipid species were used. The yield obtained using this novel technique was compared with the conventional heating (CH) and microwave heating (MWH) as the control method. The results revealed that the yields obtained using the novel SCMH were higher; *Nannochloropsis* sp. (83.33%) and *Tetraselmis* sp. (77.14%) than the control methods. Maximum yields were obtained using SCMH when the microwave was set at 50 °C, 800 W, 16 h of reaction with simultaneous cooling at 15 °C; and water content and lipid to methanol ratio in reaction mixture was kept to 0 and 1:12 respectively. GC analysis depicted that the biodiesel produced from this technique has lower carbon components (<19 C) and has both reasonable CN and IV reflecting good ignition and lubricating properties.

1. Introduction

Due to rapid depletion of fossil fuel, biodiesel from microalgae has become an attractive alternative energy source (Prafulla et al., 2012) due to its rapid growth rate (5–30 times more than oil crops), has high oil yields/hectare and is not a food competitor. However commercialized biodiesel production from microalgae is beleaguered with issues such as expensive dewatering and drying processes, large volumes of solvent utilization and laborious extraction processes.

Recently, replacing the conventional heating by microwave irradiation has been rapidly increasing (Idris et al., 2012). Microwave irradiation is not simply dielectric heating rather a specific activation effect of microwave was involved in the chemical reaction (Idris et al., 2012) and interaction between materials with

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microwave need to be considered. Microwave power introduced in the biochemical process played a critical role in the organic synthesis (Baghurst and Mingos, 1992). Unlike direct conventional heating (CH), MWH causes hot spots that lead to superheating effect. Microwave irradiation plays two roles in the synthesis process; non-thermal and thermal effects (Haswell and Howarth, 1999). Uneven microwave energy distribution and non-uniform increasing temperature were problems encountered in pulsed mode microwave irradiation, thus a continuous microwave irradiation mode was preferred (Baghurst and Mingos, 1992).

SCMH allows for higher levels of microwave energy to be introduced into a reaction mixture. Several researchers have reported the benefit of SCMH over microwave assisted synthesis alone and conventional heating. Maximum 85% yield of lactides (Idris et al., 2012) were obtained under SCMH. In another study (Chen and Deshpande, 2003) reported that rapid synthesis of ketoamides occurred under SCMH; both aromatic and aliphatic acyl chlorides provided good to moderate yields. In principle SCMH allows for higher levels of microwave energy to be introduced into a reaction and at the same time maintaining the reaction at a specific constant temperature. However the potential of SCMH technology has never been explored yet in biodiesel synthesis. Thus in this study an attempt was made to introduce the SCMH in the transesterification of lipids to biodiesel. Critical parameters effecting SCMH are MW settings such as temperature, power, cooling effect of the microwave, reaction duration; including reaction mixture parameters such as water content and ratio of lipid to methanol were investigated. Microalgae from the two different species (*Nannochloropsis* sp. and *Tetraselmis* sp.) were harvested upon reaching the maximum growth phase. The lipids from these species were extracted using the Bligh and Dryer method; (i) using CH (ii) MWH. The lipids obtained from the CH were then transesterified into biodiesel using CH while the lipids extracted via MWH was further transesterified using (i) MWH alone and (ii) SCMH.

2. Methods

2.1. Cultivation, harvesting and lipid extraction of microalgae

Nannochloropsis sp. and *Tetraselmis* sp. obtained from the culture collection of Borneo Marine Research Institute (BMRI), Universiti Malaysia Sabah, were cultivated in Walne medium with 10% starting inoculum taken from stock culture at conditions similar to previous study (Teo et al., 2014). The 2 L marine microalgae after 10 days cultivation were dewatered by centrifugation. Wet microalgal biomass (200 ml) was mixed with methanol-chloroform (1:2 v/v) for lipid extraction according to Bligh and Dyer (1959) method. For (i) *conventional lipid extraction*; the mixture was heated in a water bath (2400 watts) and then left to cool to room temperature. (ii) *Microwave irradiation*; the mixture was placed in the microwave (MAS-II microwave synthesis workstation; rated power of 500 watt) which was operated at 50 °C for 5 min (Teo and Idris, 2014).

2.2. Transesterification of lipids to biodiesel

Methanol was mixed with 0.5 g of sodium hydroxide (NaOH) and stirred for 20 min at 400 rpm at approximately 50 °C. The ratio of methanol to oil in the mixture was kept to 6:1. The mixture of catalyst and methanol was then poured into the conical flask containing the algae oil. In the case of (i) *CH alkali transesterification*: The conical flask containing the algae oil (obtained from the CH lipid extraction) and reactants was placed in the water bath at 50 °C. (ii) *MWH transesterification*: The flask containing reactants and microalgae lipids (extracted using microwave irradiation) was placed in the cavity of the microwave. During the transesterification process, a condenser was used in order to prevent loss of solvent due to vaporization. Temperature of condenser was maintained between 15 and 16 °C. The reaction solution was agitated at 400 rpm using a magnetic stirrer and the temperature was measured directly by using infrared (IR) thermocouple and maintained at 50 °C and 500 watt. (iii) *SCMH transesterification:* The mixture of catalyst (sodium hydroxide) and methanol was then poured into a three-neck round bottom customized jacketed type flask containing microalgae lipids (extracted using microwave irradiation). The jacket was cooled by chilled water (0–5 °C) which was produced by chiller (Julabo, 32-ME, 450 watt) during the whole process. The flask was placed in the cavity of the microwave and similarly connected to the condenser which was maintained at between 15 and 16 °C. The temperature of reaction mixture was maintained in the same manner as in (ii). The biodiesel was recovered according to Teo et al. (2014) and its composition analysis was determined using gas chromatography (GC) (Agilent Technologies, 7820A) and HP-88 capillary column (60 m × 0.25 mm × 0.2 μm) at similar settings reported by Teo et al. (2014). The percentage of efficiency was calculated using the equation reported by Zayed and Jehad (2014).

2.3. Parametric study on SCMH transesterification

In order to optimize the SCMH transesterification method, several parameters were studied; reaction temperature (30–70 °C), microwave energy input (500–900 W), water content (0–16 ml), duration of transesterification reaction (8–30 h), lipid to methanol ratio (1:4, 1:6, 1:8, 1:10 and 1:12) and cooling effect (4–35 °C).

3. Results and discussions

3.1. The productivity of biodiesel

Table 1 shows the productivity of biodiesel from *Nannochloropsis* sp.'s and *Tetraselmis* sp.'s crude oil for the three methods: CH, MWH and SCMH transesterification. Highest productivity of biodiesel was obtained from the transesterification process performed under the SCMH. The increasing productivity due to the simultaneous cooling process allowed more microwave energy waves to penetrate to the reactants (Idris et al., 2012). In principle, the setup allowed higher microwave energy to be absorbed thus causing higher oscillations of molecules to occur and at the same time the mixture temperature was maintained via cooling system. The experimental results showed increased penetration of microwave irradiations under SCMH enhanced the specific activation effects of microwave irradiation, prolonged the lifetime of the reactants and thus the rate of biodiesel production was promoted. Similar improved results were obtained by other researchers (Chen and Deshpande, 2003).

Table 1 shows a comparison of the SCMH with recently transesterification methods. The results showed that the application of SCMH during alkali transesterification achieve the highest productivity compared with the other transesterification methods. The high yield of biodiesel obtained reflects the successful setup in the lab scale thus the possibility of a pilot scale and industry scale setup based on this concept can be considered in future studies.

3.2. Energy consumption using conventional drying and microwave wet methods

Besides achieving high yields, biodiesel production using direct microwave lipid extraction and SCMH transesterification method utilizes less energy compared to the conventional heating. The