



## *In situ* heterogeneous transesterification of microalgae using combined ultrasound and microwave irradiation



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### ABSTRACT

Heterogeneous KF/CaO catalyst, prepared by the wet impregnation method with different KF loadings (15–35 wt.%) and calcination temperatures (600–1000 °C), was used to assist biodiesel production from microalgae *Chlorella vulgaris* under the combination of ultrasound and microwave (US–MW) irradiation. It was found that the catalyst calcinated at 900 °C with 25 wt.% KF loading presented the optimum performance, when the test was conducted with 12 wt.% of catalyst and a methanol to biomass ratio of 8:1 at 60 °C for 45 min. The highest fatty acid methyl esters (FAME) yield was  $93.07 \pm 2.39\%$ , which was significantly higher than that achieved by using US or MW irradiation individually. The catalysts were characterized by X-ray diffraction, scanning electron microscopy and Brunauer–Emmett–Teller.

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### 1. Introduction

Bio-fuel is a more attractive sustainable energy source than traditional fossil fuels when we are facing the increasing challenge of energy crisis and environmental pollution. Microalgae have been intensively researched in recent years as a promising feedstock for biodiesel production, owing to the properties including rapid growth, high lipid content, CO<sub>2</sub> fixation, and wastewater utilization and disposal [1–3]. One of the most common methods to produce biodiesel is the *in situ* transesterification of triglyceride (the lipid compound in microalgae) with the presence of methanol and catalysts, and the products are usually fatty acid methyl esters (FAME) or named biodiesel.

Catalysts commonly compromise homogeneous and heterogeneous catalysts. However, compared to homogeneous catalysts, heterogeneous catalysts have attracted more attention in biodiesel production from vegetable oils or animal fats, due to the easy separation, recycling, and product purification [3]. Alkaline earth metal oxide – calcium oxide (CaO) has been widely evaluated as the catalyst in biodiesel production, owing to the easy availability and prominent cost effectiveness [4–6]. However, the catalytic activity of CaO is limited because of the low specific surface area and gels formation problem in methanol [7]. Hence, the modifications of

CaO were essential: for instance, Wen et al. [8] investigated KF/CaO as heterogeneous catalyst producing biodiesel from Chinese tallow seed oil and the high conversion efficiency was more than 96%; Liu et al. [9] found cinder supported CaO/KF exhibited perfect reusability and high biodiesel yield as a catalyst in soybean oil conversion. Table 1 summarizes the heterogeneous catalyst processes of biodiesel production using different kinds of feedstock with conventional heating method, ultrasound or microwave-assisted transesterification. It was found that the reaction time of conventional heating method was usually longer than 120 min [7–18], which could cause problems in heterogeneous (KF/CaO) transesterification of microalgae due to the rigid cell wall. Conversely, it was reported that ultrasound (US) or microwave (MW) irradiation assistance could significantly reduce the reaction time [19–22].

US or MW assisted catalysis could also improve the microalgae conversion efficiency [23–27]. Iqbal and Theegala [23] reported that using a MW – mediated method could reduce energy consumption, accelerate organic synthesis, and enhance reaction rate to short reaction time, because MW radiation delivered heat more effectively than convection and conduction [24]; but MW was not able to provide energy or break bonds [25]. US, especially in the low frequency range from 20 to 50 kHz, could generate acoustic cavitations, increasing the interfacial region of the reactants and disruption of algal cells, enhancing mass transfer, and accelerating the biodiesel production [26,27]. However, the limitation of US was low effective heating transfer ability [28]. Then, the combination of US and MW (US–MW) irradiation could overcome the limitations,

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which has been successfully designed and well documented in product synthesis, owing to reaction time reduction, decrease in energy consumption, improved and enhanced yield, and selection of products [29,30]. However, there has been little research on the combining of US–MW technology employed in heterogeneous transesterification of microalgae.

The objectives of this paper were (1) to identify whether KF/CaO was an efficient catalyst for biodiesel production from microalgae and (2) to confirm the optimum *in situ* conversion conditions for the US–MW reactor, including the parameters, such as the calcination temperature of KF/CaO catalyst, KF loading, catalyst amount, methanol to biomass ratio and reaction time. Furthermore, the effect of US or MW alone on microalgae conversion was also investigated for comparison.

## 2. Materials and methods

### 2.1. Materials

Microalgae *Chlorella vulgaris* was provided by Tianjian biotechnology company (Binzhou, China) with the physical and chemical properties displayed in Table 2. Heptadecanoic acid methyl ester and FAME standards (10 mg/mL) were purchased from Sigma–Aldrich (USA). All reagents and solvents were either of HPLC or analytical grade purchased from local commercial suppliers.

### 2.2. Catalyst preparation

A series of KF/CaO catalysts with different KF loadings (15–35wt.%) were prepared by the wet impregnation method. Because CaO was difficult to dissolved in water, Ca (NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O was used as the precursor instead. The catalysts were prepared in a two-neck round bottom flask (100 mL) equipped with a temperature indicator and a magnetic stirrer. The impregnation was carried out at 60 °C under continuous stirring until the completion of the preparation process, and subsequently dried in an oven at 105 °C. The catalysts were then transferred to a muffle furnace and calcinated at different temperatures (600, 700, 800, 900 and 1000 °C) for 2 h for the optimum calcination temperature determination.

### 2.3. Catalyst characterization

To identify the crystalline phases of the catalysts calcinated at different temperature, X-ray diffraction (XRD) was performed by a Siemens D500 X-ray powder diffractometer, using a Cu K $\alpha$  irradiation, over a  $2\theta$  angle varying from 4° to 70° with a step width of 0.05° every 3 s.

The morphologies of the calcinated catalysts were investigated using Scanning Electron Microscope (SEM; S570, Hitachi, Japan). The samples were mounted on copper stubs and sputter-coated with gold–palladium by a sputter coater (IB-3, EIKO, Japan) and photographed at a 15 kV accelerating voltage.

The specific surface area was measured by the Brunauer–Emmett–Teller (BET) multipoint N<sub>2</sub> adsorption and desorption method at liquid nitrogen temperature (–196 °C) using a Micromeritics ASAP 2000 analyzer.

### 2.4. In situ transesterification

In the transesterification experiments, the mixture of dry microalgae (5 g) with a fixed amount of methanol and catalyst was employed in a US–MW synergistic extraction apparatus (CW-2000, China), with a 100 mL flask and a cooling condenser, as shown in Fig. 1. The frequency of US and of MW was 40 kHz and 2450 MHz, respectively, and the power was 50 W and 10–80 W (self-regulated by the fixed temperature of 60 °C, there was a temperature indicator at the back of US–MW reactor). After the reaction was complete, the mixture was separated into two layers by adding 6 mL hexane. The upper layer (400  $\mu$ L) contained hexane and FAME, which was then transferred into a clean vial (2 mL) with 100  $\mu$ L heptadecanoic acid methyl ester (C17: 0, 2 mg/mL) as internal standard. The obtained FAME was qualitatively and quantitatively analyzed by GC–MS (Trace GC ultra and DSO II) equipped with an automatic sampler (Thermo Fisher, USA) and a capillary column of VF-23 ms (30 m  $\times$  0.25 mm  $\times$  0.25  $\mu$ m, Agilent). Helium was used as carrier gas. The oven temperature was set at 150 °C for 1 min, and sequentially heated up to 165 °C at a rate of 1 °C/min. The yield of FAME was expressed as its weight to the transesterifiable lipid presented in the microalgae biomass and the lipid extraction method and triglyceride analysis were according to literature reported by Ma et al. [31].

**Table 1**  
Heterogeneous catalyst used in biodiesel production.

Number	Feedstock	Heterogeneous catalysts	Calcination temperature (°C)	Optimal reaction condition	Maximum yield (%)	References
1	Soybean oil	Zeolite supported CaO	600	180 min, 65 °C	95	[7]
2	Chinese tallow seed oil	KF/CaO	450, 600 and 700	150 min, 65 °C	>96	[8]
3	Soybean oil	CaO/KF supported on cinder	500	20 min, 65 °C	99.9	[9]
4	Palm oil	TiO <sub>2</sub> –ZnO <sub>2</sub>	400	300 min, 60 °C	92.2	[10]
5	Sunflower oil	Alumina/silica supported K <sub>2</sub> CO <sub>3</sub>	300, 600 and 1000	300 min, 120 °C	About 93	[11]
6	Sunflower oil	Cs/Al/Fe <sub>3</sub> O <sub>4</sub>	600	120 min, 58 °C	94.8	[12]
7	Rapeseed oil	Ca/Al composite oxide	120–1000	180 min, 65 °C	>94	[13]
8	Vegetable oil	MgAl hydrotalcites	507 and 700	240 min, 65 °C	97.1	[14]
8	Stillingia oil	KF/CaO–Fe <sub>3</sub> O <sub>4</sub>	600	180 min, 65 °C	95	[15]
9	<i>Nannochloropsis</i> sp.	Mg–Zr solid base catalyst	600	240 min, 60 °C	–	[16]
10	<i>Nannochloropsis</i> oil	Hierarchical zeolites	550	240 min, 115 °C	47	[17]
11	<i>Nannochloropsis oculata</i> lipid	CaO/Al <sub>2</sub> O <sub>3</sub> and Mg/Al <sub>2</sub> O <sub>3</sub>	500	240 min, 50 °C	97.5	[18]
12	Crude <i>Jatropha</i> oil	Alumina-supported heteropolyacid	–	50 min, 65 °C	84	[19]
13	<i>Jatropha curcus</i> oil	Na/SiO <sub>2</sub>	600	15 min, 50–70 °C	98.53	[20]
14	Free fatty acid	Sulfated zirconia	–	20 min, 60 °C	>90	[21]
15	Vegetable oil	ZnO/La <sub>2</sub> O <sub>2</sub> CO <sub>3</sub>	550	5 min, <100 °C	>95	[22]

Note: Numbers 1–11 conducted by conventional method, 12–13 by ultrasound and 14–15 by microwave irradiation.

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