Technical Feasibility of Biodiesel Production From Waste Cooking Oil: Comparison Between Electric Heating and Microwave Heating Process

Wenjing Li

Tongji University College of Environmental Science and Engineering

Guangming Li (✉ ligm@tongji.edu.cn)

Tongji University <https://orcid.org/0000-0002-0281-8258>

Fan Wang

Chinese Research Academy of Environmental Sciences

Haochen Zhu

Tongji University College of Environmental Science and Engineering

Wenzhi He

Tongji University College of Environmental Science and Engineering

Juwen Huang

Tongji University College of Environmental Science and Engineering

Research Article

Keywords: Electric heating and Microwave techniques, Kinetic analysis, Process optimization WCO, Variance Analysis

Posted Date: October 8th, 2021

DOI: <https://doi.org/10.21203/rs.3.rs-863803/v1>

License: © ⓘ This work is licensed under a Creative Commons Attribution 4.0 International License.

[Read Full License](#)

Technical feasibility of biodiesel production from waste cooking oil: Comparison between electric heating and microwave heating process

Wenjing Li^a, Guangming Li ^{a,*}, Fan Wang^c, Haochen Zhu^a, Wenzhi He^a, Juwen Huang^a

^aCollege of Environmental Science and Engineering, Tongji University, 1239 Siping Road, Shanghai, 200092, China

^bShanghai Institute of Pollution Control and Ecological Security, Shanghai 200092, P.R. China

^cChinese Research Academy of Environmental Sciences, No. 8, Dayangfang, Beiyuan, Anwai, Chaoyang District, Beijing, China.

*Corresponding Author: Prof. Guangming Li, Ph D

Corresponding Author's Affiliation: College of Environmental Science and Engineering, Tongji University, 1239 Siping Road, Shanghai, 200092, China.

Corresponding author E-mail: ligm@tongji.edu.cn; Phone: +86 13501967237; Fax: +021 65989215

Abstract: Base-catalyzed transesterification and conversion of waste cooking oil (WCO) into biodiesel is a renewable energy production technology with a wide range of applications. The most commonly used heating method is electric heating (EH). Microwave heating (MW) has the characteristics of high heat transfer efficiency and short preheating time, and has recently received attention in this field. This study compared effects of the alkali-catalyzed transesterification reaction of WCO under EH and MW processes. The maximum biodiesel yield of EH process appeared when the reaction temperature is 60 °C, the reaction time is 30

min, the molar ratio of alcohol to oil is 6:1, and the catalyst concentration is 1.0%, up to 93.4%. The maximum biodiesel yield obtained from MW technique is 80.66%, under the condition of 200W, 5min, 1wt. % KOH and the methanol/oil molar ratio of 9:1. The activation energy for CH and MW process are found to be 6 768 J·mol⁻¹ and 503.4 J·mol⁻¹, respectively. Microwave heating greatly reduced the activation energy of the reaction, as well as transesterification yield. Compared with other biodiesel producing process, EH process in this study has the advantages of high speed and low production cost, while biodiesel yield is slightly insufficient. This is likely due to the small amount of un-removed moisture contained in the WCO.

Keywords: Electric heating and Microwave techniques, Kinetic analysis, Process optimization WCO, Variance Analysis

1 Introduction

Due to rapid population growth and economic growth in the last two decades, the consumption of edible oils has increased from 7,337,900 t (1999) to 50,660,000t (2018) in China (China 2018). Waste cooking oils (WCO) weighs approximately 25% of the total mass of edible oils production, while the output of WCO can reach 12,665,000 t in 2018. WCO would be produced by pyrolysis, oxidation, and hydrolysis reactions occur during cooking and frying (Cvengros and Cvengrosova 2004, Maddikeri, Pandit et al. 2012), which bringing the increase of viscosity, specific heat, surface tension, and changes of color, and the formation of foam in oils (Kulkarni and Dalai 2006). Oils became a mixture of triglycerides with higher acid value, saturation and harmful contents (Xingguo 2013). Direct emission of WCO can cause a series of environmental problems, such as the deterioration of land and the atmospheric environment, or sewer-blocked

(Peiro, Mendez et al. 2008). Worse still, because of the huge economic benefit (around 300% (Bussness 2012)) of trench oil, the unhealthy WCO that supposed to be disposed was reused as edible oil after facile process, which seriously threatens human health (Math, Kumar et al. 2010).

WCO can be employed as raw materials to produce biodiesel, fatty acids and soaps, or as C sources in the production of single-cell proteins(Yinxia, Jian et al. 2009, fei and maiqian 2011) and bio surfactants(Jia, Xiangfeng et al. 2009, Yao and Min 2010). Transesterification into biodiesel is fast becoming a key instrument in WCO management. In the past few years, fresh edible oils and non-edible oils are common raw materials for biodiesel production (Chuah, Klemes et al. 2017, Putra, Irawan et al. 2018). However, these materials account for about 80% cost of biodiesel production, which is a lot higher than fossil fuel (Farid, Hassan et al. 2017, Naylor and Higgins 2017). This fact makes WCO an anticipated material for biodiesel production. As one of the most widely used technologies, homogeneous base catalysts-potassium hydroxide (KOH) or sodium hydroxide (NaOH) can produce biodiesel at a mild reaction temperature and pressure in short time. (Fadhil and Ali 2013, Mardhiah, Ong et al. 2017, Akram, Singh et al. 2019, Harabi, Bouguerra et al. 2019, Rajagopalachar, Joshi et al. 2019)

During the transesterification reaction, the heating method will affect the mass transfer and heat transfer coefficient, thereby affecting the reaction efficiency. Among them, electric heating (EH) and microwave heating (MW) are two common reaction processes. It was reported that MW could provide a better thermal conductivity and convection currents

generated in the mixture, and the requirement of pre-heating of reactants is not required. (Milano, Ong et al. 2018, Silitonga, Shamsuddin et al. 2020)

However, currently, there are relatively few studies on the influencing factors, yield and kinetics of the CH process and MW process. Due to the differences in the reaction materials, reaction conditions and the operating level of the experimenters, the results of different studies lack contrast, and it is difficult to scientifically reflect the difference in the transesterification yields of the two processes. Therefore, this study uses WCO obtained from canteens and nearby restaurants as raw materials, and EH and MW technologies were utilized to perform transesterification to prepare biodiesel. This study will perform single factor experiments to examine details in the influencing factors and reaction kinetics of the two technologies, and thoroughly analyze the advantages and disadvantages of the two comparison. On this basis, the acquired best yield will be compared with previous research results to have an insight on the application potential of the raw materials used in this study.

2 Materials and methods

The waste edible oil used in the experiment comes from a student canteen of Tongji University. In order to ensure the uniformity of the samples, 3 samples were taken from lunch, another 3 were taken from dinner. The collection process continued for 7 days from Monday to Sunday. Total 42 samples were gathered and mixed into one WCO sample. Before transesterification, the filtration and extraction were done to remove the contaminants and water. The procedure of pretreatment is demonstrated in Fig.1.

Fig.1. Oil Pretreatment to remove the contaminants and water

The methanol, the hexane for Gas Chromatography were obtained commercially from Sigma-Aldrich (USA) and the analytical internal standard, heptadecanoic methyl ester was purchased from Fluka (USA). The high-purity nitrogen was provided by Chunyu Special Gases Co., Ltd. (Shanghai).

2.1 Characterization of the WCO

The characterization techniques were used to indicate the feasibility of the WCO for biodiesel production. QP2010SE gas chromatography-mass spectrometer was employed to determine WCO fatty acid profile. Nicolet5700 Fourier Infrared Spectrometer was used to determine WCO molecular structure. The physical and chemical properties (density, acid value, saponification value, peroxide value, iodine value and moisture content) was determined by titration. These parameters were compared with common biodiesel raw materials.

2.2 Transesterification reaction

Three neck flat bottom borosil flasks (250 mL capacity) fitted with a condenser and a temperature sensor were used in both reaction vessels. A magnetic bar was put into the reactor for stirring and the stirrer was set at 700 rpm as well. Transesterification reaction for conventional heating (CH) process was carried in a water-bath heating system. The oil was preheated to the specified temperature to keep the reaction temperature stable, while methanol and KOH were mixed in advance. Transesterification reaction for microwave heating (MW) process was carried under 2 450 MHz microwave radiation. The oil and the KOH-dissolved methanol was mixed into the reactor at the beginning of reaction because of the high temperature rise rate.

The transesterification was carried at the fixed mixing intensity (700 rpm), varying the catalyst amount (0.5–2 wt. %), methanol/oils molar ratio (3:1–15:1), reaction time (5–60 min for CH, and 0.5–30 min for MW), reaction temperature (50–70 °C for CH). Since there was no temperature-controlled system installed in the microwave oven, it was not possible to maintain the experimental temperature at a fixed value. So microwave power was fixed in the range of 50–500W in MW process. The biodiesel was split up immediately through cool water after reaction, then filtered through 0.45 µm syringe filter.

2.4 Analytical of biodiesel yield

The FAME of biodiesel can be determined by gas chromatography mass spectrometry. The analysis conditions were as follows: HP5-MS column; injection volume 1 µL; inlet temperature 260 °C; carrier gas is high-purity nitrogen, flow rate 50 mL/min, split ratio 19.9: 1. The column

thermostat uses a column heating program: initial temperature 70 ° C, hold for 2 min, 10 ° C / min to 180 ° C, then 5° C / min to 230 ° C, hold for 10 min; detector is FID, temperature is 260 ° C; hydrogen flow rate is 25 mL / min , The air flow rate is 300 mL / min.

The analytical internal standard for the quantitative determination was heptadecanoic methyl ester. The peak areas of the internal standard and other esters were compared to quantify the fatty acid methyl ester content in the biodiesel sample. The results were calculated according to Eq.1.

$$C = \frac{\sum A - A_{EI}}{A_{EI}} \times \frac{C_{EI} \times V_{EI}}{m} \times 100\% \quad (1)$$

Where C is the fatty acid methyl content (%); $\sum A$ is the total peak area; A_{EI} is the peak area of the heptadecanoic methyl ester; C_{EI} is the concentration of heptadecanoic methyl ester in the hexane (mg/L); V_{EI} is the injection volume of heptadecanoic methyl ester solution (μ L); m is the mass of biodiesel sample (mg).

2.5 Kinetics study

In the transesterification reaction, stoichiometrically 1 mol of triglycerides (TG) reacts with 3 mol of MeOH to yield 3 mol of FAME and 1 mol of glycerol. The whole transesterification reaction process can be written as Eq.2.

The general rate equation for the transesterification reaction can be expressed as Eq.3:

$$\frac{d[TG]}{dt} = k_r [TG]^n MeOH^m \quad (3)$$

where t is reaction time, k_r represents the rate constant.

The rate equation can be rewritten as Eq.4:

$$\frac{d[TG]}{dt} = k_r [TG]^n = A \exp\left(\frac{-E_a}{RT}\right) [TG]^n \quad (4)$$

where t is reaction time, k_r represents the rate content.

In the CH process, homogeneous base-catalyzed reaction, KOH is dissolved in methanol in advance, and the effect of stirring makes the entire reaction system be regarded as a homogeneous reaction. For the molar concentration of methanol is much higher than the stoichiometric requirement during the whole reaction, the concentration of methanol can be treated as a constant. And the second-order transesterification can be regarded as a pseudo-first order reaction (Ramezani, Rowshanzamir et al. 2010, Zhang, Sheng et al. 2010).

The rate equation for a pseudo-first order model ($n = 1$) can be expressed as Eq.5:

$$[TG] = [TG]_0 e^{-k_r t} \quad (5)$$

As for the MW process, it has been reported that under certain microwave power conditions, the reaction follows pseudo-second-order reaction kinetics (Yeong, Law et al. 2019). The integrated rate equation can be written as Eq.6:

After dividing left and right by $[TG]_0$ at the same time, the rate equation can be expressed as Eq.6:

$$\frac{1}{[TG]} = \frac{1}{[TG]_0} + k_r t \quad (6)$$

The activation energy of the reaction was calculated using the Arrhenius equation (Eq.7).

$$k = A e^{\frac{-E_a}{RT}} \quad (7)$$

Take the logarithm of both sides:

$$\ln k = -\frac{E_a}{RT} + C \quad (8)$$

3 Results and discussion

3.1 WCO characterization

Table 1 provides the results of WCO characterization. To illustrate its potential for producing biodiesel, the quality parameters were compared with waste oils used in other biodiesel product reactions.

GC chromatogram showed the main chemical components of the WCO acid profile. Compared with other waste edible oils which were used in biodiesel product, the fatty acid composition of the waste oil in this study is more complex. While the main ingredients are fatty acids of C16 to C20, accounting for 96.55%, it still has the potential to be converted into biodiesel. (Yen, Hu et al. 2013)

Acid value and moisture content are important indicators to characterize the properties of WCO. Excessive free fatty acids will react with the alkali catalyst KOH, and the water in the oil will also promote the saponification reaction, reducing the yield of biodiesel produced by the transesterification reaction. The threshold values of the acid value and moisture content of the feedstock oil for homogeneous base-catalyzed transesterification are respectively 0.06% (Canakci and Van Gerpen 1999) and 1% ($2 \text{ mg KOH} \cdot \text{g}^{-1}$) (Maddikeri, Pandit et al. 2012). According to Table 1, the acid value of all feedstocks is less than the threshold value moisture content, which shows that the raw materials in the table are suitable for the production of biodiesel by homogeneous base catalytic transesterification. Especially, after pretreatment, the acid value of our WCO is $0.4 \text{ mg KOH} \cdot \text{g}^{-1}$. It is possible to obtain a higher FAME yield biodiesel in this study.

The density of the WCO is lower than other waste oils, and the saponification value is only higher than that of Hekel fish oil, indicating that WCO has a longer carbon chain and higher average molar mass. The low iodine value of WCO indicates that its degree of unsaturation is low. The WCO has longer average carbon chain and lower degree of unsaturation, its biodiesel would have a higher cetane number and strong oxidation stability.(Knothe 2005, Zhang, Pham et al. 2019) Compared with other non-edible feedstock, the WCO had higher potential for biodiesel production.

In addition, further experiments on the effect of moisture content would be discussed in 3.2.3.

Table 1 The quality parameters of WCO and the comparison with the properties of waste grease used in other studies

Quality Parameters	WCO	Fried Oil in Spain (Bouaid, Vázquez et al. 2016)	Fried Oil in Turkey (Uzun, Kılıç et al. 2012)	Hekel Fish Oil (Fadhil and Ali 2013)
Fatty acid composition				
C12:0	0.13	—	—	0.71
C14:0	1.00	0.28	—	1.48
C15:0	0.16	—	—	0.11
C16:0	13.64	15.01	7.07	10.53
C16:1	3.26	—	—	—
C17:0	0.52	—	—	1.45
C18:0	8.82	4.66	2.42	4.20
C18:1	20.05	31.88	36.68	20.90
C18:2	29.68	42.56	52.20	14.06
C18:3	3.32	—	—	9.28
C20:0	13.89	0.26	—	—
C20:1	1.79	—	—	—
C20:2	0.69	—	—	0.86
C20:4	0.89	—	—	7.07
C20:5	—	—	—	7.82

Quality Parameters	WCO	Fried Oil in Spain (Bouaid, Vázquez et al. 2016)	Fried Oil in Turkey (Uzun, Kılıç et al. 2012)	Hekel Fish Oil (Fadhil and Ali 2013)
C22:0	1.05	0.23	0.83	—
C22:5	—	—	—	3.95
C22:6	—	—	—	2.21
C24:0	0.42	0.08	—	—
Physicochemical properties				
Density (g•m ³)	0.913a	—	0.963b	0.9156c
Acid Value (mg KOH•g ⁻¹)	0.4	1.3	0.587	1.9
Saponification Value (mg KOH•g- 1)	184.1	—	185	182.15
Iodine value (g I ₂ /100 g)	36.88	115	122	107
POV (mmol/kg)	13.67	3.45	84.38	—
Moisture content (%)	0.097	0.023	—	—

*— means no data available; a means the density at 20 °C; b means the density at 15 °C; c means the density at 15.6°C.

3.2 Biodiesel production

3.2.1 Biodiesel yield of EH process

In case of EH, the optimization of the factors including reaction temperature, reaction time, catalyst amount and methanol/oil molar ratio. Fig.2 shows the variation into FAME yield. The maximum biodiesel yield obtained from CH technique is 93.45%, under the condition of 60 °C, 30min, the dosage of 1wt.% KOH and the methanol/oil molar ratio of 6:1. The detailed results are shown in table S1.

Fig.2a indicated that FAME yield increased with the increase of temperature from 50 to 60 °C, and further increase of temperature would reduce the biodiesel yield.

et al. also reported that the maximum FAME yield was achieved at the same reaction temperature. (Mercy Nisha Pauline, Sivaramakrishnan et al. 2021) Higher temperature could accelerate the reaction and shorten the reaction time by favouring the number of collisions. (Ma and Hanna 1999, Leung and Guo 2006) In addition, an increase in the temperature decreased the viscosity of the reaction mixture, increasing alcohol-oils two-phase contact as well (Gupta and Rathod 2018). Further increase of reaction temperature would accelerate methanol volatilization, which brought the decline of the FAME content. High temperature would promote the occurrence of saponification may be another important reason (Phan and Phan 2008).

When the reaction time was in the range of 5-60min, the reaction was very fast in the first 5 min, then the process slowed down and tilled the maximum methyl content at 30min (Fig.2b). To further increase the reaction time from 30 min to 60 min had no further positive effect on the methyl content, even led to a small reduction. In this study, prolonging the reaction time would slightly decrease the FAME yield, but previous studies had different results. Agarwal.et al. produced biodiesel from waste cooking oil under KOH catalyzed, and reported the best reaction time was 60min.(Agarwal, Chauhan et al. 2012) Elango, R. K., et al. reported a maximum of 94.9% FAME yield was obtained at 60 °C with 1.25% (w/v) KOH catalyst and 1:12 oil: methanol molar ratio for 60 min of reaction. (Elango, Sathiasivan et al. 2019) The reason for this difference could be that more excess methanol can promote the positive shift of the chemical equilibrium for a longer period of time, resulting in higher yields. However, considering economy, 30min was still selected as the subsequent reaction.

224 When methanol content raising from 3:1 to 15:1, the FAME yield could remain above 75%
225 (Fig.2c). The improvement of methanol/oils molar ratio could drive the reaction process in the
226 forward direction. Besides, when methanol content gets higher in the system, the more
227 methanol can stay in the system when temperature increasing. But, extra methanol would
228 dissolve more glycerin, increasing the glycerol concentration in the reaction system. (Milano,
229 Ong et al. 2018) The more methanol in the reaction system, the specific surface area of
230 methanol-oils turns less as well (Motasemi and Ani 2012). The maximum biodiesel yield of
231 93.45% was achieved for 6:1 methanol/oil molar ratio.

232 As shown in Fig.2d, the reaction would not occur without catalyst, and lower concentration (0
233 to 0.5% w/w of oils) of KOH led to lower methyl content. The increase in the amount of catalyst
234 brings more methoxy free radicals, increases the contact opportunities between free radicals
235 and oils, and promotes the transesterification reaction. The maximum content of methyl ester
236 was obtained with 1.0% KOH. An excess amount of KOH would reduce the biodiesel yield,
237 for high KOH concentrations causes more triglycerides being involved in the saponification
238 reaction and brings about the formation of soap (Chhetri, Watts et al. 2008).

Fig.2. Effects of the process parameters (temperature, time, methanol /oils molar ratio and KOH concentration).(a) Effect of temperature; (b) Effect of time; (c) Effect of methanol/oils molar ratio; (d) Effect of catalyst concentration.

Experimental yield data were given as an input of the analysis of variance (ANOVA) in table 2. The results showed that the reaction time has no obvious effect on the transesterification yield in EH process. The significant terms influencing the biodiesel yield in decreasing order are catalyst amount, methanol/oil molar ratio and reaction temperature.

Table 2 ANOVA analysis of EH process

Source of difference	Variance	Degrees of freedom	Mean square error	F value	P value	F critical value
Time	0.004321	4	0.001080	1.863	0.1663	3.007
Temperature	0.009093	4	0.002273	3.920	0.02100	3.007
RO	490.4	4	122.6	38.39	4.864E-06	3.478

Source of difference	Variance	Degrees of freedom	Mean square error	F value	P value	F critical value
CA	1907E+01	4	4767	1875	2.511E-14	3.478

RO stands for methanol/oil molar ratio; CA stands for catalyst amount.

3.2.2 Biodiesel yield of MW process

In case of MW, the optimization of the factors including microwave power, reaction time, catalyst amount and methanol/oil molar ratio. Fig.3 shows the variation into FAME yield. The maximum biodiesel yield obtained from MW technique is 80.66%, under the condition of 200W, 5min, the dosage of 1wt.% KOH and the methanol/oil molar ratio of 9:1. The detailed results are shown in table S2.

Fig.3 Effects of the process parameters (microwave power, time, methanol /oils molar ratio and KOH concentration).(a) Effect of microwave power; (b) Effect of time; (c) Effect of methanol/oils molar ratio; (d) Effect of catalyst concentration.

The curves of MW process were very similar to those of the EH process, but there was difference in value. The reaction time in MW technique was sustainably reduced, while the amount of methanol required was higher. These was because of that microwave would affect dipole rotation and ion migration, improve the thermal conductivity and convection current of the mixture. (Manco, Giordani et al. 2012, Sharma, Kodgire et al. 2021) This effect accelerated molecular level heating, would increase the volatilization of methanol while shortening the reaction time. In MW process, the temperature rised very sharply, breaking through the boiling point of methanol after 2 minutes; even if the temperature rise slowed down after 5 minutes, the system temperature had already exceeded 80°C (Fig.4). Too high reaction temperature made methanol boil violently, which seriously affected the condensation effect. Therefore, the final yield was lower than EH process.

Fig.4 Temperature rising of the reaction system in MW process

Experimental yield data were given as an input of the analysis of variance (ANOVA) in table 3. According to the results, in MW process, the microwave power and reaction time would not significantly affect the reaction yield. The significant terms influencing the biodiesel yield in decreasing order are catalyst amount, and methanol/oil molar ratio. It was worth noting that the probability value of catalyst amount were almost the same in EH process and MW process.

Table 3 ANOVA analysis of MW process

Source of difference	Variance	Degrees of freedom	Mean square error	F value	P value	F critical value
Time	7.077	2	3.539	0.4435	0.6566	4.459
Power	113.5	4	28.38	3.557	0.0597	3.838
RO	220.5	4	55.12	22.76	5.223E-05	3.478
CA	1528E+01	4	3821	1869	2.549E-14	3.478

RO stands for methanol/oil molar ratio; CA stands for catalyst amount.

3.2.3 The effect of water in both reaction system

Oleic acid triglyceride was used as model compound to determine the impact of water content on the methyl ester content. The experiments were conducted in the presence of water ranging from 0.05% to 0.5% w/w of oil. The other parameters were in constant with the experiments where the maximum methyl content was obtained in the above sections. The results are represented in Fig.5. For both CH and MW techniques, water content had obviously negative effect on biodiesel yield. Moisture would promote the saponification reaction was the main reason of FAME yield decrease. In the case of MW, water molecules would move quickly along the direction of the constantly changing microwave field, thereby accelerating the saponification and hydrolysis reactions. Higher reaction temperature would also increase saponification and reduce the yield of biodiesel. Thus, MW technique has more stringent requirements on the water content of the feedstock oil, when WCO is used as a reactant, more stringent pretreatment of water removal is required.

Fig.5 Effect of catalyst concentration on the methyl content in the biodiesel sample

3.3 Kinetics Analysis

For CH and MW, the rate constants of the transesterification reaction under different temperature or different microwave power were respectively determined by curve fitting the reaction rate equations with the biodiesel yield. Performing kinetic calculations according to 2.5, the reaction rate constant of CH process was found to increase from 0.3479 min^{-1} to 0.4048 min^{-1} . The reaction rate constant at 60°C was 0.3737 . The reaction rate constant of MW process increased from 3.623 min^{-1} to 9.965 min^{-1} . The reaction rate constant at 200W was 9.247 min^{-1} . It is worth noting that the reaction rate constant of the MW process reached the maximum when the microwave power was 300W , and decreased at 500W . It is observed that the k value was approximately 10 to 20 times higher respectively in the case MW process than that of CH. The higher rate constant means a faster reaction rate, requiring lower activation energy. (Sharma, Kodgire et al. 2021)

Activation energy values derived from Arrhenius plots using Eq. 8 for the both techniques are shown in Fig 6. The activation energy for CH and MW process are found to be $6768 \text{ J}\cdot\text{mol}^{-1}$ and $503.4 \text{ J}\cdot\text{mol}^{-1}$. Microwave heating greatly reduced the activation energy of the reaction.

Fig.6 Linear fitting of $\ln k$ to $1/T$ in transesterification reaction

3.4 Reaction efficiency comparison

A comparative study has been done on different biodiesel producing process as shown in table 6. The main advantage of homogeneous base-catalyzed transesterification is that the reaction temperature is low, the reaction time is short, the catalyst and methanol are added in a small amount, and the production cost can be saved. There is a large difference in FAME yield due to the difference in raw materials. Compared with other research, this study still has the advantages of high speed and low production cost, but FAME yield is slightly insufficient. This is likely due to the small amount of un-removed moisture contained in the WCO.

The acid catalysed transesterification or two-step esterification- trans-esterification has a wider application range, can adapt to the possible high free fatty acid content and high water content of WCO, and can obtain high FAME yield under strong acid catalyzed conditions, but the reaction conditions are harsh and the methanol consumption is larger. As compared to these reported data, at present experiment work biodiesel yield 93% was obtained at 30min reaction time, 60°C reaction time and 6:1 methanol/ oil ratio for the composition and physical properties of WCO in EH process.

The data in 3.2 shows that in this study, the transesterification yield of the MW process is lower than that of the EH process. The possible reason is that methanol is more polar and has a strong ability to absorb microwaves. The methanol in the system heats up rapidly, becoming a "hot spot" in the reaction system, and rapidly evaporates above its boiling point, causing the methanol concentration of the reaction system to drop, which affects subsequent transesterification reactions proceed; while triglycerides are just the opposite. They are less polar and have a weak microwave absorbing ability, which becomes a "cold spot" in the

reaction system, making the rate of reaction with methanol slower; in addition, with As the reaction progresses, the polarity of the intermediate products and products of the reaction system is smaller than the polarity of the initial reactants, which leads to the gradual decrease of the thermal and non-thermal effects of the microwave. Compared with previous studies, the transesterification yield of the MW process in this study is significantly lower (93.06% vs 80.66%) (Gunawan, Aznury et al. 2019, Ibrahim, Omilakin et al. 2019). This shows that the WCO used in this study is less adaptable to microwaves, and the most important factor is the water content of WCO.

Table 6

Comparison of different biodiesel produce process.

Raw Material	Reaction Method	Molar Ratio (oil: alcohol)	Reaction Temperature (°C)	Reaction Time (min)	Catalyst Concentration (wt. %)	FAME yield (%)	Ref.
Silurus triostegus Heckel fish oil	KOH	6.0	32.0	60	0.50	96.0	(Fadhil and Ali 2013)
Waste frying oil	KOH	7.3	55.3	-	0.50	96.3	(Harabi, Bouguerra et al. 2019)
Garcinia gummi-gutta seed oil (GGO)	KOH	6.0	55.0	90	1.6	97.0	(Rajagopala char, Joshi et al. 2019)
Linseed oil	KOH	20.0wt.%*	60.0	-	1.5	88.0	(Akram, Singh et al. 2019)
WCO	K ₂ O-CaO	18.0	-	300	4.0	89.5	(Zul, Ganesan et al. 2019)
WCO (through acid-catalyzed pre-esterification)	KOH	3.0	50.0	360+50	1.0	94.0	(Sahar, Sadaf et al. 2018)

Raw Material	Reaction Method	Molar Ratio (oil: alcohol)	Reaction Temperature (°C)	Reaction Time (min)	Catalyst Concentration (wt. %)	FAME yield (%)	Ref.
WCO	H ₂ SO ₄	20.0	95.0	600	4.0	90.0	(Wang, Ou et al. 2006)
WCO (through acid-catalyzed pre-esterification)	Alkali	10.0	95.0	240	2.0	97.2	(Wang, Ou et al. 2006)
WCO	KOH	6.0	60.0	30	1.0	93.4	This study

-Indicates that the component is not reported

4 Conclusions

This study systematically compared the influencing factors and effects of the alkali-catalyzed transesterification reaction of waste edible oils under EH and MW process, then compared the results with previous studies, and explained the possible reasons for the decrease in yield under MW conditions in this study eventually. The specific conclusions are list as follows.

The maximum FAME yield of CH process appeared at the reaction temperature is 60 °C, the reaction time is 30 min, the molar ratio of alcohol to oil is 6:1, and the catalyst concentration is 1.0%, reaches 93.4%. The maximum biodiesel yield obtained from MW technique is 80.66%, under the condition of 200W, 5min, 1wt. % KOH and the methanol/oil molar ratio of 9:1.

Compared with the CH process, microwave heating can shorten the reaction time, but will increase the consumption of methanol, and the final yield will also decrease. The best catalyst percentages for CH process and MW process are the same. And one-way analysis of variance results showed that the biodiesel yield was witnessed to be very sensitive to methanol/oil molar ratio and catalyst weight % for both CH and MW techniques.

The activation energy of CH and MW were respectively determined by the pseudo-first-order kinetic modeling and pseudo-second-order kinetic modeling. The activation energy for CH and MW process are found to be 6 768 J·mol⁻¹ and 503.4 J·mol⁻¹. Microwave heating greatly reduced the activation energy of the reaction. However, the transesterification yield of the MW process is lower than that of the CH process.

Compared with other biodiesel producing process, CH process in this study has the advantages of high speed and low production cost, while FAME yield is slightly insufficient. This is likely due to the small amount of un-removed moisture contained in the WCO.

Declarations

- Ethics approval and consent to participate is not applicable;
- Consent for publication is not applicable;
- All data generated or analysed during this study are included in this published article [and its supplementary information files];
- The authors declare that they have no competing interests;
- The works were financially supported by Key Project in the National Science & Technology Pillar Program in China (grant number: 2010BAK69B24).
- All authors contributed to the study conception and design. Wj L, FW and Gm L performed the material preparation, data collection and analysis. The first draft of the manuscript was written by Wenjing Li. Wz H, Hc Z and Jw H critically revised the work. All authors read and approved the final manuscript.

References

Agarwal, M., G. Chauhan, S. P. Chaurasia and K. Singh (2012). "Study of catalytic behavior of KOH as homogeneous and heterogeneous catalyst for biodiesel production." Journal of the Taiwan Institute of Chemical Engineers **43**(1): 89-94.

Akram, W., Y. Singh, A. Sharma and N. K. Singh (2019). "Experimental studies on performance and exhaust emission characteristics of a diesel engine fuelled with diesel-linseed oil methyl ester (LOME) blends." Energy Sources Part a-Recovery Utilization and Environmental Effects.

Bouaid, A., R. Vázquez, M. Martinez and J. Aracil (2016). "Effect of free fatty acids contents on biodiesel quality. Pilot plant studies." Fuel **174**: 54-62.

Bussness, S. (2012). "Gutter oil profit chain revealed: up to 300%." from <http://business.sohu.com/20120905/n352362645.shtml>.

Canakci, M. and J. Van Gerpen (1999). "Biodiesel production via acid catalysis." Transactions of the Asae **42**(5): 1203-1210.

Chhetri, A. B., K. C. Watts and M. R. Islam (2008). "Waste Cooking Oil as an Alternate Feedstock for Biodiesel Production." Energies **1**(1): 3-18.

China, N. B. o. S. o. (2018). Production of refined edible vegetable oil.

Chuah, L. F., J. J. Klemes, S. Yusup, A. Bokhari and M. M. Akbar (2017). "A review of cleaner intensification technologies in biodiesel production." Journal of Cleaner Production **146**: 181-193.

Cvengros, J. and Z. Cvengrosova (2004). "Used frying oils and fats and their utilization in the production of methyl esters of higher fatty acids." Biomass & Bioenergy **27**(2): 173-181.

Elango, R. K., K. Sathiasivan, C. Muthukumaran, V. Thangavelu, M. Rajesh and K. Tamilarasan (2019). "Transesterification of castor oil for biodiesel production: Process optimization and characterization." Microchemical Journal **145**: 1162-1168.

Fadhil, A. B. and L. H. Ali (2013). "Alkaline-catalyzed transesterification of Silurus triostegus Heckel fish oil: Optimization of transesterification parameters." Renewable Energy **60**: 481-488.

Farid, M. A. A., M. A. Hassan, Y. H. Taufiq-Yap, M. L. Ibrahim, M. R. Othman, A. A. M. Ali and Y. Shirai (2017). "Production of methyl esters from waste cooking oil using a heterogeneous biomass-based catalyst." Renewable Energy **114**: 638-643.

fei, z. and n. maiqian (2011). "Study on the production of single cell protein by discarded edible oils and fats." Ecotechnology **17**(3): 1-4.

Gunawan, I., M. Aznury and A. Husaini (2019). "Synthesis Biodiesel from Waste Cooking Oil with Microwave Irradiation Method as Alternative Renewable Energy Source." Symposium of Emerging Nuclear Technology and Engineering Novelty (Senten 2018) **1198**.

Gupta, A. R. and V. K. Rathod (2018). "Waste cooking oil and waste chicken eggshells derived solid base catalyst for the biodiesel production: Optimization and kinetics." Waste Management **79**: 169-178.

Harabi, M., S. N. Bouguerra, F. Marrakchi, L. P. Chrysikou, S. Bezergianni and M. Bouaziz (2019). "Biodiesel and Crude Glycerol from Waste Frying Oil: Production, Characterization and Evaluation of Biodiesel Oxidative Stability with Diesel Blends." Sustainability **11**(7).

Ibrahim, A. P., R. O. Omilakin and E. Betiku (2019). "Optimization of microwave-assisted solvent extraction of non-edible sandbax (Hura crepitans) seed oil: A potential biodiesel feedstock." Renewable Energy **141**: 349-358.

Jia, L., H. Xiangfeng, L. Lijun, Y. Na, G. Sainan, C. Xuyuan, Y. Dianhai and Z. Qi (2009). "Study on Dietziasp. S-JS-1 Production of Bio-Demulsifier by Using Waste Oil." Microbiology bulletin **36**(4): 491-497.

Knothe, G. (2005). "Dependence of biodiesel fuel properties on the structure of fatty acid alkyl esters." Fuel Processing Technology **86**(10): 1059-1070.

426 Kulkarni, M. G. and A. K. Dalai (2006). "Waste cooking oil-an economical source for biodiesel: A review."
 427 Industrial & Engineering Chemistry Research **45**(9): 2901-2913.

428 Leung, D. Y. C. and Y. Guo (2006). "Transesterification of neat and used frying oil: Optimization for biodiesel
 429 production." Fuel Processing Technology **87**(10): 883-890.

430 Ma, F. and M. A. Hanna (1999). "Biodiesel production: a review 1." Bioresource Technology **70**(1): 1-15.

431 Maddikeri, G. L., A. B. Pandit and P. R. Gogate (2012). "Intensification Approaches for Biodiesel Synthesis from
 432 Waste Cooking Oil: A Review." Industrial & Engineering Chemistry Research **51**(45): 14610-14628.

433 Manco, I., L. Giordani, V. Vaccari and M. Oddone (2012). "Microwave technology for the biodiesel production:
 434 Analytical assessments." Fuel **95**(1): 108-112.

435 Mardhiah, H. H., H. C. Ong, H. H. Masjuki, S. Lim and H. V. Lee (2017). "A review on latest developments and
 436 future prospects of heterogeneous catalyst in biodiesel production from non-edible oils." Renewable &
 437 Sustainable Energy Reviews **67**: 1225-1236.

438 Math, M. C., S. P. Kumar and S. V. Chetty (2010). "Technologies for biodiesel production from used cooking oil
 439 — A review." Energy for Sustainable Development **14**(4): 339-345.

440 Mercy Nisha Pauline, J., R. Sivaramakrishnan, A. Pugazhendhi, T. Anbarasan and A. Achary (2021).
 441 "Transesterification kinetics of waste cooking oil and its diesel engine performance." Fuel **285**: 119108.

442 Milano, J., H. C. Ong, H. H. Masjuki, A. S. Silitonga, W. H. Chen, F. Kusumo, S. Dharma and A. H. Sebayang
 443 (2018). "Optimization of biodiesel production by microwave irradiation-assisted transesterification for waste
 444 cooking oil- Calophyllum inophyllum oil via response surface methodology." Energy Conversion and
 445 Management **158**(FEB.): 400-415.

446 Milano, J., H. C. Ong, H. H. Masjuki, A. S. Silitonga, F. Kusumo, S. Dharma, A. H. Sebayang, M. Y. Cheah and
 447 C. T. Wang (2018). "Physicochemical property enhancement of biodiesel synthesis from hybrid feedstocks of
 448 waste cooking vegetable oil and Beauty leaf oil through optimized alkaline-catalysed transesterification." Waste
 449 Management **80**: 435-449.

450 Motasemi, F. and F. N. Ani (2012). "A review on microwave-assisted production of biodiesel." Renewable &
 451 Sustainable Energy Reviews **16**(7): 4719-4733.

452 Naylor, R. L. and M. M. Higgins (2017). "The political economy of biodiesel in an era of low oil prices."
 453 Renewable & Sustainable Energy Reviews **77**: 695-705.

454 Peiro, L. T., G. V. Mendez and X. G. I. Durany (2008). "Exergy analysis of integrated waste management in the
 455 recovery and recycling of used cooking oils." Environmental Science & Technology **42**(13): 4977-4981.

456 Phan, A. N. and T. M. Phan (2008). "Biodiesel production from waste cooking oils." Fuel **87**(17-18): 3490-3496.

457 Putra, M. D., C. Irawan, Udiantoro, Y. Ristianingsih and I. F. Nata (2018). "A cleaner process for biodiesel
 458 production from waste cooking oil using waste materials as a heterogeneous catalyst and its kinetic study." Journal
 459 of Cleaner Production **195**: 1249-1258.

460 Rajagopalachar, S., S. S. Joshi and R. P. Reddy (2019). "Biodiesel synthesis from Garcinia gumnii-quitto (L.
 461 Robson) seed oil: fuel feasibility evaluation of a novel feedstock by homogeneous and heterogeneous
 462 transesterification." Biofuels-Uk **10**(3): 403-410.

463 Ramezani, K., S. Rowshanzamir and M. H. Eikani (2010). "Castor oil transesterification reaction: A kinetic study
 464 and optimization of parameters." Energy **35**(10): 4142-4148.

465 Sahar, S. Sadaf, J. Iqbal, I. Ullah, H. N. Bhatti, S. Nouren, R. Habib ur, J. Nisar and M. Iqbal (2018). "Biodiesel
 466 production from waste cooking oil: An efficient technique to convert waste into biodiesel." Sustainable Cities and
 467 Society **41**: 220-226.

Sharma, A., P. Kodgire and S. Singh Kachhwaha (2021). "An experimental investigation of the performance of biodiesel production techniques: Optimization, kinetics, and energy analysis." Thermal Science and Engineering Progress **22**: 100842.

Silitonga, A. S., A. H. Shamsuddin, T. Mahlia, J. Milano, F. Kusumo, J. Siswantoro, S. Dharma, A. H. Sebayang, H. Masjuki and H. C. Ong (2020). "Biodiesel synthesis from Ceiba pentandra oil by microwave irradiation-assisted transesterification: ELM modeling and optimization." Renewable Energy **146**.

Uzun, B. B., M. Kılıç, N. Özbay, A. E. Pütün and E. Pütün (2012). "Biodiesel production from waste frying oils: Optimization of reaction parameters and determination of fuel properties." Energy **44**(1): 347-351.

Wang, Y., S. Y. Ou, P. Z. Liu, F. Xue and S. Z. Tang (2006). "Comparison of two different processes to synthesize biodiesel by waste cooking oil." Journal of Molecular Catalysis a-Chemical **252**(1-2): 107-112.

Xingguo, W. (2013). Oil Chemistry. Beijing, Beijing Science Press.

Yao, Z. and E. Min (2010). "A double-edged sword of the discarded edible oils: Harmful pollutants or resources utilization." Natural Gas Industry **30**(5): 123-128.

Yen, H. W., I. C. Hu, C. Y. Chen, S. H. Ho, D. J. Lee and J. S. Chang (2013). "Microalgae-based biorefinery - From biofuels to natural products." Bioresource Technology **135**: 166-174.

Yeong, S. P., M. C. Law, K. Y. You, Y. S. Chan and V. C. C. Lee (2019). "A coupled electromagnetic-thermal-fluid-kinetic model for microwave-assisted production of Palm Fatty Acid Distillate biodiesel." Applied Energy **237**: 457-475.

Yinxia, Q., C. Jian and L. Changhai (2009). "Advances in the production of single cell proteins by fermentation using waste resources." Food industry technology(5): 366-369.

Zhang, L., B. Sheng, Z. Xin, Q. Liu and S. Sun (2010). "Kinetics of transesterification of palm oil and dimethyl carbonate for biodiesel production at the catalysis of heterogeneous base catalyst." Bioresour Technol **101**(21): 8144-8150.

Zhang, R., P. X. Pham, S. Kook and A. R. Masri (2019). "Influence of biodiesel carbon chain length on in-cylinder soot processes in a small bore optical diesel engine." Fuel **235**: 1184-1194.

Zul, N. A., S. Ganesan and M. H. Hussin (2019). "Application of K-Impregnated Staghorn Coral as Catalyst in the Transesterification of Waste Cooking Oil." Sains Malaysiana **48**(4): 803-811.

Supplementary Files

This is a list of supplementary files associated with this preprint. Click to download.

- [SupplementaryInformation.pdf](#)