



Microwave assisted esterification of acidified oil from waste cooking oil by CERP/PES catalytic membrane for biodiesel production

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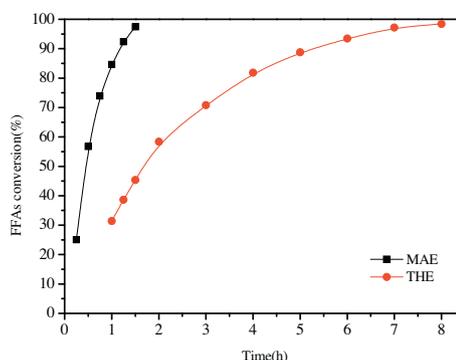
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HIGHLIGHTS

- ▶ We prepared CERP/PES hybrid catalytic membrane for biodiesel production.
- ▶ We conducted esterification of acidified oil under traditional heating method.
- ▶ We conducted esterification of acidified oil under microwave irradiation.
- ▶ Biodiesel production with microwave irradiation needs less time and catalyst.
- ▶ Esterification with microwave irradiation offers a fast, easy and effective route.

GRAPHICAL ABSTRACT

Compared with traditional heating esterification (THE), microwave assisted esterification (MAE) needs less reaction time, lower reaction temperature, less energy and lower methanol additive. Thus, manufacturing biodiesel using microwave represents a fast, easy and effective route with advantages of a short reaction time, a low methanol/acidified oil mass ratio, an ease of operation, reduced energy consumption and all with lower production cost.



ARTICLE INFO

Article history:

Received 21 March 2012

Received in revised form 23 June 2012

Accepted 25 June 2012

Available online 4 July 2012

Keywords:

Biodiesel

Cation ion-exchange resin

Hybrid catalytic membrane

Esterification

Microwave irradiation

ABSTRACT

The traditional heating and microwave assisted method for biodiesel production using cation ion-exchange resin particles (CERP)/PES catalytic membrane were comparatively studied to achieve economic and effective method for utilization of free fatty acids (FFAs) from waste cooking oil (WCO). The optimal esterification conditions of the two methods were investigated and the experimental results showed that microwave irradiation exhibited a remarkable enhanced effect for esterification compared with that of traditional heating method. The FFAs conversion of microwave assisted esterification reached 97.4% under the optimal conditions of reaction temperature 60 °C, methanol/acidified oil mass ratio 2.0:1, catalytic membrane (annealed at 120 °C) loading 3 g, microwave power 360 W and reaction time 90 min. The study results showed that it is a fast, easy and green way to produce biodiesel applying microwave irradiation.

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1. Introduction

The enormous exhaust emissions of fossil fuels lead to serious and great concerns about the energy and environment and

biodiesel has gained much attention for it is believed to be renewable and environmental friendly (Foo and Hameed, 2012; Hong, 2011). Biodiesel, a mixture of mono-alkyl esters of long-chain fatty acids, is an alternative diesel fuel derived from vegetable and

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animal oils/fats by transesterification and esterification with short-chain alcohols (e.g. methanol or ethanol). It has many advantages such as environmental friendliness, biodegradability, renewability, low toxicity, high security of use and storage, adaptability to presently used engines and good blending ability with petroleum-based diesel fuels (Wang et al., 2006; El Sherbiny et al., 2010).

However, biodiesel are not currently competitive with fossil fuels due to its higher cost of raw material and production (Yan et al., 2011). One way to reduce the cost of biodiesel is to select cheaper oil feeds like waste cooking oils (WCO) (Feng et al., 2010; Phan and Phan, 2008). WCO contains a lot of free fatty acids (FFAs) and cannot be directly used to prepare biodiesel by alkaline-catalyzed transesterification for soap formation (Shi et al., 2011; Liu et al., 2010). Therefore, the FFAs in waste cooking oils were often firstly esterified by homogeneous strong acid-catalysts, such as sulphuric and hydrochloric acid (Marchetti and Errazu, 2008; Zhang and Jiang, 2008). But liquid acids are difficult to be separated from the reaction medium and produce wastewater and strong equipments corrosion (Shi et al., 2010; Zhu et al., 2010).

Catalytic membranes, as one form of heterogeneous catalysts were developed to overcome the shortcoming of liquid acid catalysts for they have a lot of advantages, such as catalyst separation, mild reaction conditions, no corrosion to equipment and no pollution to the environment (Ding et al., 2011). Polyethersulfone (PES) is a good candidate as polymeric material for the preparation of catalytic membrane supports since it possesses good mechanical and thermal stability and good chemical resistance to aliphatic hydrocarbons, alcohols and acids. Cation ion-exchange resins can offer better selectivity towards the desired product(s) and better reusability compared with homogeneous acid catalysts (Feng et al., 2011). In our previous work, cation ion-exchange resin particles/PES hybrid catalytic membrane was prepared and used as catalyst for the esterification of acidified oil with different alcohols and the membrane showed good catalytic activity in biodiesel production (Ding et al., 2011; Zhang et al., 2012).

Microwave irradiation is an unconventional energy source which has been widely used for a large number of chemical reactions including esterification. As polar molecules can selective absorb microwave energy and non-polar molecules are inert to the microwave dielectric loss, chemical reactions can be greatly accelerated under microwave irradiation condition (Kumar et al., 2011). Microwave irradiation has a selective heating function and requires less energy input for heating compared with conventional heating method. It is possible to perform reactions quickly, efficiently and safely using scientific microwave apparatus (Kumar et al., 2011). Some previous studies on microwave-assisted synthesis of biodiesel reported that microwave irradiation can accelerate the reaction and reduce the reaction time (Hernando et al., 2007; Hsiao et al., 2011; Refaat et al., 2008; Su et al., 2010; Immacolata et al., 2012; Yuan et al., 2009). Azcan and Danisman (2008) reported a significant reduction in the reaction time and an increase in product yield in microwave irradiated transesterification. However, the esterification of high FFAs oil with catalytic membranes under microwave condition was little reported.

In the present work, we applied CERP/PES catalytic membrane for esterification of acidified oil with methanol for biodiesel production under traditional heating method and microwave irradiation. The main affecting parameters including reaction time, reaction temperature, catalytic membrane loading, methanol/acidified oil mass ratio and microwave power were analyzed to find out the optimal reaction conditions. Furthermore, the compositions of the produced biodiesel were analyzed by Gas chromatography-mass Spectrometry.

2. Methods

2.1. Materials

PES was purchased from Solvay Advanced Polymer Co. Ltd. Cation ion-exchange resin NKC-9 (average size of 0.83 mm) in acidic form with total exchange capacity of ≥ 4.7 mmol/g, average pore diameter of 56 nm and moisture content of $\leq 5\%$ was purchased from the Chemical Plant of Nankai University. NKC-9 was milled in frozen state using liquid nitrogen to obtain fragments (CERP) and the average particle size of the CERP particles analyzed by Laser Scattering Particle Analyzer (BT-9300H, Dandong Baite Instrument CO. Ltd. Dandong, China) was 24.96 μm . Acidified oil (FFAs) from waste cooking oil with an acid value of 152.3 mg KOH/g was kindly supplied by Hubei Haolin Bioenergy Company and filtered to remove impurities. No water was detected by Karl Fischer water tester with a sensitivity of 500 ppm (KF-1A, Shanghai Precision and Scientific Instrument Co. Ltd., China). The main compositions of the feedstock oil analyzed by Gas chromatography-mass Spectrometry (GC-MS: 6890N GC/5973 MS, Agilent Technologies) were dodecanoic acid, tetradecanoic acid, hexadecanoic acid and octadecadienoic acid. The other chemicals were all AR grade and used without further purification.

2.2. Membrane preparation

The PES and CERP were dried at 120 °C for 1 h and 50 °C for 24 h, respectively in a vacuum oven to remove a trace amount of water in them. Twenty grams PES was dissolved in 80 g NMP under continuous stirring for 12 h at room temperature to obtain PES solution and then 20 g CERP was added into the above solution and stirred till a homogeneous solution was obtained. The solution was cast onto glass plates and a copper wire was used to control the thickness of the membranes. The membranes were immersed into secondary distilled water to phase inversion and washed for 6 h to remove the solvents. Then the membranes were peeled off from the glass plates and dried in a vacuum oven at 50 °C for 24 h. The obtained membranes were annealed at 80, 120, 150 and 200 °C, respectively for 1 h in a heating oven. Finally, the membranes were cut into pieces for further use.

2.3. Traditional heating esterification (THE)

Traditional heating esterification (THE) was performed in a three-necked batch reactor (100 ml) equipped with a reflux condenser and mechanical stirrer at atmospheric pressure. The reactor was heated by a heating jacket and a thermocouple was inserted in the reactor to measure the reaction temperature. The catalytic membranes were cut into small pieces (3 mm \times 3 mm) to achieve better contact with reactants and to eliminate the influence of diffusion on esterification. Some amount of acidified oil was first introduced into the reactor and heated to the determined temperature. Then the desired amount of methanol and the catalytic membranes were added into the reactor and the reaction began at pre-determined conditions. The basic optimal reaction conditions discussed in our previous paper (Ding et al., 2011) were: acidified oil 20 g, methanol/acidified oil mass ratio 2.5:1 (methanol/acidified oil molar ratio 29:1), catalytic membrane loading 5 g, reaction temperature 65 °C and reaction time 8 h. The samples were taken out from the reaction system every one hour and treated by decompression distillation with a rotational evaporator to remove unreacted methanol and produced water to determinate acid value and FFAs conversion. In repeated experiments, the membranes were reused without any treatment.

2.4. Microwave assisted esterification (MAE)

As shown in Fig. 1, microwave assisted esterification (MAE) was carried out with a microwave accelerated reaction system (Beijing XiangHu Science and Technology Development Co. Ltd., XH-200A). The system is equipped with a reflux condenser, a magnetic stirrer and an infrared temperature measurement which allows continuous stirring and constant temperature control. A three-necked batch reactor (500 ml) was used for the microwave assisted reaction and a flask (250 ml) full of water was settled in the chamber to absorb microwave during each experiment. The basic reaction conditions were: acidified oil 20 g, reaction time 120 min, reaction temperature 65 °C, methanol/acidified oil mass ratio 2.0:1, catalytic membrane loading 3 g and microwave power 360 W.

2.5. Separation and purification of biodiesel

After reaction completion, the reaction mixture was cooled to room temperature and settled to separate the liquid phase (biodiesel, methanol and unreacted acidified oil) and solid phase (catalytic membrane). The liquid phase was poured into a separating funnel and settled over night to separate methanol and the biodiesel. The biodiesel was further purified by decompression distillation with a rotational evaporator under vacuum (10 ± 1 mmHg) at 50 °C to remove excess methanol and other impurities. The biodiesel was washed twice with secondary distilled water and treated by anhydrous sodium sulfate to remove moisture. The product obtained was qualitatively analyzed by Gas chromatography-mass Spectrometry (GC-MS: 6890N GC/5973 MS, Agilent Technologies). The temperatures of injector and detector were kept at 250 °C. The nitrogen was used as a carrier gas at a flow rate of 40 mL/min. Column was heated from 70 to 240 °C at heating rate of 10 °C/min and maintained at 240 °C for 10 min.

2.6. Determination of the acid value and FFAs conversion

The acid value was determined by titration according to ASTM D1980–87 (1998) (Standard Test Method for Acid Value of Fatty Acids and Polymerized Fatty Acids). The brief steps were introduced as follows: about 0.20 g samples were added into 150 ml

neutralized boiling ethanol and was fully dissolved; 0.5 ml phenolphthalein was used as indicator; the sample was then titrated by 0.1 mol/L KOH solution. The acid value was calculated using Eq. (1):

$$S = \frac{56.1 \times V_{\text{KOH}} \times C_{\text{KOH}}}{m} \quad (1)$$

where S is the acid value (mg KOH/g acidified oil), C_{KOH} is the concentration of KOH used for titration (mol/L), V_{KOH} is the volume of KOH employed for titration (ml), m is the weight of the sample taken to be analyzed (g).

FFAs conversion is defined as the ratio of acid value variation rate of acidified oil before and after reaction compares to acid value of the initial oil. The conversion is calculated according to Eq. (2):

$$\text{FFAs conversion} = \frac{S_i - S_t}{S_i} \times 100\% \quad (2)$$

where S_i refers to initial acid value (mg KOH/g acidified oil) and S_t refers to the acid value at pre-determined reaction time (mg KOH/g acidified oil). The reported values were the mean of at least five measurements and the average estimated error was $\pm 5\%$.

3. Results and discussion

3.1. Traditional heating esterification

3.1.1. Effect of membrane annealing temperature

In order to improve the catalytic activity and reusability, the membranes were annealed at 80, 120, 150 and 200 °C for 1 h, respectively. Five grams of membranes annealed at different temperatures were used in the esterification. It is found that annealing temperatures markedly affected the FFAs conversion. FFAs conversions increase from 77.86% to 90.87% and 94.98% with the annealing temperature increasing from 50 to 80 and 120 °C because removal of the absorbed water in the membranes could improve $-\text{SO}_3\text{H}$ group content in the drier membranes of unit quality. However, FFAs conversion decreases greatly from 94.98% to 74.12% when the annealing temperature rose from 120 to 200 °C mainly because $-\text{SO}_3\text{H}$ groups in CERP reacted with $-\text{OH}$ at higher temperature, such as 200 °C (Zhu et al., 2010). So the optimized annealing temperature is 120 °C.

3.1.2. Effect of stirring rate

Stirring plays an important role in biodiesel production. Esterification is a relatively slow process since this reaction can only occur in the interfacial region between the liquids and FFAs and methanol are not totally miscible. As a result, vigorous mixing is required to increase the area of contact between the two immiscible phases. Previously, researchers had reported that the stirring rate and mode were extraordinary important parameters for biodiesel production (Meher et al., 2006; Veljkovic et al., 2006). To investigate the effect of stirring rate in the reaction, esterification was conducted with different mechanical stirring rates of 120, 240, 360, 480 and 600 rpm, respectively. The FFAs conversions at different stirring rates are shown in Fig. 2. It is observed that the reactions are incomplete when the stirring rates are 120, 240 and 360 rpm and the FFAs conversions are only 71.15%, 80.24% and 85.96%, respectively after 8 h. However, FFAs conversions at 480 and 600 rpm are nearly the same of 94%. So the optimal stirring rate is 480 rpm which is in accordance with the result of Veljkovic et al. (2006).

3.1.3. Reusability of the catalytic membranes

Besides the catalytic activity, reusability of the catalytic membranes is very important in saving produce cost. The catalytic membranes annealed at different temperatures were employed

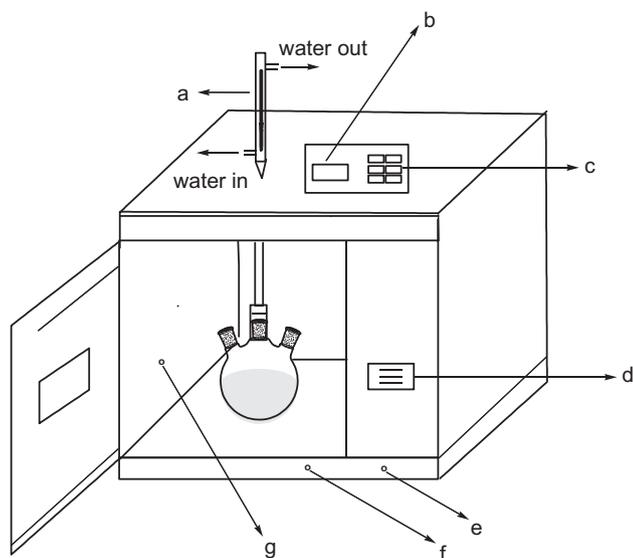


Fig. 1. Schematic diagram of the microwave accelerated reaction system. (a) Condenser pipe; (b) display panel; (c) control panel; (d) reaction chamber switch; (e) mains switch; (f) magnetic stirring knob; (g) infrared temperature measurement.

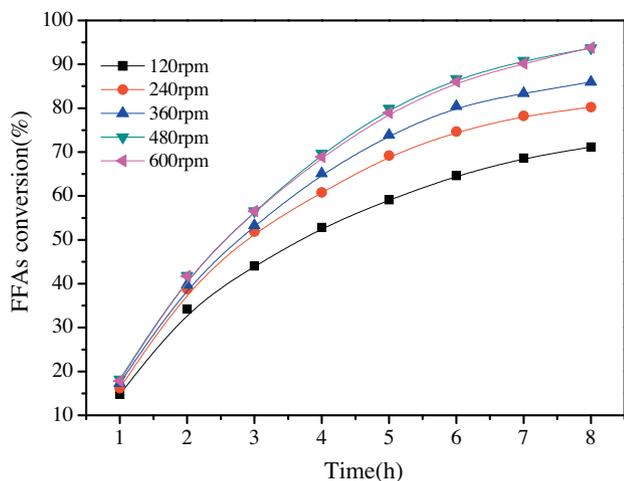


Fig. 2. Effect of stirring rate on esterification. Reaction conditions: acidified oil 20 g, methanol/acidified oil mass ratio 2.5:1, reaction temperature 65 °C, catalytic membrane loading 5 g and reaction time 8 h.

in the esterification for six runs and the results are shown in Fig. 3. It can be seen that all the membranes show good catalytic activity at the first run with FFAs conversion above 90%, higher than that reported by Özbay et al. (2008). The catalytic activity and catalytic stability of the membranes annealed at 120 °C are higher than that of others and the FFAs conversion reaches approximate 85.21% at the sixth run. It implies that the membranes annealed at 120 °C exhibit the best catalytic activity and stability for producing biodiesel. For the other four membranes, the catalytic activity decreased with the runs and the FFAs conversion is only 75.34% for the membranes annealed at 200 °C at the sixth run. The membranes become very fragile, easy broken into fine particles under stirring and lost during the repeated experiments, which would lead to the decrease of the catalytic efficiency. In addition, the saturation of absorbing water produced from the esterification may be another reason of the conversion decrease for all the membranes (Zhu et al., 2010).

3.2. Microwave assisted esterification

3.2.1. Effect of reaction temperature

Effect of reaction temperature on FFAs conversion under microwave condition is shown in Fig. 4. It is found that FFAs conversion increased with the increase of reaction temperature from 35 to

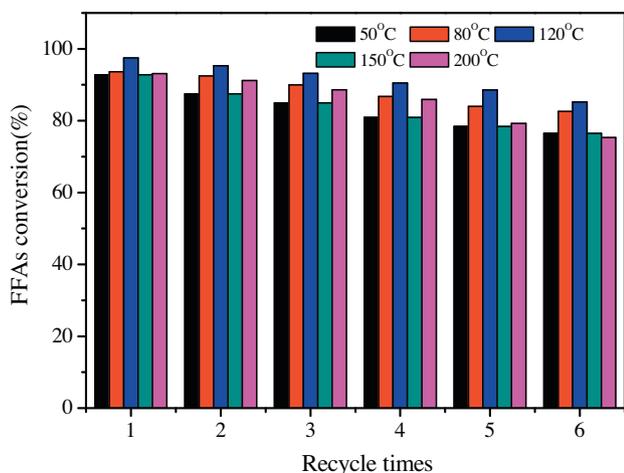


Fig. 3. Catalytic performances of the membranes versus recycling times under optimal conditions.

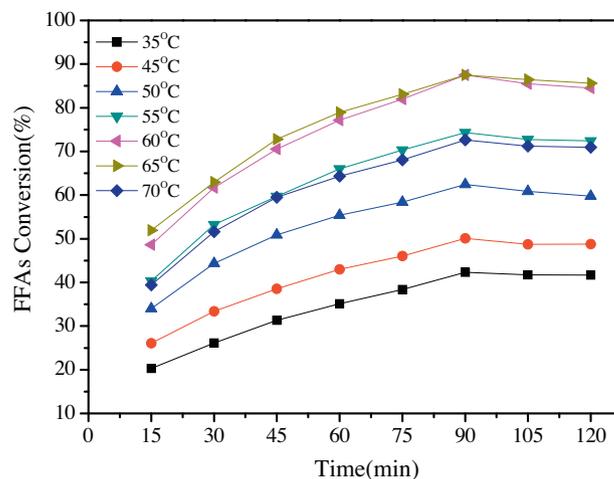


Fig. 4. Effect of catalytic membrane loading and reaction time on esterification. Reaction conditions: acidified oil 20 g, reaction temperature 60 °C, methanol/acidified oil mass ratio 2.0:1, microwave power 240 W and reaction time 90 min.

60 °C due to the promotion of the molecule motion and mass transfer rate with increasing temperature (Ding et al., 2011). FFAs conversion of 60 °C is almost the same with that of 65 °C. However, the FFAs conversion decreases greatly from 87.5% to 72.6% when the temperature further increases to 70 °C because methanol will vaporize and form a large number of bubbles which may inhibit the reaction when the reaction temperature exceeds the boiling point of methanol (El Sherbiny et al., 2010). In consideration of production cost, the optimal reaction temperature is 60 °C. This implies that microwave condition needs lower reaction temperature as the optimal reaction temperature with traditional heating method was 65 °C.

3.2.2. Effect of reaction time

To optimize reaction conditions, the effect of reaction time on the esterification was investigated and the results are shown in Fig. 4. FFAs conversion by CERP/PES catalytic membrane under microwave condition can be divided into three phases when reaction temperature is set as 60 °C. At the first phase, the FFAs conversion over 85% can be obtained within 60 min; at the second one, esterification rate slows down from 60 min to 90 min with FFAs conversion of above 95%; at the last phase after 90 min, prolonging the reaction time don't increase FFAs conversion but drive the esterification left as a result of side reaction. In view of reaction time and production cost, the optimal reaction time is 90 min.

3.2.3. Effect of methanol/acidified oil mass ratio

One of the most important variables affecting the esterification is the molar ratio of methanol to FFA. The stoichiometric molar ratio for esterification requires one mole of methanol and one mole of FFA to yield one mole of free fatty methyl ester and one mole of water. However, esterification is an equilibrium reaction which is often performed in excess methanol to drive the reaction to the right. Effect of methanol/acidified oil mass ratio on esterification under microwave condition is shown in Table 1. The FFAs conversion increases from 56.54% to 95.92% with the increase of methanol/acidified oil mass ratio rose from 0.5:1 to 2.0:1. However, the FFAs conversion decreased a lot when the mass ratio rise to 3.5:1, which is mainly because excess methanol would adsorb on the catalytic membrane surface and decrease the contact opportunities between acidified oil and the catalytic membranes and thus decrease the catalytic activity or even deactivate the catalyst. The result was in good agreement with the swelling degree value re-

Table 1
Effect of methanol/acidified oil mass ratio on the esterification.

Methanol/oil mass ratio	0.5	1.0	1.5	2.0	2.5	3	3.5
FFAs Conversion (%)	56.54	64.87	76.63	95.92	93.84	80.33	78.42

Reaction conditions: Acidified oil 20 g, reaction temperature 60 °C, 120 °C annealed catalytic membrane loading 3 g, microwave power 240 W and reaction time 90 min.

Table 2
Effect of catalytic membrane loading on the esterification.

Catalyst loading (g)	1	2	3	4	5
FFAs Conversion (%)	64.3	81.65	92.2	92.31	92.6

Reaction conditions: Acidified oil 20 g, reaction temperature 60 °C, methanol/acidified oil mass ratio 2.0:1, microwave power 240 W and reaction time 90 min.

ported in our previous work (Zhang et al., 2012). So the optimal methanol/acidified oil mass ratio is 2.0:1 in the reaction system.

3.2.4. Effect of catalytic membrane loading

In order to optimize the catalytic membrane loading, different experiments were performed with different catalytic membrane loadings and the results are illustrated in Table 2. FFAs conversion is quite low when catalytic membrane loading is 1 and 2 g as there are not enough active sites. This indicates that the reaction could not proceed efficiently with a small amount of CERP/PVA hybrid catalytic membranes as there were not enough active sites. The FFAs conversion is almost the same of 92.5% with the catalytic membrane loading of 3, 4 and 5 g and it seems meaningless for the FFAs conversion to further increase catalytic membrane loading. Thus the optimal catalytic membrane loading is 3 g in the reaction system. This strongly demonstrates that the experiments under microwave condition need low catalyst loading.

3.2.5. Effect of microwave power

Microwave power is another important parameter in analyzing the reaction process so as to evaluate the production cost. The effect of microwave power on FFAs conversion was investigated. It is found that FFAs conversion increased a lot from 83.93% to 94.76% when microwave power increased from 120 W to 360 W for the raised reaction temperature. However, it seems meaningless to increase the microwave power from 360 W to 480 W, with the FFAs conversion of 94.7%. It is also found that the FFAs conversion decreased slightly (about 90.34%) when the power further increased to 600 W, which is mainly because that with the increase of microwave power, heating rate increases greatly and methanol will vaporize promoting the side reaction and inhibiting the esterification. So the optimal microwave power is 360 W in this reaction system.

3.2.6. Effect of different alcohols

Alcohols used in acid-catalyzed esterification mainly included methanol, ethanol, propanol and butanol. Methanol and ethanol are used most frequently in both laboratory research and the biodiesel industry. The low cost of methanol makes it the first choice for the esterification reaction. Ethanol, however, is derived from agriculture products (renewable sources) and biologically less objectionable to the environment than methanol. Thus, ethanol is the ideal candidate for the synthesis of fully biogenerated fuel. To study the esterification of methanol and ethanol with acidified oil under microwave condition, different experiments were performed and the results are shown in Fig. 5. It is observed that methanol has better FFAs conversion than ethanol. This is

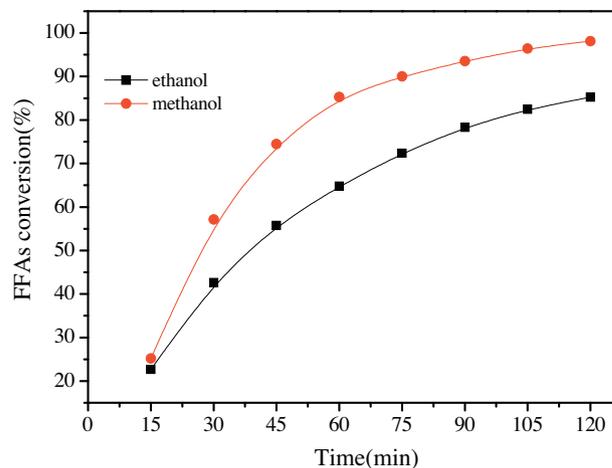


Fig. 5. Effect of different alcohols on esterification. Reaction conditions: acidified oil 20 g, reaction temperature boiling point of each alcohol, alcohol/acidified oil molar ratio 23.5:1, microwave power 240 W and reaction time 90 min.

associated with the fact that methanol has stronger microwave absorption capacity and it can easily react with acidified oil under the microwave condition (Yuan et al., 2009).

3.3. Comparison of THE and MAE catalyzed by CERP/PES membranes

The traditional heating esterification and microwave assisted reaction were performed under optimal reaction conditions, respectively and the results are shown in Fig. 6. As can be seen in Fig. 6, FFAs conversion of THE is about 98.4% under the optimized conditions for 8 h reaction time; however, FFAs conversion of MAE could reach 97.4% under the optimal conditions of reaction temperature 60 °C, methanol/acidified oil mass ratio 2.0:1, 120 °C annealed catalytic membrane loading 3 g, microwave power 360 W and reaction time 90 min. The reaction temperature, catalyst loading and methanol consumed in MAE are slightly lower and the reaction time is much lower than that in THE, which could lead to lower cost in biodiesel production. These results strongly demonstrates that the application of microwave condition could offer a fast, economical and easy route to produce biodiesel and MAE catalyzed by CERP/PES catalytic membrane is an appropriate option for biodiesel production.

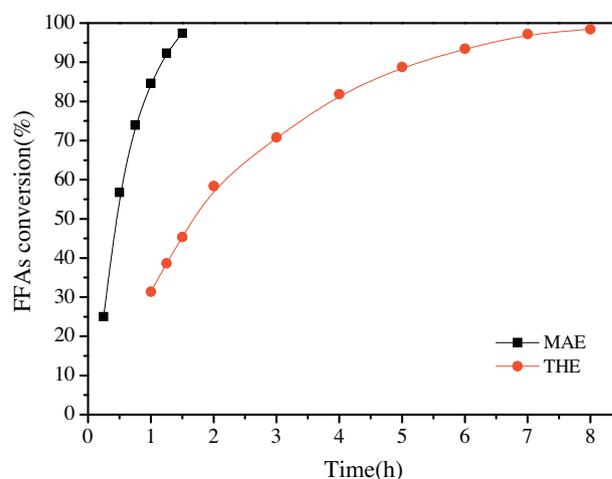


Fig. 6. Comparison of traditional heating method and microwave assisted esterification catalyzed by CERP/PES membrane under optimal conditions, respectively.

Table 3
Compositions of the product.

Peak	Retention time(min)	Constituents	Fatty acid
A	15.73	Dodecanoic acid methyl ester	C12:0 ^a
B	18.73	Tetradecanoic acid methyl ester	C14:0
C	20.69	Hexadecanoic acid methyl ester	C16:0
D	22.84	9,12-Octadecadienoic acid(Z,Z) methyl ester	C18:2
E	23.02	Octadecanoic acid methyl ester	C18:0

^a The first number stands for the number of the carbon in the compound; the second number stands for the number of C=C double bond in the compound.

3.4. Qualitative analysis of the biodiesel

The compositions of the produced FAME were investigated and are illustrated in Table 3. The reaction product mainly contained five constituents: dodecanoic acid methyl ester, tetradecanoic acid methyl ester, hexadecanoic acid methyl ester, 9, 12-octadecadienoic acid (Z, Z) methyl ester and octadecanoic acid methyl ester. The two C18 esters of 9, 12-octadecadienoic acid (Z, Z) methyl ester, octadecanoic acid methyl ester should be produced from the octadecadienoic acid in the acidified oil that are difficult to separate in the GC test. So the compositions in the acidified oil were transformed to their corresponding fatty acid methyl ester (FAME) in the reaction product by esterification with the CERP/PES catalytic membrane as heterogeneous acid catalyst under microwave condition.

4. Conclusion

In the present investigation, biodiesel was prepared by esterification of acidified oil with methanol under microwave irradiation condition. Compared with traditional heating method, microwave assisted esterification needs less reaction time, lower reaction temperature, less energy and lower methanol additive. Thus, manufacturing biodiesel using microwave represents a fast, easy and effective route with advantages of a short reaction time, a low methanol/acidified oil mass ratio, an ease of operation, reduced energy consumption and all with lower production cost. Further experiments need to be done in the future to investigate the possibility of scale-up for industrial application.

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