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Novel Technology for Bio-diesel Production from Cooking and Waste Cooking Oil by Microwave Irradiation

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Abstract

In the transitional process, acid or base catalysts are common technology to produce bio-diesel from waste cooking oil; however, the catalysts only can be use one time. Highly reaction time is requirement for the transitional technology. For improvement these concern issues, this study applied a novel technology to create bio-diesel product from cooking oil and waste cooking oil by microwave irritation. The microwave irradiation can provide strong power and reach reaction temperature in a short time. The SrO catalyst is a heterogeneous catalyst which is not dissolution into any liquid solution therefore, it can be recycling and reusing again.

In this research, the optimum conditions were using commercial SrO, 40 to 180 seconds reaction time, around 80°C reaction temperature, 6 methanol to oil ratio, and 1000W microwave power output. 99% and 93 % biodiesel conversion efficiency for cooking oil and waste cooking oil were reached within in these conditions. The determined specifications of obtained biodiesel according to ASTM D6751 and EN14214 standards were in accordance with the required limits. As a conclusion, the present study indicates that derived fuel promises being an alternative for diesel, and could be used in engines without a major modification due to its qualifications.

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Keywords: Waste cooking oil; SrO catalyst; Microwave irradiation; Bio-diesel .

INTRODUCTION

In the past three decades, the increasing world population and rapid industrial developments have drastically increased the consumption of fossil fuel derived oils. The current use of fossil fuels in various sectors for heat and power generation continues to threaten global stability and sustainability [1, 2]. Thus, countries around the world have devoted their resources to solving the shortage of fossil fuel energy and

lowering energy costs. In general, the predominant energy policies have been divided into two categories: (1) the development of renewable energy resources and (2) the recycling and reuse of waste energy.

There are increasing interest in developing alternative energy resources, which include hydrogen cells [3], solar energy [4], and wind power [5]. However, these technologies are still at the developing stage and the cost of applying them is high. Biomass is the only renewable energy resource that can lead to competitive prices for liquid fuels in transport. Many benefits of using this renewable resources are increased environmental protection, lower toxic gas emissions, lower level of oil imports (67% of oil is for transportation fuels), and increased safety of fuel supply [6].

Bio-diesel is the result of a simple trans-esterification reaction using vegetable oil and methanol as substrates (Fig. 1). The most commonly used catalysts in trans-esterification reactions are NaOH, KOH and H₂SO₄. The starting oil and methanol are generally heated and stirred with the catalyst or else, in the case of the basic catalysts, the base is first dissolved in the methanol prior to addition. Trans-esterification is not the only route to production of fatty acid methyl esters. An alternative approach is to hydrolyze all tri-glycerides to free fatty acids, and then directly esterify these fatty acids with methanol. However, trans-esterification is the process of choice in the majority, if not all, of the commercial biodiesel production facilities that have come on line. The preparation of biodiesel by trans-esterification was shown in the Fig.1.

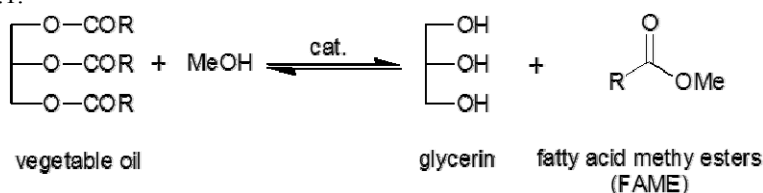


Fig 1. Preparation of biodiesel by trans-esterification

The increasing production of cooking oils from household and industrial sources is a growing problem in around the world. This residue is regularly poured down the drain, resulting in problems for wastewater treatment plants and energy loss, or is integrated into the food chain through animal feeding, thus becoming a potential cause of human health problems [7]. The cooking oil will become the major material to make bio-diesel.

Sodium and potassium hydroxide are commonly used as base catalysts, but there are many obstacles to their utilization [8-10]. Acidic catalysts are also being used for the trans-esterification reaction. However, despite the increase in the yield of the bio-diesel, the acid catalyzed reaction is much slower than the alkali catalyzed reaction, and it also requires higher temperatures and pressures [11, 12].

Heterogeneous (solid) catalysts are the general advantage of easy separation from the reaction medium and reusability. Heterogeneous catalysis is thus considered to be a green process. The process requires neither catalyst recovery nor aqueous treatment steps: the purification steps of products are then much more simplified and very high yields of methyl esters, close to the theoretical value, are obtained. Glycerin is directly produced with high purity levels (at least 98%) and is exempt from any salt contaminants [13].

Many types of alkaline earth metal oxide catalysts can catalyze trans-esterification reactions. The order of activity between alkaline earth metal oxide catalysts is BaO > SrO > CaO > MgO [14, 15]. SrO is insoluble in vegetable oil, methanol, and fatty acid methylester. Despite the lower surface area of SrO as reported elsewhere [16] there are other factors that cause the high activity of SrO. Besides the specific surface area, alkalinities, and acid/base sites of alkaline earth metal oxides affect also the activity of the catalyst [16].

An issue with using a trans-esterification approach to bio-diesel manufacture is that the reaction can be slow to reach completion and also because it is equilibrium an excess of methanol is often used to drive the reaction towards formation of products. Trans-esterification is usually conducted by conventional heating for introducing energy into reactions. Recently, the microwave dielectric heating

effect was used as an alternative heating source to conventional heating for driving the trans-esterification reaction [17, 18]. Indeed, one approach that has been taken to accelerate the reaction is the use of microwave heating as a tool.

In this research, leveraging the rapid reaction times, it is possible using microwave heating and the inherent advantages of using a heterogeneous catalyst, it will be possible to develop a very rapid, easy method to high-throughput biodiesel production from fresh cooking oil and waste cooking oil.

Materials and Methods

Materials:

The fresh cooking oil was mustard oil which was purchased in supermarket. Waste cooking oil were collected from restaurants in Taiwan and then filtered to remove any inorganic residues and suspended matters. All the chemicals used in experiments were purchased from Merck chemicals. The certified reference standards for Gas Chromatography (GC) were purchased from Sigma-Aldrich.

The microwave oven was Panasonic NN-SF550, and also was modified Taiwan. The maximum input power was 1000W. The Fig 2 was the modified microwave.

Methods:

All the experiments were carried out at least three times in order to determine the variability of the results and to assess the experimental errors. In this way, the arithmetical averages were calculated for all the results which had an experimental error of less than 0.5%. Experiments was repeated at various conditions such as, catalyst concentration (1.4 – 3.25 wt.% of Oil), reaction time (1-4 min), methanol/oil molar ratio (4:1-10:1) were studied.

Analysis Methods:

The fuel characteristics of the final biodiesel product were determined according to the ASTM D 6751, EN 14214 standard test methods. Methyl ester content is defined as below:

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

where C: Total fatty acid methyl ester content (mg mg^{-1}); A: sum of peak area of fatty acid methyl ester from C_{14} to $C_{24:1}$; A_{EI} : peak area of internal standard, heptadecanoic acid acid methyl ester; C_{EI} : concentration of heptadecanoic acid methyl ester (mg ml^{-1}); V_{EI} : Volume of heptadecanoic acid acid methyl ester (ml^{-1}); and m: mass of input biodiesel (mg). Then, biodiesel yield was calculated relative to the initial amount of waste cooking oil by weight. Similar calculations were used by others [19-22].

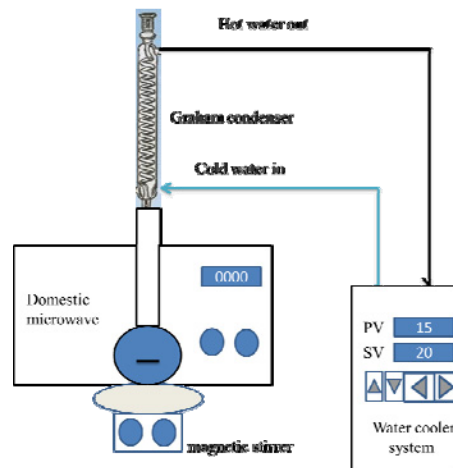


Fig. 2. The microwave reactor system for bio-diesel making

Result and Discussion:

Effects of catalyst concentration on biodiesel yield:

The catalyst concentration is an important parameter in the bio-diesel making. In this part, the reaction temperature of 80°C, reaction time of 40 sec, and methanol/oil molar ratio of 6:1, and agitation intensity of 600 rpm were maintained as constant with heterogeneous catalyst (SrO) concentrations (1.42wt%-3.25wt% of oil) for the production of bio-diesel. The results are given in Fig.3.

As shown, the maximum biodiesel yield was obtained as 99.1% with 1.85 wt. % SrO, and the biodiesel conversion efficiency was decrease dramatically as addition more than 1.85 wt. % SrO. This can be explained as addition of excess amount of catalyst caused more triglycerides participating in the saponification reaction and caused the formation of soap in presence of high catalyst concentration and a slight decrease in biodiesel yields.

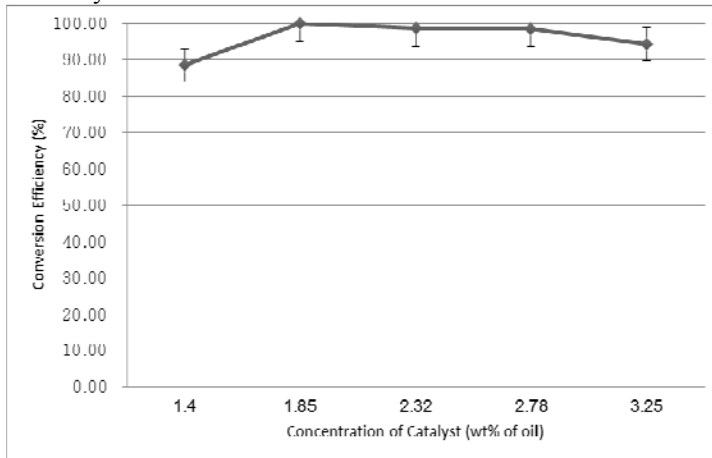


Fig.3. Effects of catalyst concentration on biodiesel

Effects of reaction time on biodiesel yield:

In this part, to measure the effect of reaction time on formation of methyl esters, various experimental reaction times were carried out from 40 to 160 sec at catalyst concentration of 1.85 wt. SrO, reaction temperature around 80° C, molar ratio of methanol to oil 6:1, and the speed of magnetic stirring in 600 rpm. The experimental results are shown in Fig. 4.

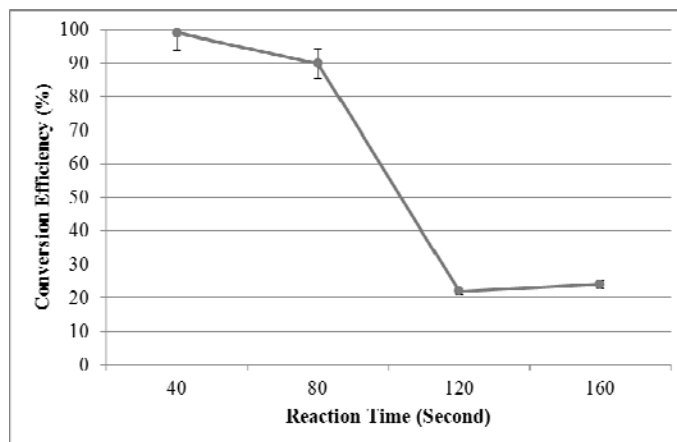


Fig.4. Effects of reaction time on the biodiesel making

As seen, biodiesel yield increased with reaction time at the beginning, reached at a yield of 99.3% in the first 40 sec and was also the best conversion efficiency, and then decreased dramatically with increasing reaction time. Due to longer reaction times led the hydrolysis of esters and caused more fatty acids to produce soap [23]. According to experiment results, reaction time had a significant effect on the conversion of the triglycerides up to 40 sec, but increasing further the reaction time had decreased the biodiesel yield. Due to reaching the maximum biodiesel yield as 99.3 %, 40 sec was selected as the optimal reaction time for cooking oil transesterification in the present conditions.

Effect of methanol-to-oil molar ratio

In order to investigate the effect of molar ratio on biodiesel yields, experiments were conducted with various molar ratios ranging from 3:1 to 12:1 with a constant catalyst concentration of 1.85 wt.% SrO, reaction time of 40 sec, reaction temperature of 80° C, and the speed of magnetic stirring in 600 rpm. The stoichiometric molar ratio of methanol to oil is 3:1. In bio-diesel making processes with heterogeneous catalysis, mass transfer and the adsorption of reactants onto the catalyst play an important role. Moreover, the transesterification reaction consists of a sequence of three consecutive reversible reactions. Thus, the methanol-to-oil molar ratio should be larger than that of stoichiometric molar ratio in order to shift the equilibrium conversion of the reaction. The effect of methanol-to-oil molar ratio on the bio-diesel conversion efficiency was shown in Fig. 5.

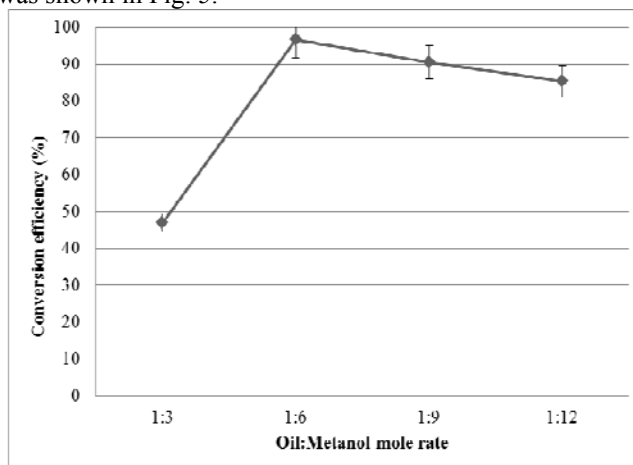


Fig.5. methanol-to-oil molar ratio on the biodiesel making

As seen, the stoichiometric ratio (3:1) was the lowest biodiesel conversion efficiency as 48.34%. During the experimental study, the best biodiesel conversion efficiency was 6:1 methanol: oil molar ratio. This result was similar with previous studies [24, 25]. Nevertheless, increasing the molar ratio more than 6:1 reduced the biodiesel conversion efficiency. Due to excess methanol increased the solubility of glycerol; this caused the interference of a little amount of glycerol with the ester phase. The diluted glycerol in ester phase led to more foam formation with the lower product [26].

The bio-diesel conversion for soybean oil and waste cooking oil

In this research, the optimal condition for the fresh cooking oil was 99.3% in the condition of 1.85 wt.% SrO, 6:1 methanol: oil molar ratio, and 40 second microwave irradiation time. In the section, the bio-diesel conversion efficiency for waste cooking oil was also evaluated in this study.

According to Freedman et al. [27](1984) studied the influence of the free fatty acids (FFA) and water content in the production process of biodiesel. They found that the oil acid value should be less than 1 mg KOH/g and that all raw materials should be anhydrous (water content <0.3%). If these requirements are not met it is still possible to produce biodiesel, but the reaction is reduced due to the deactivation of the catalyst and the formation of soaps. Due to waste cooking oil was degraded by hydrolytic and oxidative reactions, both processes being responsible for changes in the chemical and physical properties, as compared to the fresh oil [7]. In this research, the acid value for waste cooking oil was up to 2.02mg

KOH/g, and the water content was around 1%. This waste cooking condition will affect the worse bio-diesel efficiency than fresh cooking oil. Figure 6 showed the best bio-diesel conversion efficiency from waste cooking oil was around 93% in the conditions of 1.85 wt.% SrO, 6:1 methanol: oil molar ratio, and 3 minutes microwave irradiation time. This situation was similar with Costa Neto et al. experimental result.

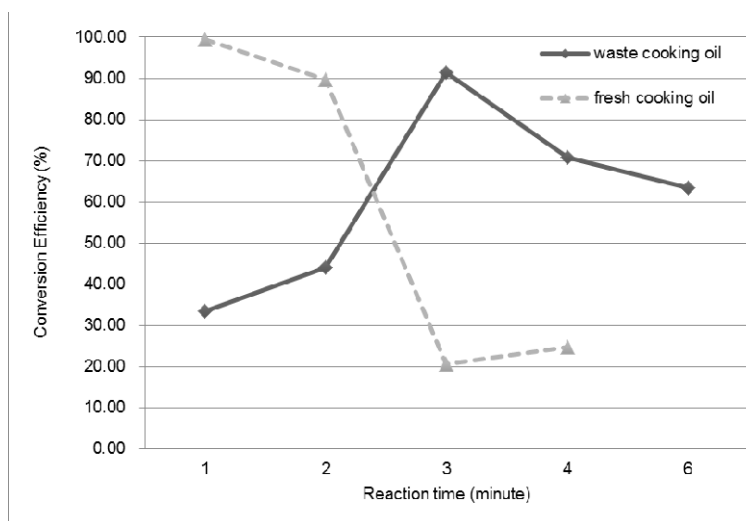


Fig. 6. methanol-to-oil molar ratio on the biodiesel making

Conclusion:

The study of transesterification reaction of fresh cooking oil and waste cooking oil showed that the main factors affecting the process are the molar ratio methanol / oil, the catalyst amount, and the reaction time. From the obtained results, using the conventional technique, the best bio-diesel 99% and 93% for the production of biodiesel from fresh cooking oil and waste cooking oil were obtained using a methanol/oil molar ratio of 6:1, SrO as catalyst (1.85%), and a reaction time 40 seconds and 3 minutes. The results showed that application of radio frequency microwave energy offers a fast, easy route to this valuable biofuel with advantages of enhancing the reaction rate and improving the separation process. The reaction time was reduced to 40 seconds for fresh cooking oil and 3 minutes for waste cooking oil instead of 150 minutes in previous experiment, because, by using the microwave technique, no pretreatment is required. The methodology also allows for the use of high free fatty acid content feedstock, including waste cooking oil. Although, the bio-diesel conversion efficiency for waste cooking oil was less than fresh cooking oil, it was still useful for bio-diesel production. The heterogeneous catalysts and microwave irradiation provide new and efficiency method to create energy sources via bio-diesel recovery and utilization technologies

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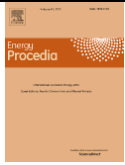
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Biography

Prof. Gedankenis a member of the Nano Materials Center at the Institute of Nanotechnology and Advanced Materials (BINA), and a recipient of the President of Israel Achievement Award for coordination of a European Funded Research. He is included in the ISI International list for Highly Cited Researchers in the field of Material Science for his outstanding research