

Production of Ethyl Ester (Biodiesel) from used Frying Oil: Optimization of Transesterification Process using Microwave Irradiation

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Abstract : A process for the production of the ethyl ester of used frying oil for use as a biodiesel fuel has been studied. The essential part of the process is the transesterification of the used frying oil with ethanol, in the presence of a catalyst, to yield the ethyl ester as a product and glycerine as a by-product. Experiments have been performed to determine the optimum conditions for the preparation of the biodiesel. The optimum conditions were: (1) 0.5% sodium hydroxide catalyst (dissolved in ethanol) based on weight of used frying oil and 100% excess of the stoichiometric amount of required anhydrous alcohol; (2) Extremely vigorous agitation with a little splashing until the reaction mixture (oil and ethanol) becomes thoroughly mixed; (3) Microwave irradiation of the mixture at 50% of its exit power of 750 W. Viscosity, cloud point and pour point of the used frying oil ester produced were measured.

Keywords: Biodiesel, Transesterification, used frying oil, microwave irradiation, catalyst, ethyl ester, methyl ester.

Abstrak : Satu proses penghasilan etil ester dari minyak goreng terpakai untuk kegunaan sebagai bahanapi biodisel telah di kaji. Bahagian utama proses ini ialah transesterifikasi minyak goreng terpakai dengan etanol, dengan kehadiran pemangkin, untuk menghasil etil ester sebagai hasil utama dan gliserina sebagai hasil sampingan. Setelah keadaan optima telah dikenalpasti, pengoptimuman lanjutan proses ini menggunakan kaedah transesterifikasi bantuan gelombang micro. Keadaan optima adalah (1) 0.5% pemangkin natrium hidroksida bersadar kepada berat minyak masak terpakai yang digunakan dan 100% berlebihan jumlah alkohol ; (2) pencampuran secara cergas campuran minyak dan alkohol sehingga ia menjadi sebat. (3) Sinaran gelombang micro terhadap campuran sebat pada 50% daripada kuasa maksima 750 W. Kelikatan, takat awan dan takat tuang ester minyak goreng terpakai yang dihasilkan telah diukur.

Received : 11.08.03 ; accepted : 13.12.04

Introduction

Biodiesel was introduced in South Africa before World War II to power heavy-duty vehicles. Recent environmental and domestic economic concerns have prompted a resurgence in the use of biodiesel throughout the world. Biodiesel can be produced through "transesterification"; a process that combines vegetable oils, animal fats, and/or microalgal oils with alcohol in the presence of a catalyst to form fatty esters. Products are separated into phases which provide easy removal of glycerol, a valuable industrial by-product, in the first phase. The remaining alcohol/ester mixture is then separated and the excess alcohol is recycled. Then the esters are sent to the clean-up or purification processes, which consist of water washing, vacuum drying, and filtration.

Across the globe environmental concerns and energy security issues have prompted legislation and regulatory actions spurring demand for alternative fuels such as biodiesel. However, the greatest driving force for the use of biodiesel and

biodiesel blends is the need to have a fuel that fulfills all of the environmental and energy security needs which does not sacrifice operating performance. Biodiesel possesses several distinct advantages over petro-diesel in the following safety, biodegradability and environmental aspects [1]:

- A renewable fuel with a net gain of energy producing it;
- Higher flash point makes its safer in transport and storage
- Greatly reduces particulate matter and carbon monoxide emissions
- Reduces carcinogenic polycyclic aromatic hydrocarbons (PAH) and nitrated PAH;
- Contains essentially no sulfur, therefore greatly reduces sulfur dioxide emissions from diesel vehicles;
- Biodegrades as fast as dextrose;

Numerous studies have been conducted on biodiesel production and emission testing in the past two decades [2]. Most of the current challenges are targeted to reduce its production cost, as the cost of biodiesel is still higher than its petro-diesel counterpart. This opens a golden opportunity for the use of waste or recycled oils as its production feedstock. Everywhere in the world, there is an enormous amount of waste lipids generated from restaurants, food processing industries and fast food shops everyday. Reusing of these waste greases can not only reduce the burden of the government in disposing the waste, maintaining public sewers and treating the oily wastewater, but also lower the production cost of biodiesel significantly [2].

Transesterification is a process of displacement of an alcohol group from an ester by another alcohol. In vegetable oil almost 90–95% is glycerides, which are basically esters of glycerol and fatty acids [3]. Previous publications reported the use of methyl, ethyl, and butyl alcohols for the transesterification of rape oil, sunflower oil, cotton seed oil, peanut oil, soybean oil, and palm oil to produce methyl, ethyl, and butyl esters. The transesterifications were enhanced by the use of potassium hydroxide, sodium hydroxide, sodium methoxide, or sodium ethoxide as catalysts [4-6]. Important reaction parameters for the transesterifications are: (a) ratio of alcohol to vegetable oil, (b) temperature, (c) rate of agitation, and (d) amount of water present in reaction mixture. Earlier work has concentrated on methyl esters. Ethanol rather than methanol can be used to produce ethyl ester of vegetable oils as shown in Fig. 1. Although use of different alcohols present few differences with regards to the kinetics of reaction, the final yield of esters remains more or less unchanged. Therefore, selection of the alcohol is based on cost and performance consideration. Ethanol can be produced from agricultural renewable resources, thereby attaining total

independence from petroleum-based alcohols. Consequently, a process for the production of the ethyl ester of used frying oil for use as a biodiesel fuel has been studied.

In this work, the production of ethyl esters from used frying oil has been optimized. Optimum conditions for the transesterification of waste cooking oil to produce ethyl ester were determined. The variables were: (a) Temperature of reaction; (b) Catalyst; (c) Rate of agitation of reaction mixture; (d) Water content of alcohol (ethanol); and (e) Amount of excess alcohol. After getting the optimum conditions further enhancement of the process was studied using microwave-assisted transesterification method.

Experimental Setup and Procedures

Three operations were studied in the experimental work namely (a) transesterification, (b) phase separation, and (c) washing. Figure 1 shows the transesterification process; in this study ethanol, in presence of a catalyst, was used and ethyl esters were produced. After the reaction was complete, the reaction products separated into two layers; the ester product formed the upper layer and the by-product glycerine formed the lower layer. The residual catalyst and unreacted excess alcohol were distributed between the two phases. After separation of the phases, the catalyst and alcohol were washed from the ester with water.

1. Preparation of used frying oil

The raw material (i.e. used frying oil) was collected from several restaurants and cafeterias in Malaysia. The used cooking oil was filtered to remove food residues and solid precipitate in the oil. In this transesterification process it is important that the oil contains very minimal amounts of water because every molecule of water will destroy a

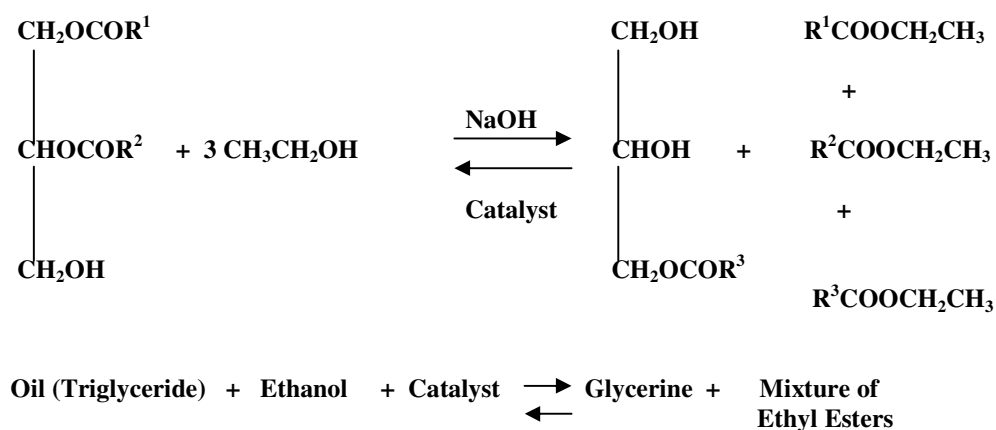


Figure 1 : Transesterification Process

molecule of catalyst. Hence the filtered used frying oil (300–400 g) subjected to drying by heating at 60°C for 10 min using microwave oven (model RM 800, Plazmatronika, Wroclaw, Poland; operating frequency 2.5 GHz) equipped with magnetic stirrer and non-contact infrared continuous feedback temperature system at high power (output power 750 Watts).

2. Ester preparation

2.1. Two-step Transesterification reaction

The transesterification experiments were performed in conical flasks using 250 g of used frying oil prepared as above. The ester preparation involved a two-step transesterification reaction [7]. The two-step reaction utilized 2.5 g (1% by weight of the oil) of potassium hydroxide (powder) or 1.25 g (0.5% by weight of oil) of sodium hydroxide as catalysts. The catalyst was first dissolved in 72 g of ethanol (6:1 molar ratio of anhydrous ethanol to oil), which represented a 100% excess of the stoichiometric amount required for the transesterification. The required amount of catalyst was quickly weighed, protecting it as much as possible from atmospheric moisture and carbon dioxide. The solid catalysts were dried using microwave oven for 1 min at high power (output power, 750 Watts). Dryness is absolutely essential as any water in the system will consume some of the catalyst and slow the transesterification reaction. The solid catalyst was added to the ethanol and was vigorously stirred with slight heating until completely dissolved. The ethanol and dissolved catalyst were then added to the oil and was stirred vigorously. Reaction was performed at room temperature. Six sets of the reaction mixtures were prepared and allowed react for 3, 15, 30, 45, 60 and 75 min respectively. The reaction was arrested in each sample by adding ten to fifteen drops of water. The reaction mixture was poured into a separatory funnel; the top ester layer was poured into another flask and transesterified a second time using the same method as the first reaction.

2.3. Two-step Transesterification reaction with microwave irradiation

Microwave irradiation is a well-established methodology to improve extraction and to accelerate chemical reactions such as those of hydrolysis and esterification [8]. Experiments were carried out to see the effect of microwave irradiation on the transesterification process. For this experiment 250 g of the filtered used frying oil and 72 g of ethanol, which represented a 100% excess of the stoichiometric amount required for the transesterification was used. The catalyst used was

0.5% sodium hydroxide prepared as described above. The oil and alcohol were heated at 60°C using microwave oven. The oven was equipped with magnetic stirrer and non-contact infrared continuous feedback temperature system, which allowed continuous vigorous stirring and constant temperature control. The reaction mixture was irradiated using 25 % of an exit power of 750 W. Five sets of the reaction mixtures were prepared and allowed react for 1, 2, 3, 4, and 5 min respectively. Each of the reaction was arrested by adding ten to fifteen drops of water. Experiments were repeated for 50%, 75% and 100% exit power of 750 W for all the five different reaction time. Additional 25 ml of water was added to each set of reaction mixture whose reaction was already terminated previously as mentioned above. After allowing it to stand at room temperature for 5 min. the reaction mixture was poured into a separating funnel; the top ester layer was poured into another flask and transesterified a second time using the same method as the first reaction.

2.4. Washing

The crude ester (225 g) was separated and excess alcohol and residual catalyst were washed from the ester with 100 ml of water. This step was repeated twice. The ester phase was placed in a glass cylinder. Water was sprayed into the top of the cylinder at a low velocity. The excess alcohol and catalyst were removed by the water as it percolated through the cylinder. Microwave heating at maximum power (750 Watt) for 3 - 4 min was again used to speed up the separation process. It is well established that phase separation can be achieved by microwave irradiation [8]. After microwave irradiation the cylinder was left to stand at room temperature for 10 min. After 10 min the water phase containing the un-reacted alcohol and catalyst would settle, leaving a clear ester phase on top. Finally, the ester (211 g) was dried with anhydrous sodium sulphate.

2.5. Analyses

The weight percentage of ethyl ester in the product was determined using a HP 6890 Series II Gas Chromatography installed with a flame ionization detector. A HP-INNOWax (Cross-linked polyethylene glycol) capillary column, (length: 30 m, film thickness: 0.5 μ m and ID: 0.32 mm) was used. Nitrogen was used as the carrier gas at flow rate of 50ml/min. In the GC, the temperature of the detector and injector were maintained at 250°C and the temperature of the oven was maintained at 200°C. One micro-liter of the biodiesel sample was injected manually. Glycerol, monoglyceride, diglyceride, triglyceride and ethyl palmitate were used as standards. The conversion was defined as the

concentration ratio of transformed oil to initial oil $\times 100\%$. All samples were measured in triplicate.

The kinematic viscosity measurements of the ester were made according to ASTM standards (ASTM D445 or IP 71). The ester was analyzed for cloud and pour points using ASTM Standards D2500-81 and D97, respectively [9].

Results and Discussion

1. Optimum Conditions for Ethyl Ester Preparation

Transesterification

Temperature had no detectable effect on the ultimate conversion to ester. However, higher temperatures decrease the time required to reach maximum conversion. A high degree of conversion could be obtained only if the oil and alcohol phases have been well mixed. This required extremely vigorous agitation with some splashing at the start of the reaction. The presence of water in the reaction mixture markedly reduces the conversion of oil to ester. Anhydrous ethanol must be used in order to obtain a high degree of conversion. Based on our previous work 100% excess alcohol was required to achieve a high degree of conversion and good phase separation from the glycerin [10].

Both sodium ethoxide (mixture of sodium hydroxide and ethanol) and potassium hydroxide (mixture of potassium hydroxide and ethanol) gave good conversions during transesterification, however, sodium ethoxide was chosen as the most promising

catalyst due to phase separation considerations described below. Experiments were performed in which the concentration of sodium methoxide varied from 0.3% to 0.5% with respect to the weight of used cooking oil. Maximum conversion was obtained when 0.5% concentration of catalyst was used. Figure 2. is a chromatogram of biodiesel sample at time equal to 4 min. As can be seen clearly the first peaks are glycerol followed by ethyl esters and mono, di and triglycerides. Only the chromatogram with glycerol as the standard is shown here. This GC chromatograph confirms that the reaction has taken place and calculations show that a conversion of up to 87% is achievable.

The microwave irradiation of the reaction mixture inside a microwave oven greatly reduced the time required to achieve maximum conversion. Fig. 3 shows a power level of 50% of an exit power of 750 W was required to achieve maximum conversion. While the conventional process required 75 min., the microwave assisted process only required 4 min. On increasing the power percentage, for the same fixed irradiation time, the conversion amount was somewhat constant. The use of microwave-assisted transesterification process dramatically reduces the reaction time from 75 min to 4 min., (at 60°C) thus involving a dramatic save of time. Irradiation times must be controlled in order to avoid overheating which can destroy some organic molecules. Radiation power levels must not be too high, which may cause damage to the organic molecules.

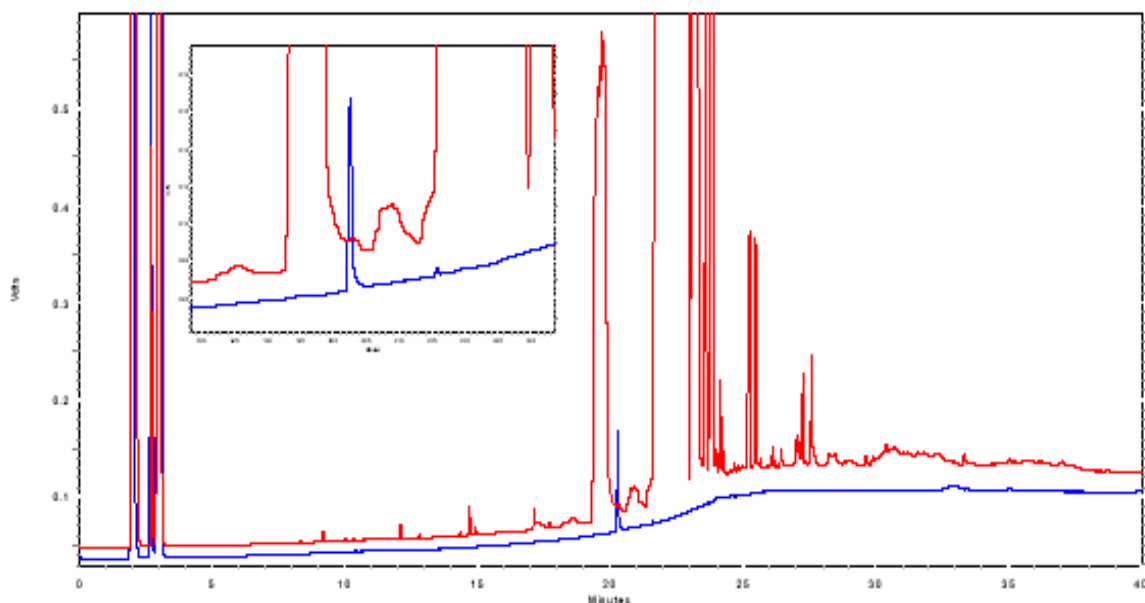


Figure 2 : Upper trace: Injection of 1µL of Biodiesel; Lower trace: injection of 1µL of 500 ppm glycerol; Insert: Close-up of glycerol peak.

During microwave irradiation, polar molecules such as alcohol (in the sample) align with the continuously changing magnetic field generated by microwaves. The changing electrical field that interacts with the molecular dipoles and charged ion, cause these molecules or ions to have rapid rotation and heat is generated due to friction of this motion. The increase in the reaction rate most probably is due to an elevated temperature at local reaction site: the catalytic surface. This is supposed to accelerate various chemical, biological, and physical processes [11-14]. Microwave treatment brings about greater accessibility of the susceptible bonds and hence a much more efficient chemical reaction [15].

During the washing of the ester phase care must be taken to add water slowly in a fine spray. Agitation of the ester with the flow of water caused a loss of as much as 18% of the ester due to the formation of an emulsion [16]. The importance of washing is the removal of residual catalyst and excess alcohol from the ester. The effluent wash water was monitored for sodium content and washing continued until the sodium content of the effluent

was the same as the sodium content of the entering wash water. After washing, separation of the ester phase and the water phase is usually done by allowing it to stand for 45-60 min. Microwave irradiation can greatly help in achieving a good phase separation. After 2 - 3 min irradiation and then standing at room temperature for 3 min, complete separation of the two phases was achieved. Microwave separation technique has been used for oily-wastewater separation processes, which are waste discharged from industries such as petrochemical, metallurgical and transportation [10]. Without the microwave irradiation the separation would take 45-60 min. [17].

2. Physical properties of waste frying oil ethyl ester

The measured kinematic viscosity of the ethyl ester was 5.9 centistokes (cSt) at 25°C. The viscosity was 4.8 cSt at 40°C and 1.82 cSt at 100°C [9]. The viscosity of #2 diesel is 3.2 cSt at 40°C and 1.26 cSt at 100°C [12]. The cloud and pour points of the ethyl ester was found to be -7°C and -16°C, respectively.

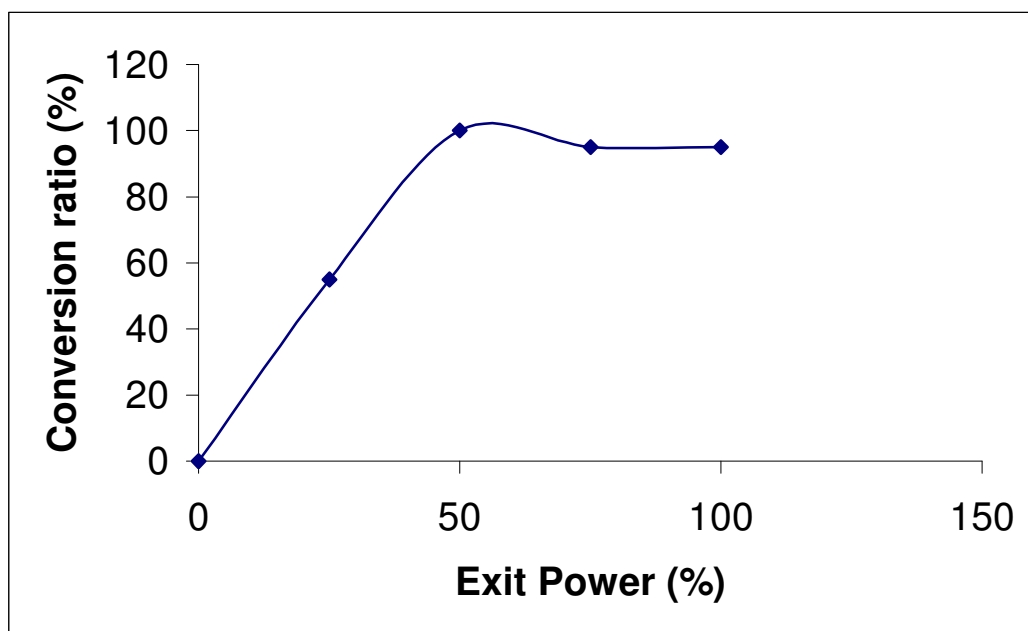


Figure 3 : Effect of microwave power level on transesterification of waste cooking oil.

Conversion ratio was established as a quotient between total conversion obtained after microwave-assisted transesterification (irradiation time 3 min) and conventional transesterification at room temperature. Both processes were performed under optimal conditions: alcohol 50% excess of the stoichiometric ratio, 0.5% sodium methoxide as catalyst with respect to the weight of used cooking oil.

Conclusions

Used frying oil ethyl ester was successfully produced using microwave-assisted transesterification reaction. Microwave assisted reaction offers a fast and safe alternative to the usual process. The mechanism of the microwave effect on a chemical reaction, whether thermal or nonthermal, is debatable, however these results clearly establish that there is considerable enhancement in reaction rates [11-13, 18]. This brings about considerable time saving as well as cost.

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