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# Batch Esterification of Free Fatty Acid in Crude Palm Oil with Ethanol Assisted by Ultrasonic Irradiation

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**Abstract-** One of the obstacles in transesterification of crude palm oil (CPO), a raw material in biodiesel production, is its free fatty acid (FFA) content which causes soap formation and lowers the ester yield. This study investigated FFA reduction using batch esterification of FFA with ethanol, having sulfuric acid as a catalyst together with ultrasonic irradiation. Taguchi method was used in the experimental design. Results showed that FFA content could be reduced from 5.1 to 0.5 wt%. The optimum conditions were: sulfuric acid content at 60 wt% of FFA, 30:1 molar ratio of ethanol to FFA, 60 °C reaction temperature, 1 h reaction time, and 75% amplitude of acoustic power. The esterification not only reduced the FFA content, but also simultaneously lowered the phosphorus content from 11.24 to 1.46 mg/kg. One obvious advantage of this method is that no external source of heat is required for the reaction; the heat could be generated by cavitation resulting from ultrasonic activity. Comparing with the traditional stirring method, esterification by ultrasonic irradiation yielded no significant difference on FFA reduction. The esterification process had also been proven an efficient alternative to simultaneously reduce FFA and phosphorus content in the CPO.

**Keywords-** Biodiesel Production, Crude Palm Oil, Esterification, Free Fatty Acid, Ultrasonic Irradiation.

## 1. Introduction

Energy crises and global warming are factors prompting many countries to focus on developments of alternative sources of energy, biodiesel included. Biodiesel can be used as a substitute for petroleum diesel in any proportion. It can be produced from various plant and animal oils and fats, which mainly contain triglycerides. Some main advantages of using biodiesel are renewability, better-quality exhaust gas emission, and biodegradability. Given that all the organic carbon present is photosynthetic in origin, it would not contribute to a rise in the level of carbon dioxide in the atmosphere and consequently to the greenhouse effect [1].

Crude palm oil (CPO) has high potential in southern Thailand for biodiesel production since there are large oil palm plantations. Palm oil renders the highest oil yield (5,000 kg/ha/y) compared to other oil plants [2,3]; thus CPO is the promising raw material for industrial scale biodiesel production. Productions are performed mainly via alkali catalyzed transesterification to convert glycerides to ester or biodiesel. Transesterification of this kind yields a good result when the raw material has low FFA content. If the oil contains a high amount of FFA (>1 wt%), soap would form from the reaction with the alkali catalyst, and ester conversion would decrease. If ethanol is used as a reactant, this soap formation will prevent glycerin phase separation of the biodiesel [4]. Raw material pretreatment thus becomes necessary, especially on FFA reduction, often described as the de-acid step. Commercial CPO, unfortunately, has high phosphorus and FFA content (~5 wt%). If it is processed using alkali catalyzed transesterification, it will need certain pretreatments to reduce phosphorus (degumming process) and FFA content (de-acidification process). In order to maximize ester yield by transesterification, FFA content of the feedstock should be lower than 0.5 wt% [5,6]. There are three common chemical methods to reduce FFA content: saponification, glycerolysis, and esterification. Saponification is neutralization of FFA with an alkali solution (sodium or potassium hydroxide); the process is also called FFA stripping. Glycerolysis transforms FFA to glycerides under high temperatures and low pressure. Esterification uses an acid catalyst to yield fatty acid alkyl ester as the main product and water as a byproduct. The main product from saponification is soap, which is troublesome in further processing since it is difficult to separate the soap from the oil, and hence a higher yield loss. Esterification increases the yield; acid and water can be separated from the oil before the oil is fed into the subsequent transesterification process. Glycerolysis process needs to be conducted at high temperature (200 °C) and under vacuum pressure, whereas the other two processes can be carried out at atmospheric pressure and at a much lower temperature (60-70 ºC). Clearly, esterification could be regarded as the most suitable method to reduce FFA content of the feedstock, particularly since acid degumming and phosphorus removal can be carried out simultaneously.

Low-frequency high-intensity ultrasound can be efficiently utilized to optimize conversion of triglycerides to biodiesel and has been widely used for base-catalyzed transesterification [7]. An ultrasound can also be used for esterification of FFA with methanol using sulfuric acid ($H_2SO_4$) as catalyst [8]. Low frequency ultrasonic irradiation has both physical and chemical effects based on the acoustic cavitational phenomenon. When bubbles cavitate, localized hot spots are generated (temperature >5000 K with heating and cooling rate > $10^{10}$ K/s, and pressure >500 atm), and micro jets and shock waves are also created during implosion of cavities. These phenomena take place in a short time span (less than a microsecond), but the local hot spots promote the reaction and the jet and shock waves enhance the mixing effect [9,10]. Rokhina et al. [11] investigated the influence of low-frequency ultrasounds (28 and 40 kHz) on biodiesel production from triglycerides, FFAs and fatty acid cut (C8–C10) using either methanol or ethanol in the presence of different catalysts, such as sodium hydroxide (NaOH), potassium hydroxide (KOH) and sulfuric acid, and compared them to conventional transesterification process. Their experiments demonstrated that the use of ultrasound significantly reduced the amount of catalyst required, whilst eliminating saponification and dramatically shortened the reaction time from 2 h to 30 min. Moreover, the molar ratio of methanol to fatty acids was reduced by as much as three times, resulting in high biodiesel yields of 95–97%, regardless of the initial material used. Hanh et al. [4] investigated the production of fatty acid ethyl ester (FAEE) from oleic acid with short-chain alcohols (ethanol, propanol, and butanol) under ultrasonic irradiation. The ultrasonic experiments in their study were carried out using a Honda Electronics Ultrasonic Cleaner (WS 1200-40, 40 kHz with a maximum power of 1200 W). Their batch esterification of oleic acid was carried out to study the effect of reaction temperatures, molar ratios of alcohol to oleic acid, quantity of sulfuric acid and irradiation time, respectively in the range of 10–60 °C, 1:1–10:1, 0.5–10 wt% of oleic acid and 10 h. The optimum condition for their esterification process was a molar ratio of ethanol to oleic acid of 3:1 with 5 wt% of $H_2SO_4$ at 60 °C with an irradiation time of 2 h.

A typical biodiesel process uses oil and alcohol (methanol or ethanol) as main reactants. The normal short chain alcohol used is methanol because it promotes the highest activity and is also a low cost product. On the other hand, the disadvantages of methanol are its lower solubility with oil, toxicity, as well as the fact that it is generally not locally produced in Thailand, so most of it has to be imported. Ethanol, however, is available locally and is also non-toxic together with good solubility. This study has focused on using ethanol instead of methanol because of these natures. Moreover, ethyl ester produced from the use of ethanol is a totally natural product and a recyclable source of energy.

Taguchi method is a Design of Experiments (DOE) developed by Dr. Genichi Taguchi. Based on statistics principle, it emphasizes engineering judgment by adapting orthogonal array as an effective experimental design tool to reduce the size of the experiments.

This research aims to determine the optimum conditions for batch esterification of FFA in commercial CPO reacted with ethanol in the presence of sulfuric acid catalyst assisted by low-frequency high-intensity ultrasonic irradiation. Comparison of the ultrasonic method and stirring method was presented together with investigation of the reaction mixture images under a digital microscope. A preliminary study of this complete research was earlier reported in Reference [12].

## 2. Materials, Equipment and Methods

### *2.1. Materials*

Commercial CPO (5.0-5.5 wt% of FFA and 0.16 wt% of water), used as the feedstock in the experiments, was purchased from Krabi Oil-Palm Farmers Cooperatives Federation Ltd., a local Thai palm oil mill supplier. Commercial grade 99.5 wt% ethanol ($C_2H_5OH$), used as the reactant, was obtained from Union Intraco Pcl. Commercial grade 98 wt% sulfuric acid, used as the catalyst, was acquired from S.T. Chemical Business Co., Ltd.

### *2.2. Equipment*

The equipment was set up as shown in Fig. 1. An ultrasonic processor, model UP400S 24 kHz (Hielscher, Germany), fitted with a 22 mm dia. sonotrode, was used as the ultrasound generator. The acoustic power of the processor was fixed by the manufacturer at 400 W. The amplitude, however, could be adjusted to vary across the full range - up to a maximum of 100 micrometers. It can produce an acoustic power density of 0.85 W/mm$^2$ and has a maximum submerged depth of 45 mm. The reactor, a 400-mL glass bottle with a plastic sealed lid, has an inner diameter of 60 mm and a nominal height of 155 mm. Attachment between the sonotrode and the reactor lid was secured and sealed with a synthetic rubber o-ring to prevent gas leakage. A monitoring digital thermometer (Templog

Temperature Data Logger version 1.0) with 8 channels was purchased from the Scientific Equipment Center (SEC), Prince of Songkla University (PSU), Songkhla, Thailand. The thermometer probe was positioned in the reaction solution. A thermostat-controlled water chiller was also provided by the SEC, PSU. The cooling bath, where the glass reactor is partially submerged, has an inner diameter of 100 mm and a height of 140 mm. A circulating pump assembled with the cooling bath, was used as the temperature controlling system. A watt-hour meter, type PL 10053, was employed for monitoring the power consumption. Drying of samples from the experiment was conducted via the use of a hot air oven, whilst investigation of the mixtures was carried out via an LCD digital microscope (NOVEL, model NLCD-307).

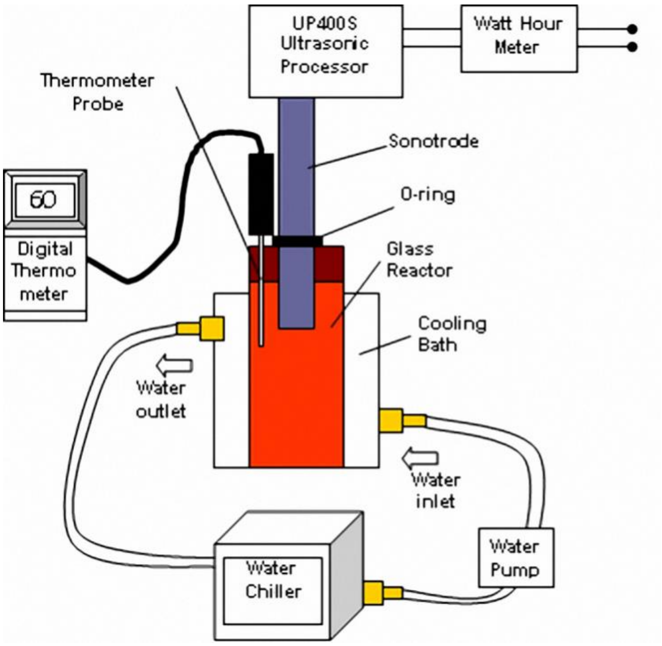

**Fig. 1.** Schematic diagram of the experiment

### 2.3. *Methodology*

The experiment consists of six parts. The first two, preliminary and secondary experiments, were designed using Taguchi method [13]. The other four parts are, respectively, the reaction time optimization, the two-stage experiment, the stirring experiment, and the investigation of the liquid-liquid phase mixtures using a microscope. These are briefly described in the following sections.

#### 2.3.1. *The preliminary experiment*

Preliminary experiments were conducted with five randomly selected factors, each at four levels. The preliminary experimental design, using the Taguchi method, produced a $L_{16}(4^5)$ orthogonal array. This part aims to survey the significant effect of each factor and to estimate its appropriate level ranges which should be focused on in the secondary step.

#### 2.3.2. *The secondary experiment*

Secondary experiments employed the previous results by considering significant factors affecting the esterification to specify new order and focused levels. These have led to five prioritized factors plus two additional interaction factors, i.e. Cat x Temp (Catalyst interacting with Temperature) and Cat x MR (Catalyst interacting with Molar Ratio of ethanol to FFA), each at two appropriate levels. This would produce a $L_8(2^7)$ orthogonal array.

#### 2.3.3. *The reaction time optimization*

Based on the set of best conditions from the secondary part, experiments with varying reaction times were further carried out to determine the best possible reaction time in reducing the FFA.

#### 2.3.4. *The two-stage experiment*

Experiments were set up to investigate the effect of ester hydrolysis by using two-stage esterification. The experiments were conducted based on results from the previous experiments in 2.3.3 which had produced the lowest FFA in the first esterification. While esterification of FFA in CPO is still in the process, water as a by-product would react with ester and convert it back to FFA, since the reaction is reversible. If some water could be removed from the system, the esterification reaction could further undergo to produce even less FFA content. Thus, after finishing this first stage esterification, the reaction mixture was washed with warm water until the washing water was neutral. The sample was then dried at 60 °C while its weight was intermittently monitored. No significant weight loss of the mixture was observed at the above specified temperature after 1 h, and hence the one hour period was adopted. The second esterification was then conducted using the same optimal conditions as previously described, but at same amounts of ethanol and catalyst.

#### 2.3.5. *The stirring experiment*

For comparison with the ultrasonic method, stirring experiments were performed instead in the one-stage and two-stage batch esterification using optimal conditions obtained from section 2.3.3.

#### 2.3.6. *The investigation of the liquid-liquid phase mixtures using the microscope*

The LCD digital microscope was used to investigate the dispersed phase (catalyst in alcohol droplets) and the continuous phase (TG phase) of both the reaction mixtures by ultrasonic and stirring methods.

Energy consumption was recorded and compared with theoretical energy consumption. Phosphorus content analysis of promising samples was conducted by SEC, PSU in accordance with ASTM D 4951. Subsequently, phosphorus contents of the initial CPO and the final product were compared.

### *2.4. Procedures*

#### *2.4.1. The ultrasonic method (Sections 2.3.1 through to 2.3.4)*

CPO used in this research had 5.0-5.5 wt% FFA content. Both CPO and ethanol were calculated to make up a total amount of 300 g per batch suitable for a controlled 20 mm sonotrode submerged depth. The esterification reactions were carried out in the glass reactor placed in a circulating water bath. The reaction temperature was generated by cavitation of ultrasonic irradiation in the reaction mixture; no external heat was required for heating the mixture up to the desired temperature. The temperature increased to the 60 °C reaction temperature within 5 min, and this desired temperature was regulated constant by adjusting the flow rate of the cooling water. The temperature was monitored using the digital thermometer and these were periodically logged throughout the experiments. The preliminary and secondary experiments were run according to each parameter designed in their orthogonal arrays. The third set of the experiments, using the best conditions of the secondary experiments, was run by varying the reaction time. The fourth set of experiments was conducted using the optimal conditions derived from all prior experiments.

#### *2.4.2. The stirring method*

Esterification, 150 g per batch in the reactions, was carried out in a 250 ml screw-cap bottle placed in a water bath on a heater. Temperature was raised by the heater and mixing was conducted with a magnetic stirrer operating at 750 rpm. The molar ratio of ethanol:FFA was 30:1 and the catalyst were 60 wt% of FFA for the one-stage esterification. The reaction conditions used in both the one-stage and the two-stage esterification were the same; these are the optimal conditions of 60 °C reaction temperature and 1 h reaction time obtained from Section 2.3.3. For the two-stage esterification, water in the reaction mixture was removed employing the procedures defined earlier in Section 2.3.4.

#### *2.4.3. FFA content analysis*

FFA content of the samples was determined by AOCS Ca 5a-40 titration method. CPO samples were tested for FFA prior to esterification, and again after esterification. For the latter, samples of 30 mL were drawn from the final reaction solutions and immediately washed with warm water in a 250 mL separatory funnel to stop the reaction and to remove all contaminants such as ethanol, gum and sulfuric acid. The washing step was repeated until the washing water was neutral. The clean samples containing saturated water were then dried at 60 °C for 30 min in the hot air oven. The FFA content of the dried samples was then determined.

#### *2.4.4. Data analysis*

The results of FFA, defined as quality characteristics (y), were analyzed by level average analysis based on the-smaller-the-better principle. This analysis is performed to determine the average response for factors and interaction levels. The analysis presents the significance of factors and interactions based on these computed values. The goal behind the level average analysis is to identify the strongest effects and to determine the combination of factors and interactions investigated that produce the most desirable results [13]. The calculation steps are as follow:

(1) Determine the overall experiment average (T); $T = \sum y_i/n$.
(2) Determine the mean responses of all factors for each level, e.g. the mean response of A1 is $(\sum y_{A1})$/number of A1, when A1 is the factor A in level 1.
(3) Establish response table and graph using the mean responses.
(4) Establish the effect of each factor by calculating the difference of maximum and minimum responses (Delta) in their levels; Delta = Max-Min.
(5) Prioritize each factor by its significance. The higher the delta, the higher the significance.
(6) Select the target level of each prioritized significant factor; the target level selected is the level having the least mean response value.
(7) Check interactions by joining the maximum and the minimum points of each pair of factors. Interactions are detected when intersections occur in the plots.
(8) Define a predicted FFA, using a prediction equation $(\mu)$ only on significant factors at the selected target levels.
(9) Conduct a confirmation (conf.) run according to the target level.

## 3. Results and Discussion

### *3.1. The Preliminary Experiments*

Table 1 and Table 2 for the preliminary experiments respectively tabulate the orthogonal array and results, and the responses, thus:

**Table 1** Orthogonal array and results of the preliminary experiments

| Run No. | Factors | | | | | y |
|---|---|---|---|---|---|---|
| | Cat | Amp | MR | Temp | Time | (%FFA) |
| 1 | 1 | 35 | 5 | 50 | 0.5 | 5.34 |
| 2 | 1 | 55 | 10 | 60 | 1 | 4.78 |
| 3 | 1 | 75 | 20 | 70 | 2 | 3.27 |
| 4 | 1 | 100 | 40 | 80 | 4 | 1.77 |
| 5 | 2 | 35 | 10 | 70 | 4 | 2.59 |
| 6 | 2 | 55 | 5 | 80 | 2 | 3.58 |
| 7 | 2 | 75 | 40 | 50 | 1 | 4.54 |
| 8 | 2 | 100 | 20 | 60 | 0.5 | 4.46 |
| 9 | 5 | 35 | 20 | 80 | 1 | 1.72 |
| 10 | 5 | 55 | 40 | 70 | 0.5 | 3.06 |
| 11 | 5 | 75 | 5 | 60 | 4 | 3.47 |
| 12 | 5 | 100 | 10 | 50 | 2 | 3.66 |
| 13 | 20 | 35 | 40 | 60 | 2 | 0.74 |
| 14 | 20 | 55 | 20 | 50 | 4 | 1.03 |
| 15 | 20 | 75 | 10 | 80 | 0.5 | 2.27 |
| 16 | 20 | 100 | 5 | 70 | 1 | 2.89 |
| Average, T | | | | | | 3.07 |
| Conf. run | 4 | 1 | 4 | 4 | 4 | 1.15 |

Remarks:
Cat: wt% $H_2SO_4$ catalyst by wt. of FFA
Amp: % Amplitude of acoustic power
MR: Molar ratio of ethanol:FFA
Temp: Reaction temperature (°C)
Time: Reaction time in h

**Table 2** Response table of the preliminary experiments

| Level | Factors | | | | |
|---|---|---|---|---|---|
| | Cat | Amp | MR | Temp | Time |
| 1 | **3.79** | **2.6** | **3.82** | **3.65** | **3.79** |
| 2 | 3.79 | 3.11 | 3.32 | 3.36 | 3.48 |
| 3 | 2.98 | **3.39** | 2.62 | 2.95 | 2.81 |
| 4 | **1.73** | 3.20 | **2.53** | **2.34** | **2.22** |
| Delta | **2.06** | **0.79** | **1.29** | **1.31** | **1.57** |
| Order | **1** | **5** | **4** | **3** | **2** |
| Select | **Cat4** | **Amp1** | **MR4** | **Temp4** | **Time4** |

m = T+(Cat4-T)+(Time4-T)+(Temp4-T)+(MR4-T)+(Amp1-T)
= Cat4+ Time4+ Temp4+ MR4+ Amp1-4T
= 1.73+2.22+2.34+2.53+2.60-4(3.07) = -0.86

Remark:
Those shown in bold lettering in the Table indicate the chosen options according to the set criteria.

The final FFA (wt%) of each run, or the quality characteristics (y), in the preliminary experiments are shown in the last column of Table 1. These runs all started off with 5.1 wt% of FFA. The y values were used to determine the overall experiment average (T), and the mean responses, as respectively described earlier in steps 1 and 2 in Section 2.4.4. The response table, step 3 of the preliminary experiments, was shown in Table 2. Analysis of the delta values in steps 4 and 5 reveal that the factors, in order of significance, were: the amount of catalyst, the reaction time, the reaction temperature, the molar ratio of ethanol to FFA, and the amplitude of acoustic power. All factors were used in subsequent steps until the $\mu$ value was reached in step 8. The resulted $\mu$ value, however, yielded a negative value, which cannot be possible, whereas the confirmation run using the selected factors at their respective selected level yielded a value of 1.15 wt%. This infers that there must be some other significant interactions that had not been accounted for. Upon closer inspection on the interaction graphs it was found that those between Cat x Temp and Cat x MR, having interactions as shown in Fig. 2, were significant. These interactions were thus taken into consideration later in the secondary stage in the search for optimum result. As of now, the results show that as the levels went up most effective factors lowered the FFA content, while the amplitude of acoustic power exhibited generally otherwise.

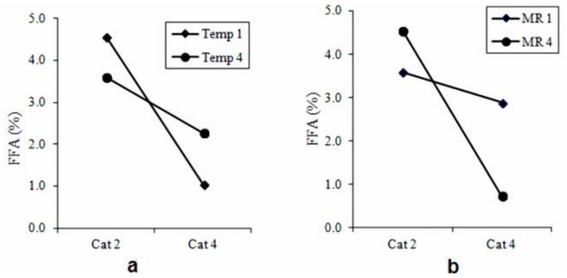

**Fig. 2.** Interaction graphs between Cat x Temp (a) and Cat x MR (b)

It should be noted here that the quality characteristic of the first run of this experiment, at 5.34 wt%, was found to be higher than the 5.1 wt% initial FFA. It is thought to have been affected by hydrolysis reaction because of the mild conditions involved: The low concentration of sulfuric acid adsorbed less water than at higher concentration; The MR, also at its lowest level with a low amount of ethanol, produced a higher ratio of water to ethanol, and lower the solubility of ethanol in the oil phase; The low temperature also enhanced hydrolysis reaction instead of esterification.

### 3.2. The Secondary Experiments

As for the secondary experiments, Table 3 and Table 4 respectively tabulate the associated orthogonal array and results, and the responses, thus:

**Table 3** Orthogonal array and results of the secondary experiments

| Run No. | Factors | | | | | | | y |
|---|---|---|---|---|---|---|---|---|
| | Cat | Time | Temp | Cat x Temp | R | Cat x MR | Amp | (%FFA) |
| 1 | 0 | 1 | 60 | 1 | 0 | 1 | 35 | 1.41 |
| 2 | 0 | 1 | 60 | 2 | 0 | 2 | 75 | 0.96 |
| 3 | 0 | 2 | 80 | 1 | 0 | 2 | 75 | 1.41 |
| 4 | 0 | 2 | 80 | 2 | 0 | 1 | 35 | 1.21 |
| 5 | 0 | 1 | 80 | 1 | 0 | 1 | 75 | 0.66 |
| 6 | 0 | 1 | 80 | 2 | 0 | 2 | 35 | 1.10 |
| 7 | 0 | 2 | 60 | 1 | 0 | 2 | 35 | 0.46 |
| 8 | 0 | 2 | 60 | 2 | 0 | 1 | 75 | 0.61 |
| Average, T | | | | | | | | 0.98 |
| Conf. run | | | | | | | | 0.47 |

Remarks:
Cat: wt% $H_2SO_4$ catalyst by wt. of FFA
Time: Reaction time in h
Temp: Reaction temperature (°C)
MR: Molar ratio of ethanol:FFA
Amp: % Amplitude of acoustic power

**Table 4.** Response table of the secondary experiments

| Level | Factors | | | | | | |
|---|---|---|---|---|---|---|---|
| | Cat | Time | Temp | Cat x Temp | MR | Cat x MR | Amp |
| 1 | 1.25 | 1.03 | 0.86 | 0.98 | 1.13 | 0.97 | 1.04 |
| 2 | 0.70 | 0.92 | 1.09 | 0.97 | 0.82 | 0.98 | 0.91 |
| Delta | **0.54** | 0.11 | **0.23** | 0.02 | **0.31** | 0.01 | 0.13 |
| Order | **1** | 5 | **3** | 6 | **2** | 7 | 4 |
| Select | **Cat2** | Time 2 | **Temp 1** | | **MR2** | | Amp2 |

m = T + (Cat2-T) + (MR2-T) + (Temp1-T)
= Cat2 + MR2 + Temp1 - 2T
= 0.70+0.82+0.86-2(0.98) = 0.42

Remark:
Similar to that labeled in Table 2, those shown in bold lettering here in the Table indicate the chosen options according to the set criteria.

The secondary experiment set was conducted based on the preliminary results by re-ordering the significant factors, taking into account the interactions and focusing on more appropriate levels as shown in Table 3. The response was shown in Table 4. Data analysis was performed in the same manner as for the preliminary part. The factors and interactions were considered, using the Taguchi method, by comparing each effect to the next strongest effect. Only three factors, in order of their significance, were found: the amount of catalyst, the molar ratio of ethanol to FFA, and the reaction temperature. Based on the delta values in this secondary experiment set, the acoustic power amplitude, the reaction time, and even the Cat x Temp and the Cat x MR interactions were disregarded in accordance with the one-half rule of thumb (the fourth factor - the amplitude - was approaching half the effect of the third and was discarded in FFA prediction, and hence its subsequent factors had to be ignored too). The predicted FFA content, 0.42 wt%, corresponded well to the 0.47 wt% value obtained from the confirmation run.

The response gives the effect of the five factors and the two interaction factors. The amount of catalyst, the molar ratio of ethanol to FFA, and the amplitude exhibited positive effects at a higher level, yielding lower FFA values. Negative effect was evident only on the reaction temperature; implying that esterification or FFA reduction was better at the lower reaction temperature of 60 ºC than at 80 ºC. The rest of the factors exhibited no significant changes on FFA reduction when the level was changed. The results, nevertheless, show only the mean responses under the designed conditions which were analyzed using the level average method; it does not purely represent the influence of each factor. FFA results, hence, were contributed by the level of each factor. The optimum conditions for this secondary experiment were: catalyst at 60 wt% of FFA, 30:1 molar ratio of ethanol to FFA, 60 ºC temperature, 2 h reaction time, and 75% of acoustic power amplitude. According to the delta values in Table 4, it is apparent that the reaction time, either 1 or 2 h, rendered nearly insignificant difference on the mean response results. Since there were no optimum conditions associated with the 1 h reaction time in the designed experiment, further experiments were conducted, as outlined in Section 2.3.3, using the optimum conditions with different reaction times to fine-tune this parameter.

### *3.3. The Reaction Time Optimization Experiments*

Figure 3 shows the results of reaction time vs. wt% FFA under the secondary experiment, the reaction time optimization, and two-stage experiments that were carried out (the last one is discussed in Section 3.4). From the figure, comparison between the Secondary expt: Conf. run line and the Time optimization line shows that they are overlapping, indicating almost the same level of FFA reduction. At 2 hour, the reaction of the secondary experiment could reduce FFA content down to 0.47 wt%, same as that of the 1-h reaction of the time optimization. This reveals that reaction time can be taken as 1 h since equilibrium has already been reached. Fig. 3 also shows further that FFA content could be rapidly reduced in the first 15 min, and can only be slightly reduced over reaction time beyond 30 min. The reaction time optimization experiments resulted in less than 0.5 wt% of FFA within the designed one hour reaction time and under all other optimum conditions conducted in the secondary experiment. For this experiment, the optimum conditions were: catalyst at 60 wt% of FFA, 30:1 molar ratio of ethanol to FFA, 60 ºC temperature, 1 h reaction time, and 75% of acoustic power amplitude.

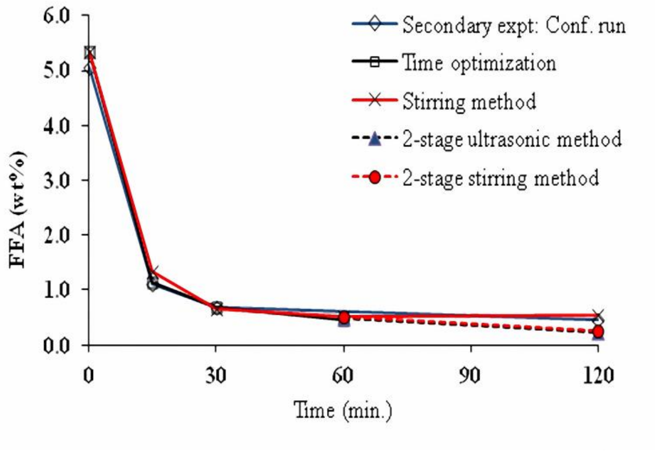

**Fig. 3.** FFA reduction with different reaction time and two-stage esterification

### *3.4. The Two-Stage Experiments*

In hydrolysis/esterification reaction, Equation (1) is a reversible process, with the undesirable water by-product. In the presence of triglyceride (TG), diglyceride (DG) and monoglyceride (MG) in Equations (2) to (4), respectively, hydrolysis could produce more FFA, especially under acidic condition. Thus, if water could be further removed, the reaction should shift to the product side, and further FFA reduction should be possible. This was verified in the fourth experiment.

$$R_1COOCH_2CH_3 + H_2O \overset{H_2SO4}{\longleftrightarrow} R_1COOH + CH_3CH_2OH \quad (1)$$

$$TG + H_2O \overset{H_2SO4}{\longleftrightarrow} DG + R_1COOH \quad (2)$$

$$DG + H_2O \overset{H_2SO4}{\longleftrightarrow} MG + R_1COOH \quad (3)$$

$$MG + H_2O \overset{H_2SO4}{\longleftrightarrow} C_3H_8O_3 + R_1COOH \quad (4)$$

The forth experiments involved twice the esterification process; the first conducted under conditions detailed in Section 3.3, water was then removed, and esterification was again repeated with the same quantities of CPO, ethanol and catalyst. To recapitulate, the conditions employed in the first esterification were: catalyst at 60 wt% of FFA, 30:1 molar ratio of ethanol to FFA, 60ºC temperature, 1 h reaction time, and 75% acoustic power amplitude. The FFA reduction graphs of the second esterification were continuously plotted to the first esterification. The result (dotted line with triangle points in Fig. 3) showed that FFA content could be further reduced down to 0.22 wt% from 0.47 wt% obtained in the first esterification. The outcome supports the hypothesis that equilibrated esterification is resulted from reversible and/or hydrolysis reactions; and that the presence of water interrupts the process of esterification. Complying with the general principle of a reversible reaction, when a product is removed, reaction will shift to the product side. This experiment serves to further confirm the hypothesis in deriving the end result of FFA content.

### 3.5. The Stirring Method

The esterification by the stirring method employed the same conditions as those in the ultrasonic experiment, except that stirring was carried out with a magnetic stirrer. These conditions were: catalyst at 60 wt% of FFA, 30:1 molar ratio of ethanol to FFA, 60ºC temperature, 1 h reaction time, and 750 rpm stirring speed. The results of the stirring method are also shown in Figure 3. For both the one-stage and the two-stage esterifications, the continuous plotting was done in the same manner as that described in Section 3.4. FFA reductions by the stirring method do not significantly differ from the corresponding stage esterification by the ultrasonic method. Although, the latter employs no physical agitator, its mixing is achieved by effects of micro cavity implosions, i.e. micro jets and shock waves [14]. These can produce *a very fine dispersed phase*, resulting in more interfacial area to enhance the reaction rate. The stirring method requires an extra heating source whereas the ultrasonic method needs only an ultrasonic generator to generate acoustic cavitation, and hence the heat. The FFA reduction outcomes were not significantly different, thus one advantage of the ultrasonic method is the efficient energy consumption, and this is to be further discussed in Section 3.7.

### 3.6. Investigation of the Liquid-Liquid Phase Mixtures using the Microscope

Esterification is a biphasic liquid system consisting of a dispersed phase (catalyst in alcohol droplets) and a continuous phase (TG phase) which resembles the base-catalyzed transesterification system [15]. Because reaction rate depends on interfacial area, it could be referred to as the dispersion and the size of alcohol droplets; the more dispersion and the smaller alcohol droplets, the higher rate of reaction. Investigation by microscope shown in Figures 4 and 5, respectively for the ultrasonic method and the stirring method, revealed the liquid-liquid phase of the esterification reaction, having alcohol droplets dispersed in the TG phase. Although alcohol droplets by the ultrasonic method are apparently smaller than those by the stirring method, their FFA reduction results are not significantly different.

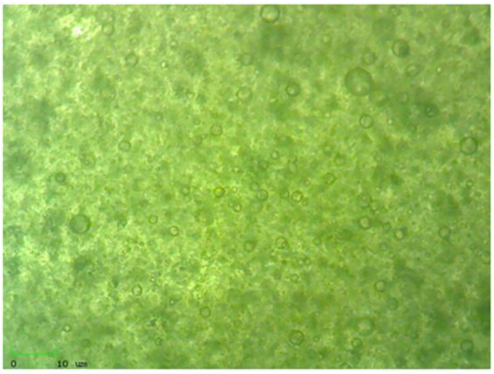

**Fig. 4.** The reaction mixture obtained by ultrasonic method after 1 h reaction time, 100X magnification.

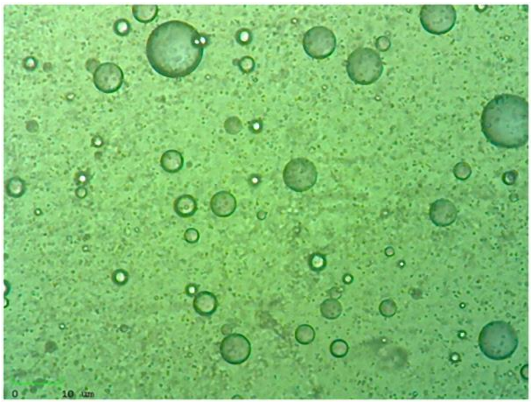

**Fig. 5.** The reaction mixture obtained by stirring method after 1 h reaction time, 100X magnification.

### 3.7. Energy Consumption

Ultrasonic esterification requires no external heat source; heat is generated by cavitation. Energy consumption in the experiment to mix and heat up the CPO to 60 ºC was measured using the watt hour meter. A theoretical energy consumption was worked out for the same time duration needed. The theoretical and experimental energy consumptions were 256 and 260 Wh/kg of CPO, respectively, indicating more than 98% energy efficiency for the ultrasonic device. The experimental energy consumption, 260 Wh/kg of CPO, could be compared to consumption of 250 Wh/kg of oil for transesterification of soybean oil using ultrasonic method [16]; indicating good consistency.

It should be noted here that the heat of reaction for esterification and transesterification is neglected when computing heat consumption or comparing to the process sensible heat. The heat of reaction could be calculated using data from references [17,18]. The derived value for esterification was -32.69 kJ/mol, and -38.85 kJ/mol for transesterification. The heat of reaction for esterification of 5% palmitic acid in CPO was -1.77Wh/kg CPO, and -8.70Wh/kg for transesterification of tripalmitin. Both reactions were shown to be exothermic, having values considerably smaller than the process sensible heat. Thus, only the process sensible heat was considered in our study.

### 3.8. Phosphorus Contents

Phosphorus contents of the initial CPO and the product after reactions were found to be 11.24 and 1.46 mg/kg, respectively. Thus, phosphorus content could be much reduced concomitantly with esterification reaction. This lower phosphorus content meets the methyl ester standard (EN 14214: 2008) of not more than 4 mg/kg. Hence, the esterification process could reduce the phosphorus content to an acceptable level without having to separately perform a degumming step.

## 4. Conclusion

Batch esterification of CPO with an initial FFA content of about 5.0-5.5 wt% using ethanol, assisted by ultrasonic irradiation achieved a final FFA content of less than 0.5 wt%

in the one-stage reaction. The optimum conditions found are: catalyst content at 60 wt% of FFA, 30:1 molar ratio of ethanol to FFA, 60 ºC temperature, 1 h reaction time, and 75% acoustic power amplitude. Amplitude of acoustic power was found to impose the least significant impact. This esterification reached equilibrium at approx. 0.5 wt% FFA with the presence of water. On FFA reduction, the stirring method yields similar efficiency to the ultrasonic method. When water is removed, the reaction shifts to the product side. As a result, the FFA content further declined until it reached a new equilibrium; at 0.22 wt% by the ultrasonic method, and 0.26 wt% by the stirring method. These results indicate that esterification of both methods can reduce FFA content of CPO with similar efficiency. The ultrasonic method is proven an alternative for pretreatment of CPO before a transesterification process; it cuts down the FFA content as well as the phosphorus content simultaneously during the reaction. The method alleviates the use of external oil heating unit since heat is generated by cavitation.

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