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Rapid Esterification of Fatty Acid using Dicationic Acidic Ionic Liquid Catalyst via Ultrasonic-assisted Method

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Abstract – Biodiesel production via esterification/transesterification reactions can be catalyzed by homogenous or heterogeneous catalysts. Development of heterogeneous catalysts for biodiesel production is highly advantageous due to the ease of product purification and of catalyst recyclability. In this current work, a novel acidic [DABCO]DBS][CF₃SO₃]₂ dicationic ionic liquid (DIL) was used as heterogeneous catalyst to produce biodiesel using oleic acid as model oil. The esterification was conducted under ultrasonic irradiation (20 kHz) using a 14 mm ultrasonic horn transducer operated at various duty cycles at ambient temperature. It was observed that the duty cycle, amplitude, methanol to oil molar ratio, catalyst amount and reaction temperature were the major factors that greatly impact the necessary reaction time to lead to a high yield of biodiesel. The reaction conditions were optimized with the aid of Response Surface Methodology (RSM) designed according to the Quadratic model of the Box Behnken method. The optimum conditions were found to be at catalyst amount of 0.64 mol%, methanol to oil ratio of 14.3:1, temperature of 59°C, reaction time of 83 min and amplitude of 60% in continuous mode. The results showed that the oleic acid was successfully converted into esters with conversion value of 93.20% together with significant reduction of reaction time from 7 h (using mechanical stirring) to 83 min (using ultrasonication) . The results also showed that the acidic DIL catalyst we designed purposely was efficient to catalyze the ultrasonic-assisted esterification yielding high conversion of oleic acid to methyl oleate on short times. The DIL was also recycled and reused for at least five times without significant reduction in performance. Overall, the procedure offers advantages including short reaction time, good yield, operational simplicity and environmentally benign characteristics.

Keywords - Biodiesel, ultrasound, pulse, continuous, ionic liquids, dicationic

1. Introduction

The future exhaustion of petroleum reserves and concern over global warming issue has led to the urgent requirements for exploring alternative renewable energy sources that are environmentally more acceptable. Biodiesel derived renewable resources such as vegetable oils and animal fats have been known to be among the alternatives to the highly polluting petroleum-based fuels [1]. Typically, biodiesel feedstock can be divided into several classes comprising of edible and non-edible oils, animal fats, waste oil, micro-algal oil and fungi oil [2]. Up to recently, the main feedstock for biodiesel production were mainly from highly available edible oils, such as from palm, soybean, and sunflower oil as the biodiesel produced showed comparable properties to diesel. Nevertheless, their large scale production would impact the supply balance between food and fuel which potentially may lead to a crisis or at least to ethical issues [3,4]. Use of non-edible oils, such as *Jatropha curcas*, *Pongamia pinnata*, and more recently *Calophyllum inophyllum*, could overcome the problem as they are not suitable for human consumption and their crops could be grown in wastelands unsuitable for food crops. However, they produce low biodiesel yield and contain high free fatty acids, thus requiring multiple reaction steps to produce biodiesel, leading to an increase in operating cost [5-7]. Waste cooking oil (WCO) is a more environmental friendly and potentially better sustainable feedstock but the biodiesel produced contain many undesired impurities and the properties are closely dependent on the fatty acids contents of the source cooking oil. The collection infrastructure and logistics also pose significant problems given that the sources are scattered widely [8-10]. Consequently, micro-algal and fungi oils do emerge as potentially best alternative feedstock as they can afford up to 30 times more oil product than any other feedstock sources while requiring a shorter period for harvesting as compared to other oil

crops [11]. Nevertheless, the application also requires a high production cost due to the high yielding of algae strains needing effective large-scale bioreactors [3].

Biodiesel feedstocks are mainly composed of a wide range of fatty acids such as myristic acid (C14:0), palmitic acid (C16:0), stearic acid (C18:0), oleic acid (C18:1) and linoleic acid (C18:2). Among them, oleic acid is found to be the highest content in most feedstock which explains the reason for it being chosen as the model oil by researchers for lab-scale biodiesel production study.

Biodiesel is commonly produced through esterification or transesterification reactions due to their simplicity and economic viability by reacting free fatty acids or triglycerides with alcohol. However, the immiscibility between the two main reactants has proven to be one of the key reasons behind their low conversion. Typical production requires significant reaction time and is often energy consuming. The immiscibility problem can be potentially overcome by utilizing low-frequency ultrasonic irradiation which causes formation of micro bubbles, hence maximising the interfacial surface area of the molecules.

Using ultrasound for chemical reaction within the frequency range of 20 kHz to 2 MHz can improve the mixing efficiency between reactants in a liquid medium through the generation of micro-bubbles caused by cavitation effect. This unique physical phenomenon subsequently leads to several physical and/or chemical effects depending mainly on the incident frequency [16]. At low frequency, shock waves allow for harsh stirring of the medium together with jetstreams leading to an enhanced mass transfer, whilst, at high frequency, the bubble collapsing time is shorter leading to the formation of free radicals [17]. Since the reaction mixture in the esterification/transesterification process is heterogeneous in reason of the immiscibility between alcohol and oil, the reaction mixture could be considered as suitable for low-frequency ultrasound irradiation. During the process, the asymmetric collapse of the bubble disrupts the interface between the alcohol and oil with extreme energy release (heat

and pressure), creating local hotspots and microjets. This results in an enormous increase in the interfacial area between the immiscible reactants, leading to more intimate mixing and hence faster reaction kinetics [18,19].

Ultrasound reaction can be operated on either continuous or pulse mode as shown in **Figure 1**. Generally, continuous operating mode is the standard method used as it may energize the reaction by offering thermal energy suitable for reactions that require thermal excitation. Besides that, it can induce good emulsion between alcohol and oil phases within a short time. However, the mode delivers acoustic radiation continuously hence preventing time for relaxation among reactants. Thus, it increases the thermal energy of the reaction medium. The phenomenon is possibly caused by the partial loss of the applied energy converted to vibrational or cavitation energy due to absorption or scattering effect [20]. The long continuous mode also often results in difficulty in product separation [21]. On the other hand, pulse mode allows for relaxation intervals providing excitation gap to the reaction mixture to form good emulsions without increasing thermal energy. It also results in smaller sized bubbles thus avoiding energy absorption or scattering. Hence, pulse mode offers better energy distribution and efficiency and enhances mass transfer at the same time even with heterogeneous catalytic esterification or transesterification reaction [22,23]. However, the pulse mode may result in lower excitation compared to the continuous mode and may therefore require longer sonication times. So, it is important to screen the best pulse mode that could lead to comparable results (in this case is the conversion of oil to biodiesel) on continuous mode. The pulse mode is often represented by the period of *On* : *Off* ratio where the *On* period represents the time which ultrasound operates while the *Off* period refers to the interruption or interval time where the ultrasound does not operate. Many studies reported on the effect of pulse sonication on the transesterification of fresh and used oils for both direct and indirect (ultrasonic bath) irradiation modes [24-27]. Indirect mode was shown to have

much lower efficiency reflected by prolonged reaction times compared to direct ultrasound application [21]. Several studies have reported on the direct and continuous application of ultrasonic processing of biodiesel production [21,26,28,29]. Nevertheless, none of the studies compared the continuous and pulse effects of direct ultrasound application for acid-catalyzed biodiesel production.

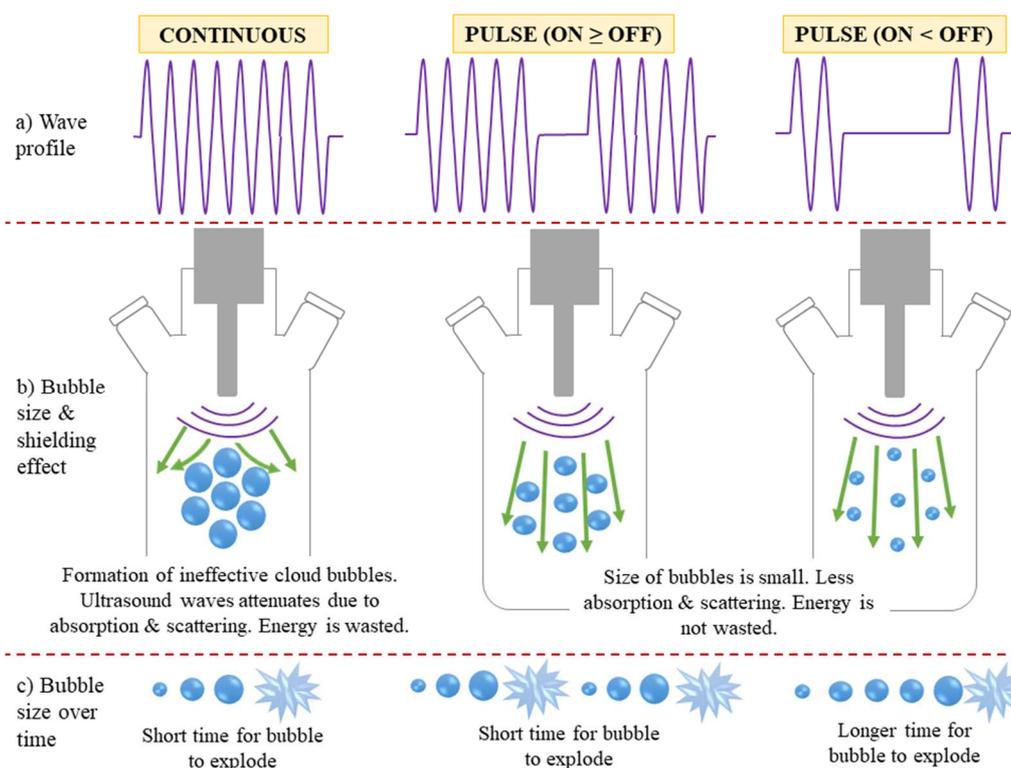


Figure 1. Ultrasonic continuous and pulse mode reaction.

In the production of biodiesel, the catalyst plays evidently an important role. Currently, ionic liquid technology has been explored as new prospect for catalyst in biodiesel synthesis [30]. Their exceptional properties such as high thermal stability, simple recovery process and negligible vapour pressure offer great alternative to volatile and hazardous materials which has attracted the attention of many researchers for utilizing them in a wide range of chemical reaction applications [31,32]. Recently, the introduction of a new class of dicationic ionic liquids (DILs) has attracted wide attention as they represent an interesting variation of the monocationic analogues in terms of properties. DILs show indubitable and several benefits as

compared to typical monocationic ionic liquids in term of volatility and thermal stability, as well as tenability of chemical and physical properties [33] exhibiting promising potential to be used in many applications [34-39].

In the field of biodiesel production, acid catalysts are highly favourable as they can simultaneously conduct esterification and transesterification reaction while avoiding soap formation. The biodiesel can be directly produced from feedstock with high free fatty acid content such as non-edible oil including *Calophyllum inophyllum* oil and cheap feedstock including grease and waste cooking oils. In acid-catalyzed esterification and transesterification reactions, added protons activate the carbonyl group of the free fatty acids or triglyceride molecules whose then undergo a nucleophilic attack of the alcohol to produce water and fatty acid alkyl esters. Several researchers highlighted that sulphonate-based catalysts either on heterogeneous [40,41] or homogenous conditions [42,43] increased the acidity of the catalyst and resembles sulfuric acid in term of acidity and activity [44,45]. Combining the aforementioned properties, this present study aims at enhancing the reaction through the utilization and reuse of sulfonic group-functionalized ionic liquids as an acid catalyst with a combination of low-frequency ultrasound cavitation.

In the present work, a SO₃H-functionalized dicationic ionic liquid as depicted in **Figure 2** is prepared and characterized. Its performance as catalyst for ultrasound-assisted esterification reaction is evaluated and compared with conventional mechanical stirring approach. The effect of different mode (pulse and continuous) and amplitude are also investigated. The reaction condition is then optimized using Response Surface Methodology (RSM) and compared with literature. The recyclability and reusability of the green IL are also studied.

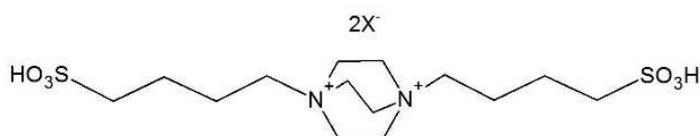


Figure 2 Structure of SO₃H-functionalized dicationic ionic liquid, X = CF₃SO₃.

2. Experimental

2.1 Reagents and materials

All chemicals (analytical reagent grade) used are commercially sourced and used as received without further purification unless otherwise stated. ^1H NMR spectra are done in deuterated water (D_2O) at 298 K, recorded on a Bruker Advance 500MHz spectrometer, and processed using the Top-Spin software.

2.2 Synthesis of ionic liquids

1,4-diazabicyclo[2.2.2]octane (DABCO) is dissolved in ethanol. A double molar equivalent of 1,4-butane sultone is added in a three-neck round-bottom flask. The mixture is reacted at 55 °C for 3 days. As the reaction progresses, a white precipitate began to form. After completion of the reaction, the precipitate is filtered off and washed with cyclohexane and diethyl ether several times and dried using a rotary evaporator to remove unreacted materials. The zwitterion precursor is obtained at a 96% yield as a white powder. The double equivalent of trifluoromethanesulfonic acids is reacted on the zwitterion precursor to produce IL having trifluoromethane sulfonate as anions. The mixture is reacted under vigorous stirring at 70 °C for 4h. The resulting product is then dried under vacuum, affording SO_3H -functionalized dicationic acidic IL as solids at room temperature. Di-(4-sulfonic acid) dibutyltriethylene diammonium di(trifluoromethanesulfonate), ($[\text{DABCODBS}][\text{CF}_3\text{SO}_3]_2$): ^1H NMR: δ 1.830 (m, 2 \times 2H), 2.009 (m, 2 \times 2H), 2.985 (t, 2 \times 2H), 3.627 (t, 2 \times 2H), and 4.009 (s, 6 \times 2H).

2.3 Ultrasonic-assisted esterification reaction

The esterification reaction is conducted under ultrasonic irradiation and conventional mechanical stirring separately under the same experimental conditions for comparison

purpose. The schematic diagram of the process flow for ultrasonic-assisted esterification reaction is shown in **Figure 3**. The reaction is performed in a 30ml double-jacketed glass flask in order to finely control the reaction temperature using cooling-fluid circulation. The reaction solution containing the feed materials is ultrasonically irradiated using a 14mm horn system connected to a Sonic Vibracell generator (20 kHz, VCX 750W, Newton, USA). The ultrasonic power received by the reaction solution is determined using a calorimetric method and set at 30 acoustic power (W) [46]. After completion of the reaction, the resulting mixture is centrifuged for 30 minutes at 4000 rpm and consequently three layers are formed within the liquid solution. Desired fatty acid methyl esters is located in the upper phase and is simply separated from the bottom layers containing a mixture of catalyst, methanol and water. The catalyst is then recovered by removal of methanol and water using rotary evaporator and then recycled for another reaction experiment. The conversion yield is calculated through titration method using the following formula:

$$Y = \frac{AV_0 - AV}{AV_0} \times 100\% \dots \dots \dots (1)$$

where Y is the conversion yield, AV_0 is the acid value of oleic acid and AV is the acid value of the esterification product.

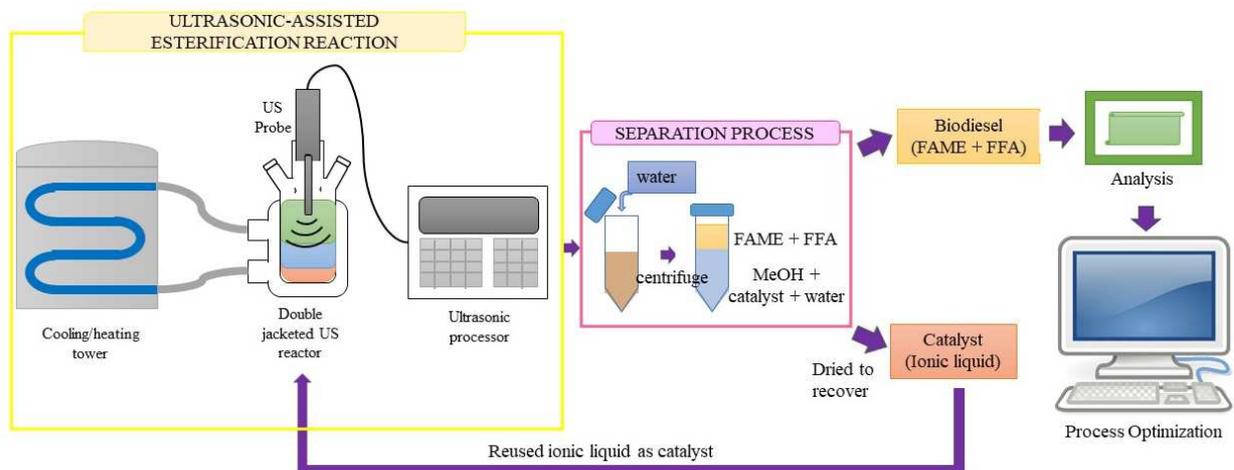


Figure 3. Schematic diagram of process flow for esterification reaction by ultrasonic cavitation.

2.4 Power calculation

The ultrasonic energy dissipated into the reaction solution is measured using a calorimetric measurement since most of the ultrasonic energy is converted to several forms of mechanical energy that ultimately produces heat [47]. The ultrasonic power is calculated using the equation below:

$$P = mC_p \frac{dT}{dt} \dots\dots\dots(2)$$

Where m is the mass of the irradiated solution, C_p is the heat capacity per unit mass of solution (J/kg K) and dT/dt is the slope of the temperature rise versus time (K/s).

2.5 Experimental design

In the present investigation, a Box-Behnken method is used as the tool to optimize the four independent variables namely time (A), temperature (B), catalyst amount (C), and methanol to oil molar ratio (D). The range of variables is decided based on literature studies and initial experimentations conducted. The range of experimental values used are as follows: 25-60 °C, 15-120 min, 3-15 methanol to oil molar ratio and 0.2 to 1.0 mol % catalyst amount. Experimental data from the Box-Behnken method is analyzed using regression (Design Expert™ 8.0) and fitted to a second-order polynomial model in order to identify all possible interactions between the selected factors using a response function as follows:

$$Y = \beta_0 + \sum_{i=1}^3 \beta_i x_i + \sum_{i=1}^3 \beta_{ii} x_i^2 + \sum_{i=1}^2 \sum_{j=i+1}^3 \beta_{ij} x_i x_j \dots\dots\dots(3)$$

where, Y is a response (conversion, %), β_0 is a constant and β_i , β_{ii} and β_{ij} are the regression coefficients, x_i and x_j are independent variables. The fitness and adequacy of the quadratic regression model are investigated through analysis of variance (ANOVA). The coefficients of the fitted model is tested for their significance using Fisher's F -test F -value and p -value (Prob > F) [49,50]. Also, the F -value for each terms namely linear (A, B, C, D), interactive

(AB, AC, AD, BC, BD, CD) and quadratic (A^2 , B^2 , C^2 , D^2) terms are evaluated. A high F -value and p -value < 0.05 indicate that the model is significant. Besides that, if the p -value for lack-of-fit of the model > 0.05 , it means that the model fits well. Additionally, influence of process variables in linear, interactive and quadratic terms towards methyl oleic conversion are studied using the sum of squares of all factors generated in ANOVA table. After the model is derived from the Box Behnken method, a confirmation reaction is conducted to test the validity of the model. The procedure is repeated for three times to evaluate the relative error. The relative error of the model was calculated using the equation as follows:

$$\text{Relative error (\%)} = \frac{|\text{experimental value} - \text{theoretical value}|}{\text{theoretical value}} \times 100\% \dots \dots \dots (4)$$

3. Results and Discussion

3.1 Comparison of ultrasonic-assisted reaction with the conventional method

The performance of ultrasonic-assisted reaction is firstly compared to a conventional mechanical stirring method with and without the presence of a catalyst. The reaction is done using oleic acid as a model oil. The reaction is conducted at 60 °C in a 1-hr duration with 0.4 mol% of [DABCODBS][CF₃SO₃]₂ and a methanol to oleic acid molar ratio of 9. Results, depicted in **Figure 4**, show that ultrasonic irradiation produced at least 16% conversion of oleic acid to methyl oleate even in the absence of catalyst in comparison to the conventional mechanical stirring which only attained 7%. This can be explained by the emulsification thus interaction between the immiscible oil and alcohol phase through the physical effects brought up by cavitation bubbles formation issued from ultrasonic irradiation [29].

When the IL catalyst is used, the amount of oleic acid converted to methyl oleate significantly increase to 89% and 59% respectively for ultrasonic-assisted and mechanical stirring reaction. This phenomenon can be explained by the fact that the IL catalyst provides

more proton to accelerate the reaction. The simultaneous effect of the catalyst and ultrasonic cavitation synergized the reaction.

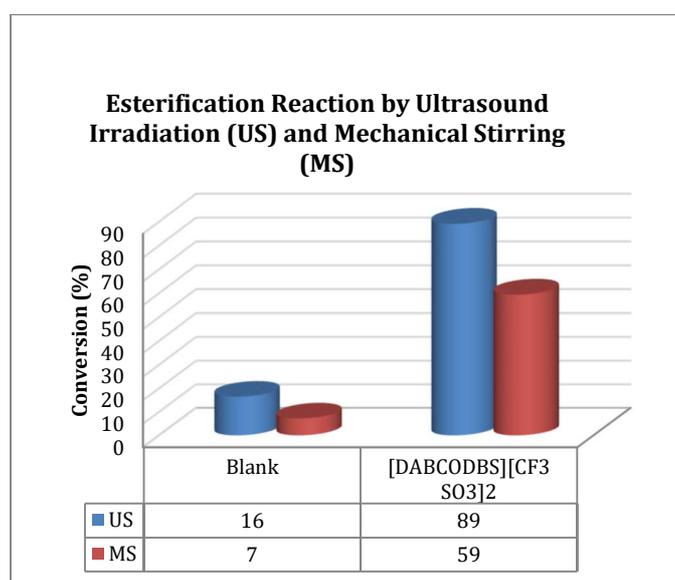


Figure 4. Esterification reaction by ultrasonic irradiation and conventional mechanical stirring with and without IL catalyst.

3.2 Effect of pulse and continuous modes of ultrasonication

To investigate the impact of continuous and pulsed ultrasonic irradiation modes on the biodiesel conversion, experiments with pre-determined operating conditions were conducted on both modes. **Figure 5** displays the results of biodiesel conversion and respective powers consumed under both modes. The result shows that the reaction conducted under continuous mode leads to a better conversion as than under pulse mode. Under pulse mode, by reducing the *On* : *Off* ratio, the conversion value also significantly decreased. This result is in agreement with Ji *et al* [48] where they found that at lower pulse *On* : *Off* ratio, less power is supplied by ultrasound to the reaction and hence less mixing effects occurred preventing a good and rapid conversion. Therefore, continuous mode is chosen for the next optimization of the amplitude.

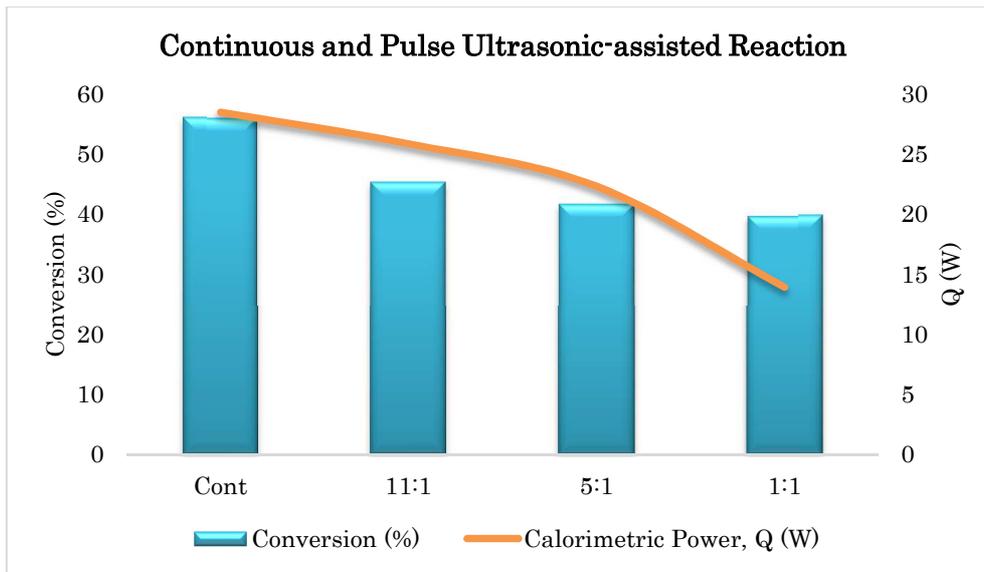


Figure 5. Conversion of biodiesel and power consumption at continuous (cont) and various pulse (on:off, i.e 11:1, 5:1, 1:1) modes.

3.3 Effect of amplitude

Since this amplitude represents the power applied to the system, therefore in theory, the higher the amplitude, the higher the amount of energy supplied and hence favoring the reactions. Higher amplitude causes higher mixing due to fast bubble formation and explosion, overcoming the mass transfer barrier between the immiscible oil and alcohol phases. However, a very high amplitude may also result in ineffective cloud bubbles. In this case, ultrasonic waves are attenuated by the absorption and scattering effect of too numerous bubbles due to high turbulent conditions. Therefore, energy supplied to the system is wasted and will not improve the reaction. Hence, the esterification reaction is investigated at various amplitude levels within the range of 40% to 70%. The calorimetric power is calculated based on Equation (2) as discussed in section 2.4. The results on the effect of amplitude against power and conversion of biodiesel are depicted in **Figure 6**. From the figure, it is shown that the calorimetric power increased from 20.8 W to 28.5 W when changed from 40% to 60% amplitude setting, respectively. But, increasing the amplitude to 70% reduces the calorimetric power to 26.2 W. This power trend is in line to the conversion of biodiesel studied for the same range of amplitude. As for 40% to 60% amplitude ultrasound system, the conversion of

oleic acid to methyl oleate increased from 71.9% to 93.2%. This can be attributed to the improved mixing and emulsification of oleic acid and methanol layers at higher power dissipation. However, increasing the amplitude of the ultrasound to 70% onwards, the conversion reduces to 82.8% of methyl oleate highlighting the already mentioned scattering effect. Similar trend was also observed by Ji and his co-workers [48]. Therefore, for further optimization process through RSM, the ultrasonic amplitude is fixed at 60% amplitude under continuous mode.

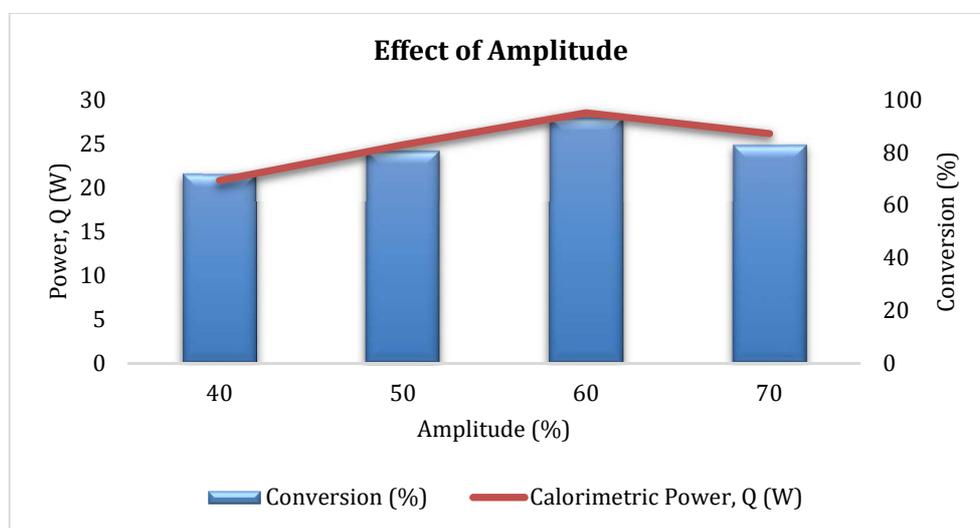


Figure 6. Conversion of biodiesel at a various amplitude in continuous mode.

3.4 Experimental results and statistical analysis

3.4.1 Response Surface Methodology

A set of experimental designs is executed using Box-Behnken method to study the effect of all process variables and at the same time, determine the optimum condition for the esterification of oleic acid using dicationic [DABCO DBS][CF₃SO₃]₂ IL as a catalyst. For ease of evaluation, the relation between predicted and actual conversion values of the biodiesel produced is represented in **Figure 7**. The quadratic regression model is fitted with the actual experimental results obtained using the Box-Behnken method. The figure showed a

good correlation between the predicted and actual values of the oleic acid conversion to methyl oleate for all the experimental data. The final equation in term of actual factors is as follows:

$$Y = -33.1540 + 0.6236t + 2.0087T + 58.3828C - 0.5204M + 0.0007Tt - 0.1646Ct + 0.0195Mt - 0.1311TC + 0.0611TM + 2.0135CM - 0.0032t^2 - 0.0233T^2 - 25.5532C^2 - 0.1977M^2. \dots\dots(4)$$

where Y is conversion, T is temperature, t is time, M is methanol to oil molar ratio and C is amount of catalyst.

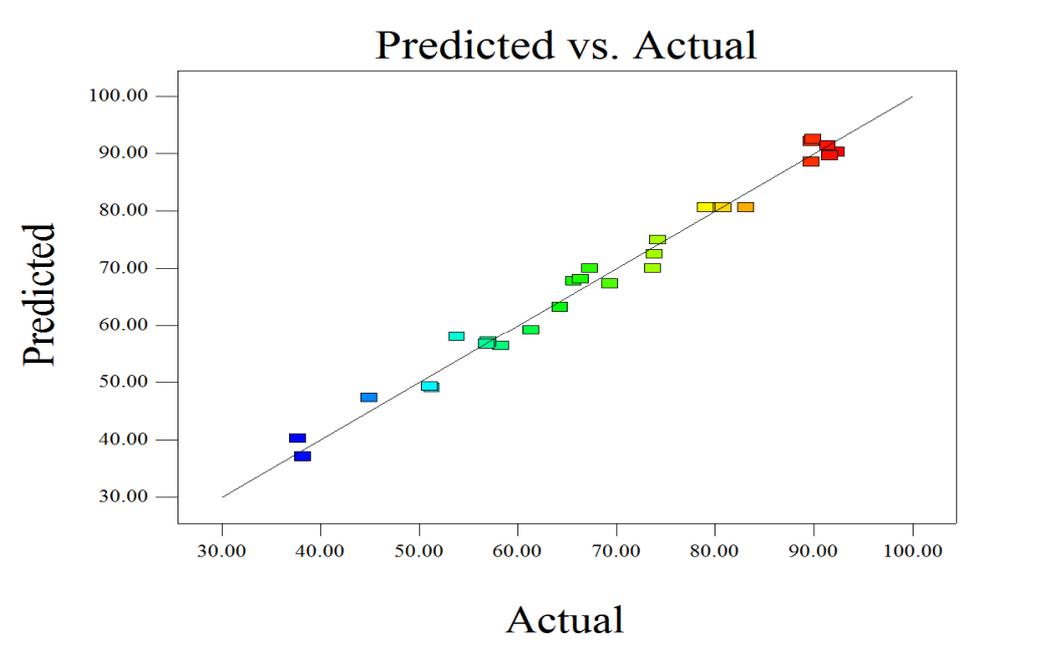


Figure 7. The actual and predicted conversion for optimization of esterification reaction using dicationic ILs as a catalyst.

The ANOVA table is shown in **Table 1**. The ANOVA result shows that a high Fisher’s F -test F -value of 64.01 and very low p -value of < 0.0001 are achieved. It implies that the model is highly significant [51]. Besides that, the F -value for each terms namely linear (A, B, C, D), interactive (AC, AD, BD, CD), and 15quadratic (A^2 , B^2 , C^2 , D^2) terms indicates high influence towards the methyl oleate conversion.

Table 1 ANOVA for quadratic regression model for optimization of esterification reaction using dicationic IIs as a catalyst

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	
Model	7380.12	14	527.15	64.01	< 0.0001	significant
A-Time	2875.21	1	2875.21	349.11	< 0.0001	
B-Temperature	1084.57	1	1084.57	131.69	< 0.0001	
C-Catalyst amount	1632.41	1	1632.41	198.21	< 0.0001	
D-Methanol to oil molar ratio	467.17	1	467.17	56.72	< 0.0001	
AB	1.54	1	1.54	0.19	0.6722	
AC	47.81	1	47.81	5.81	0.0303	
AD	150.20	1	150.20	18.24	0.0008	
BC	3.37	1	3.37	0.41	0.5329	
BD	164.67	1	164.67	19.99	0.0005	
CD	93.41	1	93.41	11.34	0.0046	
A²	508.61	1	508.61	61.76	< 0.0001	
B²	330.88	1	330.88	40.18	< 0.0001	
C²	108.43	1	108.43	13.17	0.0027	
D²	328.44	1	328.44	39.88	< 0.0001	
Residual	115.30	14	8.24			
Lack of Fit	105.96	10	10.60	4.54	0.0790	not significant
Pure Error	9.34	4	2.33			
Cor Total	7495.42	28				
Std. Dev.	2.87		R-Squared	0.985		
Mean	69.41		Adj R-Squared	0.969		
C.V. %	4.13		Pred R-Squared	0.917		
PRESS	624.94		Adeq Precision	26.851		

Influence of process variables in linear, interactive and quadratic terms towards methyl oleate conversion with respect to the sum of squares (SS) of all factors in ANOVA is shown in **Figure 8**. The figure shows that the linear term possesses the predominant effect of 77.72% towards the conversion, followed by the quadratic term that has a marginal effect of 16.37%, and interactive term that has the least effect of 5.91%. The trend agrees with those found in past literature. Maran and co-worker used central composite rotatable design

(CCRD) to optimize the reaction conditions for biodiesel production. They obtained the highest linear effect of 54.32%, followed by the quadratic effect of 39.24% and lastly the interactive effect of 6.22% [52]. In another study by Maran and co-worker, investigation of the biodiesel production from neem (*Azadirachta indica*) oil through the same two-step esterification-transesterification reaction, using CCD design, they also achieved the highest linear effect of 54.93%, followed by the quadratic effect of 36.53% and interactive effect of 7.56% [53].

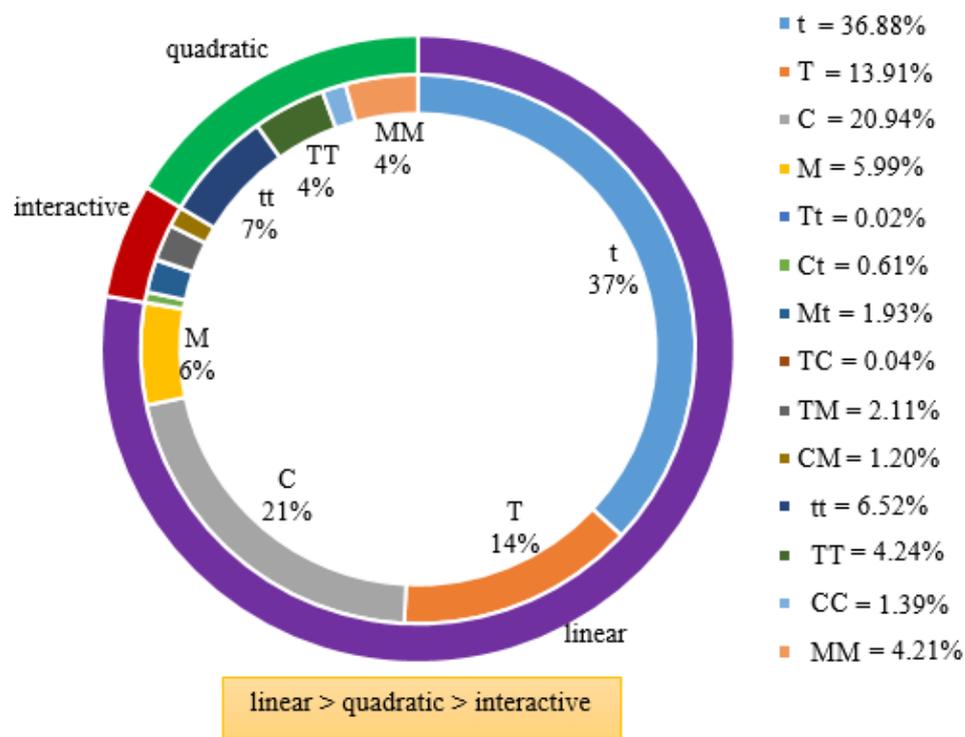


Figure 8. Influence of process variables (parameters/factors) in Linear (Independent), interactive and quadratic terms on FAME conversion (t = reaction time, T = temperature, C = catalyst amount and M = methanol to oil molar ratio).

In this study, all four linear factors (A = time, B = temperature, C = catalyst amount and D = methanol to oil molar ratio) is found to significantly influence the response of the model (conversion), especially reaction time. Their influence strength are as follows: reaction time > catalyst amount > temperature > methanol to oil molar ratio. At the same time, the interactive

except for time*temperature and temperature*catalyst amount and the quadratic factors also are significantly influencing the model output. The significance is that all the factors affect the biodiesel conversion independently and there is a high interaction between mechanisms of effects of the factors. In addition, the p -value for lack-of-fit of 0.0790 implies that it is not significant relative to the pure error. This essentially means that the model is fit and there is only a 7.9% chance that a Lack of Fit value (F -value = 4.54) this large could occur due to noise. The value of R^2 is calculated to be 0.985. The high value of adjusted R^2 of 0.969 which is very close to R^2 value of 0.985 indicates that the sample factors and the sample size are large enough to represent the model and the model is highly significant. The low coefficient of variation (CV) of 4.13% does not only indicate a high degree of precision but also a good reliability in the experiments conducted [54]. The adequate precision reflex the measure of signal to noise ratio. A value greater than 4 is desirable to support the fitness of the model [55]. For the present study, the adequate precision is found to be 26.851 which shows it supports the fitness of the quadratic model.

The interaction between the variables are further studied using the three dimensional response surface plots. The plots are constructed for various combinations of two variables change whilst keeping the other two variables constant and are shown **Figure 9** where the value of conversion decreases in the following colors: red > orange > yellow > green > blue. Based on previous ANOVA result, the trending for the influence of all parameters independently decreases in the following order: reaction time > catalyst amount > temperature > methanol to oil molar ratio.

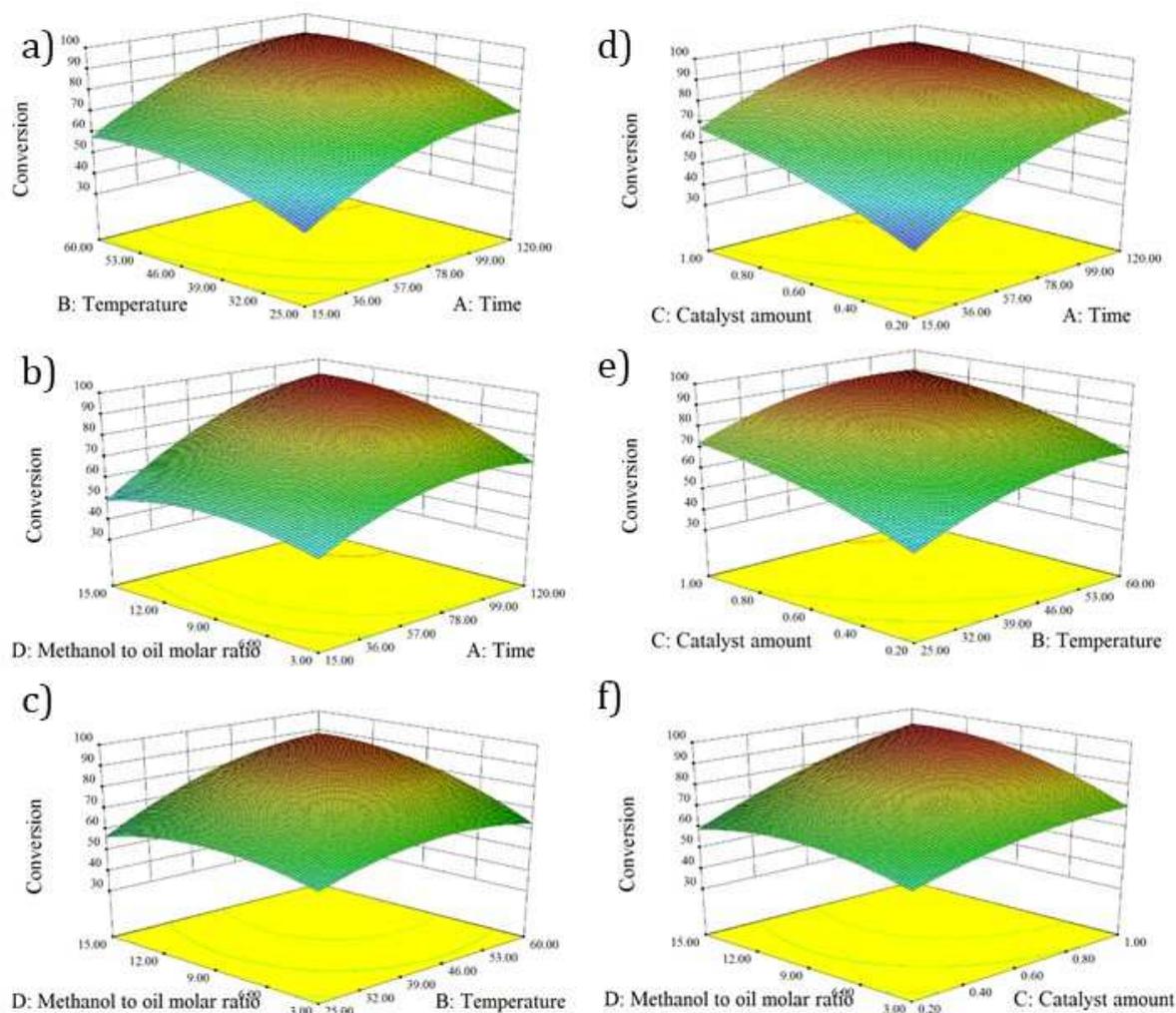


Figure 9. Response surface plot for conversion (%) for optimization of esterification reaction using dicationic IIs as a catalyst.

3.4.2 Effect of reaction time

The effect of reaction time on the conversion of oleic acid was investigated within the range of 15 to 120 min. The influence of reaction time interactively with other factors comprising of temperature, catalyst amount and methanol to oleic acid molar ratio can be observed in Figure 9a, b and d, respectively. In Figure 9a, even at a low temperature, the conversion increases with time from approximately 40% to 70%. With the addition of heat, at the highest setting temperature which is 60°C, the conversion increases significantly from 58.1% to 90.3%. In Figure 9b, at low catalyst amount, the reaction increases from 37.1% to 75.0% with time. With high amount of catalyst, the reaction speed up and the conversion increases from

67.4% to 91.4% with time until reaching the 78th minute where it has reached maximum value. In Figure 9d, at low methanol to oil molar ratio, the conversion increases from 49.1% to 67.8% with time whilst at high methanol to oil molar ratio, the conversion increases from 49.3% to 92.5%. In all cases, by increasing the time, more oleic acid is converted to methyl ester until it reaches equilibrium.

Kouzu et al stated that as the reaction started with high oil concentration, the reaction accelerated to produce methyl ester, following zero-order kinetic at the early phase. By the time, the oil concentration reduced, the esterification reaction became slower. Hence the speed in the conversion of oleic acid to methyl oleate also reduced [56]. According to Martinez-Guerra and co-workers [57], biodiesel production may require a long time due to heterogeneity and poor solubility of methanol in the oil phase requiring harsh mixing to form a homogeneous suspension to allow the proton taking part to the esterification reaction. This harsh and necessary mixing effect can be brought obviously by low-frequency ultrasound as long as key operating parameters (frequency, amplitude, temperature, etc.) have been correctly optimized.

3.4.3 Effect of catalyst amount

The use of catalyst can speed up the reaction remarkably and reduced the alcohol requirement. Hence, it will improve the esterification process economically and environmentally [58]. In this study, the use of dicationic IIs having twice the amount of SO₃H-functionalized group compared to the monocationic IIs is to enhance the reaction by providing a double amount of proton to the reaction. The study on the catalyst impact is conducted within the range of 0.2 to 1.0mol% (based on the mole of oleic acid). The results are shown in Figure 9 (d,e,f), which demonstrate the interactive effect of the catalyst amount with time, temperature and methanol to oil molar ratio, respectively. In all cases, initially, a

low amount of catalyst results in low conversion of oleic acid to methyl oleate. As the amount of catalyst is increased, even at low reaction time of 15 min, temperature of 25°C and methanol to oil molar ratio of 3, the conversion of oleic acid to methyl oleate increases. The same trend is observed for the effect of the catalyst at high reaction time (120 min), temperature (60°C) and methanol to oil molar ratio (15). This can be explained by the mechanism of acid-catalyzed based reaction through the mechanism shown in **Figure 10**. Increasing the number of catalyst molecules will increase the acidity and active sites of the catalyst hence increasing the number of available proton from the sulphonate functional group needed for the protonation of oleic acid to form a carbocation. Hence, the conversion increases [59-61]. With the aid of ultrasound, the catalyst is also well dispersed in the reaction system thus enhancing the acid-catalyzed esterification process.

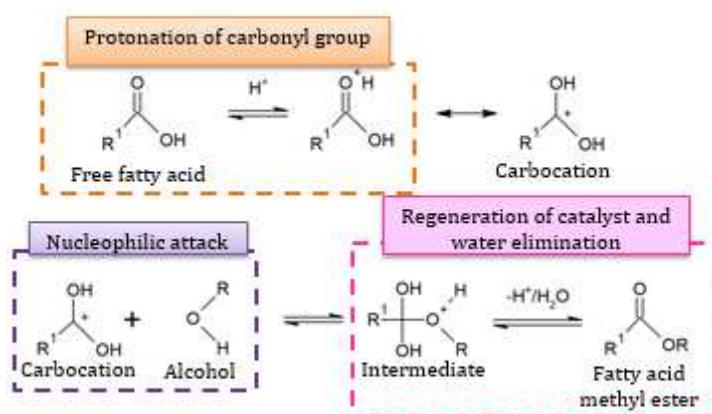


Figure 10. Mechanism of acid-catalyzed esterification reaction.

3.4.4 Effect of temperature

The effect of operating temperature is investigated within the range of 25°C to 60°C to ensure that the reaction proceeds below the boiling point methanol (64.7 °C). The trend showing the effect of temperature can be observed in Figure 9 (a,c,e) which represented the interactive effect between the operating temperature with the reaction time, the methanol to oil molar ratio and the catalyst amount, respectively. Generally, at lower temperature, the conversion achieved is understandably low. As the temperature increases, the solubility of

methanol in oil is enhanced thereby allowing better mass transfer between the reactants, hence improving catalytic activity and improved reaction conversion. In addition, by increasing the temperature, the reaction rate also increases and consequently increases the conversion of oleic acid to methyl ester [62]. The same trend was observed by Gronroos et al who also studied the effect of operating temperature on ultrasonic-assisted esterification reaction [63].

3.4.5 Effect of methanol to oil molar ratio

The methanol to oil molar ratio is one of the most influential factor in determining the extent of conversion. Commonly, a significance and excess amount of methanol is required to drive the reaction forwards to the product direction [10]. The effect of methanol to oil molar ratio is investigated within the range of 3 to 15 molar ratio. Theoretically, only a minimum molar ratio of 1:1 is required to achieve a full reactivity. However, as the reaction is reversible, higher methanol to oil molar ratio is required to shift the reaction equilibrium forwards and to speed up the reaction [64-66]. The trend showing the effect of the methanol to oil molar ratio can be observed in Figure 9 (b,c,f) which represents the interactive effect of the methanol to oil molar ratio with the reaction time, the operating temperature and the catalyst amount, respectively. At a lowest reaction time of 15 min, there was no significant effect of methanol to oil molar ratio towards the conversion of oleic acid to methyl oleate. This indicates that a longer reaction time is required to ensure better mixing of the methanol and oil hence producing higher conversion. At the lowest operating temperature of 25°C and lowest catalyst amount of 0.2 mol%, a similar trend was observed. This can be due to the insufficient energy of the reaction system and lack of catalyst to provide the proton in order to initiate the esterification reaction. However, with the aid of other parameters at the highest level, the increase of the methanol to oil molar ratio increases the cavitation intensity hence

enhancing the reaction conversion. The same trend was observed by Stavarache and co-workers who investigated the effect of the methanol to oil molar ratio on the ultrasonic-assisted the transesterification of vegetable oil [67].

3.5 Optimization process and data validation

The model equation (4) is used to find the optimum values of parameters to get the highest reaction conversion and 55 solutions are found. The selected optimum values of all variables to get a predicted conversion of 95.43% are found to be the temperature of 59 °C, the time of 83 min, the methanol to oil molar ratio of 14.3 and the catalyst amount of 0.64 mol%. **Table 2** shows the reaction conversion achieved and the relative errors as compared to the predicted value. A minimum average relative error of 2.23% is obtained hence the model can be considered as accurate.

Table 2 Corresponding measured and predicted data for the statistical model validation.

No.	Condition	Conversion (%)		Relative error (%)
		Predicted	Measured	
1	Temperature: 59 °C, time: 83 min, methanol		93.20	2.34
2	to oil molar ratio: 14.3, and catalyst	95.43	93.11	2.43
3	amount: 0.64 mol%		93.59	1.93
			Average relative error (%)	2.23

The optimized conditions and conversions are compared with the past literatures that also used sulfonated ionic liquid catalysts and ultrasound as tabulated in **Table 3** [68-71]. Our proposed ionic liquid is able to catalyze the biodiesel production at a comparable conversion with the literature that used higher amount of catalyst, temperature and reaction time. This could be explained by the higher number of sulphonate group in the catalyst that increases the number of the proton that can be donated during the esterification reaction. Therefore, the production cost and the energy consumption can possibly be reduced.

Table 3 Ultrasound-assisted biodiesel production using various types of SO₃H-functionalized ionic liquids.

Reference	This study	[68]	[69]	[70]	[71]
Ionic Liquid	DABCO DBS CF ₃ SO ₃	TMAPS HSO ₄ ^a	TEAPS HSO ₄ ^b	BMIM HSO ₄ ^c	BMIM HSO ₄ ^c
Feedstock	Oleic acid	Soybean oil	Soybean oil	Corn oil	Soybean oil
Temperature (°C)	59	60	60	90	100
Time (min)	83	60	20	50	50
Methanol to oil molar ratio	14.3	9	14	11	10
Catalyst amount	0.64 mol% (~1.55 wt%)	3.2 mol%	2.7 mol%	40.7 mol% (11 wt%)	37.2 mol% (10 wt%)
Ultrasound frequency (kHz)	20	24	24	-	40
Power (W) ^d	12.4	200	80	360	280
Conversion/yield (%)	93.3±0.29%	93.2%	96%	91.85%	92.5%

^a Trimethylamino-propanesulfonic hydrogen sulfate

^b Triethylamine-propanesulfonic hydrogen sulfate

^c 1-Butyl-3-methylimidazolium hydrogen sulfate

^d The power for the current study is acoustic power while other literatures refer to electrical power

3.6 Catalyst recyclability & reusability

High cost is one of the main restriction for the vast usage of IL in many applications. Therefore, to tackle this issue, the recyclability and the reusability study of the IL in the system are very essential. In this study, five successive runs were performed using the recovered IL to determine its recyclability and reusability. The result of oleic acid conversion to methyl oleate using the recovered IL is shown in **Figure 11**. As shown in Figure 11 the conversion reduces from 93.11% to 89.03% after the fifth cycles which is considered as insignificant. The reduced conversion might be attributed to the loss of IL during the phase separation process, in which subsequently effect the amount of IL for the next reaction [61].

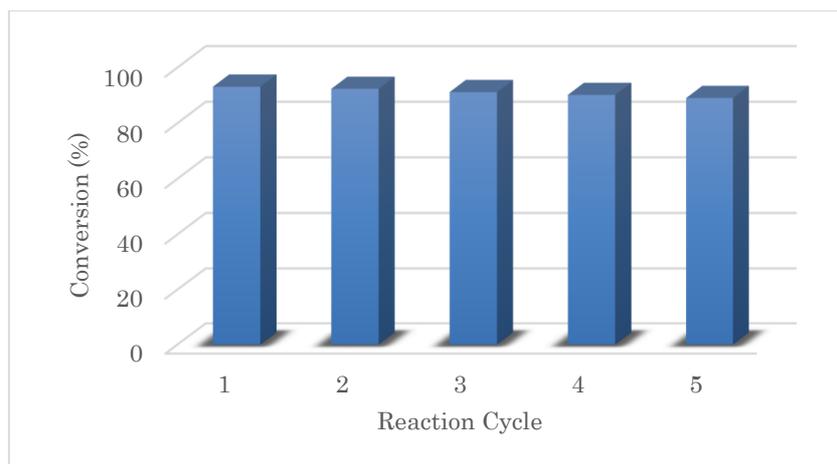


Figure 11. Reusability of [DABCODBS][CF₃SO₃]₂ IL catalyst for the esterification reaction.

4. Conclusion and Future Work

In conclusion, the continuous ultrasonic irradiation affords a better conversion than pulse mode. The SO₃H-functionalized dicationic IL is found to be a potential catalyst to replace conventional catalyst to produce biodiesel. At the optimized conditions were found to be at temperature of 59 °C, 83 minutes of reaction with methanol to oil molar ratio of 14.3 and 0.64 mol% catalyst, a high conversion of 93.2% is attained. The separation of the biodiesel and IL is successfully achieved by simple liquid-liquid extraction followed by centrifugation. The ability of the IL to be reused as an esterification catalyst for at least five times without significant reduction in performance indicates its potential for cost saving and sustainable used.

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