



Optimization of Potassium Carbonate-based DES as Catalyst in the Production of Biodiesel via Transesterification

AbdulwasIU Abdurrahman^{a,*}, Saidu Muhammad Waziri^a, Olusegun Ayoola Ajayi^a, Fadimatu Nyako Dabai^b

^aDepartment of Chemical Engineering, Ahmadu Bello University, Zaria, Nigeria

^bDepartment of Chemical Engineering, University of Abuja, Nigeria

Abstract

Increasing energy demand necessitates the production of sustainable fuels, which can be in the form of bio-fuels. One of such bio-fuels is biodiesel, which is typically produced via transesterification. The development of homogeneous catalyst that is relatively easy to synthesize, cheap, reusable, and environmentally friendly, is a major issue in transesterification reaction. The use of Deep eutectic solvent (DES) as catalyst, is believed to be a significant step in the direction of attaining a sustainable bio-economy. In this study, deep eutectic solvent was synthesized from different mole ratios of K_2CO_3 /glycerol. The synthesized DES was used as catalyst in the transesterification reaction to produce biodiesel from *Jatropha curcas* oil. Box-Behnken design (BBD) was used to determine the factors that significantly affect the biodiesel yield. Optimum fatty acid methyl ester (FAME) yield of 98.2845% was achieved at optimum conditions of 1:32.58 mole ratio of K_2CO_3 /glycerol, 8.96% w/w concentration of DES, and 69.58 minutes. GC-MS analysis revealed that the produced biodiesel contained 98.87% ester content. The properties of the biodiesel produced were characterized and found to agree with those of ASTM D6751-12 standard. Thus, suggesting the synthesized DES is a promising catalyst in the transesterification reaction to produce biodiesel from *Jatropha curcas* oil.

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1. Introduction

Due to the continuous rise in the world's population, the demand for global energy keeps growing. Increasing energy demand necessitates the production of sustainable energy, which can be in the form of bio-fuels [1-2]. One of such bio-fuels is biodiesel. The direct usage and mixing of raw oils, thermal cracking, micro-emulsions, and transesterification are the

basic ways of producing biodiesel [3]. In particular, transesterification is the most prevalent process for making biodiesel because the resulting biodiesel has higher cetane number, lower emissions, higher combustion efficiency and renewability [4]. Acids, alkalis, enzymes, and ionic liquids are used to catalyze the reaction[5]. Acid and alkali catalysts are more commonly utilized in the manufacture of biodiesel because of their low cost compared to enzyme catalysts. However, the acid-catalyzed transesterification process necessitates a large mole ratio of methanol to oil, it takes a long time to complete the reaction

*Corresponding author tel. no: +243 7036088332

Email address: ac1645035@gmail.com (AbdulwasIU Abdurrahman)

compared to alkali catalysts, and the acidic catalysts are caustic and unfriendly to the environment [4, 6-7].

When considering biodiesel production, it is also important to consider the physical state of the catalyst to be employed. While homogeneous catalysts make it difficult to separate catalyst from liquid mixtures, heterogeneous catalysts require harsh operating conditions (such as longer reaction time and high temperature) to produce biodiesel. As already mentioned, Ionic liquids (ILs) have the potential to be used as catalysts in biodiesel production. The ability to recycle ILs at the conclusion of the reaction, and the ease with which products may be separated, are two advantages of using a typical heterogeneous catalyst. Therefore, as a result of combining the benefits of homogeneous and heterogeneous catalysts, ILs have gained appeal as a catalyst in biodiesel synthesis [8-11]. However, large-scale commercial applications of ionic liquids remain a challenge due to complicated synthesis techniques and high cost of the raw materials needed for the synthesis [12]. A cheaper alternative to ILs are the deep eutectic solvents (DESs) [13]. Due to their potential as an ecologically friendly solvent with favorable features over ionic liquids, such as simplicity of production in high purity at reduced cost, low toxicity, biodegradability, and non-reactivity with water, DESs are currently in use in both research and industry [14].

DESs have gained much attention in the biodiesel industry, where they may be used as an extracting solvent, catalyst, or co-solvent [15-16]. DESs are excellent solvents for the separation of glycerol (by-product) from biodiesel [17]. Abott et al. [18] demonstrated that a glycerol-based deep eutectic solvent is effective in separating glycerol and biodiesel from the final reaction mixture generated by ethanolysis in the presence of KOH from rape seed and soybean oils. DESs were found to be successful in removing glycerol, mono- and diacyl glycerols, and also as an alkali catalyst, for crude biodiesel made from palm oil by Hayyan et al. [19] and Shahbaz et al. [20-21]. Zhao & Baker [22] analyzed the feasibility of producing biodiesel by mixing traditional ILs with DESs. Huang et al. [23] discovered a simple and energy-efficient method to initiate commercial CaO for biodiesel synthesis with no pre-treatment by adding a novel DES that can detach the inert layers of CaCO₃ and Ca(OH)₂ on the commercial CaO surface during the reaction to obtain good FAME yield, while the reaction was still running. Hayyan et al. [24] used a phosphonium-based deep eutectic solvent (P-DES) combined with alkali treatment to esterify poor quality crude palm oil. Using ideal circumstances, the oil's free fatty acid content was reduced from 9.5 to 1%. Gu et al. [25] developed a choline-based deep eutectic solvent with glycerol as a co-solvent to catalyze transesterification of rape-seed oil for biodiesel synthesis. Under optimal circumstances, a 98 % FAME yield was attained. Granados et al. [26] reported excellent yields of fatty acid alkyl esters of 90.3 and 92.4 by using potassium carbonate at concentrations of 2 and 3mol percent. Excess methanol was used to move the reversible reaction's equilibrium to the product side, while a co-solvent (such as tetrahydro-furan, THF) was added to overcome the mass transport limit in a heterogeneous system [27]. However, these organic solvents (such as methanol and THF) are often volatile,

flammable, poisonous, and environmentally hazardous [28]. In addition, the little amount of soap created reduces yield and increases the creation of emulsions in the product, making separation of biodiesel from glycerine more difficult. In an alkali catalyzed chemical transesterification reaction, Petracic, [7] investigated the usefulness of a DES (choline-chloride: ethylene-glycol with a molar ratio of 1: 2.5) for the extraction of glycerol from biodiesel. It was determined that the DESs had little to no effect on the extraction efficiency, hence a further process adjustment to lower the amount of total glycerol and glycerides was advised.

In the area of catalysis, Alhassan et al. [29] successfully employed ChCl:KOH, ChCl:p-Toluenesulfonic acid monohydrate, ChCl:Glycerol and ChCl:FeCl₃ as catalyst and co-solvent for hydrothermal liquefaction of de-oiled *Jatropha curcas* cake, and later applied ChCl:p-Toluenesulfonic acid as heterogeneous and homogeneous catalysts to produce biodiesel from *Pongamia pinnata* seed oil [30]. Also, ChCl:p-Toluenesulphonic acid was used as catalyst in co-liquefaction of *Jatropha curcas* seed [31], while, Yong et al. [32] utilized ChCl:Oxalic acid to convert biomass furfural to fumaric acid and maleic acid in the presence of H₂O₂. Although the aforementioned DESs performed well as catalyst in the biodiesel production, a side reaction between hydroxyl groups of the salt, and the acids from some types of DESs composed of ChCl and carboxylic acids was observed [5]. As a result of side esterification reactions observed in choline chloride based-DESs, Petračić et al. [29] prepared Eutectic mixtures DES (K₂CO₃ : C₂H₆O₂ = 1 : 10) which was used for feedstock deacidification. A total acid value of the waste cooking oil was reduced from 2.362 mg KOH/g to 0.574 mg KOH/g. While Sander et al. [33] employed potassium carbonate-based solvent (potassium carbonate:ethylene Glycol) to lower the total acid number of crude biodiesels using coffee feedstock. The time and mass ratio of DES to oil were optimized, and these were shown to be favourable variables for the prospective industrial scale-up of the process.

The industrial applications of DESs, which are comprised of an organic salt and a hydrous metal salt, are limited [5, 34], hence, there is need to further explore the uses of these classes of DESs. Since glycerol is a key by-product of the production of biodiesel and the *Jatropha* plant is vastly available and recognized as a significant source of biodiesel [1], DES, produced from glycerol and potassium carbonate, was employed as a catalyst in the transesterification reaction to produce biodiesel. In particular, the aim of this research is to investigate the impact of mole ratio, time and concentration of potassium carbonate DES on the yield of biodiesel synthesized from *Jatropha curcas* oil. In previous studies, KOH was used as the primary catalyst for transesterification, and potassium carbonate based-DES as a secondary catalyst for purification, deacidification, separation, and extraction, while in this study, the DES was produced from glycerol and potassium carbonate, and it was employed as a catalyst in the transesterification reaction.

2. Experimental Procedure

2.1. Materials

Jatropha curcas oil, with a free fatty acid (FFA) content of 6.68% was obtained from National Research Institute for Chemical Technology NARICT, Zaria, Nigeria, while glycerol, methanol, and K_2CO_3 were obtained from Romtech Scientific Supplies Company Limited, Zaria. The chemicals had 98% purity and were employed for the preparation of DESs without additional purification or drying.

2.2. Synthesis and characterization of DES

2.2.1. Synthesis of DES

Different molar ratios of potassium carbonate to glycerol (as shown in Table 1) were used to produce DES samples. In order to combine the salt with the hydrogen bond donor, a magnetic stirrer hot plate was utilized. Each DES mixture was shaken for 2 hours at 400 rpm at 353 K until a homogeneous transparent colorless liquid was obtained. DES samples were produced at atmospheric pressure with moisture content tightly controlled.

2.3. Determination of viscosity

Viscosity and density of DES play significant roles in processes involving mass transport. The viscosity of the oil was measured using a brookfield rotary digital viscometer NDJ-8S at 40°C. A spindle was attached to the viscometer and set at 60 rpm. 200 mL of the oil was poured into a beaker and the spindle was lowered into the beaker and allowed to attain the same temperature with the sample. The reading at 25% shear rate was taken.

2.3.1. Fourier transform infrared (FTIR) spectroscopy analysis

FTIR was utilized to investigate the interactions between the DES's constituents, and determine if DES was formed through hydrogen bonding, by observing the stretch or shift in each functional group. The FTIR spectroscopy experiments were carried out using microlab PC software of Fourier-transform infrared spectrometer (model 630, Agilent Technology). All samples were scanned over a wave number range of 400-4000 cm^{-1} . The spectra of the samples were recorded in 16 scans at 4 cm^{-1} resolution and plotted in the transmittance mode. Prior to each measurement, the quality of the background signal was evaluated and a background spectrum was recorded using the same settings as for the sample measurement if necessary (residual peaks after cleaning > 0.2 % transmittance). The spectra were submitted to an automatic baseline correction performed with microlab PC software.

2.4. Reduction of free fatty acid (esterification)

The *Jatropha* oil employed in this study has a significant amount of free fatty acid (FFA) (6.68 %), which is not suitable for the production of biodiesel via transesterification. As a result, it became essential to lower it via esterification. Crude *Jatropha* oil was put into a conical flask and heated to 60°C. A combination of concentrated H_2SO_4 (1% w/w) and methanol (30% v/v) was heated separately at (60°C) before being added

to the heated oil in the flask. The mixture was agitated for an hour and then allowed to settle for another two hours, and then FFA value of the oil was determined.

2.5. Experimental design

In this study, the reaction temperature was kept constant at 60°C and the agitation rate was kept constant at 300 rpm, as indicated in the esterification experiment [35]. Response surface methodology (RSM) and Box–Behnken Design (BBD) were used to investigate the primary reaction parameters (such as K_2CO_3 /Glycerol ratio, catalyst (DES) concentration, and reaction duration) and optimize the reaction conditions for fatty acid methyl ester yield (FAME) production. In the regression and graphical data analysis, the Design Expert 6.06 program was employed. The model's statistical analysis was carried out in order to evaluate the analysis of variance (ANOVA).

2.6. Transesterification

40g of the esterified *Jatropha* oil was transesterified in conformity with the design layout matrix, shown in Table 3. The mole ratio of K_2CO_3 /glycerol was in the range of 1:20 to 1:40, time was varied from 30 to 120 minutes and concentration of DES varied from 8 to 10% w/w. The mixture was stirred at 300 rpm with a magnetic stirrer hot plate at a temperature of 60°C. The reaction mixture stabilized into a biphasic system at the end of the reaction. Due to variances in viscosity and density between the two products, two layers developed in the separating funnel. The topmost layer was biodiesel (FAME), whereas the lower layer was crude glycerol. The separation was allowed to run overnight in order to allow the separation of the FAME layer and the free glycerol and other contaminants that can degrade the final quality of biodiesel.

3. Result and Discussion

3.1. Characterization of DES

Different molar ratios of glycerol to potassium carbonate were used to prepare the DESs. Table 1 shows these ratios along with their abbreviations and observations, during the preparation process. During the synthesis stage, DESs samples were formed in a white viscous gel within the first 30 min. After 60 min of mixing, a liquid phase started to appear with some precipitation. Therefore, the period of mixing was extended to 120 min in order to get a homogenous liquid phase DES. DES1 to DES8 were not successful, as the two components did not form DES, as the products were in either turbid white liquid or a mixture of colourless liquid and solid, throughout the process and after cooling to room temperature. Adding more glycerol achieved the necessary balance between the two DES constituents and guaranteed complete miscibility. Thus, DES9, DES 10 and DES11 remained in colourless liquid phase at room temperature, and the unsuccessful DESs were not considered for further investigation in this study.

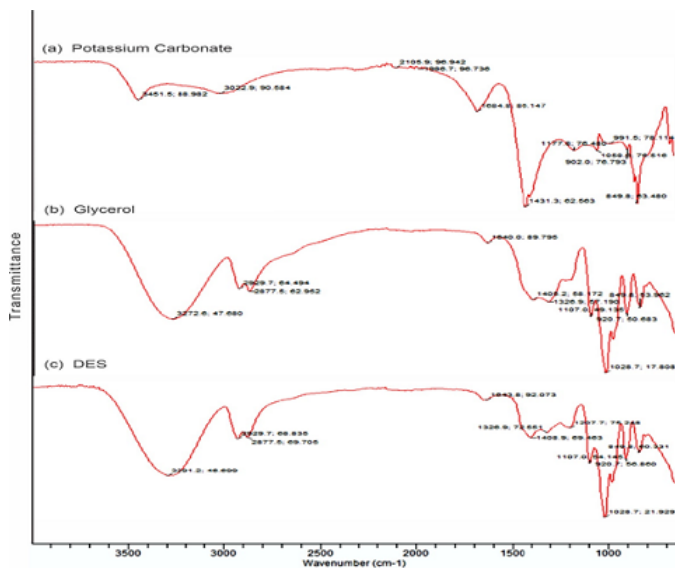
The physical properties of the synthesized DES (in particular, DES 9) are shown in Table 2. DES 9 was considered,

Table 1. Mole ratio and Abbreviations of DES synthesized

| Mole Ratio | Abbreviation | Appearance |
|------------|--------------|------------------------------|
| 1:3.5 | DES 1 | turbid white liquid |
| 1:4 | DES 2 | turbid white liquid |
| 1:5 | DES 3 | turbid white liquid |
| 1:6 | DES 4 | turbid white liquid |
| 1:7 | DES 5 | colorless liquid with solids |
| 1:8 | DES 6 | colorless liquid with solids |
| 1:9 | DES 7 | colorless liquid with solids |
| 1.10 | DES 8 | colorless liquid with solids |
| 1.20 | DES 9 | colorless liquid |
| 1.30 | DES 10 | colorless liquid |
| 1.40 | DES 11 | colorless liquid |

Table 2. Properties of DES Synthesized

| Property | DES synthesized |
|------------------|-----------------|
| Viscosity @ 40°C | 0.428 Pa.s |
| Density | 1.322g/mL |
| pH | 10.53 |

Figure 1. FT-IR result of (a) K_2CO_3 , (b) Glycerol, and (c) DES

since it was successfully synthesized at a lower mole ratio than DES 10 and DES 11. The density and viscosity conform to that reported by Naser *et al.* [36]. The pH is important in applications related to catalytic reactions. A pH of 10.53 was obtained, which indicates the basicity of the mixture. This implies that when the DES is used as catalyst, the reaction will follow a base-catalyzed transesterification mechanism.

Figure 1 shows the FT-IR of K_2CO_3 , Glycerol, and synthesized DES.

In Figure 1 (a, b and c), the region between 3000 and 2800 cm^{-1} shows the existence of C–H stretching bands of the alkanes CH_3 and CH_2 for the DES. The peak at 3022.9 cm^{-1} indicates the absence of O–H in K_2CO_3 in Figure 1a, while the presence of O–H stretching bands between 3200 and 3500 cm^{-1} in Figure

1 (b and c) is attributed to hydroxyl group. Figure 1 reveals that a shift in the O–H stretching vibration of glycerol indicates that the change in vibrational state occurred because a portion of the cloud of electrons of the oxygen atom was transferred to the hydrogen bond, reducing the force constant. Thus, the shift of the O–H stretching vibration (3209.1 cm^{-1}) indicates the existence of a hydrogen bond between the glycerol and K_2CO_3 when the DES was formed. This is in agreement with the observation reported in the literature [37–41]. Thus the FT-IR spectra reveal the intermolecular attraction between the salt and the hydrogen bond donor (Glycerol).

3.2. Production of biodiesel using DES as catalyst

Prior to the production of biodiesel, the FFA of the *Jatropha curcas* oil was reduced from its initial value (of 6.68%) via esterification. The FFA of the *Jatropha curcas* oil were reduced after the first 3 hours to 2.427 %, after 4 hours to 1.112 %, and then to 0.409 %, which is within the range of standard oil for the production of biodiesel.

Box–Behnken Design (BBD) was used to optimize the reaction conditions for the production of fatty acid methyl ester yield (FAME), based on the primary reaction parameters (such as K_2CO_3 /Glycerol mole ratio, catalyst (DES) concentration, and reaction duration), as shown in Table 3.

The esterified oil was transesterified with methanol at a molar ratio of 1:6, utilizing K_2CO_3 /glycerol DES as a catalyst; with the reaction temperature set at 60°C, and the system agitated at 300 rpm. FAME yields in the range of 88.97–98.15% were obtained at DES component ratios of 1:20, 1:30, and 1:40, reaction times ranging from 30 to 120 minutes, and DES concentrations ranging from 8 to 10% w/w, as indicated in Table 3.

3.2.1. Modified quadratic model for transesterification process

Response surface methodology (RSM), based on BBD, was used to investigate the primary reaction variables. To match the experimental data, a quadratic polynomial equation in terms of real components was established using response surface methods, as illustrated in Equation (1).

$$\% \text{ Biodiesel Yield} = +98.00 + 2.95A + 0.64B + 0.44C - 4.21A^2 - 0.90B^2 - 1.31C^2 + 0.50AB + 0.20AC - 0.38BC \quad (1)$$

where: A - mole ratio of K_2CO_3 /glycerol, B- conc. of DES C - reaction time.

As already mentioned, for the regression and graphical data analysis, the Design Expert 6.06 program was employed. The model's statistical analysis was carried out in order to evaluate the analysis of variance (ANOVA). Based on the analysis of variance (ANOVA) results (Table 4), a second-order polynomial model (Equation 1) appears to illustrate the relation between the yield and the important factors. The regression model's significance is shown by a very high F value (204.34) and a modest p-value (0.0001). A, B, C, A^2 , B^2 , C^2 are significant model terms. A reasonable determination coefficient ($R^2 = 0.9962$) indicates that the independent variables (K_2CO_3 /glycerol

Table 3. Design layout for the transesterification reaction

| Serial No. (in order of lowest to highest biodiesel yield) | Run No. | Mole ratio of K ₂ CO ₃ /glycerol | Conc. of DES (% w/w) | Time (min) | Actual Yield of Biodiesel (% w/w) |
|---|---------|--|----------------------|------------|-----------------------------------|
| 1 | 7 | 20.00 | 9.00 | 30.00 | 88.97 |
| 2 | 1 | 20.00 | 8.00 | 75.00 | 88.98 |
| 3 | 10 | 20.00 | 9.00 | 120.00 | 89.65 |
| 4 | 17 | 20.00 | 10.00 | 75.00 | 91.32 |
| 5 | 14 | 30.00 | 8.00 | 30.00 | 94.48 |
| 6 | 13 | 40.00 | 9.00 | 30.00 | 94.90 |
| 7 | 6 | 40.00 | 8.00 | 75.00 | 95.45 |
| 8 | 2 | 40.00 | 10.00 | 75.00 | 95.80 |
| 9 | 12 | 30.00 | 8.00 | 120.00 | 95.90 |
| 10 | 5 | 30.00 | 10.00 | 120.00 | 96.35 |
| 11 | 11 | 40.00 | 9.00 | 120.00 | 96.39 |
| 12 | 8 | 30.00 | 10.00 | 30.00 | 96.45 |
| 13 | 3 | 30.00 | 9.00 | 75.00 | 97.67 |
| 14 | 15 | 30.00 | 9.00 | 75.00 | 97.93 |
| 15 | 16 | 30.00 | 9.00 | 75.00 | 98.10 |
| 16 | 4 | 30.00 | 9.00 | 75.00 | 98.15 |
| 17 | 9 | 30.00 | 9.00 | 75.00 | 98.15 |

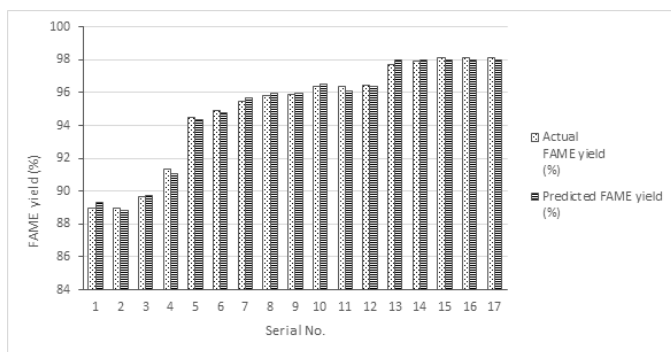


Figure 2. Comparison between the actual (experimental) FAME yield and predicted yield

molar ratio, catalyst concentration, and reaction duration) can account for 99.62 % of the sample variation in biodiesel generation.

To confirm the model validity, the model prediction was compared with experimental data as shown in Figure 2. It was found that the model was successful in capturing the correlation between the process parameters to the response with a correlation coefficient. The high adjusted determination coefficient ($\text{Adj.}R^2 = 0.9913$) verifies the model's importance, and the comparatively low variation coefficient ($\text{CV} = 0.32\%$) suggests the good accuracy of the experimental data. A precision greater than 4 establishes the model's adequacy by assessing the signal-to-noise ratio.

The three-dimensional graphs of a second-order prediction model for the FAME yield response are shown in Figures 3 (a, b and c). As shown in Figures 3 (a) and (b), the FAME production improved significantly when the mole ratio of K₂CO₃/glycerol

was adjusted to its midpoint. This is consistent with the results shown in Table 4 (the mole ratio of K₂CO₃/glycerol has the highest calculated F-value and the lowest p-value). This is due to the fact that the quantity of salt supplied to glycerol has a substantial impact on the creation of hydrogen bonding, which can lead to improved DES activity as a catalyst in the transesterification reaction. When the surplus mole ratio is utilized, it means that the amount of salt utilized was greater than the matching hydrogen bond donor, resulting in the precipitation of the additional salt that was unable to form hydrogen bonds with the hydrogen bond donor.

FAME yield increases as the concentration of the catalyst (DES) increases, as seen in Figure 3 (a) and (c). A low catalyst dose does not generate enough methoxide to achieve a high FAME yield. While due to probable side reactions such as saponification, an excessive catalyst dose does not result in a high yield. As a result, the optimal concentration zone is depicted in Figures 3 (a), (b) and (c).

It is important to note that reaction time is a significant operating parameter because of its direct impact on the cost and quality of biodiesel. To obtain a complete reaction, sufficient but not excessive response time must be supplied. The optimal transesterification reaction time was determined to be between 30 and 120 minutes, as indicated in (b) and (c). In particular, after 75 minutes of response time, there is no discernible influence on yield.

3.3. Optimization solution

One of the main goals of the optimization process is to maximize FAME yield. Table 6 depicts several optimization solutions. As previously stated, the amount of time and catalyst concentration have a direct impact on the cost and quality of

Table 4. ANOVA for Selected Factorial Model

| Source | Sum of squares | DF | Mean squares | F Value | Prob > F |
|----------------|----------------|----|--------------|---------|------------------------|
| Model | 167.03 | 9 | 18.57 | 204.13 | < 0.0001 significant |
| A | 69.74 | 1 | 69.74 | 766.80 | < 0.0001 |
| B | 3.27 | 1 | 3.27 | 35.96 | 0.0005 |
| C | 1.53 | 1 | 1.53 | 16.79 | 0.0046 |
| A ² | 74.78 | 1 | 74.78 | 822.27 | < 0.0001 |
| B ² | 3.40 | 1 | 3.40 | 37.34 | 0.0005 |
| C ² | 7.21 | 1 | 7.21 | 79.22 | <0.0001 |
| AB | 0.99 | 1 | 0.99 | 10.89 | 0.0131 |
| AC | 0.16 | 1 | 0.16 | 1.80 | 0.2212 |
| BC | 0.58 | 1 | 0.58 | 6.39 | 0.0393 |
| Residual | 0.64 | 7 | 0.91 | | |
| Lack of Fit | 0.47 | 3 | 0.16 | 3.70 | 0.1195 not significant |

Table 5. Predicted and Adjusted R-squared

| Std. Dev. | 0.30 | R-Squared | 0.9962 |
|--------------------|-------|----------------|--------|
| Mean Variation | 94.98 | Adj R-Squared | 0.9913 |
| Coefficient (C.V.) | 0.32 | Pred R-Squared | 0.9538 |
| PRESS | 7.75 | Adeq Precision | 39.784 |

biodiesel. The mole ratio of K_2CO_3 /glycerol also has a significant impact on biodiesel production, therefore a mole ratio of 1:32.58, a concentration of 8.96 percent w/w of DES, and a duration of 69.58 minutes are identified as the optimal reaction conditions.

Based on numerical optimization, as shown in Table 6, the optimum FAME yield of 98.2845 % is predicted to be attained at a 1:32.58 mole ratio of K_2CO_3 /glycerol, 8.96 % w/w concentration of DES, and 69.58 minutes. Experiments were conducted at the indicated optimal conditions, producing FAME yields of 98.20 %, 98.20 %, 98.22 %, with an average value of 98.21 %, as shown in Table 7. Thus, the experimental and predicted value(s) are in good agreement. The relative error between the anticipated and real data is 0.0789 %, indicating that BBD and RSM successfully achieved the optimization of DES-catalyzed biodiesel synthesis from *Jatropha curcas* oil.

3.4. Effect of the effluent DES as catalysts

The ability to reuse a catalyst is considered vital to lowering biodiesel production costs. Thus the catalytic performance of the DES, utilized as a catalyst, is an essential metric to consider. The performance of reused DES in the transesterification process is reported in Table 8. The performance of the DES as a catalyst changed significantly after it was reused. Deactivation of the hydrogen bond in the DES, inability to separate the DES from the reaction effluent, and the existence of residual reaction mixture in DES might have contributed to a decrease in the DES catalytic strength.

Table 8 shows the FAME yield(s) obtained from the initial (synthesized)DES (98.22%), from the DES obtained from the first run (71.98%), and the DES obtained from the second run (53.24%). Therefore, following the application of DES in two cycles, the yield of FAME decreased.

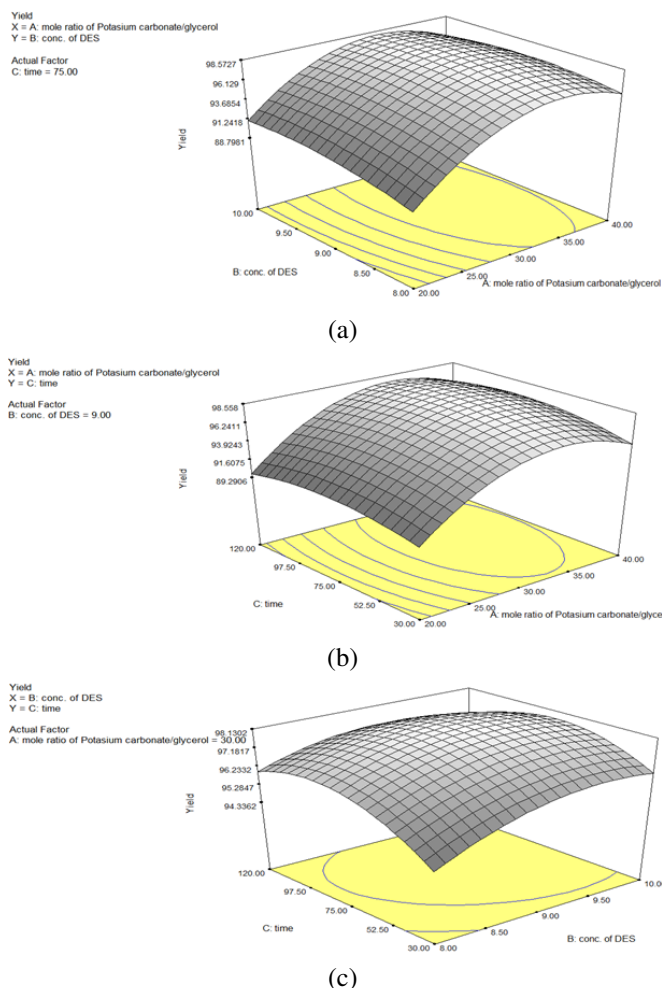


Figure 3. Plots of response surface of FAME yield against reaction parameters: (a) K_2CO_3 -glycerol mole ratio and conc. of DES interaction; (b) K_2CO_3 -glycerol mole ratio and time; and (c) time and conc. of DES interaction

3.5. Properties of the biodiesel produced

The produced biodiesel was subjected to analysis, to verify its properties. The properties were then compared to the expected standards (ASTMD6751), as shown in Table 9.

The biodiesel produced in this study has a viscosity of $4.27 \text{ mm}^2/\text{s}$,

Table 6. Optimized Parameter for the Transesterification

| Mole ratio of Potassium carbonate/glycerol | conc. of DES(% w/w) | Time (min) | Yield of Biodiesel (% w/w) | Desirability |
|--|---------------------|------------|----------------------------|--------------|
| 34.96 | 8.63 | 84.67 | 98.1643 | 1.000 |
| 32.13 | 8.84 | 74.77 | 98.2353 | 1.000 |
| 33.79 | 9.20 | 103.67 | 98.3144 | 1.000 |
| 35.31 | 9.41 | 65.35 | 98.1606 | 1.000 |
| 34.22 | 8.69 | 103.56 | 98.1709 | 1.000 |
| 33.69 | 8.77 | 99.53 | 98.2959 | 1.000 |
| 34.69 | 8.84 | 80.65 | 98.3464 | 1.000 |
| 32.58 | 8.96 | 69.58 | 98.2845 | 1.000 |
| 35.66 | 8.81 | 95.63 | 98.2006 | 1.000 |
| 34.34 | 8.76 | 85.51 | 98.3365 | 1.000 |

Table 7. Optimized conditions and validation for transesterification process

| Predicted optimal conditions and yield | | | |
|--|----------------|---------------------|----------------------|
| A(ratio) | B (wt.%) | C(min) | Yield (%w/w) |
| 32.58 | 8.96 | 69.58 | 98.2845 |
| Actual experiments (validations) | | | |
| Yield 1 (%w/w) | Yield 2 (%w/w) | Yield 3 (%w/w) | Average yield (%w/w) |
| 98.20 | 98.20 | 98.22 | 98.207 |
| Predicted yield (%w/w) | | Actual yield (%w/w) | Deviation |
| 98.2845 | | 98.207 | ± 0.1% |

Table 8. Comparison of FAME yield from the synthesized DES and the reused DES at optimized conditions

| S/No | Catalyst | FAME Yield (% w/w) |
|------|----------------|--------------------|
| 1 | DES | 98.22 |
| 2 | DES from run 1 | 71.98 |
| 3 | DES from run 2 | 53.24 |

which is within the ASTM biodiesel standard range [21]. This is relevant, considering that the atomization of the fuel being injected into an engine combustion chamber is affected by the viscosity of the fuel [42]. Another crucial aspect for optimum engine performance is fuel density; the higher the density, the more difficult it is to pump the gasoline. The produced biodiesel has a density of 0.882g/cm^3 , which is also within the standard range [20]. Another essential attribute of fuels is the cetane number, which is a measurement of a diesel's combustion quality during compression ignition. Engine performance, cold starting, warm up, and engine combustion roughness are all affected by the ignition quality, which is determined by the cetane number. The volatility of the fuel is related to the cetane rating, with higher ratings for more volatile fuels. If a high cetane fuel ignites too quickly, it may result in incomplete combustion and smoke; by not giving enough time for the fuel to combine with air for full combustion [42]. The synthesized biodiesel has a value of 51.18 cetane number, which is within the acceptable range for use in diesel engines. The acid value, pour point, and cloud point of the *Jatropha* oil biodiesel were all within ASTM D6751 specifications. Despite the fact that ASTM does not specify a limit for biodiesel saponification value or iodine value, the attributes of the biodiesel generated are very similar

to those reported in the literature [15].

GC-MS analysis reveals that the biodiesel produced contains 98.87% ester content and 1.13% non-ester composition, as shown in Table 10. This further confirms the quality of the biodiesel produced.

4. Conclusion

In the transesterification process to produce biodiesel from *Jatropha curcas* oil, DES (made from glycerol and K_2CO_3) was utilized as a catalyst, in this study. The work shows that the DES is a promising catalyst in the transesterification reaction, with a biodiesel yield of 98.22%, with ester content of 98.87%. Using Response surface methodology (RSM) and Box-Behnken Design (BBD) to investigate the primary reaction parameters, the mole ratio of K_2CO_3 /glycerol of 1:32.58, concentration of DES of 8.96% w/w and time of 69.58 minutes served as the optimum conditions for the transesterification reaction. Also, the study shows that after the third run of reusing the catalyst, a 53.24% yield of biodiesel was obtained, which shows there is a certain (albeit low) level of reusability of catalyst. Nevertheless, the study shows that the synthesized DES is a promising catalyst in the transesterification reaction to produce biodiesel.

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Table 9. Physical properties of Jatropha oil biodiesel

| Property | Produced Biodiesel | ASTMD6751 STANDARD |
|---|--------------------|--------------------|
| Density at 40 ⁰ C (g/cm ³) | 0.882 | 0.86–0.90 |
| Viscosity at 40 ⁰ C (mm ² /s) | 4.27 | 1.6–6.0 |
| Acid value (mg KOH/g) | 0.74 | ≤ 0.8 |
| Cetane number | 51.18 | ≥ 47 |
| Pour point ⁰ C | -2 | -15 to 16 |
| Cloud point ⁰ C | 10 | -3.0 to 12 |
| Iodine value (mg I/100g oil) | 104.133 | — |
| Saponification value (mg KOH/g oil) | 192.8 | — |

Table 10. GC-MS of the produced biodiesel

| Peak No | Name of the compound | Molecular formula | Retention time (min) | Peak Area (%) |
|------------------------------------|--|--|----------------------|---------------|
| 1 | Dodecanoic acid, methyl ester | C ₁₃ H ₂₆ O ₂ | 24.408 | 0.03 |
| 2 | Methyl tetradecanoate | C ₁₅ H ₃₀ O ₂ | 29.271 | 0.09 |
| 4 | Hexadecanoic acid, methyl ester | C ₁₇ H ₃₂ O ₂ | 33.791 | 16.38 |
| 5 | Heptadecanoic acid, methyl ester | C ₁₈ H ₃₆ O ₂ | 35.717 | 0.22 |
| 6 | 8,11-Octadecadienoic acid, methyl | C ₁₉ H ₃₄ O ₂ | 37.332 | 30.43 |
| 7 | 9-Octadecenoic acid, methyl ester | C ₁₉ H ₃₆ O ₂ | 37.479 | 22.44 |
| 8 | Methyl stearate | C ₁₉ H ₃₈ O ₂ | 37.797 | 8.96 |
| 9 | 9,12-Octadecadienoic acid, ethyl ester | C ₂₀ H ₃₆ O ₂ | 38.392 | 0.08 |
| 10 | Oleic Acid* | C ₁₈ H ₃₄ O ₂ | 39.908 | 0.30 |
| 11 | Glycidyl palmitate | C ₁₉ H ₃₆ O ₃ | 40.857 | 4.94 |
| 12 | 9-Octadecenoic acid (Z)-, 2,3-dihydroxypropyl ester | C ₂₁ H ₄₀ O ₄ | 43.125 | 2.72 |
| 13 | Glycidyl oleate | C ₂₁ H ₃₈ O ₃ | 43.987 | 9.99 |
| 14 | Adipic acid, butyl 3-heptyl ester | C ₂₂ H ₄₂ O ₄ | 44.154 | 0.85 |
| 15 | 6-Octadecenoic acid, (Z)- * | C ₁₈ H ₃₄ O ₂ | 44.571 | 0.50 |
| 16 | Docosanoic acid, methyl ester | C ₂₃ H ₄₆ O ₂ | 44.721 | 0.21 |
| 17 | Tetracosanoic acid, methyl ester | C ₂₅ H ₅₀ O ₂ | 47.856 | 1.52 |
| 22 | 2,2-Dimethyl-3-(3,7,16,20-tetramethyl-heneicosa-3,7,11,15,19-pentaenyl)-oxirane* | C ₂₉ H ₄₈ O | 49.525 | 0.34 |
| Total composition | | | | 100 |
| Total Non-ester content (*) | | | | 1.13 |
| Total ester content | | | | 98.87 |

* indicates non-ester compounds

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