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Synthesis and Characterization of a Deep Eutectic Solvent Catalyst Using Oxalic Acid Extracted from *Averrhoa bilimbi* L. for Biodiesel Production

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Article info

Article history:
Received 5 October 2026
Revised 12 October 2026
Accepted 20 October 2026
Available online xxx

E–ISSN:
P–ISSN:

How to cite:
N. Haryani, D. Agustini, R. Mahmudah, "Synthesis and Characterization of a Deep Eutectic Solvent Catalyst Using Oxalic Acid Extracted from *Averrhoa bilimbi* L. for Biodiesel Production," Eco Chemical Engineering Journal, Vol. 1 No. 1.

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http://doi.org/10.26594/register.v6i1.idarticle

Abstract

Deep eutectic solvents have attracted many researchers' attention as alternative catalyst for production of biodiesel. This research has synthesized and characterized DES based on choline chloride–oxalic acid by using *Averrhoa bilimbi L* as natural source of oxalic acid. Oxalic acid was extracted at various temperatures and then combined by choline chloride at molar ratio 1:1, 1:2, and 1:3. The content of oxalic acid then was determined by using titration procedure, while the product of extraction and DES synthesized were examined by using Fourier-transform infrared spectroscopy (FTIR), scanning electron microscopy coupled with energy-dispersive X-ray spectroscopy (SEM–EDX), and also measurement of pH. The highest content of oxalic acid measured was 33.8 % at 90 °C. SEM results showed solid morphology which relatively well ordered, while EDX analysis showed the content of carbon and oxygen were 15.22% and 50.69%, respectively. The synthesized DES was still in the liquid state and had pH between 1.22 to 2.05, with the lowest pH was obtained at molar ratio of 1:3 and temperature 90 °C. Analysis of FTIR confirmed the existence of unique functional group due to choline chloride and oxalic acid. The analysis also showed the change of hydrogen bond environment. Experimental result exhibited that the development of DES based on choline chloride–oxalic acid by using *Averrhoa bilimbi L* feasible to be investigated for next step, especially in application of esterification process in order to biodiesel production.

Keywords: Deep eutectic solvent, Oxalic acid, *Averrhoa bilimbi* L., Choline chloride, Biodiesel

1. Introduction

The increasing of energy demand due to the increasing of population growth number, industrialization, economic development has raised the need of alternative energy source. The continued dependence of fossil fuel due to the emission of greenhouse gases and various environmental impact, strengthening the need for development of technology for renewable and sustainable fuel. Biodiesel became the high attention as the renewable liquid fuel since can be produced from various sources such as: vegetable oil, animal fat, and used cooking oil then can be used as conventionally alternative fuel for diesel engine [1], [2]. Biodiesel production generally involved transesterification reaction of triglyceride with short chain of alcohol, while esterification reaction was required when reactant contained free fatty acids (FFAs) in large amount. Therefore, the choice of catalyst is one of the urgent factors to effect reaction kinetics, conversion and performance in general [2].

The conventional homogenic acid and base catalysts have been largely used in production of biodiesel due to their high catalytical activities. However, homogenic catalyst has several problems, such as: operational limitation, catalyst separation, corrosion, generation of wastewater, and the need of extra purification steps. For the reactants having high content of FFA, esterification reaction with acid catalyst commonly applied as pretreatment stage prior to transesterification stage using base catalyst [2], [3]. For instance, Wang et al. [3] showed two stages process for used cooking oil, where ferric sulphate was used to accelerate the reaction of FFA esterification before potassium hydroxide was used in transesterification stage. The use of conventional

catalytic system, even though effective, this system has increased the development of alternative catalyst which enable to give the effective esterification and also to simplify the handling process and separation of catalysts.

Ionic liquids (ILs) have subsequently attracted considerable interest as alternative reaction media and catalytic systems because their physicochemical properties can be tailored through appropriate selection of cations and anions [4], [5]. Their application in catalysis has been explored for various organic transformations, including esterification. Nevertheless, the synthesis and purification of certain ILs can involve multiple processing steps and relatively high costs, which may limit their practical application on a larger scale [4], [5]. These considerations have contributed to growing interest in deep eutectic solvents (DESs), which offer an alternative approach to designing tuneable liquid systems.

DES are usually created by mixing a hydrogen bond donor (HBD) with a hydrogen bond acceptor (HBA) in a particular molar ratio, which leads to robust intermolecular interactions and a significant lowering of the melting point compared to the separate components [6]–[8]. DESs share several characteristics with ionic liquids and are therefore often described as ionic–liquid analogues; however, they constitute a distinct class of eutectic systems with different compositions and formation mechanisms [6], [8]. Their relatively simple preparation, compositional flexibility, low vapor pressure, and tuneable physicochemical properties have stimulated extensive research into their applications in catalysis, extraction, separation, synthesis, and other chemical processes [7], [8]. In particular, the physicochemical properties of DESs depend strongly on the chemical nature of the HBA and HBD, their molar ratio, intermolecular interactions, and preparation conditions [7]–[9].

The potential of DESs for biodiesel production has been demonstrated particularly in the esterification of high–FFA feedstocks. Hayyan et al. [10] developed an ammonium–based DES consisting of N, N–diethyl ethanol ammonium chloride and p-toluene sulfonic acid monohydrate for the pretreatment of low–grade crude palm oil. Under optimized conditions, the DES reduced the FFA content from 9.5% to below 1% and could be reused for several cycles [10]. In another study, Hayyan et al. [11] developed a choline chloride–based DES containing p-toluene sulfonic acid monohydrate as the hydrogen bond donor. The DES reduced the FFA content of acidic crude palm oil from 9% to below 1%, and three recycling cycles were achieved without significant loss of catalytic activity [11]. These studies demonstrate the feasibility of DES–based acidic catalytic systems for esterification pretreatment before biodiesel production.

The use of renewable or naturally derived components in DES formulation has attracted additional interest because it may provide opportunities to develop catalytic systems from locally available resources. *Averrhoa bilimbi* L., commonly known as bilimbi and locally as *belimbing wuluh* in Indonesia, is a tropical fruit containing several organic acids, including oxalic acid. Earlier experiments have particularly identified oxalic acid as one of important acid components in *A. bilimbi* fruit. Lima et al. [12] researched to characterize physicochemical *A. bilimbi* fruit at several ripe level and reported that the content of oxalic acid varied accordingly with the ripe level. Joseph and Mendonca [13] also investigated the content of oxalic acid in *A. bilimbi* fruit and stated its concentration 10.5–14.7 mg g^{-1} in unripe fruit and 8.45–10.8 in ripe fruit, in different harvest season. These outcomes showed that *A. bilimbi* fruit is natural sources of oxalic acid and its acid composition varied depend on biology condition and environment.

The existence of oxalic acid in *A. bilimbi* fruit is appropriate for the DES development which has acid properties, because carboxylic acids can be operated as hydrogen bond donors when joined with suitable hydrogen acceptor, like choline chloride [6]–[8]. Accordingly, in the DES developed in this study, choline chloride serves as the hydrogen bond acceptor, whereas oxalic acid extracted from *A. bilimbi* L. serves as the hydrogen bond donor. Interactions between these components are expected to contribute to the formation of an acidic eutectic system. The resulting properties are influenced by the chemical characteristics and relative proportions of the two components, making the composition and preparation conditions important considerations in DES development [7], [8]. The use of oxalic acid obtained from a locally available fruit therefore provides an opportunity to investigate a naturally sourced acid component for the formulation of a choline chloride–derived DES catalyst.

Despite the demonstrated potential of DESs as acidic catalytic systems for biodiesel related esterification, the use of oxalic acid extracted from *A. bilimbi* L. as the hydrogen bond donor in a choline chloride–based DES remains insufficiently explored. In particular, information linking the extraction conditions of oxalic acid from *A. bilimbi* with the characteristics of the resulting DES is limited. Therefore, this study aimed to synthesize and characterize an oxalic acid based deep eutectic solvent catalyst using oxalic acid extracted from *A. bilimbi* L. and choline chloride for potential application in biodiesel production. Oxalic acid was extracted from *A. bilimbi* fruit at different temperatures, and the oxalic acid content was determined by titration. The resulting DES was subsequently characterized using Fourier-transform infrared spectroscopy (FTIR), scanning electron microscopy coupled with energy-dispersive X-ray spectroscopy (SEM-EDX), and pH measurement.

The study provides an initial assessment of the suitability of oxalic acid obtained from *A. bilimbi* as a natural acid component for developing a DES-based catalytic system for the esterification of used cooking oil as a pretreatment step toward biodiesel production.

2. Materials and methods

2.I Materials

The materials used for the preparation of the DES catalyst from oxalic acid extracted from *Averrhoa bilimbi* L. included oxalic acid obtained directly through the extraction of *A. bilimbi* fruit, NaOH, $CaCl_2$, H_2SO_4, distilled water, and choline chloride (ChCl).

2.2. Equipment

Equipment used in this experiment included heating mantle, hot plate, beaker glass, oven, centrifuge, fine mesh sieve, filter paper, analytical balance, Erlenmeyer flasks, volumetric flasks, pH meter, magnetic stirrer, litmus paper, glass stirrer rod, burette and clams.

2.3. Extraction of oxalic acid from Averrhoa bilimbi L. *fruit*

Extraction of oxalic acid from *A. bilimbi* fruits was conducted by stages of sedimentation and filtration steps. At first fresh *A. bilimbi* fruits were blended by using blender, and then filtered components were filtered to separate liquid fraction from solid residue. Next, filtrate was centrifuged to eliminate suspended solid, then refiltered. A 200 mL of filtrate was inserted into beaker glass, then 1 N NaOH solution was added until neutral pH achieved. Next, $CaCl_2$ was added into the neutral extract until precipitate was formed. Mixture was heated on the hot plate at temperatures of 70, 80, or 90 ^oC until boiled, after that filtered by using filter paper, followed by washing the precipitate intermittently retained using distilled water. All precipitate were put into Erlenmeyer flask, then 50 ml 98% H_2SO_4 was added to facilitate next precipitation step. The resulted mixture was then filtered and collected to determine the content of oxalate acid by titration procedure.

2.4. Synthesis of the choline chloride–oxalic acid DES

The DES was synthesized by mixing choline chloride and oxalic acid of previous extraction at molar ratio of 1:1, 1:2, and 1:3. For each mixture, ChCl and oxalic acid were mixed in accordance to molar ratio which have been determined while keep on being mixed and heated at 100 ^oC until homogenous and clear liquid obtained. The resulting liquid was determined as choline chloride DES–oxalic acid and next to be characterized.

3. Result and discussion

Experimental results gave a general idea about oxalic acid product from *A. bilimbi* fruit and its next use in production of DESs base on choline chloride–oxalic acid. Results were discussed in an order, started from the effect of extraction temperature on the measured oxalic acid content. The extracted product then analysed by using Fourier-transform infrared spectroscopy (FTIR) and scanning electron microscopy coupled with energy dispersive X-ray spectroscopy (SEM-EDX) to identify its characteristic functional group and elemental composition. Characteristic of synthesized DES obtained from FTIR was then discussed to observe the change due to interaction between choline chloride and oxalic acid. At last, the physical condition and pH of DES were analysed due to its molar composition and preparation temperature. Overall, these findings described physicochemical of synthesized and give a fundamental concept for further research about the suitability for esterification application related to production of biodiesel.

3.1. Effect of temperature on oxalic acid extraction

The effect of heating temperature on the oxalic acid content obtained from *Averrhoa bilimbi* L. fruit is presented in Table 1. The extraction was conducted at 70, 80, and 90 °C to evaluate the influence of heating temperature on the measured oxalic acid content.

Table 1. Effect of heating temperature on the measured oxalic acid content.

Heating temperature (^oC)	Oxalic acid content (%)
70	27.40
80	29.95
90	33.80

Effect of heating temperature on oxalic acid obtained from *A. bilimbi* fruit is presented in Table 1. Extraction process was conducted at temperature of 70, 80, and 90 ^{o}C to evaluate the effect of heating temperature on measured oxalic acid content. The content of oxalic acid increased gradually with the rising of temperature, from 27.40% at 70 ^{o}C to 29.95% at 80 ^{o}C, and 33.80% at 90 ^{o}C, Therefore, in the range of experiment temperatures, at 90 ^{o}C the experiment produced the highest measured oxalic acid content. The content at 90 ^{o}C showed the increment 23.4% if compared to the content obtained at 70 ^{o}C. The increasing of oxalic acid content with the increasing of temperature perhaps associated with the increasing of molecule mobility and mass transfer during the extraction process. At the higher temperature generally increases the molecular activities and provides the transfer of suspended component from plant structure into the extraction solution. Moreover, higher temperature can increase molecular fraction which having enough energy to overcome activation resistance, thus to facilitate the process associated with the release and transport of solute. Extraction system in this experiment, these effects may have contributed to the increasing of oxalic acid content measured at higher temperature.

The existence of oxalic acid in *A. bilimbi* fruit has been reported previously, therefore supporting the use of this fruit as natural source of oxalic acid. The progressive improvement observed from 70 to 90 ^{o}C showed that in the experimental condition applied, the increasing of heating temperature will support the increasing of the measured content of oxalic acid. However, because only three temperature levels were evaluated, the present results do not establish the optimum temperature beyond the investigated range. Therefore, 90 °C is considered the temperature that produced the highest measured oxalic acid content in this study, namely 33.80%. The oxalic acid obtained under this condition was subsequently used as the acid component for the synthesis of the DES catalyst based on choline chloride.

3.2. FTIR analysis of extracted oxalic acid

The extracted oxalic-acid-containing material was characterized using Fourier-transform infrared spectroscopy (FTIR) to identify the characteristic functional groups present in the sample. The FTIR spectrum of the extracted material is presented in Figure 1, while the spectrum of the standard oxalic acid is presented in Figure 2. Comparison of the two spectra was performed to evaluate the similarity of the characteristic absorption bands associated with oxalic acid, which has been reported as an organic acid component of *Averrhoa bilimbi* L. [12]. FTIR has also been used as a complementary technique for identifying oxalate-related functional groups in plant-derived materials [14].

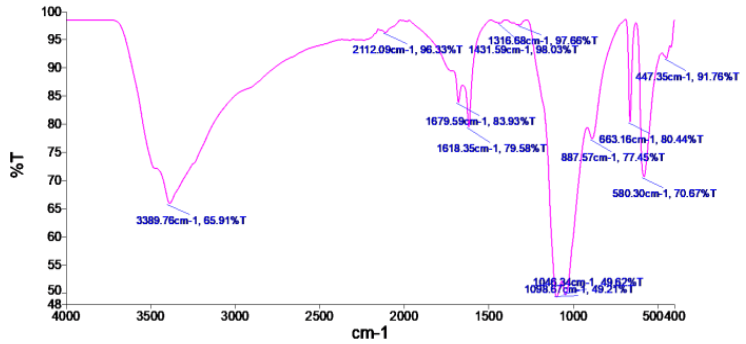


Figure 1. FTIR spectrum of the extracted oxalic acid containing material.

The FTIR spectrum of the extracted material showed characteristic absorption bands at 3,389.76; 1,679.59; 1,098.67; and 887.57 cm^{-1}. The FTIR spectrum exhibited a band at 3,389.76 cm^{-1}, indicating O–H stretching vibrations, while the prominent peak observed at 1,679.59 cm^{-1} corresponded to the C=O stretching vibration of the carboxylic acid functional group. The band at 1,098.67 cm^{-1} was associated with C–O vibration. The absorption at 887.57 cm^{-1} was located within the fingerprint region. These spectral features are consistent with the principal functional groups expected for oxalic acid and provide qualitative evidence for the presence of an oxalic acid related component in the extracted material.

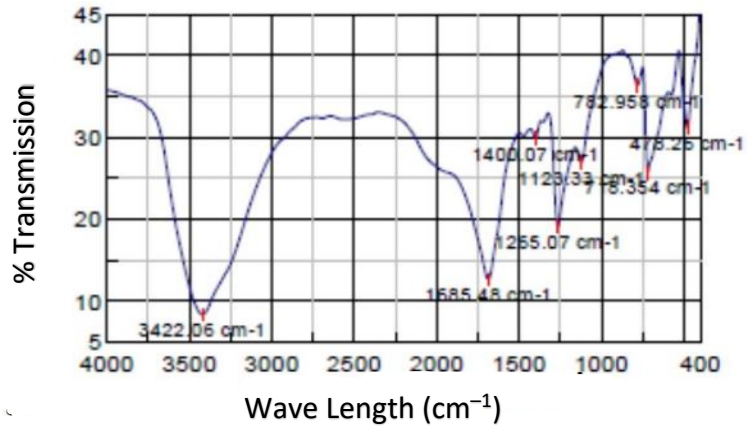


Figure 2. FTIR spectrum of standard oxalic acid.

For comparison, the standard oxalic acid showed absorption bands at 3,422.06; 1,685.48; 1,123.33; and 718.35 cm^{-1}. The band at 3,422.06 cm^{-1} was assigned to O–H stretching, while the absorption at 1,685.48 cm^{-1} corresponded to C=O stretching. The band at 1,123.33 cm^{-1} was associated with C–O vibration, whereas the absorption at 718.35 cm^{-1} was located in the fingerprint region.

Table 2. Comparison of characteristic FTIR bands of standard and extracted oxalic acid.

Functional group/spectral region	Standard oxalic acid (cm^{-1})	Extracted material (cm^{-1})
O–H	3,422.06	3,389.76
C=O	1,685.48	1,679.59
C–O	1,123.33	1,098.67
C–H	718.35	887.57

The spectral profiles in Table 2 reveal a close correspondence between the extracted material and the reference oxalic acid with respect to their major functional-group absorptions. The differences between the corresponding bands were 32.30 cm^{-1} for O–H, 5.89 cm^{-1} for C=O, and 24.66 cm^{-1} for C–O. The relatively small difference in the C=O absorption band, together with the comparable O–H and C–O absorption regions, supports the presence of oxalic-acid-related functional groups in the extracted material.

The absorption at 887.57 cm^{-1} in the extracted material was not assigned to C–H stretching because oxalic acid ($H_2C_2O_4$) does not contain C–H bonds. Instead, this band was considered a feature within the fingerprint region. Its different position relative to the 718.35 cm^{-1} band of the standard may reflect differences in the molecular environment and/or the presence of additional constituents in the extracted material. Accordingly, the difference should not be interpreted as evidence of a different compound solely on the basis of this band.

The extracted material also showed spectral features that were not identical to those of the standard. These differences may be related with compounds naturally present in the *A. bilimbi* fruit matrix or residual components introduced during the extraction step. Because the extraction procedure involved $CaCl_2$ and H_2SO_4, the possibility of residual inorganic or other complementary components should also be considered. Hence, although the FTIR spectrum supports the existence of functional groups characteristic of oxalic acid, FTIR alone cannot establish the quantitative purity of the extracted material.

Taken together, the observed correspondence of the O–H, C=O, and C–O absorption features with those of the reference standard reveals that the extracted material contains oxalic acid related functional groups. The FTIR results are complementary to the oxalic acid content determined by titration and the subsequent SEM–EDX characterization.

3.3. SEM–EDX analysis of extracted oxalic acid

Scanning electron microscopy coupled with energy-dispersive X-ray spectroscopy (SEM-EDX) was employed to examine the surface morphology and elemental composition of the material obtained from *Averrhoa bilimbi* L. extraction. SEM offers details about surface structure and microstructural characteristics, while EDX delivers qualitative or semi-quantitative data on the elemental makeup of the examined area [15], [16]. The SEM images obtained at magnifications of 500; 1,000; 5,000, and 10,000× are presented in Figure 3(a) – 3(d), respectively.

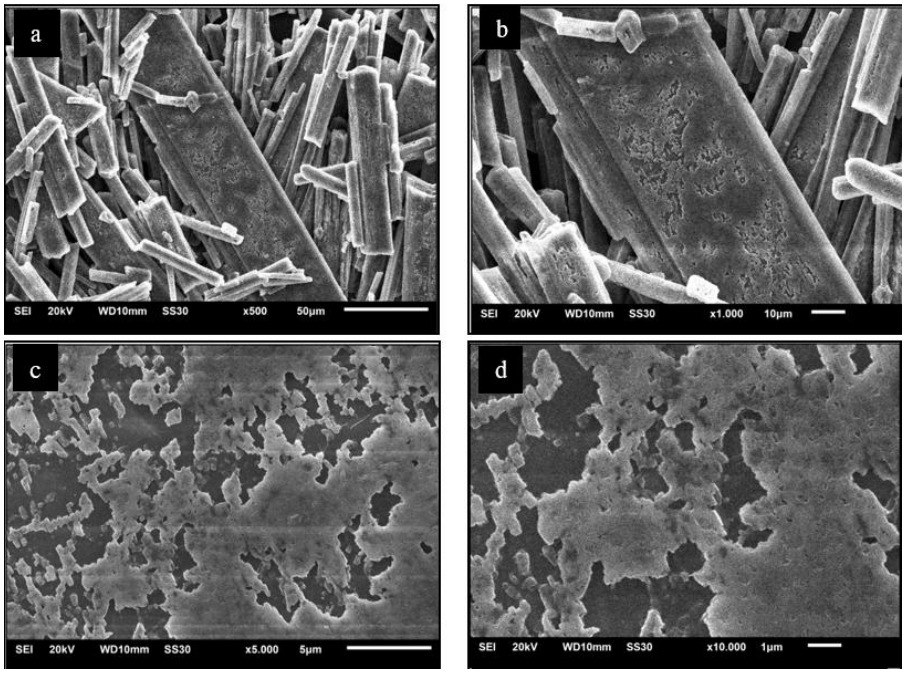


Figure 3. (a). Surface morphology of extracted oxalic acid at (a) 500×; magnification; (b) 1000× magnification; (c) 5000× magnification; (d)10,000× magnification.

SEM images show the solid structure which relatively tidy in the range of observed SEM magnification. At magnification of 500× and 10,000×, particles showed a clear characteristic morphology, while the higher magnification 5,000× and 10,000×, detailed surface of particle showed much better. The observed morphology showed the formation of structured solid material after extraction and precipitation process. However, only SEM morphology cannot be used to ensure the crystallography identity or the purity of material phase. Confirmation on crystallin phase needs addition of crystallography characterization, such as X-ray diffraction (XRD).

EDX analysis showed that carbon (C) and Oxygen (O) were major detected element, with carbon fraction 15.22% and 50.69%, respectively. The existence of carbon and oxygen was consistent with the elemental constituent of oxalic acid. However, the measured elemental proportion did not directly consistent with theoretical composition of pure oxalic acid. This difference showed that there was other elemental component also exist inside the material which need to be analysed. It needs to be noticed that conventional EDX cannot detect hydrogen, while quantitative result in the detected result can be affected by instrument condition, sample preparation, matrix effect, then characteristic of analysed surface [15], [16].

Beside carbon and oxygen, there were also detected sulphur (S), calcium (Ca), iron (Fe), and copper (Cu) by 16.12, 17.15, 0.15, and 0.68%. Sulphur and calcium content which relatively high showed the present of additional inorganic components inside the analysed material. Their existence might be correlated with the residual species from extraction process, considering calcium chloride and sulfuric acid were used during the isolation process. Yet, only EDX analysis cannot confirm the chemical formation or the exact source of these elements. Therefore, their existence should be considered as evidence of the additional elements presence, not as conclusive evidence of contaminations from specific reagent.

Analysis based on oxide showed the existence of sulphur trioxide around 19.35% and calcium chloride 21.03%, together with other oxide components at lower concentration. These findings also showed the presence of inorganic elements in the analysed material. However, basically EDX gave information about elemental composition and did not independently determine molecular structure, chemical bonds, and then crystallin phase [15], [16]. Because of that, reported oxide composition should be understood as definitive confirmation about the existence of SO_3 phase or separated CaO.

The detection of additional elements was also consistent with FTIR results, showing that extraction result of material might contain other component excluded the main functional group related to oxalic acids. However, the result of SEM-EDX gave supporting evidence that extracted material contained carbon and oxygen in large quantity and showed solid morphology which relatively ordered. The existence of sulphur and

calcium further indicated that additional inorganic components were still exist in analysed material, thus further purification step was required if the production of oxalic acid at higher purity as target.

In overall, characterization by SEM-EDX supported the formation of solid material which contained oxalic acids with relatively ordered morphology, then carbon and oxygen as dominant element were also detected. Yet, because only SEM-EDX cannot ensure molecular identity and crystallographic purity, these results should be interpreted together with FTIR and titration results. Further purification process and XRD analysis as additional characterization will give stronger evidence due to crystalline phase and purity of the extracted oxalic acid.

3.4. FTIR analysis of the synthesized eutectic solvent

FTIR was used to characterize the functional groups and observe molecular interactions in the synthesized DES. The FTIR spectra were recorded over the wavenumber range of 4500–500 cm^{-1}. Three DES compositions made with choline chloride (ChCl) for extracting oxalic acid at molar ratios of 1:1, 1:2, and 1:3 was studied, and the associated spectra are shown in Figure 4(a) – 4(c).

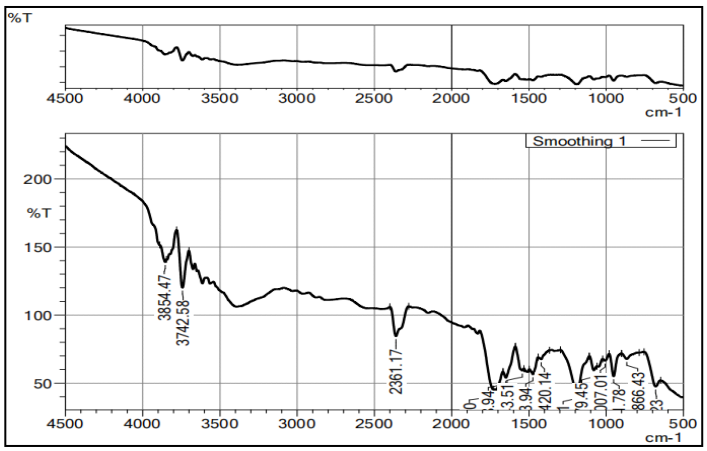


Figure 4 (a). FTIR spectrum of the DES prepared at a ChCl: oxalic acid molar ratio of 1:1.

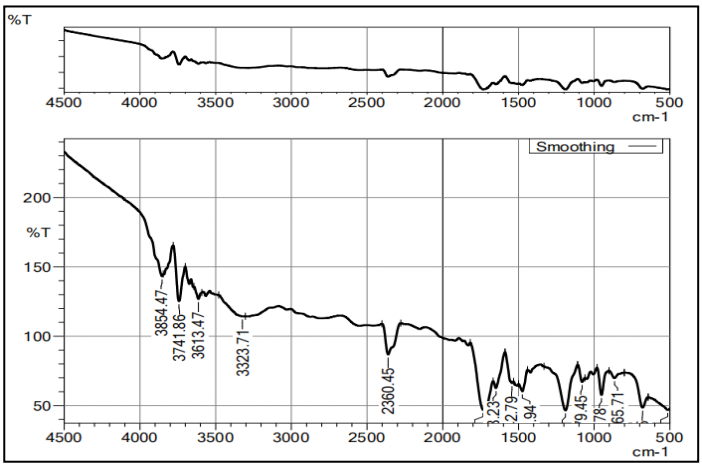


Figure 4 (b). FTIR spectrum of the DES prepared at a ChCl:oxalic acid molar ratio of 1:2.

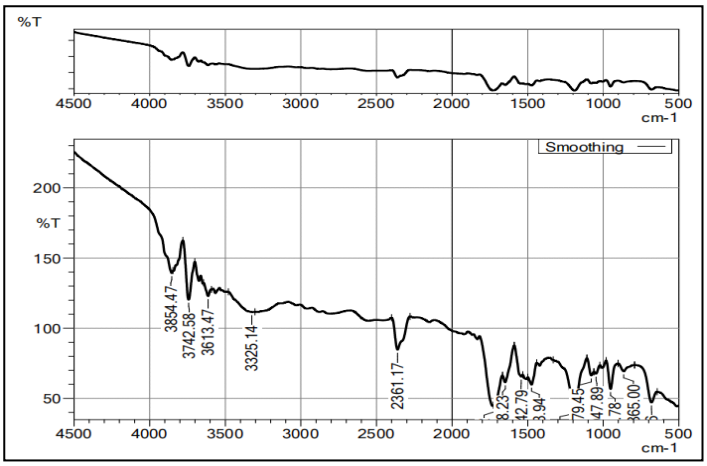


Figure 4 (c). FTIR spectrum of the DES prepared at a ChCl: oxalic acid molar ratio of 1:3.

The FTIR spectra of the three DES compositions exhibited absorption bands associated with functional groups originating from both ChCl and oxalic acid. A band was observed at approximately 3,854.47 cm^{-1}, within the O–H stretching region. Hydroxyl related absorption is commonly observed in DES systems containing hydrogen-bond-donor components, and changes in the position and profile of the O–H band can reflect changes in the hydrogen-bonding environment within the DES [17]. Nevertheless, the comparatively high wavenumber noted in the current sample should not be seen as proof of the lack of crystalline water.

An absorption band was also observed at approximately 1,189 cm^{-1}. This region is associated with C–O related vibrations and is consistent with the presence of oxygen containing functional groups originating from the oxalic acid component. Comparable C–O vibrational features have been reported for ChCl–oxalic acid DES systems, together with O–H and carbonyl related absorptions associated with the hydrogen-bond-donor component [18].

Recorded spectrum at ChCl:oxalic acid molar ratio of 1:1, 1:2, and 1:3 showed intensity variations and broadened several absorption bands along with the increasing of oxalic acid proportion. The spectrum change can be associated with environmental change of hydrogen bond which appeared because of interaction hydrogen bond acceptor (ChCl) and hydrogen bond donor (oxalic acid). Experimental and theoretical research of DES based on choline chloride–oxalic acid has showed that the change of vibration characteristic on FTIR can reflect the change of hydrogen bond interaction among DES components. Therefore, the increasing of oxalic acid proportion can change DES's relative composition and affect molecular environment which reflected in FTIR profile.

Several absorption characteristics were observed in the range 2,800–3,500 cm^{-1}, including band at 2,361; 3,323; and 3,325 cm^{-1} at various DES composition. Bands near 3,323–3,325 cm^{-1} was fit with the O–H stretching vibration, related to hydroxyl groups and interaction through hydrogen bonding. On the contrary, band near 2,361 cm^{-1} should not be linked directly with C–H stretching vibration since this area in general influenced by atmospheric CO_2 absorption and overlapping vibrational contributions. Therefore, band at 2,361 cm^{-1} was not considered as direct evidence of C–H bond existence in synthesized DES.

The existence of ChCl was also reflected by FTIR spectrum. The absorption band at near 1,479 cm^{-1} can be connected with the vibration which involving methyl groups in choline cation. Characteristic vibration due to ChCl has been reported in the range 1,400–1,500 cm^{-1}, while additional band on the lower wave number can be associated with vibration which involving structure of choline cation [18]. The presence of bands associated with ChCl, together with absorption band related to oxalic acid, showed that the both components contributed on FTIR spectrum from synthetised DES.

The absorption observed near 951 cm^{-1} is also relevant to the choline component. Vibrational bands in this region have been associated with asymmetric stretching involving the choline cation, including C–N related vibrations [18]. The persistence of characteristic ChCl related bands after synthesis indicates that the choline chloride component remained detectable in the resulting DES. However, FTIR alone cannot demonstrate that the catalytic activity of ChCl has been retained or establish a specific molecular structure. Rather, the observed spectral features provide supporting evidence for the coexistence and interaction of the DES components.

The differences among the 1:1, 1:2, and 1:3 compositions are therefore primarily reflected in changes in the O–H region and other characteristic absorption bands. These changes are consistent with modifications in

the hydrogen-bonding environment as the relative amount of oxalic acid is increased. Similar hydrogen-bond-related spectral changes have been reported for ChCl based DESs containing carboxylic acids [17]. Because hydrogen bonding is an important feature in the formation of many ChCl based DES systems, the observed FTIR changes provide supporting evidence for molecular interactions between ChCl and extracted oxalic acid.

The potential relevance of ChCl–based DESs to free fatty acid (FFA) removal from used cooking oil has also been reported. Dzakiroh et al. demonstrated that a ChCl–based DES could reduce FFA in used cooking oil, with the extent of reduction influenced by the DES to oil ratio and operating conditions [19]. However, the present FTIR results do not quantify FFA removal and therefore cannot be used to conclude that increasing the proportion of oxalic acid directly produces greater FFA reduction. Such a relationship should be established through independent esterification or FFA removal experiments.

Overall, the FTIR spectra demonstrate characteristic absorption features attributable to both ChCl and oxalic acid and show changes in the vibrational environment with variation in the ChCl:oxalic acid molar ratio. In particular, the changes in the O–H absorption region are consistent with altered hydrogen bonding interactions between the hydrogen bond acceptor and hydrogen bond donor components. These findings support the formation of an interacting ChCl–oxalic acid DES system under the investigated preparation conditions.

3.5. Effect of DES molar ratio on pH

The pH of the produced DESs was assessed to determine the effects of the choline chloride (ChCl):oxalic acid (OA) molar ratio and the preparation temperature on the acidity of the resulting mixtures. All compositions remained in the liquid state under the investigated conditions. The corresponding physical state and pH values are presented in Table 3.

Table 3. Effect of molar ratio and temperature on the characteristics of the synthesized DESs.

ChCl:OA molar ratio (mol)(mol)	Temperature (°C)	Physical state	pH
1:1	70	liquid	2.05
	80	liquid	2.05
	90	liquid	1.92
1:2	70	liquid	1.76
	80	liquid	1.87
	90	liquid	1.92
1:3	70	liquid	1.38
	80	liquid	1.71
	90	liquid	1.22

OA: Oxalic acid

The synthesized DESs exhibited pH values ranging from 1.22 to 2.05, confirming their acidic character under the investigated conditions. The effect of composition was evident from the generally lower pH observed as the relative proportion of oxalic acid increased. At 70 °C, increasing the ChCl:OA molar ratio from 1:1 to 1:3 decreased the pH from 2.05 to 1.38. A similar trend was observed at 90 °C, where the pH decreased from 1.92 to 1.22. This behaviour indicates that increasing the relative contribution of oxalic acid increased the apparent acidity of the DES. Earlier research indicated that the acidity of DES is greatly affected by the chemical properties and the relative amount of the hydrogen bond donor (HBD), with organic acid based systems typically displaying acidic traits [20], [21].

The lowest pH recorded in this study was 1.22 for the ChCl:OA ratio of 1:3 at 90 °C, whereas the highest pH of 2.05 was obtained for the 1:1 composition at 70 and 80 °C. The measured values are within the acidic range reported for several organic acid based DESs. Škulcová et al. [20] reported pH values of approximately 1.2–2.74 for DESs containing organic acids and observed a pronounced temperature dependence in choline chloride–oxalic acid systems. However, direct comparison among DES studies should be made cautiously because measured pH can depend on composition, water content, temperature, concentration, and measurement procedure [20], [21].

In contrast to the consistent effect of molar ratio, the influence of temperature was not uniform across the investigated compositions. For the 1:1 system, the pH remained at 2.05 between 70 and 80 °C before decreasing to 1.92 at 90 °C. The 1:2 system showed an increase in pH from 1.76 at 70 °C to 1.87 and 1.92 at 80 and 90 °C, respectively. Meanwhile, the 1:3 system exhibited a non-monotonic response, with pH values of 1.38, 1.71, and 1.22 at 70, 80, and 90 °C, respectively. Thus, the present data do not support a general linear relationship between increasing temperature and decreasing pH for all ChCl:OA compositions.

The temperature dependent behaviour observed for some compositions is nevertheless consistent with the reported sensitivity of DES acidity to temperature. Škulcová et al. [20] demonstrated that the pH of DESs can vary with temperature and reported particularly pronounced temperature dependence for choline chloride–oxalic acid systems. Jančíková et al. [21] further noted that the apparent acidity of DES like systems is influenced by component identity, composition, and water content. Therefore, the variations observed in the present study are more appropriately interpreted as composition dependent responses rather than as evidence of a universal temperature effect.

The non–monotonic behaviour of the 1:3 composition, particularly the increase in pH from 1.38 at 70 °C to 1.71 at 80 °C followed by a decrease to 1.22 at 90 °C, may also reflect the characteristics of the extracted oxalic acid used in the DES preparation. In this study, oxalic acid was obtained from *Averrhoa bilimbi* L. fruit rather than from a reagent grade source. Consequently, residual components associated with the extraction and precipitation procedures may have contributed to variations in the measured pH. However, the available data do not permit the contribution of individual residual components to be quantified. The observed variation should therefore be regarded as an experimental characteristic of the extracted acid-based DES rather than as evidence of a specific impurity related mechanism.

The acidic character of the synthesized ChCl–OA systems is associated with the use of oxalic acid as the hydrogen bond donor (HBD) and ChCl as the hydrogen bond acceptor (HBA). The chemical nature and relative proportion of the HBD are important factors governing the acidity of DES systems [20], [21]. Accordingly, the lower pH observed at higher oxalic acid proportions is consistent with the greater relative contribution of the acidic HBD in the 1:2 and 1:3 compositions. The measured pH should not, however, be interpreted as indicating that oxalic acid is a strong mineral acid. Rather, the values demonstrate the strongly acidic character of the resulting ChCl–oxalic acid DESs under the conditions investigated.

The acidic character of these systems is relevant to their potential application in biodiesel production, particularly in esterification of free fatty acids (FFAs) in used cooking oil. Previous experimental work has demonstrated the application of a ChCl–based DES for FFA reduction in used cooking oil. Dzakiroh et al. [19] investigated a ChCl–ethylene glycol DES and reported that FFA reduction was affected by the oil to DES ratio, stirring speed, and treatment time, with the FFA content decreasing to 0.55% under their reported optimum conditions. Despite the differences in the DES formulation compared to the current research, these results offer experimental support for the possible use of ChCl based DESs in FFA remediation.

The pH results obtained here therefore indicate that the synthesized ChCl–OA systems provide an acidic medium suitable for further investigation as an esterification catalyst. However, pH alone does not establish catalytic activity or quantify FFA conversion. Demonstrating catalytic performance would require independent esterification experiments involving measurements such as initial and final FFA concentration, acid value, FFA conversion, and biodiesel yield. Accordingly, the present results should be interpreted as evidence of the acidic character and potential catalytic applicability of the synthesized DES, rather than as direct evidence of FFA removal or biodiesel production.

Overall, all ChCl–OA compositions remained liquid under the investigated conditions and exhibited pH values between 1.22 and 2.05. Increasing the relative proportion of oxalic acid generally increased the apparent acidity of the DES, with the lowest pH of 1.22 obtained at a ChCl:OA molar ratio of 1:3 and 90 °C. The effect of temperature, however, varied among the compositions and was not uniformly monotonic. The observed pH behavior is consistent with the reported influence of HBD identity, DES composition, temperature, and water content on DES acidity [20], [21]. Together with the FTIR results presented in Section 3.4, these findings support the formation of an acidic ChCl–oxalic acid system and provide a basis for further evaluation of its performance as a potential acid catalytic medium for biodiesel related esterification.

4. Conclusion

Oxalic acid was successfully obtained from *Averrhoa bilimbi* L. fruit and used as the hydrogen bond donor component for preparing choline chloride (ChCl)–oxalic acid deep eutectic solvents (DESs). Among the investigated extraction temperatures, 90 °C produced the highest measured oxalic acid content of 33.80%. FTIR analysis supported the presence of oxalic acid related O–H, C=O, and C–O functional groups, while SEM revealed a relatively ordered solid morphology. EDX showed carbon and oxygen as the predominant detected elements, at 15.22% and 50.69%, respectively, together with sulphur and calcium indicating the presence of additional inorganic components.

The synthesized ChCl–oxalic acid DESs at molar ratios of 1:1, 1:2, and 1:3 remained liquid under the investigated conditions and exhibited pH values of 1.22–2.05. The lowest pH (1.22) was obtained at a 1:3 molar ratio and 90 °C. FTIR results further supported interactions between ChCl and oxalic acid, particularly in the O–H absorption region. Overall, the findings demonstrate the feasibility of using *A. bilimbi* derived

oxalic acid to develop ChCl–oxalic acid DESs with potential for further investigation as acid catalytic media in biodiesel related esterification. Catalytic performance, FFA conversion, and biodiesel yield remain to be experimentally verified.

Conflict of interest

The authors declare no conflict of interest.

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