Catalytic Esterification of Levulinic Acid to Alkyl Levulinates: Liquid Product Analysis and Separation Study via Extraction

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The present work unlocks the full potential of sulfonated lignin-based carbon (SLBC) catalyst in the esterification of levulinic acid (LA) with different alcohols such as methanol, ethanol, and n-butanol to alkyl levulinates (ALs), followed by liquid product analysis and product separation. Lignin was calcined to produce carbon material, modified into the SCLB catalyst by hydrothermal sulfonation, and finally characterized. The reaction was performed over SLBC catalyst in selected reaction conditions of 6 molar ratio of alcohol-to-LA, 0.3 g catalyst, and 5 h at respective alcohol reflux temperatures. The liquid products were examined by acid-base titration and then quantified using gas chromatography coupled with mass spectrometry (GC-MS) for comparison of data. The separation of the synthesized ALs and simulated ALs-LA mixture was conducted via liquid-liquid extraction, utilizing 9:1 hexane-water (v/v) mixture as the extraction solvent. The SLBC catalyst successfully yielded ALs (methyl, ethyl, and butyl levulinates) of 73.5–83.3 mol%. The hexane-water mixture was able to extract ALs from the liquid mixtures and the percentage extraction increased for longer alkyl chains of ALs. The acid-base titration demonstrated a minimal percentage difference with GC-MS data for LA conversion and could be suggested as a reliable liquid product analysis, especially for LA esterification reaction.

1. Introduction

ALs are top-notch chemicals that are potentially employed for various applications, including as fuel additives for biodiesel-diesel blends. These esters, methyl (ML), ethyl (EL), and butyl levulinate (BL) act as oxygenated additives which can enhance the physiochemical properties of the fuel blend and emission profiles (Samion et al., 2023). There exist different chemical synthesis pathways to produce ALs, yet, the acidic catalytic esterification of LA is commonly practiced due to moderate reaction conditions with high product selectivity (Badia et al., 2021). The reaction between alcohols with LA to ALs can be facilitated by the solid acid catalyst. In previous work, the SLBC catalyst was developed and catalyzed the LA esterification to EL, reaching 84.3 mol% of EL yield at the optimum reaction conditions (Hassan et al., 2023). The use of SLBC catalyst in the esterification of LA to ML and BL is considered an opportunity to unlock the full potential of SLBC catalyst through the ALs synthesis. For liquid product analysis, acid-base titration is an attractive alternative to determine the amount of LA in the mixture. This analysis has been used to determine the total amount of various types of weak organic acids such as acetic acid (Wang et al., 2010), polycarboxylic acid (Yang and Wang, 2000), oleic acid (Zhou et al., 2016), and citric acid (Ramírez et al., 2017). The acid-base titration could be used to quantify the presence of LA, and fewer reports about the competency of the method, especially for LA esterification.

The synthesized liquid product is required to be purified before being directly employed for various applications, especially as a fuel blend additive. The presence of other components such as unreacted LA causes low solubility and poor atomization of the fuel blend in the engine which impacts poor diesel engine performance and emissions profiles (Appaturi et al., 2022). The extraction of ALs from the synthesized liquid product emerges as an important step to separate the desired product from the product mixture. The liquid-phase properties of ALs and their mixture are essential to help the researcher suggest an economical separation method. According

to Tetrisyanda et al. (2021), EL and BL exhibit low solubility in water and are established as heterogeneous phases. LA is a polar molecule that tends to dissolve in polar solvents like water because of the existence of ketone and COOH groups. The alkyl chain of ALs provides a non-polar part and is generally soluble in non-polar solvents such as hexane (Guan et al., 2018). As reported by Przypis et al. (2020), the pentyl levulinate separation was achievable via extraction up to a certain efficiency with hexane, depending on its natural pure liquid properties. The large differences in boiling points between hexane and ALs make further separation via evaporation easier, and reusability of hexane is feasible.

The objective of this work is to prepare the SLBC catalyst and characterized. The esterification of LA is carried out over the SLBC catalyst with methanol, ethanol, and n-butanol to synthesize ML, EL, and BL in selected reaction conditions at their respective alcohol boiling points. These primary alcohols are readily available, widely employed in esterification reactions and also to meet the synthesis of specific ALs for targeted applications. The effects of different alcohols on the reaction performance were assessed according to ALs yield and LA conversion. The liquid products were examined by acid-base titration to determine the LA components and further quantified using GC-MS for data comparability by percentage difference. The separation study was performed over two sets of samples such as the synthesized ALs from the reactions and simulated 80 mol% ALs via extraction using a 9:1 hexane-to-water (v/v) mixture. The applicability of the separation method of synthesized products are validated through the comparison results obtained from the simulated samples.

2. Methodology

2.1 Materials and chemicals

Lignin, sulfuric acid, (H_2SO_4, 97 %), and standard of ethyl levulinate, ($C_7H_{12}O_3$, 99 %) were bought from Sigma-Aldrich, China. Levulinic acid, ($C_5H_8O_5$, 98 %) was obtained from Merck KGaA, Germany. Methanol (CH_4O), ethanol (C_2H_6O), n-butanol ($C_4H_{10}O$), and sodium hydroxide pallet (NaOH) were supplied from Vchem and Systerm Chemicals, Malaysia. Hexane (C_6H_{14}), sodium chloride (NaCl), and phenolphthalein ($C_{20}H_{14}O_4$, 1 %) were bought from Fisher Chemical and Bendosen, Malaysia.

2.2 Catalyst preparation and characterization

The method of SLBC catalyst preparation from lignin follows the process explained elsewhere (Hassan et al., 2023). Lignin-based carbon was produced from the calcination of lignin at 400 °C for 1 h and modified with concentrated H_2SO_4 at 180 °C for 6 h via hydrothermal sulfonation. The catalyst was characterized and directly employed in the LA esterification to ALs.

The chemical bonding of LC and SLBC catalyst was evaluated by Fourier transform infrared (FTIR) spectrometer model of Spectrum One Perkin-Elmer at 500–4,000 cm^{-1} of infrared (IR) wavenumber. The physical surface morphology of lignin, LC, and SLBC catalyst were carried out by scanning electron microscopy (SEM) model of JEOL JSMIT300 LV at 2,000 X and 3,000 X magnifications.

2.3 Catalytic reaction of LA esterification to ALs

The LA esterification was carried out in a batch reaction set-up assisted with a magnetic stirrer (200 rpm) as illustrated in Figure 1a. The selected reaction conditions referred from Hassan et al. (2023); 6 molar ratio of alcohol-to-LA, 0.3 g catalyst SLBC catalyst, and 5 h. The reaction temperatures were according to reflux temperatures of methanol, ethanol, and n-butanol for achieving the maximum LA conversion. After the reaction was completed, the mixture was cooled down to ambient temperature, and then the catalyst was removed.

2.4 Separation study via Extraction

The separation study of the synthesized products from the catalytic LA esterification to ALs and the simulated ALs liquid mixtures of 80 mol% were performed through liquid extraction method. The selection of mol ratio (mol%) for the simulated liquid mixture was based on the average value of ALs yield obtained in this work. The sample was mixed at 100 rpm stirring with extraction solvent of 9:1 hexane-to-water (v/v) mixture for 10 min, poured into the 250 mL separatory funnel, and let the liquid separated for 30 min at room temperature until two-layer liquid formed (Figure 1b). The final volume of hexane and water were recorded for subsequent liquid product analysis.

2.5 Liquid product analysis

Two analytical methods were carried out, namely acid-base titration and GC-MS. The acid-base titration was conducted to examine the mass of LA in the sample. The mol of titrated NaOH is equivalent to the mol of LA. The mass and conversion of LA were calculated using Eq(1) and Eq(2), V_f is the final volume of product (mL). The GC-MS of Varian 450 equipped with 5MS column was used to quantify standard chemicals representing ALs and LA, followed by liquid product samples.
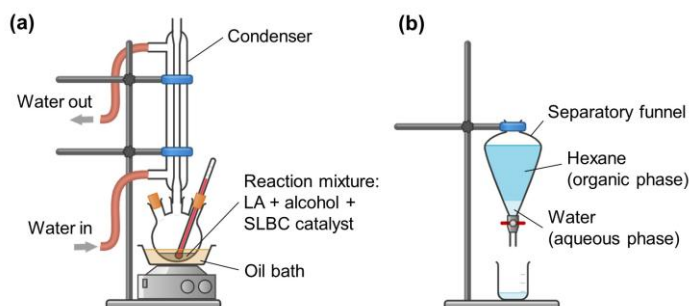
Figure 1: Set up of (a) LA esterification to ALs and (b) separation via extraction

The oven conditions of GC-MS with 1.0 mL/min of helium gas flowrate from 40–120 °C (3 °C/min) and elevated to 120–280 °C (50 °C/min). The calibration curves (i.e., ML, EL, BL, and LA) were established related to GC-MS peak area to the known standard concentrations (mg/L). These curves act as references to determine the concentrations of ALs and LA in the samples through graph interpolation. The LA conversion and ALs yield were determined through Eq(2) and Eq(3). The competency of acid-base titration was validated by comparing the GC-MS data through the percentage difference of LA conversion as defined in Eq(4).

$$\text{Mass of LA (g)} = \left[\frac{\text{Moles of NaOH x Molar mass of LA}}{\text{Sample volume}} \right] \text{x } V_f \tag{1}$$

$$\text{LA conversion (\%)} = \frac{\text{Initial mass of LA - Final mass of LA}}{\text{Initial mass of LA}} \text{ x 100 \%} \tag{2}$$

$$\text{ALs yield (mol\%)} = \frac{\text{Moles of EL}}{\text{Moles of LA}} \text{ x 100 \%} \tag{3}$$

$$\text{Percentage extraction (\%)} = \left| \frac{\text{LA conversion by GCMS - LA conversion by titration}}{\text{LA conversion by GCMS}} \right| \text{x 100 \%} \tag{4}$$

3. Results and discussion

3.1 Catalytic characterization

Figure 2a-b displays the FTIR spectra with the corresponding molecular vibrations of LC and SLBC catalyst. For LC, the vibrational band around 1,050 cm^{-1} relates to the stretching of S–O due to the existence of sulfur-based components in the sample. The band detected at 1,600 cm^{-1} is linked to the stretching of C=C aromatic ring and the broad band around the region of 3,400 cm^{-1} can be attributed to –OH. The S–O and S=O band spectra were observed at the IR range of 1,250–1,000 cm^{-1} to determine the presence of –SO$_3$H on the SLCB catalyst, resulting from the sulfonation of LC. The S=O stretching was spotted at 1,200 cm^{-1} and S–O stretching at 1,050 cm^{-1}, as mentioned by Zainol et al. (2021). The appearance of the S=O peak of SLCB catalyst indicates the –SO$_3$H was successfully functionalized on the LC structure. The C=C (aromatic) and C=O (COOH) stretching bands were observed at 1,600 cm^{-1} and 1,700 cm^{-1} (Kamyab et al., 2018). The observable C=O peak is due to the oxidation of the LC surface to form –COOH. The higher intensity of the broad peak of the SLCB catalyst around 3,400 cm^{-1} pertains to the –OH, functionalized –SO$_3$H, and water absorption.

The effects of catalyst preparation are shown by SEM images. In Figure 2c, lignin is naturally fibrous with a non-porous surface that requires transformation via calcination before conducting SO$_3$H functionalization for catalyst production. The calcination results in the development of porous and rough surface structures through the degradation of volatile and light organic components (Figure 2d). The improved size of the porous structures (Figure 1e) due to the use of H$_2$SO$_4$ under high-pressure conditions promotes further surface modification by creating new pores or enlarging the existing pores with different sizes and volumes including meso-micropores. The results of this work are supported by the additional catalyst characterizations (e.g., 1.32 mmol/g catalyst acidity, 193.0 m^2/g surface area, and thermal stability) reported by Hassan et al. (2023). These catalyst properties are crucial to serve sufficient acid sites on the surface which facilitates the LA esterification mechanism. The SLBC catalyst is suitable to catalyze at different reaction temperatures of 64–117 °C (reflux temperature of alcohols) as thermal stability was suggested up to 200 °C.
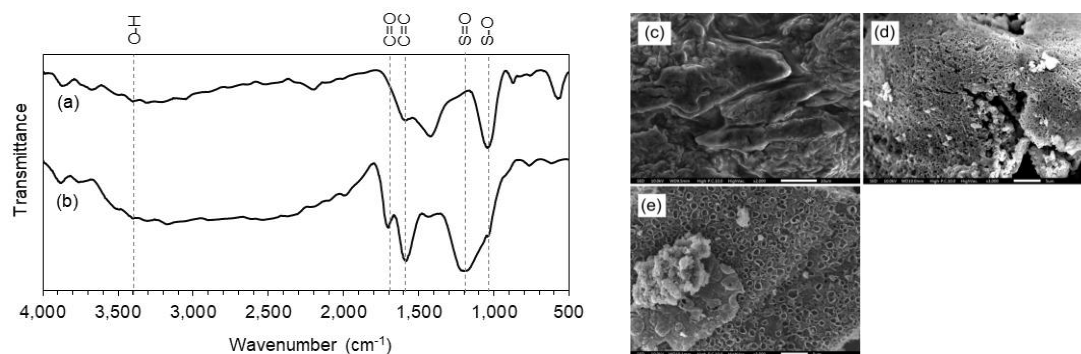
Figure 2: FTIR spectra of (a) LC, (b) SLBC catalyst, and SEM images of (c) lignin, (d) LC, and (e) SLBC catalyst

3.2 Reaction performance of LA esterification with different alcohols

Figure 3a–d show the retention time of the GC-MS peak area of standard chemicals (e.g., methanol, ethanol, n-butanol, and LA). The retention time of methanol (15.5 min), ethanol (18.5 min), n-butanol (27.5 min), and LA (19.5 min) served as a key parameter to identify the targeted compounds in the synthesized liquid product with accurate identification. In Figure 3e–g, the observable peaks at the same retention times as the standards (ML, EL, BL, and LA) in the samples verified the formation of the ALs along with unreacted LA.
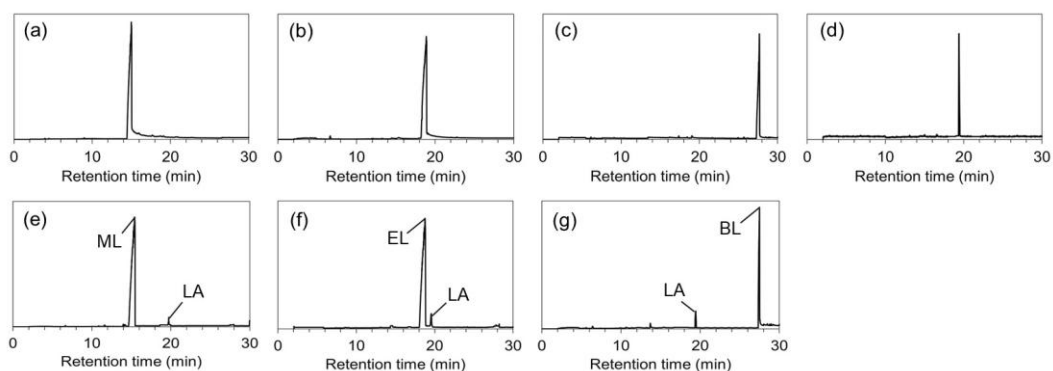

Figure 3: Retention time (min) of GC-MS peak area for (a) ML, (b) EL, (c) BL, and (d) LA standards. The detection of (e) ML, (f) EL, and (g) BL of synthesized liquid products at respective retention times

The reaction performance of LA esterification to ALs over SLBC catalyst is according to the ALs yield and LA conversion shown in Figure 4a. From the known concentrations of corresponding compounds, the ALs yield was calculated with the values of 77.4, 83.3, and 73.5 mol% for ML, EL, and BL, which are equivalent to 4.28, 5.18, and 5.43 g for the same ALs. The LA conversions display the values of 80.2–85.7 %. The reaction with short-chain alcohols (methanol and ethanol) generally produced higher ALs (ML and EL) yields than the reaction with n-butanol which provided slightly lower BL yield.

The short-chain alcohols are more reactive in esterification reactions due to less steric hindrance around the OH. These molecules allow for a closer approach to the carbonyl of the LA which induces the nucleophilic attack and reaction rate (Jurkiewicz Cortada, 2023). The reaction mechanism proposed by Kim et al. (2023), the protons of the acid catalyst are moved to the carboxylic (COOH) of LA to produce an intermediate, then the attack of nucleophilic oxygen of alkyl alcohol to the resulted intermediate to yield ALs, elimination of water, and catalyst regeneration (Figure 4b). The longer carbon chain of n-butanol that relates to the size of the molecule otherwise causes slow access to LA due to higher steric hindrance. This impacts lower reaction rate of n-butanol which is agreed by Boffito et al. (2015). The high reaction temperature of using n-butanol (117 °C) not only pushes the reaction toward equilibrium according to Le-Chatelier's principle, but the condition also leads to increased side reactions and product degradation (Khan et al., 2021).

The use of ethanol for LA esterification affords a higher yield (mol%) compared to methanol. Higher ML can be achieved as the reaction is conducted at suitable optimum conditions. As the overall comparison, the LA conversion by acid-base titration demonstrates comparable results with calculated data from GC-MS analysis with a small percentage difference. The results acquired by acid-base titration are 84.7–89.2 % with the highest LA conversion with ethanol to EL which similar pattern demonstrated by GC-MS. The agreement between these sets of data provides a minimal percentage difference of 4–7.3 % which is considered satisfactory.
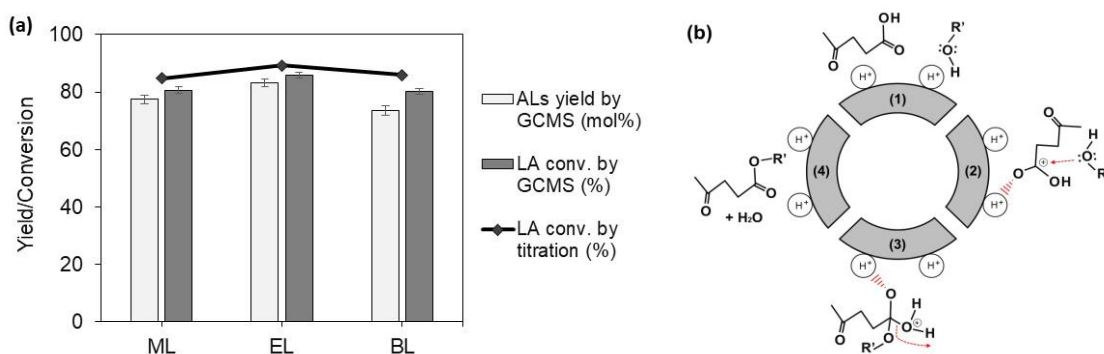
Figure 4: (a) ALs yield and LA conversion from the esterification of LA with methanol, ethanol, and n-butanol to ALs over SLBC catalyst quantified by acid-base titration and GC-MS analysis, (b) Illustration of reaction mechanism of LA esterification to ALs on catalyst surface

3.3 Separation of ALs via solvent extraction

Table 1 displays the percentage of extracted ALs as quantified by GC-MS. For both sets of samples of synthesized liquid products from experimental and simulated product mixtures, the percentage of ML, EL, and BL are observed generally higher (69.0–85.0 %) and (70.8–91.3 %) in the hexane phase. This finding shows the effectiveness of the hexane in separating the ALs from the mixture. The ALs are more soluble in the low-polarity organic solvent. The existence of relatively non-polar alkyl chains of ALs helps to mix better with the hexane (Guan et al., 2018). Specifically to each ALs, the ability of hexane to extract EL and BL from the synthesized liquid products is higher than ML. The trends are also consistent for the simulated mixtures, suggesting the extraction using the hexane is more compatible with the longer alkyl chain of ALs (EL and BL). The length of the non-polar alkyl chains has a good affinity with the solubility of organic compounds in hexane (Hosseinabadi et al., 2014). BL and EL exhibit more hydrophobic character owing to their molecules containing longer alkyl chains than ML which enhance the solubility and extraction into the hexane phase.

The LA component is undetected by GC-MS in the hexane phase. This implies that LA is mainly distributed to the water (100 % of LA in aqueous phase) because of higher polarity than hexane (organic phase). LA is an organic acid that has good solubility in water. The molecule contains highly polar functional groups such as –COOH and keto (C=O). The carboxylic acid group of LA creates a hydrogen bond with water molecules, making LA highly soluble in water (Yang et al., 2022). Based on the results, the application of 9:1 hexane-water (v/v) mixture has shown as a promising method to extract ALs, especially EL and BL from the liquid mixtures.

Table 1: The extraction of synthesized and simulated mixtures using 9:1 hexane-water quantified by GC-MS

	ML	EL	BL
Synthesized liquid product from catalytic LA esterification reaction			
ALs in hexane (%)	69.0 ± 1.1	80.3 ± 0.8	85.0 ± 0.7
ALs in water (%)	29.2 ± 0.9	18.3 ± 1.3	13.3 ± 1.2
LA in hexane	LA component is undetected in hexane		
Simulated liquid product of 80 mol% ALs			
ALs in hexane (%)	70.8 ± 1.4	85.9 ± 1.1	91.3 ± 0.7
ALs in water (%)	27.4 ± 0.7	12.1 ± 1.6	6.9 ± 1.3
LA in hexane	LA component is undetected in hexane		

4. Conclusions

The characterizations of SLBC are consistent with previous report and the catalyst showed the potential in synthesizing ALs of 73.5–83.3 mol% (ML, EL, and BL) via LA esterification. The difference in ALs yield and LA conversion in similar reaction conditions at respective reflux temperatures showed the catalytic activity is significantly influenced by the nature of alcohols. The acid-base titration is a competent method and can be put forward as a liquid product analysis, while the GC-MS remains the top-notch method for more accurate data analysis. The ALs can be extracted by hexane and the extraction percentage increased with the alkyl chain of ALs. The use of the hexane-water mixture for extraction could be a valuable technique in the separation of ALs and the extraction of ML could be suggested using other types of extraction solvent, yet more research needs to be done at the optimum condition of the extraction to maximize the extraction efficiency.

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