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OPTIMISATION OF REACTION PARAMETERS FOR THE SYNTHESIS OF SOLKETAL LEVULINATE AS POTENTIAL BIODIESEL ADDITIVE

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ABSTRACT

Glycerol is a major by-product of biodiesel production and finding new uses for glycerol is crucial to ensure the sustainability and continuance of the biodiesel industry. Thus, the transformation of glycerol into ketal compounds that have potential as additive to improve biodiesel properties, could be an option to provide an outlet for increasing glycerol stock. This study aims to optimise the transesterification reaction to afford solketal levulinate ester (SoLE) in highest yield by reacting solketal with methyl levulinate (ML). The reaction parameters varied are type of base catalyst, catalyst concentration, reaction temperature, reaction time and reactants molar ratio. Under optimised reaction conditions: 1.5% sodium carbonate (Na_2CO_3) catalyst loading, reaction temperature of 140°C, reaction time of 4 hr and molar ratio of 3:1 (solketal:ML), as high as 74.5% yield and 95.0% purity of SoLE was obtained.

Keywords: glycerol, levulinate, lignocellulosic biomass, palm oil, solketal ester.

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INTRODUCTION

Glycerol (propane-1,2,3-triol) is the simplest alcohol with three hydroxyl (OH) group. It is also known as glycerin. Glycerol demonstrates versatile uses in numerous fields such as in food improver, pharmaceutical product, polymer industries, fuel and diesel additive (Anitha *et al.*, 2016). Glycerol (Gly) is made as a by-product commonly from biodiesel production where approximately 10% by volume for every tonne of biodiesel (Karinen and Krause, 2006).

The global growth of biodiesel production over the last decade had caused surplus of glycerol in the marketplace which resulted in decline of glycerol price, hence threaten the economic viability of biodiesel plants. Other than that, glycerol also comes from oleochemical plant. There are currently 19 oleochemical plants operating in Malaysia, which exported approximately 3.28 million tonnes of oleochemicals in 2019 (Parveez *et al.*, 2020). Therefore, new uses of glycerol are needed if the present and future glycerol stock is to be managed (Lapuerta *et al.*, 2015). Glycerol ketals and acetals are among interesting compounds to be explored, as they have been demonstrated as potential additive in the formulation of gasoline, diesel and biodiesel fuels to improve fuel properties (Nanda *et al.*, 2016). Solketal improves cold flow, ignition properties and cetane number of fuels (Kumar *et al.*, 2021), while the use of glycerol acetals in diesel fuels (biodiesel) reduces the viscosity, pour point and particles emission (Torres *et al.*, 2012). Solketal is derived from condensation of glycerol and acetone in the presence of acid catalysts (Deutsch *et al.*, 2007; Li *et al.*, 2012; Suriyaprapadilok and Kitiyanan, 2011). Solketal can be used as a fuel additive to reduce the particulate emission and to improve the cold flow properties of liquid

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transportation fuels (Pariente *et al.*, 2009). It helps to reduce the gum formation, improves the oxidation stability, and enhances the octane number when added to gasoline (Mota *et al.*, 2010). Maksimov *et al.* (2011) reported its use as a versatile solvent and a plasticiser in the polymer industry and a solubilising and suspending agent in pharmaceutical preparations.

The free –OH in solketal can also be further reacted to give solketal fatty esters (SFE) via base-catalysed transesterification with fatty acid methyl esters (FAMEs) (Trifoi *et al.*, 2016). Solketal ester and their cyclic group family correspondingly have been reported as a useful fuel additive for enhancing octane number of gasoline (Lozano *et al.*, 2016). Other than that, biodiesels formulations based on mixtures of FAME and fatty acid glycerol formal esters (FAGE) have been described as very efficient for diesel engines. Biodiesel blends up to 20% volume fraction of FAGE, exhibited an excellent suitability as liquid fuel (*e.g.* viscosity, cetane number, adiabatic flame temperature, *etc.*), as it was demonstrated by testing in an automotive engine (Lozano *et al.*, 2016; Nanda *et al.*, 2016; Perosa *et al.*, 2016).

The oil palm industry generates a large quantity of oil palm biomass on yearly basis and it was estimated that in year 2016, the Malaysian palm oil industry generated 80 million tonnes of oil palm biomass (Din *et al.*, 2019). Levulinic acid (LA) is a value-added chemical that can be obtained from lignocellulosic biomass. LA and its derivatives have been used as building blocks for the preparation of new compounds such as levulinate esters, α-valerolactone, acrylic acid and 1,4-pentanediol (Bozell *et al.*, 2000; Girisuta and Heeres, 2017; Rackemann and Doherty, 2011).

The most highlighted LA derivatives are their esters (Adeleye *et al.*, 2019; Castro and Fernandes, 2021; Din *et al.*, 2019; Tiong *et al.*, 2019). The properties of levulinate esters such as methyl and ethyl levulinate (EL) have been investigated for application as gasoline and diesel additives (Liang *et al.*, 2020; Unlu *et al.*, 2018; Vázquez-Castillo *et al.*, 2019; Xu *et al.*, 2020). EL is considered as a bio-based cold flow improver for biodiesel, as it has shown to reduce cloud point of biodiesel and the resultant mixture of biodiesel and EL showed better cold flow properties. It also has additional excellent properties such as clean combustion and low toxicity for fuel additive (Joshi *et al.*, 2011).

High-efficiency process parameters is an inevitable topic of discussion in synthesis process for sustainable synthetic chemistry (Castro and Fernandes, 2021). The synthesis of levulinate ester using LA and short chain alcohol is reported to be conducted mostly via esterification reaction employing different mineral acid catalysts, such as sulphuric acid (H_2SO_4), hydrochloric acid (HCl) and phosphoric acid (H_3PO_4) (Bart *et al.*, 1994; Liu *et al.*, 2006; Pileidis *et al.*, 2014), and various solid acids, such as sulphonic acid functionalised materials (Oliveira and Teixeira da Silva, 2014; Song *et al.*, 2015). However, we found that the esterification of solketal with LA in the presence of acid catalyst gave unsatisfactory yield of solketal levulinate ester (SoLE). This is due to possibility of hydrolysis of solketal under acidic condition forming undesirable side product. This is in agreement with the work reported by Pouilloux *et al.* (2000), where they reported utilisation of acid catalyst favours side reactions such as degradation of the fatty acid (oxidation, dimerisation) or from the glycerol (polymerisation, dehydration into acrolein, oxidation). Hence, we adopt based-catalysed transesterification of solketal with methyl levulinate (ML), where base catalyst and mL were utilised instead of acid catalyst and LA. Thus, this article reported the further optimisation of reaction parameters such as type of catalyst, effect of reaction duration, temperature and molar ratio of solketal/ML to attain maximum yield of solketal levulinate. To the best of authors' knowledge, no literature reported on the optimisation of transesterification reaction of solketal and levulinic ester for the synthesis of solketal levulinate, which potentially can be used as fuel additive in biodiesel.

MATERIALS AND METHODS

Materials

Refined solketal (99.8% purity) and mL (98.0%) were obtained from Sigma Aldrich, USA. Sodium carbonate (Na_2CO_3) and potassium carbonate (K_2CO_3) were obtained from Systerm, Malaysia. Sodium hydroxide (NaOH) was obtained from R&M Chemicals, Malaysia, and potassium hydroxide (KOH) was obtained from Chemiz, Malaysia. Magnesium oxide (MgO) and sodium methoxide (30% in MeOH, NaOMe) both were obtained from Sigma Aldrich, USA. All the reagents were used without further purification.

Methods

General procedure for the synthesis of solketal levulinate (SoLE). Reactions were carried out in a 50 mL one-neck round bottom flask equipped with a magnetic stirrer. A condenser was attached to the round bottom flask and connected to a vacuum pump to facilitate removal of methanol from the reaction system. Desired amount of solketal, mL and Na_2CO_3 (catalyst) were placed in the flask and heated to the desired temperature. An oil bath equipped with a thermometer was used to monitor the reaction temperature. *Figure 1* is the diagram of the reaction setup. The amount of reagents was calculated according to the desired mole ratio. The reaction progress was monitored via thin-layer chromatography analysis. After the reaction was completed, the crude mixture was washed with distilled water to remove the basic catalyst, followed by addition of diethyl ether to extract SoLE. The organic layer was concentrated under vacuum using roto-evaporator. Thereafter, the product was evaluated using gas chromatography (GC), proton (^{1}H) and carbon (^{13}C) nuclear magnetic resonance (NMR) spectroscopy and Fourier transform infrared (FTIR) spectroscopy.

Analysis and Characterisation of SoLE

FTIR. A convenient analytical method for determining the functional groups of the SoLE was conducted using Perkin Elmer Spectrum 100 FT-IR Spectrometer equipment with attenuated total reflectance (ATR). Samples were scanned on ATR top plate between 4000 to 650 cm^{-1} wave number with 8 scans per sample at 4 cm^{-1} resolution.

GC analysis. Quantitative analysis of the reaction mixture was conducted using GC. The GC (Agilent System 6890N Network GC System) was equipped with a ZB-5HT INFERNO (30 m x 250 µm x 0.2 µm) capillary column and flame ionisation detector. The following temperature programming was used: oven temperature, 80°C; initial temperature, 80°C; heating rate at 10°C min^{-1}; final temperature, 315°C; injector temperature, 300°C; detector temperature, 325°C; carrier gas, helium at 40.0 mL min^{-1}. The composition of products was determined according to the percent area under the respective peak in the GC chromatogram.

^{1}H and ^{13}C NMR analysis. ^{1}H and ^{13}C NMR spectroscopy were recorded on JOEL JNM-ECZ600R at 600 MHz and 150 MHz, respectively at 298 K with approximately 10% w/v solutions in deuterated NMR solvents. Chemical shifts were quoted in ppm relative to internal standard tetramethylsilane (TMS) and reference to the residual solvent. All coupling constants were quoted in hertz (Hz).

RESULTS AND DISCUSSION

Effect of Reaction Parameters on the Yield of SoLE

Influence of different types of catalysts. SFE can be prepared by the catalytic esterification of fatty acids with solketal (Sankaranarayanan *et al.*, 2017). Acidic homogeneous catalysts, such as H_2SO_4, HCl, hydrogen fluoride (HF) and *p*-toluenesulphonic acid, can be applied for this process. Although the homogeneously acid catalysed processes give high conversion of solketal, they also generates a large amount of waste from the neutralisation and separation of the acidic catalyst (Ilgen *et al.*, 2017). Conversely, the use of base catalysts (*Figure 1*) has advantages that can overcome the drawbacks of acid catalyst. Therefore, in this study, the influences of base catalyst on transesterification of solketal with mL were studied. In this work, base catalysts were tested instead of the acidic catalyst in order to prevent several side reactions associated with acid catalyst such as cleavage of the acetonide of solketal. The following reaction parameters were fixed while several base catalysts were evaluated: mole ratio (ML:solketal) – 1:1.5; reaction temperature of 140°C; reaction duration of 6 hr.

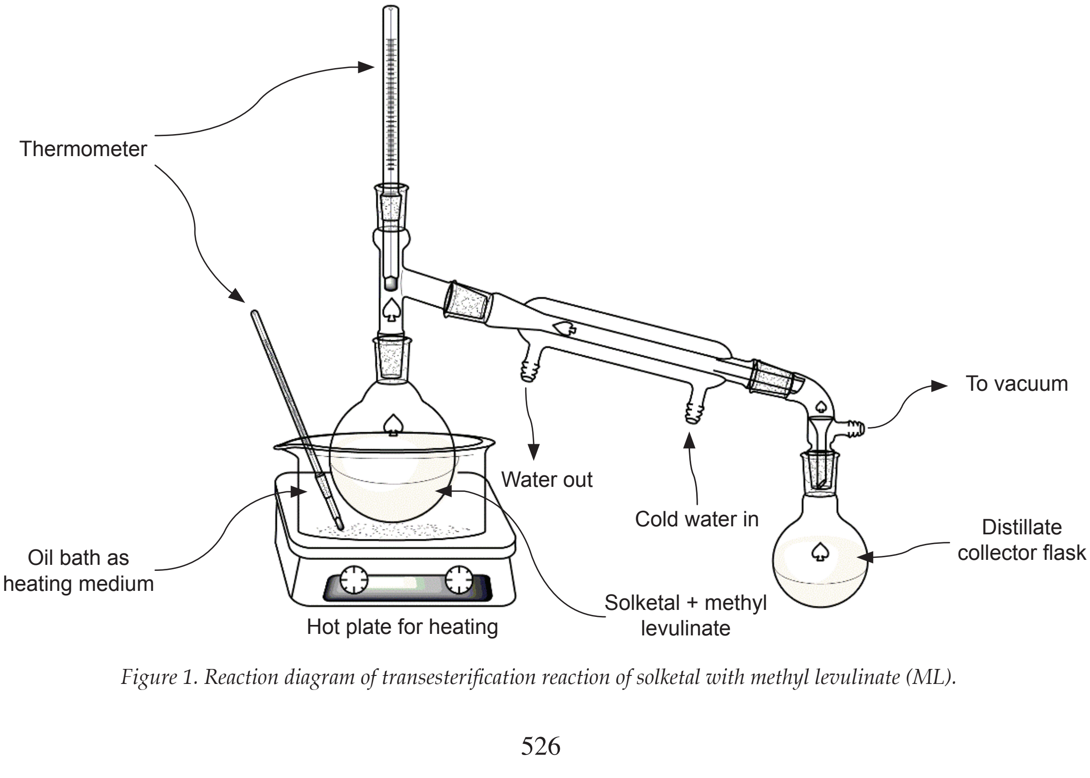

Figure 1. Reaction diagram of transesterification reaction of solketal with methyl levulinate (ML).

Application of base catalyst in transesterification reaction provides faster rate, nearly 4000 times faster than that catalysed by the same amount of an acid catalyst (Fukuda *et al.*, 2001). In this reaction, six homogeneous base catalysts were tested: Na_2CO_3, K_2CO_3, NaOH, KOH, MgO and NaOMe. The effect of different catalysts on the yield of SoLE is illustrated in *Figure* 2.

K_2CO_3 exhibited the best catalytic activity affording the highest yield of SoLE (57.29%), followed by Na_2CO_3 (49.88%) (*Figure* 3). On the other hand, both hydroxide and oxide bases gave low yield of SoLE between 3.80% and 17.36%, respectively. NaOMe was notable to be the paramount catalyst in transesterification of vegetable oil with methanol to produce methyl ester as biodiesel (Atadashi *et al.*, 2013). However, in this reaction, NaOMe generated only 29% yield of SoLE as shown in *Figure 3*. Therefore, we selected the two carbonate bases, K_2CO_3 and Na_2CO_3 as the catalysts for further optimisation.

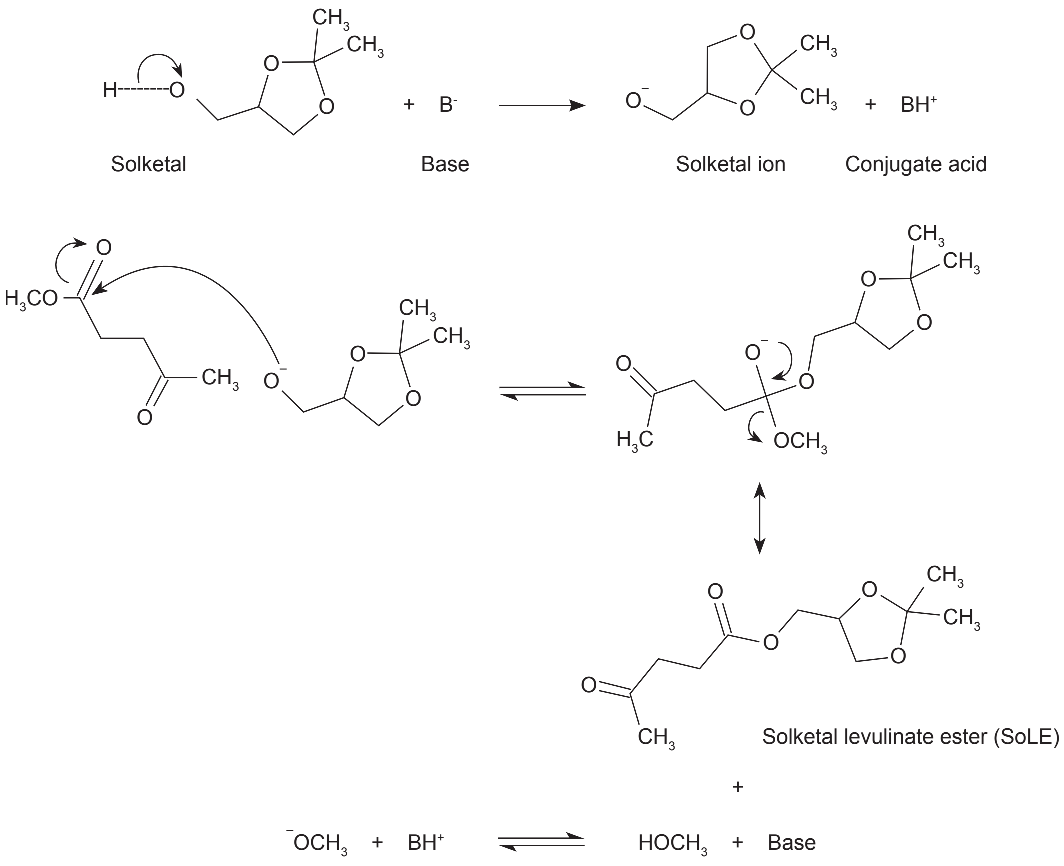

Figure 2. Reaction mechanism of based-catalysed transesterification reaction of solketal with methyl levulinate (ML).

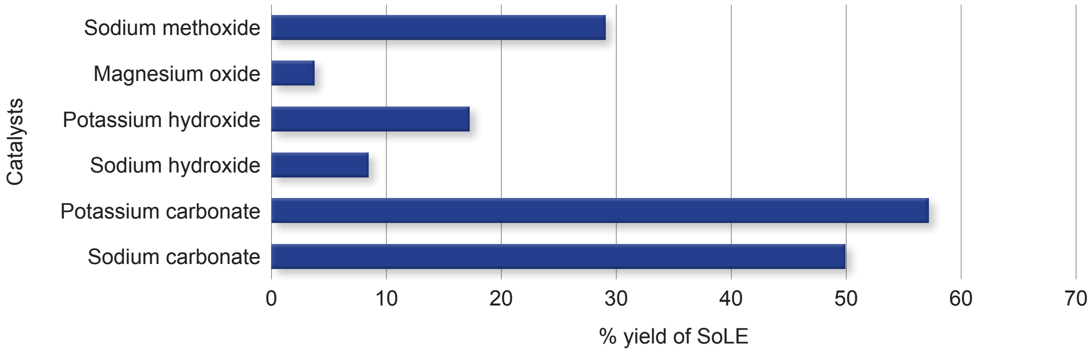

Figure 3. Effect of different type of base catalyst on the yield of SoLE.

Influence of Reaction Time on Yield of SoLE

We then investigated the effect of reaction time on the yield of SoLE, while keeping the following reaction parameters constant throughout this set of the experiments and two types of catalysts were used: molar ratio of ML:solketal = 1:3; reaction temperature of 140°C; 1% catalyst loading of K_2CO_3 and Na_2CO_3.

The reaction between solketal and mL was terminated at predetermined reaction duration, which were 2, 3, 4, 6 and 8 hr. The reaction mixture was stirred vigorously in order to achieve perfect contact between the reagents and the catalyst through the process (Ramadhas *et al.*, 2005). The effect of reaction time on the yield of SoLE is shown in *Figure 4*. The results essentially indicated that the yield of SoLE increased with longer reaction time. The result clearly showed that the maximum yield of SoLE was obtained after 4 hr of reaction for Na_2CO_3-catalysed reaction and 6 hr of reaction for K_2CO_3-catalysed reaction. Reaction time of 4 hr is more favourable due to time and cost effective of the reaction. Thus, Na_2CO_3 and reaction time of 4 hr were selected as the catalyst and optimum reaction time, respectively for the transesterification process. The selected catalyst is in agreement with a study reported by Yu *et al*. (2003) that employed Na_2CO_3 as the catalyst in transesterification of solketal with fatty acid such as stearic acid.

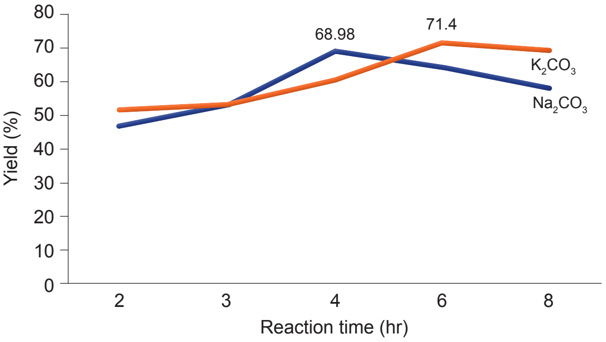

Figure 4. The effect of reaction time on the yield of SoLE.

Influence of Catalyst Loading

It is well documented that esterification/transesterification reactions require acid/base catalysts and the strength of the acid/base used is an important factor affecting the kinetics of the reaction (Rastegari and Ghaziaskar, 2015). The amount of catalyst in a reaction system will greatly influence the effectiveness of the catalyst. Therefore, in order to study the effect of catalyst loading on the yield of SoLE, the following reaction parameters were fixed as follow: molar ratio of ML:solketal = 1:3; reaction temperature of 140°C; reaction time of 4 hr.

The catalyst loading was varied from 1.0% to 3.0%. The change of yield of SoLE in respect to catalyst concentration is shown in *Figure 5*. The result showed that the yield of SoLE increased gradually with higher catalyst loading up to 1.5% and slightly decreased at catalyst loading higher than 1.5%. The highest yield of SoLE obtained with 1.5% catalyst was 74.6%. Other than that, excess addition of catalyst will lead to SoLE with darker colour. In the next stage of study, Na_2CO_3 loading amount of 1.5% will be used in subsequent sections of the study.

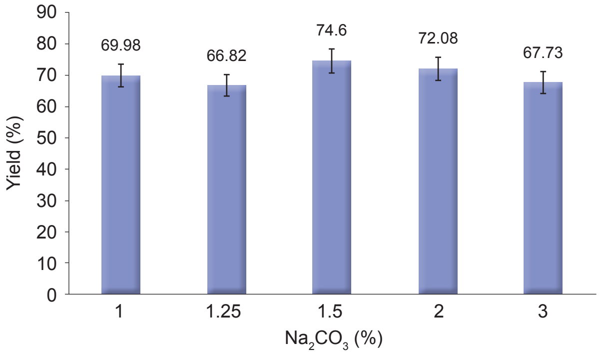

Figure 5. Effect of catalyst loading on the yield of solketal.

Influence of Molar Ratio of mL to Solketal

The mole ratio of mL to solketal is one of the most important variables affecting the yield of SoLE. Stoichiometrically, one mole of solketal is required per mole of ML, but in practice an excess of alcohol is employed in order to displace the equilibrium to produce more ester. The molar ratio of mL to solketal was varied from 1:2 to 1:4.5, while the other reaction parameters were kept constant as follow: Na_2CO_3 (1.5%); reaction temperature of 140°C; reaction duration of 4 hr. *Figure 6* shows the yield of SoLE against molar ratio of mL to solketal. Molar ratio of 1:3 (ML:solketal) was the optimum mole ratio that gave best yield of SoLE of 74.6%. When the amount of solketal was increased above or reduced below the optimal amount, the reaction condition did not increase the yield of SoLE. Hence, molar ratio of 1:3 will be used for the next section of the study.

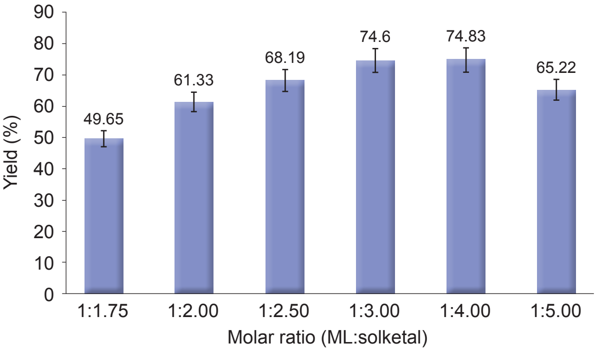

Figure 6. Effect of molar ratio (ML:solketal) on the yield of SoLE.

Effects of Reaction Temperature

Temperature is a significant factor that affects the transesterification reaction, where relatively it will influence the yield of product. To determine the effect of reaction temperature on the yield of SoLE, the reaction temperature was varied from 80°C to 160°C, while the other reaction parameters were kept constant as follow: molar ratio of ML:solketal = 1:3; Na_2CO_3 (1.5%); reaction time of 4 hr. *Figure 7* shows the yield of SoLE against reaction temperature. The figure shows that the yield of SoLE gradually increased until the reaction temperature of 140°C, giving 74.6% yield. As the reaction temperature continue to increase, the yield of SoLE slightly decreased. According to results, reaction temperature of 140°C gave the highest yield of SoLE and it was regarded to be the optimum value.

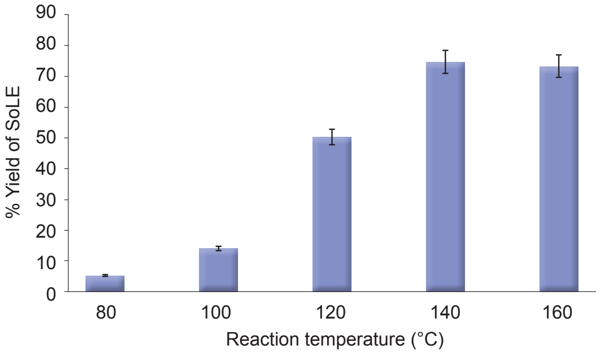

Figure 7. Effect of reaction temperature on the yield of SoLE.

Characterisation of SoLE

FTIR spectra. FTIR spectra of both solketal and mL were compared with the product in order to prove that the esterification reaction between solketal and mL had taken place. In the FTIR spectra (*Figure 8*), the absorption band at 3421 cm^{-1} assigned to C-OH stretching of hydroxyl group of solketal had almost flattened, indicating reaction had happened at the -OH group and SoLE was produced.

^{1}H and ^{13}C NMR analysis. *Figure 9* shows the ^{1}H- and ^{13}C-NMR spectra of SoLE. The chemical shift at 1.32 and 1.4 ppm in ^{1}H-NMR spectrum (*Figure 9a*) correspond to two prominent methyl groups ($-CH_3$) in solketal. The protons attached adjacent to ketone-carbonyl and ester-carbonyl in mL were featured at 2.16 (H), 2.58 (G) and 2.73 (F) ppm, respectively. Peaks between 3.70 (C) and 4.30 (D) ppm were related to the protons of $–CH_2–$ and –CH– central carbon in the glyceride unit correspondingly. Lost of $CH_2–OH$ protons peak in this region marked the occurance of transesterification reaction between mL and solketal. For the ^{13}C-NMR spectrum (*Figure 9b*), the prominent paired methyl group in solketal (B and A) appeared at 25.4 and 26.7 ppm, respectively. The glyceride carbons present in $–CH_2–$ groups (C) and central carbon (D) can be observed at 64.9 to 73.6 ppm, correspondingly. In addition, peaks at 27.8 ppm and 37.9 ppm (F) correspond to the $–CH_2–$ group adjacent to ester and ketone group, respectively. While peak at 29.9 ppm (H) relates to $–CH_3$ group of ML.

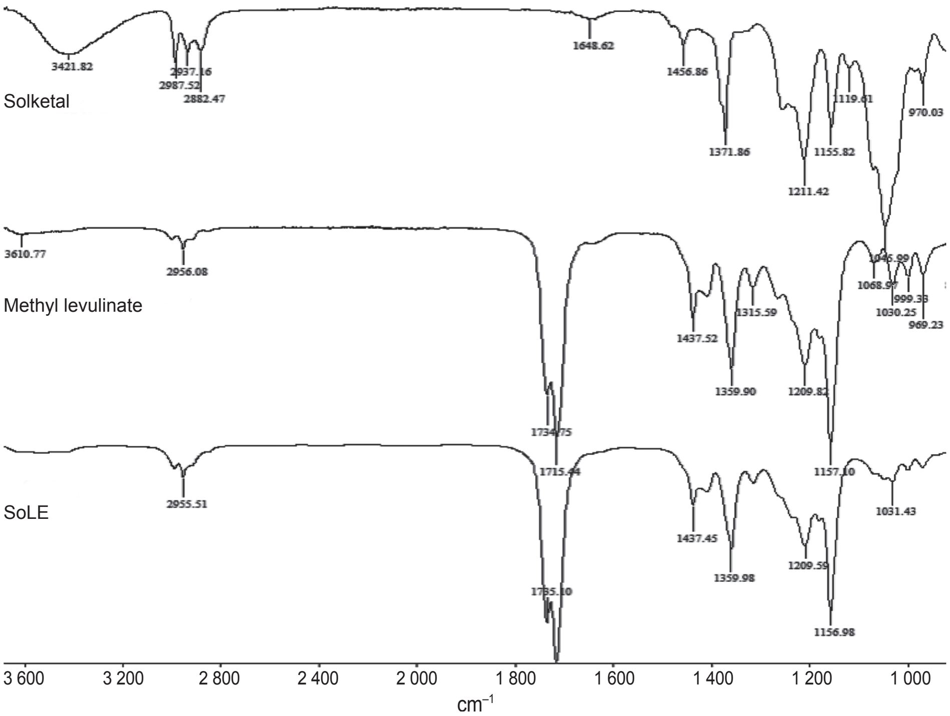

Figure 8. Fourier transform infrared (FTIR) spectrum of SoLE obtained from Na_2CO_3-catalysed transesterification between solketal and methyl levulinate (ML) at 1:3 molar ratios and at 140°C for 4 hr.

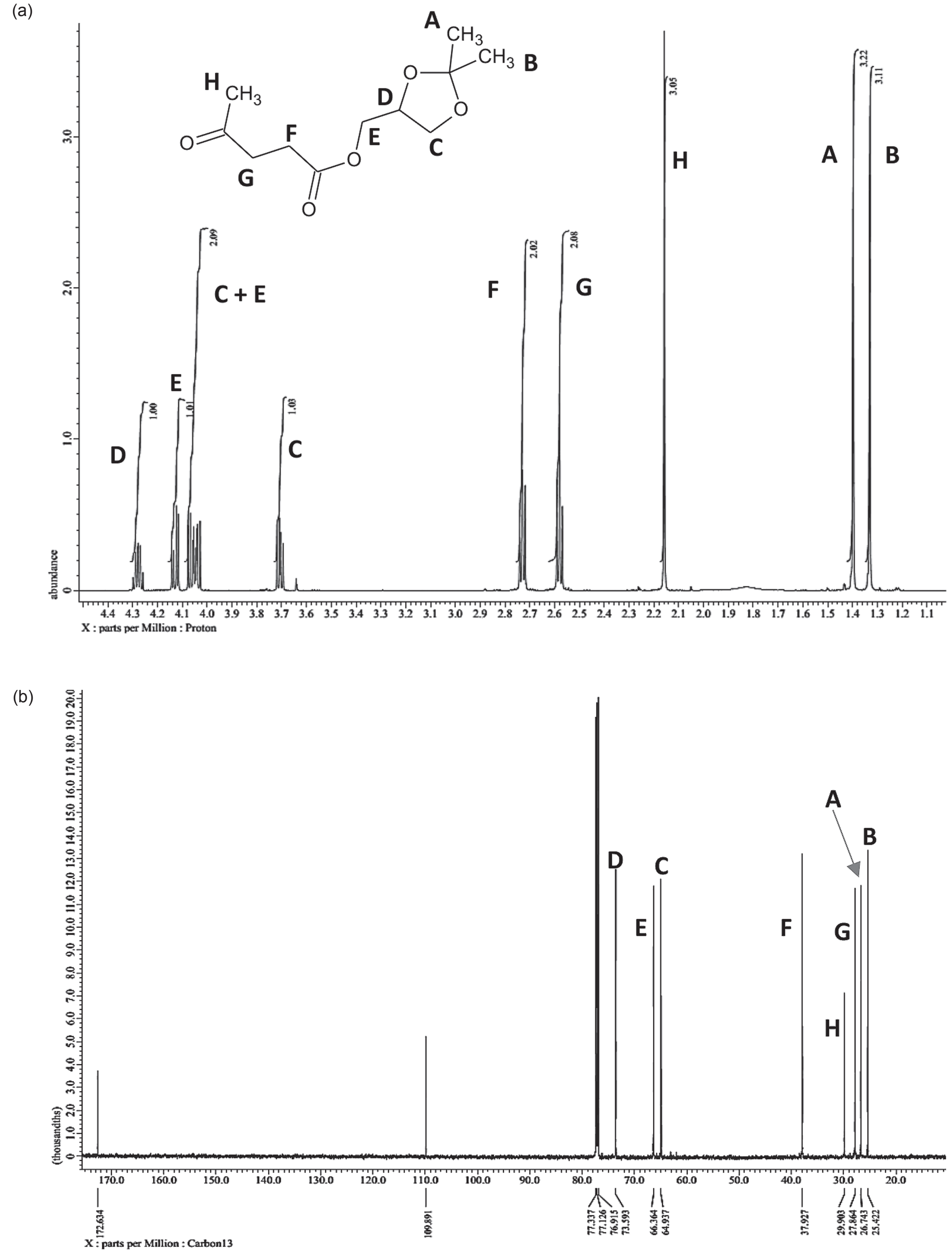

Figure 9. (a) The ^{1}H-NMR and (b) ^{13}C-NMR spectrum of SoLE obtained from Na_2CO_3-catalysed transesterification between solketal and mL at 1:3 mole ratio, 140°C for 4 hr.

GC analysis of SoLE. The formation of SoLE was confirmed qualitatively via GC analysis. The GC chromatogram of the product confirmed that the synthesised product contains high percent composition of SoLE (95%) as represented by a peak at retention time at 11.79 min (*Figure 10*). The chromatogram also indicated the existence of two other minor products with low percent composition namely methly levulinate and solketal, which appeared at 4.63 min and 5.83 min, respectively.

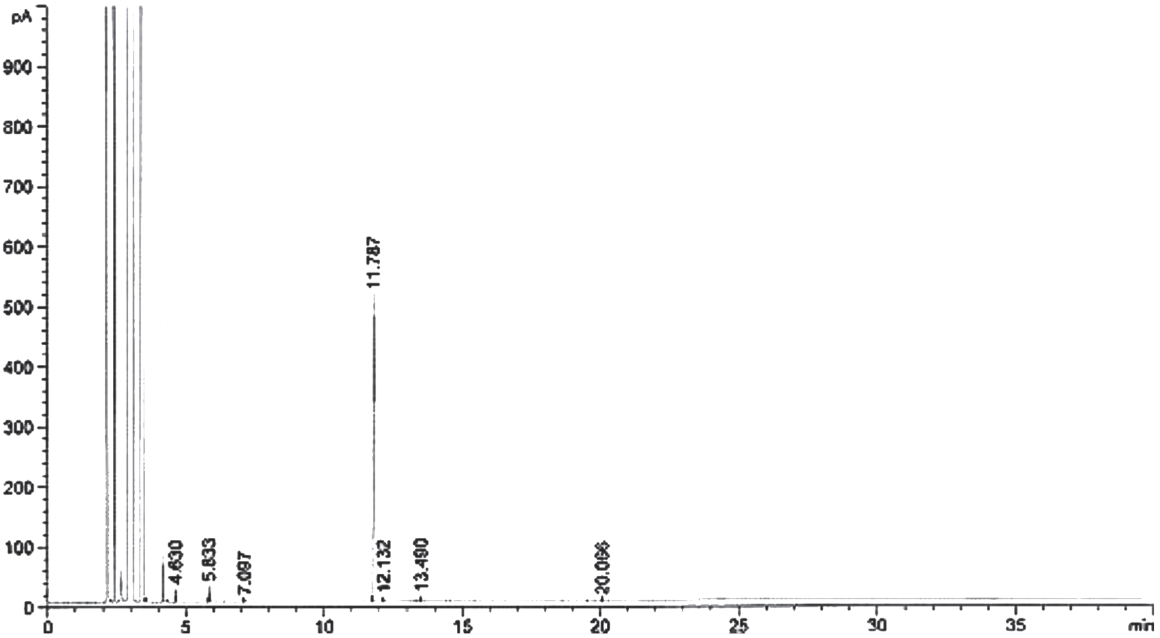

Figure 10. Gas chromatography (GC) chromatogram of solketal levulinate ester (SoLE) obtained from sodium carbonate (Na_2CO_3)-catalysed esterification between solketal (Sol) and methyl levulinate (ML) at 1:3 mole ratios and at 140ºC for 4 hr.

Potential Uses of SoLE

Solketal esters has interesting properties that are between those of cyclic acetal and glycerol ester. While current uses of solketal ester are still limited, solketal ester is proposed as a promising bio-based alternative in both direct and indirect applications.

Solketal has been reported to be applied as a fuel improver. Solketal was showed to decrease the particulate emission and enhanced the cold flow properties of liquid transportation fuels (Pariente *et al*., 2009). It helps to reduce the gum formation, improves the oxidation stability, and enhances the octane number when added to gasoline (Mota *et al*., 2010). Maksimov *et al*. (2011) described its use as a multipurpose solvent and a plasticiser in the polymer industry and a solubilising and suspending agent in pharmaceutical preparations.

Solketal and their cyclic group members has been reported as a useful fuel additive for enhancing octane number of gasoline. It was reported to reduce the gum formation and increased the octane number of gasolin (Lozano *et al*., 2016; Mota *et al*., 2010; Nanda *et al*., 2016). Lozano *et al*. (2016) has reported on producing oxygenated biofuels, based on FAME and fatty acid solketal ester mixtures, by lipase-catalysed transesterification of several vegetable oils or direct esterification of free fatty acid with methanol or solketal in ionic liquid. Other than that biodiesels formulations based on mixtures of FAME and FAGE have been described as very efficient for diesel engines. Biodiesel blends up to 20% volume fraction (vol.%) of FAGE, exhibitied an excellent suitability as liquid fuel (*e.g*., viscosity, cetane number, adiabatic flame temperature, *etc*.), as it was demonstrated by testing in an automotive engine (Lapuerta *et al*., 2015; Lozano *et al*., 2016; Nanda *et al*., 2016; Perosa *et al*., 2016).

Since solketal ester has attracted considerable attention in the fuel and biodiesel sector. We have evaluated the fuel properties of biodiesel blend with SoLE. The density of the mixture increased upon addition of SoLE. The blended biodiesel became slightly viscous with increasing SoLE amounts. The acid number of biodiesel increased upon blending with SoLE. The pour point of biodiesel was lowered to 14°C by the addition of 20 vol. % SoLE. The blending with SoLE had improved the cold flow performance of the biodiesel. The cloud point of biodiesel was also improved with the addition of 20 vol. % SoLE. This work will assist in further evaluation of SoLE as cold flow improver of biodiesel fuel.

On the other hand, solketal ester also has been reported to show potential as antimicrobial agent by Mendoza-Ortiz *et al*. (2020). In their study, they reported that solketal palmitate had showed antifungal activity against *Candida albicans* and *Candida parapsilosis*, with minimum inhibitory concentration (MIC) between 200 and 400 µg mL^{-1}.

CONCLUSION

In this study, SoLE was successfully synthesised in the presence of basic catalyst, Na_2CO_3 (1.5%). Optimum reaction temperature and reaction time to obtain high yield of SoLE were 140°C for 4 hr reaction. The best molar ratio to obtain high yield of SoLE was 1:3 of ML:solketal. Analysis by GC, FTIR and NMR confirmed the structure and composition of SoLE. The highest yield of SoLE obtained using the optimised parameters was 75% with the purity of 95%. The optimised reaction procedure to synthesise SoLE may give opportunity to industrial players in specialty chemical for production at larger scale. As described in potential application of SoLE, this research prospective will increase the uses of glycerol and chemical derived from biomass, which can boost the momentum of green chemical usage in fuel industry.

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