Optimization of the synthesis of levulinic acid and levulinic acid derivatives from sugarcane bagasse using ionic liquids

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Declaration

I, Lethiwe Debra Mthembu, declare that I performed the work described in this dissertation at Durban University of Technology, Durban, South Africa, from 2016-2020. It is an original work, and it has not been submitted in any form to another university. Where use is made of the work of others, it has been clearly stated in the text.

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James 1:17

Contents

List of tables

List of figures

List of abbreviations

$[C_5H_8O_3]$/LA	: levulinic acid
SB	: sugarcane bagasse
DSB	: depithed sugarcane bagasse
g	: grams
h:	: hour/hours
°C	: degrees celsius
MTHF	: methyltetrahydrofuran
DALA	: δ-amino levulinic acid
SL	: sodium levulinate
AL	: α-angelica lactone
CL	: calcium levulinate
EL	: ethyl levulinate
GVL	: gamma-valerolactone
DPA	: diphenolic acid
IL	: ionic liquid
ILs	: ionic liquids
FAME	: fatty acid methyl esters
[EMim][HSO_4]	: 1-ethyl-3-methylimidazolium hydrogen sulfate
[BMMim][BF_4]	: 1-butyl-2,3-dimethylimidazolium tetrafluoroborate
[BSMim][HSO_4]	: 1-butyl (4-sulfonic acid)-3-methylimidazolium hydrogen sulfate
RSM	: response surface methodology
BBD	: box-behnken design
$[C_7H_8O_3S]$/TsOH	: tosylic acid
[BMim][HSO_4]	: 1-butyl-3-methylimidazolium hydrogen sulfate
[BMim][OTs]	: 1-butyl-3-methylimidazolium tosylate
H_2O_2	: peroxide
H_2SO_4	: sulfuric acid

CaO	: calcium oxide
%	: percentage
w/w	: weight per weight
mol%	: mole percent
min	: minute
M	: molarity
R^2	: coefficient of determination
AA	: acetyl acrylate
$[C_4H_6O_4]$/SA	: succinic acid
RC(= O)R	: ketone
R–COOH	: carboxylic acid
EV	: ethyl valerate
VA	: valeric acid
VOCs	: volatile organic compounds
NREL	: National Renewable Energy Laboratory
$[C_2H_6OS]$/DMSO	: dimethyl sulfoxide
$[C_6H_{12}O]$/MIBK	: methyl isobutyl ketone
ml	: millilitre
L	: litre
µl	: microliter
mM	: millimolar
eq	: equation
Y_{act}	: actual yield
Y_{th}	: theoretical yield
ml/min	: millilitre per minute
$g.mol^{-1}$	: grams per mole
HPLC	: High performance liquid chromatography
FTIR	: Fourier-transform infrared
ANOVA	: analysis of variance
rpm	: revolutions per minute

[CH_3SO_3H]/MsOH	: methanesulfonic acid
[H_2SO_4]	: sulfuric acid
CH_3OH	: methanol
C_3H_8O	: 2-propanol
$C_4H_{10}O$	: 2-butanol
C_2H_5OH	: ethanol
DIBANET	: Development of Integrated Biomass Approaches NETwork
[PSMim][H_2PW]	: 1-(1-propylsulfonic acid)-3-methylimidazolium phosphotungstic acid
[PSMim][Cl]	: 1-(1-propylsulfonic acid)-3-methylimidazolium chloride
[SMim][$FeCl_4$]	: 1-sulfonic acid-3-methyl imidazolium tetrachloroferrate
Amberlyst-15	: 1,2-bis(ethenyl)benzene, 2-ethenylbenzenesulfonic acid
TiO_2	: titanium dioxide
ZrO_2	: zirconium dioxide
H-MCM-22	: hydrogen form-mobil combination of matter
H-MOR	: hydrogen form-mordenite
$H_4S_1W_{12}O_{40}$	: tungstosilicic acid hydrate
SiO_2	: silicon dioxide
40 WD-S	: Wells-Dawson-silica
DTPA	: dodecatungstophosphoric acid
DH-ZSM-5	: desilicated zeolite socony mobil-5
H-ZSM-5	: hexagonal zeolite socony mobil-5
Hbr	: hydrobromic acid
SA	: South Africa

Abstract

Globally, the effects of climate change due to natural sources and human activities that releases greenhouse gases has led to a greater need for a sustainable and renewable resource called biomass. In South Africa (KwaZulu-Natal) there is an excess of sugarcane bagasse (SB) therefore this study was undertaken using SB. SB was valorised to replace chemicals obtained from fossil fuel processing. Levulinic acid (LA) was identified by the National Renewable Energy Laboratory (NREL) as a chemical that can be produced from biomass. LA is a platform chemical therefore many compounds are produced from LA hence in this work three LA derivatives namely diphenolic acid (DPA), γ-valerolactone (GVL) and ethyl levulinate (EL) production were studied.

The main purpose of this work was to optimize the production of LA from depithed sugarcane bagasse (DSB) using ionic liquids (ILs), which are environment benign compared to sulfuric acid which is currently used in commercial production of LA from biomass.

Firstly, the optimal reaction conditions to produce LA from DSB using 1-ethyl-3-methylimidazolium hydrogen sulfate [EMim][HSO_4] ionic liquid (IL) were investigated. The effect of temperature (100-220 ^oC), reaction time (2-12 h), and ionic liquid loading (1- 4 g) was assessed using response surface methodology (RSM) based on the Box-Behnken design (BBD). The optimum conditions were found to be 100 ^oC, 7 h, and 4 g of IL, which yielded 54.6 % of LA from DSB. The analysis of variance (ANOVA) indicated that the design model was significant at the 95 % confidence level. The pareto chart revealed that IL loading had the most significant effect on the production of LA, followed by temperature and reaction time. The P-values also showed that these were the significant model terms. There is a strong correlation between temperature and IL loading. Solvent optimization revealed that the type of solvent used in the LA production has a significant effect on LA yield. Water was used as the control solvent for this study. Methyl isobutyl ketone (MIBK) yielded the highest LA (62 %) from all the solvents that were used.

Secondly, an environmentally friendly catalyst: 1-butyl-2,3-dimethylimidazolium tetrafluoroborate ([BMMim][BF_4]) was used to optimize the LA production from DSB. The Box-Behnken design (response surface methodology) was used to design the set of experiments with three variables, namely, time, temperature, and catalyst loading. The investigated

conditions were temperature (100 - 220 ^oC), time (2 – 12 h), and catalyst loading (1 – 4 g). The optimum condition was found to be at 100 ^oC, 7 h and 4 g of a catalyst which yielded a maximum amount of 44.8 % of LA from DSB. This study also showed that the IL is capable of theoretically producing 62.1 % of LA. The reusability study showed that [BMMim][BF_4] can be used for up to four times without losing it activity.

Thirdly, an environmentally benign method to produce a LA derivative called ethyl levulinate (EL) was investigated. EL can be produced from LA using heterogeneous catalysts replacing the highly active, corrosive, and toxic homogeneous catalyst sulfuric acid. This work uses an environmentally friendly homogeneous catalyst: methanesulfonic acid (MsOH) as the control catalyst and ILs. The esterification of commercial LA into EL was first optimized using MsOH and response surface methodology. The optimum condition for the esterification of commercial LA into EL was 5.25 h, 90 ^oC, and 2.75 g of MsOH loading. The EL yield and selectivity obtained were 92.2 % and 94 %, respectively, at a LA conversion of 98 %. The optimized conditions were then utilized to produce EL from DSB derived LA with a EL yield of 75% using MsOH.

Fourthly, gamma-valerolactone (GVL) production was optimized by a Box Behnken design from commercial LA with an environmentally friendly catalyst methanesulfonic acid. The optimum parameters were a temperature of 112.5 ^oC, reaction time of 6 h, and catalyst loading of 2.75 g yielding 78.6 % GVL with 97 % LA conversion and an 81 % selectivity. Thereafter the optimised conditions were used to produce GVL from LA derived from DSB. The hydrogen required for the reduction of LA to GVL was formed in-situ by formic acid and triethylamine in the presence of MsOH. Different solvents (including water and alcohols) were also tested to determine their effect on GVL yield, water yielded the highest GVL of 78.6 %. Different types of catalysts which included mineral acids and ionic liquids were used to determine their effect on GVL yield, and to provide a benchmark against MsOH. Sulfuric acid gave the highest GVL yield (80.9 %).

Fifthly, the production of diphenolic acid (DPA) which is one of the LA derivatives was studied. DPA has a potential to replace bisphenol A, a plasticizer. To determine the optimum conditions for DPA production, commercial LA was used with a mild environmentally benign acid namely, methanesulfonic acid. The optimized reaction parameters were time (6 h), temperature (75 ^oC), and catalyst loading (5.5 g) yielding 65.8 % DPA at 90 % LA conversion. The response surface methodology study indicated that the temperature had the most significant effect on DPA yield followed by time and catalyst loading. The analysis of variance (ANOVA) revealed that the model was able to satisfactorily predict the DPA yield. To determine the effect of catalyst on DPA production from commercial LA, ionic liquids (ILs), MsOH, and sulfuric acid were used. IL catalysts produced 59-68 % of DPA, MsOH produced 65.6 % of DPA, and sulfuric acid produced the maximum DPA of 74 %. The study also investigated the effect of the LA: phenol ratio using the optimised reaction conditions. The LA: phenol ratio of 2:5 yielded the most DPA (86.35%). The optimized reaction conditions were then used to produce DPA from LA derived from depithed sugarcane bagasse (DSB), which yielded 64.5 % of DPA. This indicates that the DSB derived LA is a good starting material for DPA production.

The LA production from depithed sugarcane bagasse was successfully optimized by using two ionic liquids namely 1-ethyl-3-methylimidazolium hydrogen sulfate and 1-butyl-2,3-dimethylimidazolium tetrafluoroborate, where for both ILs the same conditions yielded a maximum LA yield. MIBK was found to be the optimum solvent for both ILs, giving a higher LA yield compared to when water is used as a solvent. This study also revealed that at the optimum conditions there was no formation of humins, but humins were observed at maximum reaction conditions. Both ILs showed that they can be reused up to four times, which is very important for any catalysts especially for the ILs because they are known to be expensive. This study also illustrates the first-time optimization of three LA derivatives namely EL, GVL, and DPA using methanesulfonic acid.

List of conferences

1. Oral Presentation at 8th IUPAC International Conference on Green Chemistry at Shangri-La Hotel (Thailand, Bangkok), 2018

   Title: Optimization of reaction conditions for the production of levulinic acid from depithed sugarcane bagasse in 1- Ethyl-3-methylimidazolium hydrogen sulfate [EMim][HSO_4] using a Box-Behnken Design.

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   Title: Optimization of reaction conditions for the production of levulinic acid from depithed sugarcane bagasse in 1- Ethyl-3-methylimidazolium hydrogen sulfate [EMim][HSO_4] using a Box-Behnken Design.

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   Title: Valorization of Sugarcane Bagasse to a Platform Chemical Levulinic Acid catalysed by 1-Butyl-2,3-Dimethylimidazolium Tetrafluoroborate [BMMim][BF_4]

4. Poster Presentation at Durban University of Technology Faculty of Applied Sciences Research day at Southern Sun Elangeni/ Maharani hotel (South Africa, Durban), 2019

   Title: optimization of levulinic acid from depithed sugarcane bagasse using ionic liquids

List of publications

1. **Mthembu, L.D.**, Lokhat, D., Gupta, R. and Deenadayalu, N., 2021. Optimization of Levulinic Acid Production from Depithed Sugarcane Bagasse in 1-Ethyl-3-methylimidazolium hydrogen sulfate [EMim][HSO_4]. *Waste and Biomass Valorization*, *12*(6), pp.3179-3191. DOI: 10.1007/s12649-020-01221-z

2. **Mthembu, L.D.**, Lokhat, D. and Deenadayalu, N., 2021. Valorization of sugarcane bagasse to a platform chemical (levulinic acid) catalysed by 1-butyl-2, 3-dimethylimidazolium tetrafluoroborate ([BMMim][BF_4]). *Waste and Biomass Valorization*, 12(1), pp.199-209. DOI: 10.1007/s12649-020-00997-4

3. **Mthembu, L.D.**, Lokhat, D. and Deenadayalu, N., 2021. Esterification of levulinic acid to ethyl levulinate: optimization of process conditions using commercial levulinic acid and extension to the use of levulinic acid derived from depithed sugarcane bagasse. *Biomass Conversion and Biorefinery*, pp.1-10. DOI: 10.1007/s13399-021-01632-5

4. **Mthembu, L.D.**, Lokhat, D. and Deenadayalu, N., 2021. Catalytic Condensation of Depithed Sugarcane Bagasse Derived Levulinic Acid into Diphenolic Acid. *BioResources*, 16(2), pp.2235-2248. DOI: 10.15376/biores.16.2.2235-2248

5. **Mthembu, L.D.**, Lokhat, D., Deenadayalu, N.: Hydrogenation of Sugarcane Bagasse Derived Levulinic Acid to γ-valerolactone. In preparation.

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7. **Mthembu, L.D.**, Gupta, R. and Deenadayalu, N. Conversion of Cellulose into Value-Added Products. In Cellulose Science and Derivatives. *Intechopen*. Accepted. DOI: http://dx.doi.org/10.5772/intechopen.100022

Chapter 1: Introduction

1.1 Background

The environmental concerns and depletion of fossil fuels have driven scientists to research biomass which is a renewable resource for chemical productions [1, 2]. In this work, sugarcane bagasse (SB), a bio-based was used to produce levulinic acid (LA) instead of using fossil-based chemicals that contribute to climate changes resulting in an increase in global atmospheric temperatures. Bagasse is a residue, which consists of cellulose, hemicellulose, and lignin [3]. There are different types of biomass such as wheat straw, corn, water hyacinth, wood, pulp slurry, rice husk, sorghum grain, tobacco chops, olive tree pruning, poplar sawdust, paper sludge, and sugarcane bagasse [4-8].

The use of biomass was not only a solution for the limitations of fossil fuels, but it was also a solution to minimise waste which is another problem contributing to climate change. Climate change results from global warming which is caused by the release of greenhouse gases (carbon dioxide, nitrous oxide, methane and water vapour) to the atmosphere, natural sources such as plant and animal respiration, volcanic eruption, and forest fires. Humans also contribute to climate change by their actions such as burning fossil fuels, deforestation, and urbanization [9]. Therefore, the use of a renewable resource such as biomass has become a solution to both the depletion of fossil fuels and the reduction of waste.

The South African sugarcane industries have been focusing on producing sugar, paper, furfural, and alcohol such as ethanol from sugarcane. When the juice from the sugarcane is extracted to make sugar the solid residue that is left is called sugarcane bagasse (SB). Sugarcane bagasse consists of important chemical compounds such as cellulose (40%), hemicellulose (25%), and lignin (25%) [10]. Sugarcane industries have an opportunity to diversify in line with the global demand to produce alternative, renewable bio-based fuels and chemicals to those derived from petroleum to make them more sustainable. Also, the recent South Africa (SA) government law on sugar tax offers another opportunity for the diversification of the sugar industry.

In 1988, Anastas and Warner [11] developed 12 principles of green chemistry, also known as sustainable chemistry, for the safety of people and the environment. Green chemistry requires sustainable development. This was defined by the Brundtland Commission in 1987 [12] as a "development that meets the needs of the present without compromising the ability of future generations to meet their own needs" [13].

Green chemistry focuses on how the manufacture of any products can reduce or eliminate hazardous chemicals [14]. However, there are challenges in developing a profitable product that complies with green chemistry principles, since some of the environment-friendly catalysts or solvents are more expensive. Therefore, the use of biomass residue, as the feedstock reduces the cost of green processes because it is an agricultural residue that is available almost everywhere and does not compete with the food chain [7, 15].

Intensive research has been conducted on the use of biomass residue components in numerous chemical reactions. Besides the starting material, there are other materials involved in a chemical reaction such as catalysts and solvents. Catalysis plays a key role in the chemical industry because most chemical processes need catalysts to accelerate the speed of reactions, enhance selectivity and lower energy requirements. Current catalysts are costly, toxic, harmful, or noble metals [16].

In order to obey green chemistry principles, there are properties a catalyst should have such as high activity, selectivity, stability, ease of separation, reuse, environmentally benign, and be of a widely available raw material. The exploration and development of new synthetic routes and chemical processes rely strongly on progress in catalysis. The design and use of green catalysts and catalytic systems to achieve the dual goals of environmental protection and economic benefits is an important task, and it is essential for the sustainability of the chemical industry [16, 17].

Solvent selection for chemical processes is also important in green chemistry. A solvent is a substance that dissolves a solute (a chemically distinct liquid, solid or gas), resulting in a solution. A solvent is usually a liquid but can also be a solid, a gas, or a supercritical fluid [18]. Solvents can have an effect on solubility, stability and reaction rates and choosing the appropriate solvent allows for thermodynamic and kinetic control over a chemical reaction [18]. Physical properties such as high solubility also increase reaction rates. Solvent polarity can either increase or decrease the reaction rate of a reaction, but increasing solvent viscosity generally decreases reaction rates [19]. Therefore, it is important to select a suitable catalyst and solvent as they play an important role in a reaction, increasing the reaction rate and it is important to select an environmentally friendly catalyst and solvent.

The sugarcane bagasse in South Africa is currently used to power sugar mills. Sugarcane bagasse produces enough heat energy to supply all the needs of a typical sugar mill. Sugarcane bagasse used to power a sugar mill is carbon neutral because the carbon dioxide that is released during the production of energy is equal to the carbon dioxide that is absorbed by the sugarcane during its growing phase [20].

Conventional processes of paper manufacturing use wood. Energy, water consumption, greenhouse gases (GHG) and methane emissions, chlorine and raw materials used for non-virgin papers (bagasse) is less than virgin material (wood) [21]. Approximately 30 countries use sugarcane bagasse for the paper manufacturer and the application of non-wood material for paper manufacture is eco-friendly because it is alkali-free and it is a non-polluting process thus preventing global warming unlike conventional processes [22]. Bagasse is an eco-friendlier option when compared with trees because bagasse only takes 1 year to grow and harvest whereas trees can take up to 20 years to grow. It takes 5000 kg of wood to produce 1000 kg of pulp and 1500 kg of bagasse for the same amount [23].

Two to four tons of trees are used to produce one ton of paper or tissue, which is a critical concern because forests are being destroyed at an unstainable pace. Deforestation accounts for 20% of all greenhouse gas emission worldwide, therefore, the use of sugarcane bagasse to make paper and tissue is a sustainable method and trees takes longer to grow unlike sugarcane bagasse [24].

Levulinic acid (LA) is one of the top twelve value-added chemicals that can be produced from biomass. LA is a platform chemical meaning many chemicals can be produced from levulinic acids such as methyltetrahydrofuran (MTHF), δ-amino levulinic acid (DALA), sodium levulinate (SL), α-angelica lactone (AL), calcium levulinate (CL), ethyl levulinate (EL), gamma-valerolactone (GVL) and diphenolic acid (DPA) [1, 25, 26]. The currently known method for the industrial-scale production of LA is the Biofine process which uses sulfuric acid as a catalyst. Sulfuric acid is highly corrosive and toxic therefore a more environmentally friendly catalyst needs to be investigated to replace it. Other limitations of the Biofine process includes extensive water usage, cumbersome acid recovery, and production of humins. Hence more research is required to overcome these limitations.

Ionic liquids (ILs) are a diverse group of salts that are liquid at room temperature. ILs are salts that can be used as a solvent or a catalyst [8]. ILs are also known as ‘‘designer solvents’’ because their specific properties for a particular requirement can be achieved through appropriate modification of cations or anions [27]. For example, the ILs with anion such as chloride or acetate with a high hydrogen bond basicity is capable of dissolving a high yield of cellulose [28]. Sulfonic acid (SO_3H) or carboxylic acid groups increases the acidity and water solubility, which makes the acidic ionic liquid an environmentally friendly acidic catalyst [27, 29]. ILs have negligible vapour pressure in contrast to the volatile organic solvents normally used in industry, and hence the evaporation of ILs into the atmosphere is low which decreases the contamination of the environment. This is why ILs are regarded as green solvents [8, 30]. Other important properties of ILs include a wide range of temperatures in the liquid phase which can improve the control of kinetics in liquid phase reactions; high thermal and electrical conductivity; wide electrochemical windows and high electrochemical stability against redox reactions [31]. Most ILs are non-flammable, thermally and chemically stable, can be recovered and recycled. LA is highy reactive hence it has many derivatives. Three of the most interesting LA derivatives with important applications are further described below:

1. **Diphenolic acid (DPA)** also known as 4,4-bis (4-hydrophenyl) pentanoic acid is prepared by reaction of LA with phenol [32, 33]. DPA has extensive application value in polymeride and other materials [34]. DPA can serve as feedstock for the production of water-soluble resins that are used in industrial Millipore filters and oil filter paper [35]. DPA is also a widely used chemical intermediate in paint formulations, protective, decorative coatings, finishes, lubricating oil additives, cosmetics, surfactants, plasticizers, and textile chemicals [36, 37]. DPA is a structural analogue of bisphenol A (BPA) and it can serve in many of the same applications as BPA, namely for the synthesis of industrially important epoxy resins and polycarbonates that are used in the production of reinforced plastics and other chemical materials [33].

2. **γ-Valerolactone (GVL)** also known as 5-methyldihydrofuran-2-(3H)-one is produced from the hydrogenation of LA [38]. GVL is useful in industry as a solvent for lacquers, insecticides, adhesives, cutting oil, brake fluid, and as a coupling agent in the dye bath [39]. GVL is a highly promising carbohydrate-based sustainable solvent and fuel additive which is due to its favourable properties such as inertness towards oxygen and water, high boiling and flash point, low melting point, low vapour pressure and decent smell [40, 41].

3. **Ethyl levulinate (EL)** also known as ethyl 4-oxopentanoate has an oxygen content of 33 wt% and properties similar to the biodiesel fatty acid methyl esters (FAME), which

make it suitable to be used as an oxygenate diesel additive. Addition of EL into the diesel results in a cleaner-burning fuel with high lubricity, flashpoint stability, reduced sulfur content and improved viscosity that can be used in regular diesel engines [42]. Ethyl levulinate is also used in the flavouring and fragrance industries or as a blending component in biodiesel [43-46].

1.2 Problem statement

The commercial production of LA from biomass is the Biofine process (a one-pot reaction) which uses sulfuric acid as a catalyst [10, 32]. However, sulfuric acid is highly corrosive and toxic; therefore, a more environmentally friendly catalyst needs to be investigated as a replacement. Moreover, some other limitations of the Biofine process include the production of humins, inefficient separation, cumbersome acid recovery and extensive water usage [47]. The production of humins leads to clogging of the reactor, which thus lowers the LA yields [4]. Besides sulfuric acid, several homogeneous, as well as, heterogeneous catalysts have also been reported for the production of LA [39, 48-52]. The disadvantages of homogeneous catalysts are its toxicity and corrosiveness and its advantage is the high LA yield. Heterogeneous catalysts allow for easy separation of LA, but they lower the LA yield.

Given the above concern, it is, therefore, advisable that when choosing a solvent or a catalyst for a reaction; the selected solvent or catalyst must be less harmful to the environment. Hence, the main purpose of this study is to determine an environmentally friendly and efficient alternative catalyst for LA production from biomass (sugarcane bagasse). Ionic liquids (ILs) have received enormous attention because of their properties which make them environmentally friendly. ILs have negligible vapour pressure when compared to conventional volatile organic solvents, usually used in industry. Therefore, the evaporation of ILs into the atmosphere is low and the contamination of the environment is negligible. This is one of the reasons ILs are regarded as green solvents.

Furthermore, ILs are nonflammable, thermally and chemically stable, recoverable, and recyclable [53, 54]. While many papers have been published on heterogeneous and/ or homogenous catalysts for LA production, but few papers have been published on the use of ILs [8, 55]. More so, there is a dearth of empirical studies on the optimum conditions in LA production using ILs and a one-pot reaction.

1.3 Aims and Objectives

Aim

The purpose of this study was to investigate an alternative catalyst that is efficient and environmentally friendly to replace sulfuric acid which is currently used to catalyse the commercial production of LA from biomass. Part of the inquiry this study sought to address was to upscale the reaction and study the application of LA as a platform chemical by producing LA derivatives such as diphenolic acid, ethyl levulinate, and γ-valerolactone.

Objectives of the study

- Studying the effect of the alternative catalysts on the reaction conditions such as temperature, time, and catalyst loading; solvents effect on LA yield; interaction of the reaction conditions, to determine the reaction condition that has more effect on LA yield using response surface methodology (RSM) and a Box-Behnken design (BBD) and also determine the reusability of the catalyst.
- Application of synthesized levulinic acid to produce LA derivatives namely diphenolic acid (DPA), ethyl levulinate (EL) and γ-valerolactone (GVL). Investigate environmental friendly and efficient catalysts for the conversion of LA into derivatives; study the interaction of the reaction conditions, to determine the reaction conditions that have more effect on DPA, EL, and GVL yield using RSM (BBD).

1.4 Rationale

The main method for the production of high purity LA in South Africa and in other countries involves the petrochemical conversion route from maleic anhydride or hydrolysis of furfuryl alcohol [5, 56]. These conversion routes are more complex than the acid hydrolysis of biomass and result in the relatively high market price of LA [57]. Affordable feedstocks are required as techno-economic evaluations show that the raw materials are the largest cost contributor to the production process [58].

The use of a renewable material such as SB to produce LA is the best option when compared with using maleic anhydride because in SA approximately 500 million wet tons (~250 million dry tons) of sugarcane bagasse are produced annually [59]. Currently, GF*Biochemicals* (Italy) is the only company that commercially produces LA from biomass using sulfuric acid [60], which is corrosive and toxic. Therefore, alternate catalysts must be sourced to produce LA from biomass using green chemistry principles.

1.5 Structure and outline of the dissertation

Chapter 2, Literature review

Chapter 3, Experimental methods

Chapter 4, Results and Discussion

Conclusion and Recommendation

References

Chapter 2: Literature review

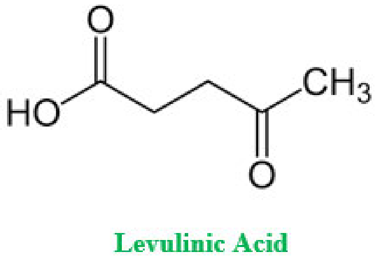
2.1 Introduction

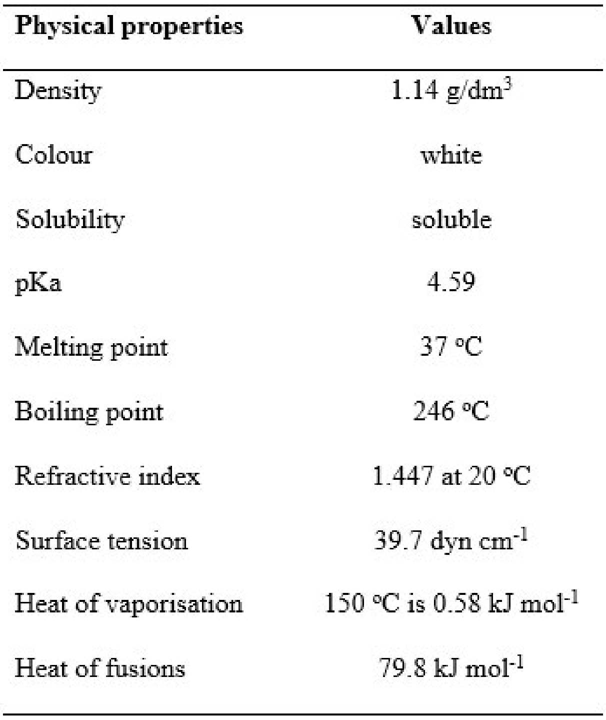
For the last more than a decade, the research on lignocellulosic biomass is gaining extensive attention for the production of biomass-based platform chemicals such as LA. LA is a keto acid, owing to its functional groups, specifically carboxylic acid (RCOOH) and ketonic ($R_2C=O$) groups, serve as a highly reactive platform chemical to generate secondary chemicals. The chemical structure and the physical characteristics of LA are shown in figure 2.1 [26, 61]. It is used as feedstock material for the synthesis of diphenolic acid, γ-valerolactone, esters of LA, amino LA, angelica lactone, 2-methylene -valerolactone, 1,4-pentanediol, 2-methyltetrahydrofuran, hydroxyvaleric acid, acetyl acrylic acid, and succinic acid. Moreover, it is also utilized in the manufacturing of food additives, medicines, biofuels, cosmetics, and agricultural chemicals.

Traditionally, LA is manufactured by the petrochemical process of hydrolysis and hydrogenation of maleic anhydride or furfuryl alcohol [62]. However, the conventional method was cumbersome and cost-intensive, leading to a comparatively high market price for LA of US$10/kg. Techno-economic analyses reveal that raw materials are the most expensive component of the manufacturing process [63], hence the LA conventional method which uses maleic anhydride or furfural alcohol as a raw material is expensive. Besides, to reduce the chemical industry's dependency on fossil fuel-based resources the focus of LA production is gradually shifted towards renewable resources such as biomass residue. Although several studies have been performed throughout the years to generate LA from biomass residue rather than maleic anhydride or furfural alcohol, however, the commercialization of biomass-based LA is still in-fancy. The reasons for the restricted production of levulinic acid include [63].

- Low yield: This is due to levulinic acid's intrinsic physicochemical characteristics, which prevent effective recovery. Furthermore, the non-selective nature of catalysts causes unwanted side reactions and re-polymerized products at every stage of the reaction pathway.
- Costs of equipment: Both the reactor and the acid recovery facility require costly building materials.
- To convert feedstocks, high temperatures are necessary, resulting in significant heating inputs.

- Issues with waste disposal or high running costs for catalyst recovery.





Physical properties	**Values**
Density	1.14 g/dm^3
Colour	white
Solubility	soluble
pKa	4.59
Melting point	37 °C
Boiling point	246 °C
Refractive index	1.447 at 20 °C
Surface tension	39.7 dyn cm^{-1}
Heat of vaporisation	150 °C is 0.58 kJ mol^{-1}
Heat of fusions	79.8 kJ mol^{-1}

Figure 2.1 Illustrate LA structure with its physical properties

Besides, there were drawbacks such as humins production, ineffective separation, laborious acid recovery, and excessive water use in the Biorefinery process, which was the first commercial method for LA from low-cost feedstock (biomass residue) [62]. As a result, research into LA synthesis is underway in order to identify catalysts that will overcome the limits of the Biorefinery process.

Although there are several reviews comprising the production strategies and the commercial aspect of LA production from lignocellulosic biomass, however, a detailed review of different catalytic processes and their role in process optimization is lacking. Therefore, the current review is an attempt to summarize the role of different components used in biomass-based LA production. Besides, brief details about few secondary chemicals produced from LA have also been discussed.

2.2 Production of levulinic acid from biomass

LA may be synthesized from any of the three generations of biomass. The first generation consists of food crops, starchy materials, and sucrose-containing biomass. The second generation consists of food waste and lignocellulosic biomass residue, whereas the third generation consists of algal biomass [64]. Chemically biomass is composed of carbohydrates polymers, cellulose (35-55 wt.%), hemicellulose (25-35 wt.%), and aromatic polymer lignin (15-30 wt.%), with minor amounts of ashes or extractives [63, 65]. Cellulose is a very stable (figure 2.2), crystalline homopolysaccharide polymer comprised of anhydroglucopyranose monomers produced by -1,4-D-glucose linkage of glucose units and containing numerous intra and inter molecular hydrogen bonds, with an average molecular weight of about 100,000 [66, 67].

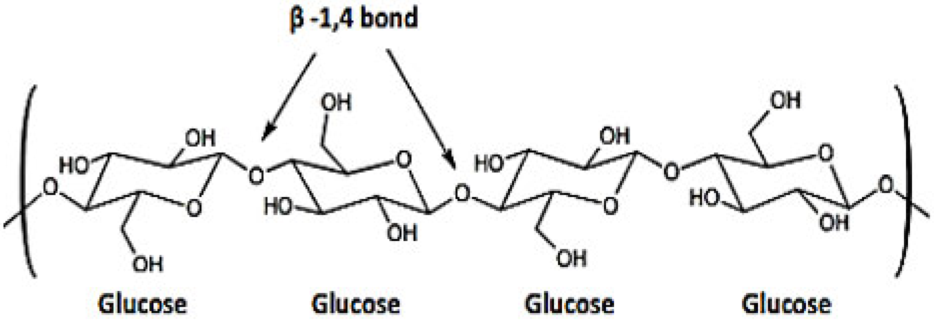


Figure 2.2 Illustrates the chemical structure of cellulose

Hemicellulose has a lower molecular weight than cellulose and is made of 5-carbon monosaccharides. Examples include; D-xylose, D-arabinose; and 6-carbon monosaccharides; D-mannose; D-galactose; and D-glucose [68]. The structure of bagasse hemicellulose is shown in figure 2.3. Hemicellulose, unlike cellulose, is soluble in both water and alkaline solutions [69-71].

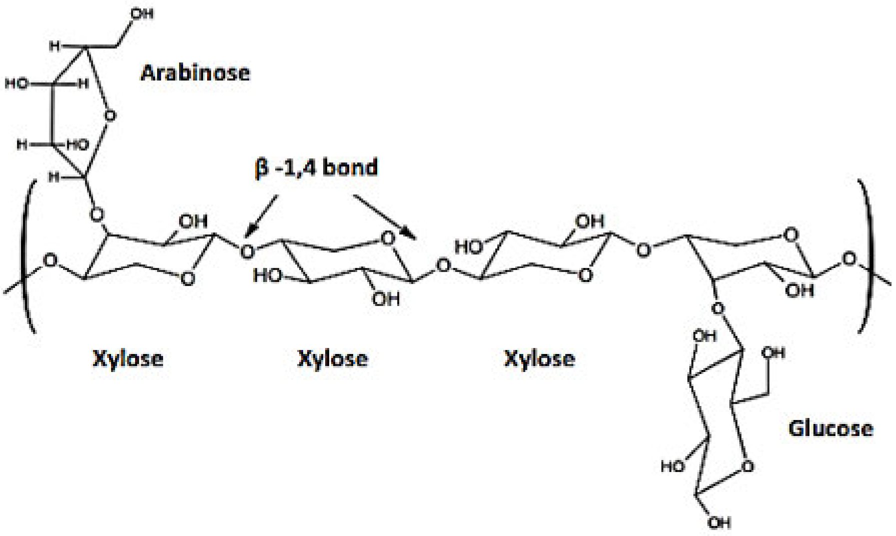


Figure 2.3 Demonstrates the chemical structure of hemicellulose

In addition, lignin (figure 2.4) acts as a binding agent in the cellular structure, keeping cellulose and hemicellulose fibers together and providing great stability and flexibility. It is an aromatic, water-insoluble complex network polymer that offers waterproofing, structural strengthening, and resistance to biological or physical assault on plant cell walls [72, 73].

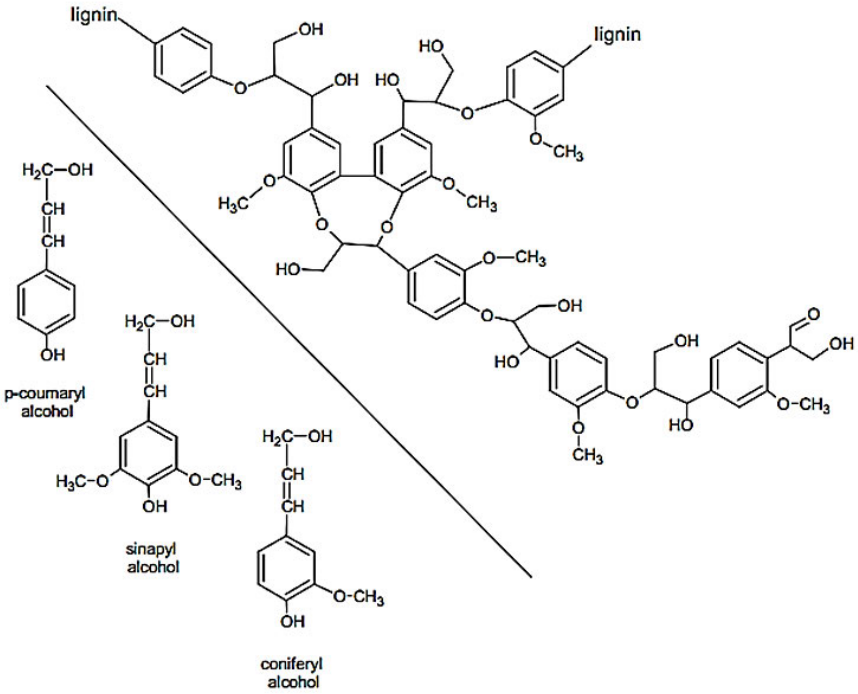


Figure 2.4 Illustrates the chemical structure of lignin (right). On the left are the chemical structure of the p-coumaryl, coniferyl, and sinapyl alcohol aromatic phenylpropane units that form lignin.

2.2.1 Sugarcane bagasse: source, definition, and composition

Sugarcane bagasse falls under energy crop which is sugarcane (*Saccharum officinarum*). Sugarcane is a perennial crop comprised of roots, leaves, and stalks which are rich in sugar sucrose that is used to make sugar (figure 2.5). Sugarcane is the world's largest crop by production, with about ~ 1.9 billion tonnes produced yearly [74]. Depending on the growth conditions, undried sugarcane contains 9-15 wt.% sucrose, 73-76 wt.% water, and 11-16 wt.% fibers [75]. Table 2.1 shows the composition of dried sugarcane.

Figure 2.5 Photograph of sugarcane

When the sugarcane stalks are mixed with water and crushed to make sugar, the solid residue that result is called sugarcane bagasse, which consists of hemicellulose (25.63 wt.%), lignin (30.36 wt.%) and cellulose (39.53 wt.%) [76].

Table 2.1 Composition of dried sugarcane

Component	**Dry mass (wt. %)**
Carbohydrates	75 – 92
Sucrose	70 – 88
Glucose	2 – 4
Fructose	2 – 4
Salts	3.0 – 4.5
Of inorganic acids	1.5 – 4.5
Of organic acids	1.0 – 3.0
Free organic acids	1.5 – 5.5
Carboxylic acids	1.1 – 3.0
Amino acids	0.5 – 2.5
Other organic non-sugars	
Proteins	0.5 – 0.6
Starch	0.001 – 0.0050
Gums (soluble polysaccharides)	0.30 – 0.60
Wax, lipids, phosphatides	0.05 – 0.15
Other non-sugar materials	3.0 – 5.0

LA is mostly produced from the second generation of biomass because of the continuous dispute over food vs. fuel or food vs. chemicals, global research is concentrating on utilizing lignocellulosic wastes [2]. LA has been derived from a variety of biomass, including wheat straw, maize stover, water hyacinth, sorghum grain, empty fruit bunch, kenaf, corn stover, and sugarcane bagasse [77]. It can either be produced directly from biomass or its carbohydrate polymers/monomers (cellulose, glucose, fructose).

2.2.2 Methods used to produce LA from biomass.

There are two techniques for producing LA from biomass residue. The first is a one-step process in which LA is directly generated from the biomass residue, also known as a one-pot synthesis. The alternative technique comprises of two or more stages in which the biomass residue is pre-treated to remove hemicellulose and lignin, followed by cellulose or glucose hydrolysis, depending on the kind of pre-treatment used.

2.2.2.1 Pre-treatments used prior LA production.

Biomass is recalcitrant due to crystallinity and strong packaging of the biomass structural polymers, which makes it resistant to chemical and/or microbial degradation [78] hence an effective pre-treatment to access each component is a prerequisite. Liu et al. [79] reported that cellulose that has undergone pre-treatment such as ball-milled has a low crystallinity thus it has a quick reaction rate compared to un pre-treated cellulose that is due to high crystallinity which limits the availability of β-1 and 4-glycosidic bonds. A pre-treatment method is required to reduce the crystallinity, break the lignin and hemicellulose seal to expose the cellulose to produce different chemicals [78, 80, 81] and reduce the mass transfer limitations of catalysts. Table 2.2 shows some of the pre-treatments utilized prior to levulinic acid synthesis.

Pre-treatments are classified into mechanical, physical, chemical, biological, and physicochemical. Mechanical pre-treatments are commonly utilized to enhance the surface area for efficient biomass pre-treatment. Mechanical pre-treatment procedures include chipping, grinding, milling, and other techniques. Physical pre-treatments aim to minimize biomass recalcitrance by raising the temperature or pressure, producing changes in the structure of lignocellulosic materials [82]. Steam explosion [83], wet air oxidation [84], ammonia fiber explosion [85], ammonia recycle percolation, liquid hot water [86], lime treatment, and other types of physical pre-treatment typically operate at higher temperatures and pressures. While chemical pre-treatments utilize organic or inorganic chemicals to interact with the intrapolymer or interpolymer linkages of

Table 2.2 Pre-treatments used for LA productions.

No.	Substrate	Pre-treatments		After pre-treatments	LA yield (wt.%)	References
1.	Sugarcane bagasse	Liquid hot water (LHW) hydrolysis: The volume flow of 250 ml/min. Temp of 200 ^oC, for 30 min at 50 bars.	Enzymatic hydrolysis: An enzyme called cellic CTec2 at a concentration of 15 fpu/g was added to the mixture with a pH of 5. The reaction occurred for 72 hrs at 50^oC.	Acid hydrolysis: Methanesulfonic acid (MsOH) was used as a catalyst at 140 ^oC for 30 min.	59	[2]
2.	Eucalyptus wood chips	Acid pre-treatment: sulfuric acid (H_2SO_4) in 1.0 M		Sulfuric acid in a concentration of 0.2 M was used a catalyst.	11	[87]
3.	Rice husks	The rice husks were dewaxed by adding180 ml of n-hexane and 90 mL of ethanol in Soxhlet system at 80 ^oC for 13 h.	Alkali pre-treatment: dewaxed rice husks were treated with 10% of NaOH at 55 ^oC for 90 min.	0.01 g of Mn_3O_4/ZSM-5, 2 ml of 40% H_3PO_4 and 0.05 ml of 30% H_2O_2 at 130^oC, for 8 h.	14	[88]
			Ultrasonication: Dewaxed rice husks were dissolved in 40 % of H_3PO_4 then ultrasonicated for 30 minutes		8	
			Ball milling: ZrO_2 balls (rice husks: ZrO_2 1:2 w/w) for 30 minutes and 60 minutes.		6	

4.	Rice husks	Soxhlet extraction: 100 °C, 12 h,		4.5 % HCl, 170 °C and 60 min	59	[89]
5.	Gelidium amansii	Acid pre-treatment: 9 % H_2SO_4, 70 °C,72 h		3 % H_2SO_4, 180 °C, 40 h	21	[90]
6.	Ecotype torviscosa	Acid pre-treatment: HCl, 80 °C, 2h		37% HCl, 190 °C, 1 h	23	[91]
7.	Rice straw	Steam explosion: 200 °C (1.5 MPa) for 6 min by saturated steam	Superfine grinding of RS and SERS using a fluidized bed opposed jet mill. to perform superfine grinding at 15 kg h^{-1} of feed load, 4544 rpm of rotational speed and 25 min of grinding time.	S_2O_2-8 /ZrO_2-Sm_2O_3, 200 °C, ~0.17 h	23	[92]
8.	Cotton straw	Dilute acid pre-treatment: 0.2 M H_2SO_4, 120 °C, 20 min		0.2 M H_2SO_4, 180 °C, 60 min	10	[93]
9.	Bagasse	Dilute acid pre-treatment: 0.4 M HCl, 110 °C, 40 min		0.4 M HCl, 200 °C, 20 min	59	[94]

lignin, hemicellulose, and cellulose, causing the structure of lignocellulosic materials to be disrupted [82]. Chemical pre-treatments that are often used include dilute and concentrated acid pre-treatment, alkaline hydrolysis, organosolv pre-treatment, and so on [95-97]. Biological pre-treatments use microorganisms and/or enzymes and are conducted at mild conditions (around ambient temperature and pressure), consuming less energy and chemicals, and producing fewer inhibitors. The ligninolytic enzyme system, a collection of oxidoreductases that can enhance the decomposition of lignin, is used in the majority of biological pre-treatments.

However, several elements of biological pre-treatment, such as incubation duration and overall efficiency (i.e., sugar yield), still need to be improved before it can be considered a viable alternative to thermochemical pre-treatment [98, 99]. Physicochemical pre-treatments are techniques that combine the benefits of physical cellulose disturbance with chemical processing [100].

2.2.2.2 Biomass-based levulinic acid production (one-pot synthesis)

Table 2.3 shows the one-pot synthesis of LA from several kinds of biomass, with different catalysts and reaction conditions utilized in most cases. Experiments 15 and 18 by Galletti et al. [4] in table 2.3 show two experiments with different types of biomass but the same reaction conditions that yielded a 9 % difference in LA yield, demonstrating that substrate has an impact on LA yield and that these results may be due to different cellulose content in biomass.

Yan et al. [5] utilized different biomass and the same reaction conditions, resulting in a 1% variation in LA production. Table 2.3 further demonstrates that several types of catalysts, such as homogeneous, heterogeneous, and ionic liquids, were employed in the one-pot synthesis of LA from biomass. Table 2.3 also demonstrates that there are many factors to consider in a reaction before it can be commercialized; it is not just a high yield of the end product, as experiment numbers 2 and 5 have the highest LA yield in the reported data, but those catalysts have not been commercialized, and the research into LA production is still ongoing.

The availability and cost of the substrate, environment impact, activity and cost of the catalyst and solvent, utilization of energy and water during the reaction while taking into account the temperature, time, and water flow of the reaction are all factors to consider in a reaction. Developing a sustainable approach for LA manufacture from biomass is critical, and one of the benefits of one-pot synthesis is that it saves time and energy necessary to generate the LA, lowering the overall cost of the process. The drawback is that lignin and hemicellulose are not removed to be used independently, even though the mixed solids are evaluated for energy supply via burning [2].

Table 2.3 Illustrate one-pot synthesis of LA from biomass.

No.	Substrate	Catalyst	Temperature (ºC)	Time (minutes)	LA yield (wt.%)	Reference
1.	Bagasse	4.45 wt% HCl	220	45	23	[5]
2.	Bamboo shoot shell	0.9 M $[C_4mim]HSO_4$	145	104	18	[101]

3.	Barley straw	H_2SO_4	158	900	0.003	[102]
4.	Bamboo	$[C_4(Mim)_2][2HSO_4)(H_2SO_4)_4]$	100	60	48	[103]
5.	Cotton straw	H_2SO_4	180	60	10	[93]
	Corn stover	$HCl/ClCH_2CH_2Cl$	80-100	180	5-9	[104]
7.	Corn stalk	$FeCl_3$	230	10	49	[105]
8.	Corncob	Acid modified zeolites	200	60	0.01	[106]
9.	Eucalyptus wood chips	H_2SO_4	180	90	57	[87]
10.	Empty fruit bunch	Hybrid of HY zeolite and $CrCl_3$	145	146	53	[77]
11.	Eucalyptus wood chips	H_2SO_4	180	90	57	[87]
12.	Empty fruit bunch	Hybrid of HY zeolite and $CrCl_3$	145	146	53	[77]
13.	Giant reed	0.4 M HCl	180	60	23	[91]
14.	Kenaf	Hybrid of HY zeolite and $CrCl_3$	145.2	147	66	[77]
15.	Olive tree pruning	37 % HCl	200	60	20	[4]
16.	Oil palm fronds	7.27 g $[SMIM][FeCl_4]$	154.5	222	25	[107]
17.	Paddy straw	4.45 wt% HCl	220	45	24	[5]
18.	Poplar sawdust	37 % HCl	200	60	29	[4]
19.	Sorghum grain	8% H_2SO_4	200	40	33	[6]
20.	Wheat straw	3% H_2SO_4	210	42	41	[108]
21.	Water hyacinth	1 M H_2SO_4	175	30	53	[7]

2.3 The impact of the catalysts, solvents, and reaction conditions on LA yield

2.3.1 Catalyst

a) Homogeneous catalysts

A homogeneous catalyst is a type of catalyst that is in the same phase as the reactants in a reaction. Hydrochloric acid [93, 109], sulfuric acid [52, 110], phosphoric acid [5], hydrobromic acid (Hbr) [110], and methanesulfonic acid are examples of widely used homogeneous catalysts for levulinic acid [52]. According to the literature, the efficacy of a mineral acid on the formation of LA is determined by the strength of their dissociation constants (pKa); HCl = -8, H_2SO_4 = -3, and H_3PO_4 = 2.15. As a result, its efficacy follows the following pattern: HCl > H_2SO_4 > H_3PO_4 [111, 112]. Other variables that influence mineral acid reactivity include the strength and concentration of the catalyst, the type and concentration of the feedstock, and the reaction conditions, which include temperature and time [64, 79].

The use of homogeneous catalysts has demonstrated high catalytic activity in the production of levulinic acid from biomass sugars; however, there are limitations such as corrosion of equipment, formation of undesirable by-products, difficulty in recovering and recycling the acid, and contributing to pollution of the environment [8]. Homogeneous catalysts are widely utilized due to their inexpensive cost, availability, and high activity. Table 2.4 shows how homogeneous catalysts affect the LA yield. It is difficult to determine which catalyst is more efficient because their efficiency varies depending on reaction conditions and feedstock type [113].

Looking at the formation of LA from monosaccharides using homogenous catalysts it is observed that a high amount of substrate leads to a lower yield of LA which may be due to humin formation since a high concentration of feedstock has a greater impact on humin production than it does on the desired products [113]. Comparing the production of LA from monosaccharides using homogeneous catalysts in table 2.4, Rackemann and Doherty. [63] was able to increase the LA yield when using monosaccharides containing glucose and xylose catalyzed by H_2SO_4, ethanesulfonic acid (ESA), and methanesulfonic acid (MsOH), yielding 66 wt.%, 62 wt.%, and 61 wt.%, respectively, which could be attributed to the addition of xylose. A similar observation was observed by Rackemann et al. [52], where production of LA from glucose when catalyzed with H_2SO_4 not only increased the LA yield (42 wt.%) but also decreased the time substantially by 50 %.

Table 2.4 Show how homogeneous catalysts affect LA yield when manufactured from monosaccharides and polysaccharides.

No.	Substrate and conc. (wt.%)	Solvents	Catalysts	Reaction conditions	LA yield (wt.%)	References
Monosaccharides						
1.	Glucose (36) and xylose (7)	Water	0.50 M H_2SO_4	180 ºC, 30 min	66	[63]
2.	Glucose (36) and xylose (7)	Water	0.50 M ESA	180 ºC, 30 min	62	[63]
3.	Glucose (36) and xylose (7)	Water	0.50 M MsOH	180 ºC, 30 min	61	[63]
4.	Glucose (2)	Water	0.5 M H2SO4	180 ºC, 15 min	42	[52]
5.	Glucose (10)	Water	0.1 M HCl	160 ºC, 4h	41	[50]
6.	Glucose (9)	Water	6 wt.% HCl	160 ºC, 15 min	41	[114]
7.	Glucose (2)	Water	0.5 MsOH	180 ºC, 15 min	41	[52]
8.	Glucose (7)	Water	7 mol% $MgCl_2$; 7 mol% HCl	3h	39	[115]
9.	Glucose (2)	Water	1 M H_2SO_4	140 ºC, 2h	38	[116]
10.	Glucose (2)	Water	1M TFA	180 ºC, 1h	37	[49]
11.	Glucose (5)	Water	5 wt.% H_2SO_4	170 ºC, 2h	34	[117]
12.	Glucose (30)	Water	5 wt.% HCl; 9 wt.% NaCl	22 h	31	[118]
13.	Glucose (12)	Water	30 wt.% H_2SO_4	100 ºC, 24 h	30	[119]
14.	Glucose (13)	Water	1M HCl	141 ºC, 1h	29	[48]

15.	Glucose (13)	Water	1M H_2SO_4	141 ºC, 1h	29	[48]
16.	Glucose (30)	Water	5 wt.% HCl	162 ºC, 1 h	24	[120]
17.	Glucose (1)	Water	72 mol% H_3PO_4	170 ºC, 4.5h	8	[51]
Polysaccharides						
1.	Cellulose (1.98)	Water: GVL(1:1)	1.25 M HCl; 17 wt.% NaCl	155 ºC, 1.5 h	52	[121]
2.	Cellulose (1.6)	Water	0.97 M HCl	180 ºC, 20 min	44	[122]
3.	Cellulose (1.7)	Water	1 M H_2SO_4	150 ºC, 2 h	43	[109]
4.	Cellulose (3)	Water	3 wt.% H_2SO_4	230 ºC, 4h	35	[123]
5.	Cellulose (10)	Water	3 wt.% HCl	250 ºC, 2h	29	[110]
6.	Cellulose (10)	Water	3 wt.% HBr	250 ºC, 2h	27	[110]
7.	Cellulose (10)	Water	3 wt.% H_2SO_4	250 ºC, 2h	25	[110]

b) Heterogeneous catalysts

A heterogeneous catalyst is a type of catalyst that is in a different phase from the reactant in a reaction. There were drawbacks to employing a homogeneous catalyst such as equipment corrosion, difficulty in recovering, and recycling the acid especially sulfuric acid, which is utilized in the commercialization of LA in a process known as Biofine. Due to these constraints, constant research into catalysts to substitute sulfuric acid was conducted, and heterogeneous catalysts were studied. According to the literature, heterogeneous catalysts used for LA synthesis do not induce corrosion in the equipment and are selective, despite the fact that they are difficult to recover, recycle, and produce poor LA yield. A variety of heterogeneous catalysts have been employed for LA synthesis, including amberlyst 70 [50], amberlite IR-120, LZY-zeolite, nafion SAC-13, and graphene oxide [124, 125], ZSM-5 and $CrCl_3$, HY zeolite [126], $CoSO_4$, $Fe(SO_4)$ [123, 127, 128]. So far, no heterogeneous catalyst has been able to overcome the limits of the Biofine process, implying that the search for a suitable catalyst continues.

Table 2.5 shows that there are solid catalysts that yield high LA and the catalyst can be reused, an example is experiment no. 9, Upare et al. [125] produced LA by catalysing glucose with Heterogeneous graphene oxide-sulfonic acid (GO-SO_3) which is a combination of Bronsted and Lewis acid. Lewis acid speeds up the conversion of glucose to fructose and Bronsted acid enhances the conversion of fructose to LA, a combination of Lewis acid and Bronsted acid is recommended for the conversion of glucose to LA [113]. The active sites are the Bronsted acid SO_3H sites, although the inclusion of additional functional groups, such as carboxyl and hydroxyl, is also significant in improving glucose adsorption for the process. The layered morphology of GO–SO_3H allows for fast diffusion of reactants and products, and the sulfonate groups are thermally stable and do not leach into the reaction mixture. The catalyst is recyclable with low activity loss and can be utilized as an initial bio-based cellulose feedstock or other biobased sugars. GO-SO_3 is a good catalyst although humins were formed which lowers LA yield but the great thing is that humins also have important applications such as organic acids, humins oils like phenolics and furans, syngas, sulfonated catalyst, and composites and resins [113].

Table 2.5 shows that the second-highest LA production in several experiments was 62%, achieved by Rackemann et al. [63] and Ya'aini et al. [126] utilizing varied catalysts, conditions, and substrate concentration. Zuo et al. [129] produced 65% of LA from cellulose catalyzed by Sulphonated chloromethyl polystyrene resin (CP-SO_3H) in a solvent combination of H_2O/GVL, although the process was prolonged. Lin et al. [130] produced 54 wt.% of LA catalyzed by Zirconium dioxide (ZrO_2). Joshi et al. [131] utilized ZrO_2 catalysts identical to Lin et al. [130], but increased parameters such as temperature, catalyst concentration, and duration, yielding 2% less LA that is 52 wt.%.

Table 2.5 Depicts the LA yield when a heterogeneous catalyst is used.

No.	Substrate and conc. (wt. %)	Solvents	Catalysts	Reaction conditions	Yield (wt.%)	References
Monosaccharides						
1.	Glucose (15)	Water	1.7 wt.% GO-SO_3H	200 ºC, 2h	79	[125]
2.	Glucose (2) and xylose (0.5)	Water	0.50 M TSA	180 ºC, 0.5 h	62	[63]
3.	Glucose (1)	Water	100 wt.% Cr/HY	160 ºC, 3h	62	[126]
4.	Glucose (13)	Water	0.2 wt.% Silphonated graphene oxide	200 ºC, 2h	50	[132]
5.	Glucose (1)	Water	12 wt.% $CrCl_3$ + HY zeolite hybrid	145.2 ºC, 2.45 h	47	[77]
6.	Glucose (15)	Water	20 wt.% Ru/HZSM-5	200 ºC, 1h	38	[133]
7.	Glucose (15)	Water	20 wt.% Ru/Al-SBA15	200 ºC, 1h	29	[133]
8.	Glucose (15)	Water	10 wt.% Ni/Al-SBA-15	200 ºC, 1h	29	[133]
9.	Glucose (15)	Water	10 wt.% Ru/Al-SBA15	200 ºC, 1h	28	[133]
10.	Glucose (10)	Water	0.1 M Zirconium phosphate	160 ºC, 3h	14	[50]
11.	Glucose	Water	3 wt.% Clay	150 ºC, 24h	12	[134]
12.	Glucose (27)	Water	19 wt.% Amberlite IR-120	25 ºC, 124 h	6	[135]
13.	Glucose	Water	3 wt.% HY-zeolite	150 ºC, 24h	6	[134]
Polysaccharides						
1.	Cellulose (5)	H_2O/GVL 10 wt%	300 wt.% CP-SO_3H	170 ºC, 10 h	65	[129]
2.	Cellulose (2)	water	100 wt.% ZrO_2	180 ºC, 3h	54	[130]
3.	Cellulose (10)	water	50 wt.% ZrO_2	240 ºC, 0.33h	52	[131]

4.	Cellulose (2)	Water-GVL (10:90)	6 wt. % Amberlyst 70	160 ºC, 16 h	49	[136]
5.	Cellulose (2)	Water	0.02 M $CrCl_3$	200 ºC, 3h	48	[137]
6.	Cellulose (4)	Water-GVL (10:90)	300 wt.% Polystyrene resin Sulfonated chloromethyl	170 ºC, 10 h	47	[129]
7.	Cellulose (2)	Water	2 wt.% ZrO_2	180 ºC, 3h	39	[131]
8.	Cellulose (5)	Water	80 wt.% Polystyrene resin Al-$NbOPO_4$	180 ºC, 24h	38	[138]
9.	Cellulose (1.25)	5 wt% NaCl-H_20	60 %Fe/H- resin	200 ºC, 5h	33	[139]
10.	Cellulose (4)	Water	500 wt.% Sulfonated chloromethyl	170 ºC, 10h	24	[131]
11.	Cellulose (1.25)	5 wt% NaCl-H_20	60 % H-resin	200 ºC, 5h	20	[139]
12.	Cellulose (4)	Water	4 wt.% Zrp	220 ºC, 2h	12	[50]
13.	Cellulose (0.5)	water	30 micro mol Lanthanum (III)chloride	250 ºC, 0.042 h	2.3	[127]

c) Ionic liquids

Ionic liquids (ILs) are a class of salts that are liquid at room temperature. ILs can be employed as a solvent or a catalyst [8]. They are often referred to as "designer solvents" because they may be tailored to meet specific needs by modifying cations or anions [27]. For example, ILs containing an anion such as chloride and acetate and possessing a strong hydrogen bond basicity are capable of dissolving a high yield of cellulose [28]. Furthermore, the inclusion of sulfonic acid (SO_3H) groups and carboxylic acid groups in the ILs improve acidity and water solubility, resulting in an ecologically favourable acidic catalyst [27, 29]. In comparison to the volatile organic solvents often employed in industry, ILs have negligible vapour pressure, thus the evaporation of ILs into the atmosphere is limited, reducing environmental pollution. As a result, ILs are considered green solvents [8, 30]. Other key features of ILs include a wide temperature range in the liquid phase, which can enhance kinetic control in liquid phase processes; strong thermal and electrical conductivity; a broad electrochemical window; and good electrochemical stability against redox reactions [31]. The majority of ILs are non-flammable, thermally and chemically stable, and may be recovered and recycled.

Catalytic conversion of biomass to LA in an ionic liquid called 1-ethyl-3-methylimidazolium chloride ([EMim][Cl]) with a hybrid catalyst ($CrCl_3$ and HY-zeolite) yielded 46 wt.% of LA from cellulose, while empty fruit bunch yielded 20 wt.% of LA in the presence of IL, but only 15.5 wt.% in the absence of IL [126]. Microwave-assisted synthesis in SO_3H-functionalized ILs yielded 55 wt.% of LA from cellulose [140]. Table 2.6 shows the production of LA from glucose, cellobiose, and cellulose catalysed by ionic liquids. Alipour and Omidvarborna. [132] illustrated the effect of a catalyst in LA production since they use fructose as a feedstock and same concentration, similar temperature and time with various catalysts which resulted in different LA yields. [BSMim]HSO_4 produced the maximum LA yield of 61 wt%, [EMim]HSO_4 produce 1.73 wt% while [EMim]CF_3O_3 didn't produce LA. The excellent performance of [BMIM-SO_3H]HSO_4 combination with water, compared to [EMIM]TFO or [EMIM]HSO_4, can be ascribed to the high acidic strength of [BMIM-SO_3H]HSO_4. Because IL acidity plays an important role in the catalytic conversion of fructose to LA and the pH of [BMim-SO_3H]HSO_4 is zero at room temperature.

Ramli and Amin. [141] also used similar reaction conditions to produce LA from glucose catalysing with different catalysts where [SMim]$FeCl_4$, [SMim]Cl, [BMim]$FeCl_4$ yielded 68 wt.%, 26 wt.% and 22 wt.% of LA respectively. The remarkable activity of [SMim][$FeCl_4$] is most likely due to its acidity, which contains both Lewis and Bronsted acid sites. It has been proven that the Lewis acid site is more active than the Bronsted acid site in catalyzing the isomerization of glucose. Bronsted acid sites, on the other hand, are required for 5-HMF rehydration to LA.

Li et al. [94] used 0.125 g of cellobiose, a disaccharide to produce LA catalysed by various ILs, utilized similar reaction conditions for all the experiments (150 ^{o}C, 3h, and O_2 at 3 Mpa), these experiments yielded different LA yield with a range of 0-46 %. Catalysing cellobiose with 4.33 wt.% [PyBS]HSO_4 resulted in 0 % of LA whereas utilizing 4.33 wt.% of $[PyBS]_5PV_2MO_{10}O_{40}$ to catalyse the reaction resulted in 46 wt.% of LA. Sun et al. [142] used similar reaction conditions for two experiments, the difference was a catalyst and the yield difference was 14 % between the two catalysts [PrSMim]$H_2PW_{12}O_{40}$ and $[PrSMim]_2$ $HPW_{12}O_{10}$, the difference was due to Bronsted acidity. $[PrSMim]_2HPW_{12}O_{10}$ had a lower Bronsted acidity. Their research showed that increasing the acidic strength of the catalysts can speed up the conversion of HMF to LA, hence [MIMPSH]H_2PW produced a significant quantity of LA (63 wt.%).

Amarasekara and Wiredu. [128] yielded 25 wt.% of LA by using prolong the time of 48 h and temperature of 150 °C catalysing the reaction with [PSMI]Cl, this showed the effect of time how long reaction time favoured low LA due to the formation of unnecessary products including humins. Ramli and Amin. [143] used Fe/HY catalyst with [BMim]Br to obtain good cellulose hydrolysis performance, since Fe/HY is a solid catalyst with acidic sites and [BMim]Br promoted cellulose dissolution. Cellulose was catalyzed with Fe/Hy in [BMim]Br at 120 °C for 3 hours, producing 72 wt.% of LA. For the conversion of cellulose to LA, Fu et al. [144] studied eighteen different types of ionic liquids with various anions. The conversion of cellulose to LA was shown to be ubiquitous in ionic liquids containing haloids and hydrogen sulfates.

In all the catalysts used [PrSMim]Cl yielded a maximum LA yield of 65 wt.% using cellulose as a substrate, the best catalytic effect showed by this catalyst is due to the IL anion, it was proven in this study that the acidities of ionic liquids are determined by the anions and have an impact on the yield of LA. The higher the acidity of ionic liquids, the larger the production of LA. Although the anion of Cl^- has a lesser acidity than HSO_4^-, it helps to disrupt the large hydrogen-bonding network of cellulose, resulting in rapid dissolution, hence higher LA was produced. In table 2.6, the catalysts of lines 25-34 in polysaccharides did not all produce LA, which may be attributed to their anions or reaction conditions were not ideal for those ILs

Table 2.6 Demonstrate the role of ionic liquids as catalysts in the formation of LA.

No.	Substrate and conc.	Solvents	Catalysts	Reaction conditions	LA Yield (wt. %)	References
Monosaccharides						
1.	2.5 wt.% Fructose	H_2O	75 wt.% [BSMim]HSO_4	95 °C, 1h	61	[132]
2.	2.5 wt.% Fructose	H_2O	75 wt.% [EMim]HSO_4	95 °C, 1h	2	[132]
3.	2.5 wt.% Fructose	H_2O	75 wt.% [EMim] CF_3SO_3	95 °C, 1h	0	[132]
4.	Glucose	H_2O	5.45 g [SMim] $FeCl_4$	154.5 °C, 4.2 h	69	[107]
5.	0.1g Glucose	10 ml H_2O	10 g [SMim] $FeCl_4$	150 °C, 4 h	68	[143]

6.	0.1 g Glucose	10 ml H_2O	10 g [SMim]Cl	150 °C, 4 h	26	[143]
7.	0.1 g Glucose	10 ml H_2O	10 g $[Bmim]FeCl_4$	150 °C, 4 h	22	[143]
Disaccharides						
1.	0.125 g Cellobiose	10 ml H_2O	5 mol% $[PyBS]_5PV_2Mo_{10}O_{40}$	150 °C, 3 h, O_2 3 MPa	46	[94]
2.	0.125 g Cellobiose	10 ml H_2O	5 mol% $[PyBS]_4SiW_{12}O_{40}$	150 °C, 3 h, O_2 3 MPa	41	[94]
3.	0.125 g Cellobiose	10 ml H_2O	5 mol% $[PyBS]_4 HPV^2Mo_{10}O_{40}$	150 °C, 3 h, O_2 3 MPa	41	[94]
4.	0.125 g Cellobiose	10 ml H_2O	5 mol% $[PyBS]_3PW_{12}O_{40}$	150 °C, 3 h, O_2 3 MPa	36	[94]
5.	0.125 g Cellobiose	10 ml H_2O	5 mol% $[PyBS]_3 H_2PV^2Mo_{10}O_{40}$	150 °C, 3 h, O_2 3 MPa	35	[94]
6.	0.125 g Cellobiose	10 ml H_2O	5 mol% $[PyBS]_3PMo_{12}O_{40}$	150 °C, 3 h, O_2 3 MPa	32	[94]
7.	0.125 g Cellobiose	10 ml H_2O	5 mol% $[BSMim]_3PW_{12}O_{40}$	150 °C, 3 h, O_2 3 MPa	29	[94]
8.	0.125 g Cellobiose	10 ml H_2O	5 mol% $[TEABS]_3PW_{12}O_{40}$	150 °C, 3 h, O_2 3 MPa	26	[94]
9.	0.125 g Cellobiose	10 ml H_2O	5 mol% $[PyBS]_6P_2W_{18}O_{62}$	150 °C, 3 h, O_2 3 MPa	10	[94]
10	0.125 g Cellobiose	10 ml H_2O	5 mol% $[PyBS]_6P_2Mo_{18}O_{62}$	150 °C, 3 h, O_2 3 MPa	9	[94]
11.	0.125 g Cellobiose	10 ml H_2O	5 mol% $H_3PW_{12}O_{40}$	150 °C, 3 h, O_2 3 MPa	3	[94]
12.	0.125 g Cellobiose	10 ml H_2O	5 mol% $[PyBS]HSO_4$	150 °C, 3 h, O_2 3 MPa	0	[94]
Polysaccharides						
1.	0.1 gm Cellulose	0.1 gm H_2O	2 mg [BMim]Br	120 °C, 3 h	72	[143]
2.	0.1 g Cellulose	2 g H_2O	2 g [PrSMim]Cl	180 °C, 3 h	65	[145]

3.	0.1 g Cellulose	10 wt.% H_2O/MIBK	0.7 mmol $[PrSMim]H_2PW_{12}O_{40}$	140 ºC, 12 h	63	[142]
4.	0.1 g Cellulose	2 g H_2O	2 g [PrSPy]Cl	180 ºC, 3 h	54	[145]
5.	25 mg Cellulose	75 mg H_2O	1 ml $[C_4(Mim)_2](2HSO_4)(H_2SO_4)_2$	100 ºC, 2 h	51	[103]
6.	0.1 g Cellulose	2 g H_2O	2 g [BSMim]Cl	180 ºC, 3 h	50	[145]
7.	0.1 g Cellulose	10 wt.% H_2O/MIBK	0.7 mmol $[PrSMim]_2HPW_{12}O_{40}$	140 ºC, 12 h	49	[142]
8.	0.1 g Cellulose	2 g H_2O	2 g $[BSMim]HSO_4$	180 ºC, 3 h	49	[145]
9.	250 mg Cellulose	2g H_2O	3.3 mmol $[PrSMim]HSO_4$	160 ºC, 30 min	45	[140]
10.	250 mg Cellulose	2g H_2O	3.3 mmol $[PrSN_{111}]HSO_4$	160 ºC, 30 min	43	[140]
11.	250 mg Cellulose	2g H_2O	3.3 mmol $[PrSPy]HSO_4$	160 ºC, 30 min	41	[140]
12.	250 mg Cellulose	2g H_2O	3.3 mmol $[BSMim]HSO_4$	160 ºC, 30 min	41	[140]
13.	0.1 g Cellulose	2 g H_2O	2 g $[BMim]HSO_4$	180 ºC, 3 h	40	[37]
14.	0.05 g Cellulose	H_2O	1.5 g $[BSMim]HSO_4$	120 ºC, 2 h	39	[27]
15.	250 mg Cellulose	2g H_2O	3.3 mmol $[PrSMim]CH_3SO_3$	160 ºC, 30 min	36	[140]
16.	0.1 g Cellulose	2 g H_2O	2 g [HOOCMim]Br	180 ºC, 3 h	36	[145]
17.	0.1 g Cellulose	2 g H_2O	2 g [HOOCMim]Cl	180 ºC, 3 h	33	[145]
18.	25 mg Cellulose	75 mg H_2O	1 ml $[C_4(Mim)_2](2HSO_4)$	100 ºC, 2 h	31	[103]
19.	0.1 g Cellulose	2 g H_2O	2 g [AlPy]Cl	180 ºC, 3 h	28	[145]
20.	150 mg Cellulose	54 wt.% H_2O/EtOH	33 wt.% [PSMI]Cl	150 ºC, 48 h	25	[146]

21.	0.1 g Cellulose	10 wt.% H_2O/MIBK	0.7 mmol $[PrSMim]_3PW_{12}O_{40}$	140 °C, 12 h	23	[142]
22.	25 mg Cellulose	75mg H_2O	1 ml $[C_4(Mim)_2]$ $(2CH_3SO_3)$	100 °C, 2h	23	[103]
23.	25 mg Cellulose	75 mg H_2O	1 ml $[C_4(Mim)_2]$ $(2CF_3SO_3)$	100 °C, 2 h	15	[103]
24.	250 mg Cellulose	2g H_2O	3.3 mmol $[PrSMim]$ H_2PO_4	160 °C, 30 min	4	[140]
25.	0.1 g Cellulose	2 g H_2O	2 g $[BMMim]CH_3SO_3$	180 °C, 3 h	0	[145]
26.	0.1 g Cellulose	2 g H_2O	2 g $[BMim]CH_3SO_3$	180 °C, 3 h	0	[145]
27.	0.1 g Cellulose	2 g H_2O	2 g [BMim]Ts	180 °C, 3 h	0	[145]
28.	0.1 g Cellulose	2 g H_2O	2 g [BMMim]Ts	180 °C, 3 h	0	[145]
29.	0.1 g Cellulose	2 g H_2O	2 g [EMim]Ts	180 °C, 3 h	0	[145]
30.	0.1 g Cellulose	2 g H_2O	2 g $[HexMim]CF_3SO_3$	180 °C, 3 h	0	[145]
31.	0.1 g Cellulose	2 g H_2O	2 g $[BMMim]CF_3SO_3$	180 °C, 3 h	0	[145]
32.	0.1 g Cellulose	2 g H_2O	2 g $[AlMim]CH_3COO$	180 °C, 3 h	0	[145]
33.	0.1 g Cellulose	2 g H_2O	2 g [AlMim]HCOO	180 °C, 3 h	0	[145]
34.	0.1 g Cellulose	2 g H_2O	2 g [EMim] $(MeO)HPO_2$	180 °C, 3 h	0	[145]

2.3.2 Solvents

Solvents such as water and organic solvents have been shown to influence the LA yield [8]. The requirements for solvents comprise the selectivity, the improvement of LA output, solvent environmental effect, mobility, acute human toxicity, chronic human toxicity, acute aquatic organism toxicity, environmental persistence, and bioaccumulation [10]. Solvents with different polarities (protic, aprotic) and extracting solvents that are involved in producing levulinic acid are discussed below:

a) Protic solvents

Water is the sole solvent that meets the above-mentioned characteristics for a suitable solvent [147], however, Qi et al. [128] found that, while water is an environmentally benign solvent, its ionization produces formic acid and humins, which reduces the levulinic acid output. Other typical protic solvents used in the production of LA include ethanol and butanol [148, 149].

b) Aprotic solvents

Dimethyl sulfoxide (DMSO), methyl isobutyl ketone (MIBK), tetrahydrofuran (THF), carbohydrachloride, ethyl acetate, dimethyl acetamide, and acetone, etc, have been utilized as polar aprotic solvents for LA's development [50]. Aprotic solvent generates increased LA output as compared to the protic solvent [148]. Shimizu et al. [150] obtained 100% of HMF yields with amberlyst-15 with DMSO in fructose dehydration. Since DMSO has a higher boiling point, the product separation and purification are more energy-intensive. This results in high process costs, recovery techniques, and energy expenses. The use of DMSO as the solvent in levulinic acid synthesis is suspected to produce sulfur with hazardous by-products [8]. Some other solvent systems that have also been explored are lithium chloride/N,N'-dimethyl acetamide (LiCl/DMAc), N-methylmorpholine-N-oxide, DMSO/ tetra-n-butylammonium fluoride (TBAF), molten salt hydrates, and sodium hydroxide/urea. However, all these systems have certain drawbacks, such as volatility, toxicity, expense, difficulties with solvent recovery, the need for high temperatures, cellulose degradation, or application instability [27].

c) Extracting solvents

γ-Valerolactone (GVL), a levulinic acid derivative, has been identified as a possible solvent for producing LA from biomass. The benefit of this reaction is that GVL concurrently transforms cellulose and hemicellulose into LA. In the presence of GVL, cellulose is converted to levulinic acid by HMF, while hemicellulose is converted to LA by furfural [132, 136]. When furfural is boiled in ethyl methyl ketone in the presence of HCl, it is transformed to furfural alcohol, which then yields around 90-93 wt.% of LA by hydroxylation [56].

Wettstein et al. [121] described a biphasic system for the synthesis of levulinic acid that included GVL and an aqueous solution of HCl (0.1-1.25 M) with a solute such as sugar or salt. The reaction was carried out at 154 ^{o}C, and the bulk of LA was extracted by GVL, producing

70 wt.% LA. Dichloromethane, secondary butanol, methyl isobutyl ketone, and other solvents have been employed in the extraction [151]. Solvents are expensive to use owing to the huge volume needs and the expense of recovery; thus, a solvent with a high partition coefficient between the phases should be used to minimize the volume of solvent required, hence minimizing the energy input [152]. As a result, novel solvents or the use of co-solvents that improve product yield and may be used on a larger scale with low-cost effects are required [8].

d) Supercritical fluids

Another kind of solvent with fascinating characteristics that can be used to enable more selective reactions and efficient product separation is supercritical fluids. Supercritical fluids are acidic and basic solvents, allowing for selective reactions and efficient elimination of LA [8, 112]. Water, carbon dioxide, and ammonia are examples of supercritical fluids, which have the characteristics of both liquids and gases at temperatures and pressures above their critical point [8]. The LA intermediate (HMF) has been generated using supercritical fluids such as water, acetone, and carbon dioxide, according to research [153, 154].

The LA yield obtained with water and acetone is lower than the yield obtained with carbon dioxide, which is due to the properties of supercritical fluids, which allow for better separation of product from the reaction mixture by limiting by-product generation. Higher operating pressures, on the other hand, raise the cost of equipment, as well as capital investment and operational expenditures.

2.3.3 Effect of reaction conditions on LA yield (namely time, temperature, and catalyst loading)

a) Effect of temperature on LA production

Temperature is vital to the efficiency of converting cellulose in biomass waste into LA during the process of reaction. When the temperature is below 320°C, cellulose is insoluble in water due to inter- and intramolecular hydrogen bonding [113]. Hence higher temperature can accelerate cellulose hydrolysis which will lead to higher conversion, but they can also have unwanted side reactions. While lower temperature affects the reaction negatively [5]. Rackemann and Doherty. [63] observed that temperature has a directly proportional relationship with LA yield and increasing temperature in the range of 150°–230°C increases the LA yield. The yield of LA from biomass increases with increasing temperatures in the range with many researchers finding an optimum temperature of 200°–220°C.

The effect of reaction temperature varies with biomass [113]. Ramli and Amin. [141] found that when glucose was catalyzed with [BMIM][$FeCl_4$] at 170 ^oC, maximum LA was produced, as compared to 150 ^oC. This is owing to the fact that higher temperatures speed up the reaction rate and improve conversion efficiency. Because atoms donate or receive electrons more easily at higher temperatures, speeding up chemical reactions. Fu and co-workers observed that at 140 °C, the LA yield was 36.3 wt.% after 210 min, while at 180 °C, the LA yield was 53.4 wt.% in 30 min [145]. Similarly, Alipour and Omidvarborna. [132] investigated the influence of temperature on the formation of LA from fructose. The experiments were carried out at various temperatures (80, 85, 90, and 95 °C). Fructose and HMF were completely converted at the highest applied temperature, 95 °C, and the LA yield was 70 wt.%.

b) Effect of time on the LA production

Yan et al. [5] used biomass and paddy straw to study the effect of time in LA production, where they observed the that low reaction time of 15 min didn’t start the hydrolysis and that there was a difference in kinetics that may be due to different cellulose content and intrinsic composition structure. It was also observed that 45 min reaction leads to the production of side reactions because of degradation of products due to long reaction time and high temperature. The effect of reaction time on LA yield was found to be dependent on the intrinsic composition of the cellulose content of the biomass source [63].

c) Effect of catalyst loading on the LA production

Increasing the catalyst loading increases LA yield up to a critical catalyst loading limit which depends on other processing conditions and the feedstock [63]. After all, it has been observed that too aggressive conditions lead to a higher prevalence of side reactions and re-polymerization of products which leads to low LA yield.

2.4 Isolation and recovery of LA

Despite several studies to enhance LA production, LA separation from the acidic aqueous solution remains problematic. Downstream processing is even considered as an impediment to the large-scale synthesis of LA through hydrolysis since it accounts for 50–70% of the overall cost of LA production. Efficient isolation procedures are required to enhance the product's recovery rate and purity. The downstream processing cost for LA separation is largely dependent on the reaction conditions. High LA yields are often achieved in solutions with low feedstock concentrations, while low LA concentration leads to high isolation costs [113].

2.5 Levulinic acid as a platform chemical

LA is used as a building block for generation of various chemicals which includes methyltetrahydrofuran (MTHF), δ-amino levulinic acid (DALA), ethyl levulinate, gamma-valerolactone (GVL), pyrrolidone and diphenolic acid (DPA) are examples of levulinic acid derivatives [63, 155, 156]. These second-generation chemicals derived from LA and LA itself has shown applications in a variety of industries, including medicines, plasticizers, perfumes, and cosmetics. In the coming section, a few LA derived chemicals have been discussed.

2.5.1 Diphenolic acid (DPA)

The typical DPA production method is the condensation of LA with phenol, which is usually catalyzed by mineral acids such as hydrochloric acid or sulfuric acid [157]. These acids often have drawbacks such as corrosivity, difficulty in handling, separation, and waste management. Environmental and economic concerns have prompted the substitution of hazardous and corrosive chemicals [26]. Hence, heterogenous catalysts and ILs have been utilized in DPA synthesis as catalysts. Guo et al. [158] synthesized DPA at 100 °C for 8 hours using tungstophosphoric acid (TPA) supported on silica ($H_3PW_{12}O_{40}$/SBA-15-C-15.7) and HCl, producing 98.4 wt.% and 96.5 wt.%, respectively. Shen et al. [37] produced 99.5 wt. % DPA for 24 hours at 60 °C using an IL catalyst named 1-butyl (4-sulfonic acid)-3-methylimidazolium hydrogen sulfate ([BSMim][HSO_4]), but when HCl was used, 96.0 wt. % DPA was produced.

2.5.2 γ-Valerolactone (GVL)

GVL is produced by hydrogenating LA with gaseous hydrogen in the presence of a catalyst such as nickel (Ni), palladium (Pd), or platinum (Pt). Li et al. [159] utilized 0.05 mol% $[Ir(COE)_2Cl]_2$ iridium complex with 0.15 mol% pincer ligands as a catalyst, ethanol as a solvent, and 3 mmol of LA for 15 hours at 100 °C and 50 atm, producing 99.3 wt.% of GVL. Ortiz-Cervantes and Garcia. [160] used water as a solvent at 130 °C and ruthenium nanoparticles (Ru-NPs) at a pressure of 25 bars for 24 hours to synthesize 99.8% wt.% GVL from 8.6 mmol of LA. Rodiansono et al. [161] used a Ni-Sn alloy as a catalyst and water as a solvent to synthesize > 99.8 wt.% GVL at 160 °C for 6 hours at a pressure of 4.0 MPa.

2.5.3 Ethyl levulinate (EL)

EL can be produced from LA at room temperature in the presence of ethanol although the process is sluggish [162]. Various catalysts were utilized to accelerate EL reactions, notably heterogenous catalysts, homogeneous catalysts, and ionic liquids [46, 163-166]. Fernades et al. [167] utilized amberlyst-15 (1,2-bis(ethenyl)benzene,2-ethenylbenzenesulfonic acid) in a 5:1 ethanol: LA mixture at 70 ^{o}C for 5 hours for the production of EL which yielded 79.3 wt.%. Similarly, Li et al. [168] used sulfated zirconium dioxide/ titanium dioxide nanocomposite (sulfated ZrO_2/TiO_2) for catalysis in 2.5:1 ethanol: LA at 105 ^{o}C for 3.5 hours, yielding 96.7 wt.% of EL. In a similar condition, a different catalyst called sulfated titanium dioxide nanorods (sulfated (TiO_2)) was utilized in the EL production for 4 hours which resulted in a yielded 93.9 wt.% yield of EL.

Yan et al. [164] used tungstosilicic acid hydrate ($H_4S_1W_{12}O_{40}$)/mesoporous silicon dioxide (SiO_2) in 18:1 ethanol: LA for 5 hours at 75 ^{o}C to synthesize 90.4 wt.% of EL. Nandiwale et al. [169] utilized dodecatungstophosphoric acid (DTPA)/desilicated zeolite socony mobil-5 (DH-ZSM-5) in 6:1 ethanol: LA for 4 hours at 78 ^{o}C to produce 93.4 wt.% EL. Later in 2014, the same group used hexagonal zeolite socony mobil-5 (H-ZSM-5) and desilicated zeolite socony mobil-5 (DH-ZSM-5) to produce EL from LA in ethanol 6:1 at 90 ^{o}C for 5 hours. The reports revealed that when H-ZSM-5 was used, it produced 43.9 wt.% of EL, whereas DH-ZSM-5 produced 66 wt. % of EL.

Further, when the ethanol: LA ratio was increased to 10:1 and the duration was increased to 6 hours, the EL yield increased substantially from 65.7 - 86.4 wt.%. Pileidis et al. [162] reported on the esterification of LA into EL catalyzed by sulfonated hydrothermal carbons (heterogeneous catalyst) at 60 ^{o}C. LA conversion to EL and EL selectivity were both greater than 96.6 wt.%. Cirujano et al. [170] used zirconium (Zr)-containing MOFs (metal organic frameworks) and amino zirconium (IV) dicarboxylate porous material (UiO-66-NH_2) in ethanol and LA at 78 ^{o}C for 8 hours to produce 98.3 wt.% of EL. Under the same conditions, zirconium (IV) dicarboxylate porous material (UiO-66) catalyzed the production of EL which yielded 98.0 wt.%, whereas tosylic acid (TsOH) yielded the maximum EL yield 99.7 wt.%.

2.6 Commercialization of LA derived from biomass residue

2.6.1 Biofine process and DIBANET design

There are two processes that have been used to produce LA from biomass in pilot-scale namely the Biofine process and DIBANET design.

(I) Biofine process

The Biofine method was developed by Dr. Stephen Fitzpatrick to manufacture levulinic acid from biomass utilizing sulfuric acid as a catalyst and water as a solvent [10, 32, 147]. The Biofine process has advantages such as a short residence time and a small reactor volume at high throughput, high feedstock flexibility within a wide range of low-grade variable composition cellulosic feedstock, continuous process control, ease of scale-up, and a 61- 69 wt.% yield of LA [32]. However, the process also has few shortcomings such as the production of humins, inefficient separation of LA, cumbersome acid recovery and extensive water usage [8]. Commercializing a method that employs a renewable resource such as biomass to manufacture LA was a significant accomplishment, however, the limits necessitate more research to enhance the Biofine process. Furthermore, the use of sulfuric acid as the catalyst for this process raises concerns because it is well known that sulfuric acid is toxic and corrosive, hence the need for a green catalyst.

(II) DIBANET design

Later DIBANET design was developed to produce levulinic acid and other compounds from biomass [171]. The process comprises the use of peroxide pre-treatment of biomass, whereby using 5 to 7.5% peroxide and high mass loadings approximately 90 wt.% lignin removal and 85 wt.% hemicellulose depolymerization was obtained in the liquor in 5 min. In comparison to the Biofine method, DIBANET design was able to extract 22.50 kg/hr (75 wt.%) of lignin and has a greater furfural yield of 28.1 wt.%. Moreover, with the DIBANET design, the LA yield improved by 22%. When compared to the Biofine process, DIBANET design consumes less energy during the production process. According to the study, the stage of LA production and recovery utilized 171,1 kW of energy in the DIBANET design, whereas the Biofine process used 543,6 kW. The DIBANET design and Biofine process were also compared in terms of product value, with Biofine process manufacturing costing less than DIBANET design and the DIBANET design gross margin being 14.8 % greater than the Biofine gross margin.

Based on their gross margin, DIBANET design produces a greater profit than the Biofine method. Haverty et al. [171] has also proposed areas to be developed by DIBANET in terms of limitation of cellulose hydrolysis (high energy input), multiple components, acidic effects on process equipment, non-processed desired products, low to water (95%), energy-intensive, sulfuric acid complicated post-processing and scalability (high-pressure CSTR).

2.6.2 Global market of LA

The global market for LA is expected to reach US$ 49.2 million by 2027, expanding at a compound annual growth rate (CAGR) of 12.7 percent between 2020 and 2027. Agriculture, medicines, food additives, and cosmetics are all anticipated to increase in the LA market. Geographically, the LA market may be found in the following continents: North America, Europe, Asia Pacific, and the rest of the globe. Biofine International US Inc, Gf Biochemicals, Avantium NV, Hefer TNJ chemical industry Co., Ltd, Lang fang triple well chemicals Co Ltd, Simagchem company, and Great chemicals Co Ltd are the main competitors in the LA market [172-174].

The generation of eco-friendly processes for the development of high-value products from renewable feedstock such as biomass is gaining extensive interest. Here we have attempted to conduct a comprehensive review on the impact of various catalysts and process conditions for the synthesis of LA. Although LA is a very attractive biorefinery platform chemical however its production from biomass often exhibit lower yields and necessitates the development of more efficient catalysts. The use of mineral acids for the production of LA suffers from the corrosive nature of acids, which not only require high-cost equipment and increase the operation cost but also create a concern for waste disposal. In contrast, heterogenous catalysts, though are easier to recover and have shown improved performance, their industrial-scale usage is observed to be quite cost-intensive. Further due to low volatility and high polarity, Ionic liquids pose to be a better solution but again the preparation of ILs for industrial scale is the limiting factor.

Overall, the literature revealed that there is still a need to develop a more ecofriendly process for LA production and new catalysts should be explored. Also, the issues such as humin production must be addressed for successful industrial-scale production of LA. Further, the optimization of process conditions and the separation and purification of LA as well as catalytic system should be studied in-depth.

Chapter 3: Experimental methods

3.1 Introduction

This chapter consists of two sections for the experimental work of this study:

Section A: Optimization of LA production from DSB catalyzed with ionic liquids.

Two following ILs were investigated to produce LA from DSB:

(i) 1-ethyl-3-methylimidazolium hydrogen sulfate ([EMim][HSO_4])
(ii) 1-butyl-2,3-dimethylimidazolium tetrafluoroborate ([BMMim][BF_4])

Section B: Application of synthesized LA from DSB.

Three LA derivatives production were optimized with various catalysts:

(i) Ethyl levulinate (EL)
(ii) γ-valerolactone (GVL)
(iii) Diphenolic acid (DPA)

3.2 Section A: Optimization of LA production from DSB catalyzed with ILs

3.2.1 Chemicals

All the chemicals were purchased from Merck (Johannesburg, South Africa), and were all used without any further purification. The chemicals used for the study were dimethyl sulfoxide (99%), methanesulfonic acid (99.5%), ethanol (99.8%), ethyl acetate (99.5%), methyl isobutyl ketone (98.5%), 1-ethyl-3-methylimidazolium hydrogen sulfate (95%), glucose (99.5%), 1-butyl-2,3-dimethylimidazolium tetrafluoroborate (97%) and fructose (99%). The chemicals used for product analysis were levulinic acid (99%), sulfuric acid (96 - 98%), acetic acid (95%), 5-hydroxymethylfurfural (99%), and formic acid (98%).

3.2.2 Preparation of DSB

The Sugar Milling Research Institute (Durban, South Africa) supplied DSB. Depithing of SB was carried out by mechanically abrading the mill-run bagasse to break the pith clusters away from the remaining portion. DSB was dried in an oven model 222 (Scientific, South Africa) at

105 ^oC for 24 h, milled by Pulverisette 16 (Fritsch, Germany), and sieved to 40-mesh particle size.

3.2.3 Compositional analysis method

Sugarcane bagasse (1.0 g) and 72 % of sulfuric acid (15 mL) were added in a 100 mL beaker for 1h while stirring at room temperature for lignin determination. The resulted mixture was placed in a 1 L flask, and then 360 mL of water was added. The mixture was boiled at 100 ^oC for 4 h, filtered, and weighed. For holocellulose determination, in a 500 mL flask, 5g of sugarcane bagasse and water were added, heated at 100 ^oC covered with a 100 mL flask for refluxing; 1.5g of $NaClO_2$ and 0.5 mL of glacial acetic acid were added. The system was set up for refluxing at 100 ^oC; $NaClO_2$ and acetic acid were added until the bagasse became white. The solids were filtered and washed with water, dried at (100 ± 5 ^oC) and weighed until the weight was constant. For ash content determination, 1.0 g of sugarcane bagasse was weighed and for moisture content 2 g of SB was used. For cellulose content determination, 2.0 g of sugarcane bagasse, 5.0 g of $NaClO_2$, and 100 mL of water were mixed, autoclaved for 30 min, cooled, and then filtered and weighed. Hemicellulose was calculated as a difference between holocellulose and cellulose. All these analyses were done in triplicate [175].

3.2.4 LA optimization from DSB

A100 mL batch Parr reactor (Parr, USA) equipped with a type J thermocouple (iron-constantan) and a magnetic stirrer was used for all the experiments. 1.0 g of the DSB, a predetermined amount of [EMim][HSO_4] or [BMMim][BF_4], and 10 mL of water was loaded in the reactor. The solution was heated to a specified temperature with continuous agitation at 250 rpm. The heat was supplied by a heater band of the reactor. After the reaction, the heater band is removed to stop the heat supply to the reactor vessel. For low temperature such as 100 ^oC, the reactor is allowed to cool but when using the maximum temperature such as 220 ^oC, ice was used to cool the reactor vessel. The mixture was further cooled to room temperature, and 10 mL distilled water was added to reduce the viscosity and ease the separation of the liquid and solid fractions. The mixture was filtered in a Buchner funnel, and the solid residue was oven-dried at 50 ^oC overnight and stored in a refrigerator at 4 ^oC for analysis. A volume of 2 x 10 mL of ethyl acetate was added to the filtrate to extract LA in a separating funnel, two layers resulted which include an aqueous layer and organic layer. The aqueous layer containing [EMim][HSO_4] or [BMMim][BF_4] was separated and oven-dried at 50 ^oC overnight to remove water and ethyl acetate, and the dried [EMim][HSO_4]/[BMMim][BF_4] was recycled for reusability test. The organic layer containing LA and other byproducts were obtained by evaporating ethyl acetate and stored in the refrigerator for analysis.

3.2.5 Experimental design

In this work, a response surface methodology (RSM), Box-Behnken design (BBD) was used to design the experiments with three variables, namely, temperature, reaction time, and IL loading. The level and range of the process variables are shown in table 3.1. The ratio of DSB to solvent was maintained at 1:10 and the pressure in the reactor was adjusted to 10 bar with nitrogen gas to maintain the IL in a liquid state at a higher temperature. The statistical analysis was carried out using design expert software version 11.

Table 3.1 Experimental range and levels for the independent variables of DSB conversion using Box-Behnken design

Variables	**Symbol**	**Range and level**		
		-1	0	+1
Temperature (°C)	A	100	160	220
Reaction time (h)	B	2	7	12
Ionic liquid loading (g)	C	1	2.5	4

3.2.6 Solvent optimization for the LA production

The production of LA from DSB using [EMim][HSO_4] and [BMMim][BF_4] in water was optimized and the optimum conditions were used as the control for the solvent optimization. The solvent optimization was carried out with other solvents, namely: ethanol, ethanol and water (1:1), dimethyl sulfoxide (DMSO), and methyl isobutyl ketone (MIBK). All the experiments were conducted in triplicate and the data reported were expressed as mean values.

3.2.7 LA production from pure glucose and fructose

LA was also produced from pure glucose and fructose using the optimum conditions: 100 ^{o}C, 7 h, and 4 g IL [EMim][HSO_4] and [BMMim][BF_4] and 1:10 (sugar: water).

3.2.8 Reusability of [EMim][HSO_4] and [BMMim][BF_4] for LA production

The optimum conditions (a temperature of 100 °C, reaction time of 7 h and IL loading of 4 g) was used for the reusability test. A 1.0 g sample of DSB and 10 mL of water were used for each reusability test reaction and the extraction was carried out as described earlier.

3.2.9 Upscaling the conversion of DSB to LA catalyzed with [EMim][HSO_4]

Two ILs were investing for the LA production from DSB, [EMim][HSO4] yielded the maximum LA hence it was used to upscale the LA production. The production was upscaled from the ratio 1:4, *i.e.*, 1 g of bagasse and 4 g of [EMim][HSO_4] to 100 g of bagasse and 400 g of [EMim][HSO_4]. The reaction was carried out in a round bottom flask immersed in an oil bath for 7 h at 100 °C.

3.2.10 Product analysis

3.2.10.1 LA yield Determination by high-performance liquid chromatography (HPLC)

The concentration of LA in the aqueous phase was determined by using HPLC (Shimadzu, Japan) using the conditions below: column – Phenomenex Rezex ROA-Organic Acid H^+ (8%) 30 x 4.6 mm, flow rate – 0.6 ml/min, mobile phase – 0.0025 mM H_2SO_4, detector – photo diode array (HPLC-PDA) at 210 nm, retention time – 40 min, column temperature – 25°C. A 0.45 µm nylon membrane was used to filter the samples before being injected into HPLC system [10]. The retention time of the LA peak is 23 minutes, determined by analyzing LA standards. The LA yield, actual yield, and theoretical yield were calculated by using equations (Eqs.) 3.1-3.3:

$$LA\ yield\ (wt\%) = \frac{Y_{act}}{Y_{th}} \times 100 \qquad 3.1$$

Where Y_{act} is the actual yield of LA and Y_{th} is the theoretical yield of LA-based on cellulose content.

$$Y_{act} = \frac{LA\ (g)}{DSB\ (g)} \qquad 3.2$$

$$Y_{th} = cellulose\ content \times 0.71 \qquad 3.3$$

The value of 0.71 in Eq. 3.3 resulted from the division of the LA molar mass (116.11 $g.mol^{-1}$) by cellulose molar mass (162 $g.mol^{-1}$).

3.2.10.2 LA Characterization by fourier transforms infrared spectroscopy (FTIR) analysis

The FTIR spectra of the organic layer samples were recorded using an FTIR 8400 (Shimadzu, Japan) in the range of 500 – 4500 cm^{-1} with a resolution of 4 cm^{-1}. The software of the FTIR is agilent resolution pro. Data was collected was used to plot the spectra with origin software.The FTIR determines the functional groups of the compounds analysed.

3.3 Section B: Application of synthesized LA from DSB.

3.3.1 Ethyl levulinate (EL)

Commercial LA was used to optimize EL production by investigating parameters namely time, temperature, and catalyst loading. The EL production was catalyzed by various catalysts which include ILs and mineral acid. The optimum conditions were then used to produce EL from the synthesized LA.

The following materials and methods were used:

3.3.1.1 Materials

All the chemicals were purchased from Merck and used without further purification: levulinic acid (98%), ethanol (98%), methanesulfonic acid (95%), ethyl levulinate (98%), 1-butyl-3-methylimidazolium hydrogen sulfate (≥ 95%), p-toluenesulfonic acid monohydrate (≥ 98.5%), sulfuric acid (98%), 1-ethyl-3-methylimidazolium tosylate (≥ 98%), methanol (99.8%), propanol (99.5%), butanol (≥ 99.4%), 2-propanol (≥ 99.5%) and 2-butanol (99.5%).

3.3.1.2 Optimization of conversion of commercial LA to EL using methanesulfonic acid

The optimization of the esterification reaction to produce EL from commercial LA was carried out in a 100 mL Parr reactor (stainless steel, USA) using the BBD of experiments. The optimization parameters were temperature, catalyst loading and reaction time. Approximately

1.0 g of commercial LA, 10 mL of ethanol and a predetermined amount of MsOH were added to the polytetrafluoroethylene (PTFE) liner and placed in a Parr reactor. The reactor heating mantle was set at a required temperature, and the PTFE liner was placed in the reactor. The reaction time was measured when the PTFE contents reached the set temperature, and once the reaction was completed, the heat was switched off and the reactor was quickly cooled to room temperature using an ice bath. All samples were stored at 4 °C in a refrigerator until analyzed.

3.3.1.3 Catalyst effect on the conversion of commercial LA to EL

The optimum condition that was determined using MsOH as a catalyst for the conversion of commercial LA to EL was used to study the effect of the other catalysts on EL production. The catalysts that were used were tosylic acid ([TsOH]), [BMim][HSO_4], [EMim][OTs] and sulfuric acid ([H_2SO_4]). The experiments were carried out in triplicate, and the reported data is the mean value.

3.3.1.4 Esterification of commercial LA to levulinic esters using various alcohols

The production of alkyl levulinate esters from commercial LA was studied using the most suitable catalyst for EL conversion from LA. This study was done to investigate the ester selectivity from LA. Alcohols that were used are methanol (CH_4O), propanol (C_3H_8O), butanol ($C_4H_{10}O$), 2-propanol (C_3H_8O), 2-butanol ($C_4H_{10}O$) and ethanol (C_2H_6O). The experiments were conducted in triplicate, and the reported data is the mean value. All esters were analyzed with HPLC.

3.3.1.5 Conversion of LA derived from DSB to EL

The studies on the most effective catalyst and the highest ester selectivity indicated that MsOH was the most suitable catalyst and EL had the highest ester selectivity. It was for these reasons that EL was synthesized from LA derived from DSB using MsOH. The experiments were carried out in a Parr reactor where 1.0 g of DSB-derived LA, 10 ml of ethanol and 2.75 g MsOH were placed in a PTFE liner at 90 °C for 5.25 h. The EL derived from DSB was analysed using HPLC.

3.3.1.6 Characterization of EL by HPLC analysis

The esterification products were analysed by HPLC (Shimadzu, Japan) equipped with an ultraviolet (UV) detector at 210 nm with a C18 column (150 mm × 4.6 mm) at a flow rate of 0.4 ml/min with a column temperature of 40 °C using a mobile phase of water and acetonitrile (50%). Using a syringe, 1mL samples and standards were filtered over a 0.45-µm filter to prevent any solids to enter the HPLC column. Both samples and standards were dissolved in distilled water. The EL yield (Y_{EL}), actual EL yield (Y_{act}), theoretical EL yield (Y_{th}), LA conversion (X_{LA}) and EL selectivity (S_{EL}) were calculated by using Eqs. (1)–(5):

where n_{LA} is the number of moles of LA and Mr_{EL} is the molar mass of EL. LA molar mass is 116.11 g/mol, and EL molar mass is 144.170 g/mol.

where $C_{LA,0}$ is the initial concentration of LA and C_{LA} is the concentration of LA after the reaction.

3.3.1.7 Characterisation of EL by FTIR analysis

The Fourier transform infrared (FTIR) spectra of the organic layer samples were recorded using an Agilent Technologies Cary 630 FTIR (Germany) in the range of 650–4000 cm^{-1} with a resolution of 4 cm^{-1}. The software of the FTIR is agilent resolution pro. Data was collected, was used to plot the spectra with origin software.This instrument determines the functional groups of the compounds analysed. The EL product from the optimized reaction using commercial LA and MsOH was compared with the EL standard by FTIR.

3.3.1.8 Statistical analysis of EL optimization by response surface methodology

In this work, response surface methodology (RSM) with BBD of experiments was used to design and analyse the optimization of EL production from commercial LA. Three reaction parameters, namely time, catalyst loading and temperature, were investigated for EL production. Table 3.2 lists the minimum and maximum conditions of the parameters to be optimized for EL production. By default, the high levels of the factors are coded as + 1 and the low levels are coded as − 1. The statistical analysis was carried out using Design Expert software, version 12.

Table 3.2 Investigated levels for the three parameters namely time, temperature, and catalyst loading, using BBD

Factors	**Symbol**	**Range and level**		
		-1	0	+1
Time (h)	A	0.5	5.25	10
Temperature (°C)	B	60	90	120
Catalyst loading (g)	C	0.5	2.75	5

3.3.2 γ-valerolactone (GVL)

The following materials and methods were used:

3.3.2.1 Materials

All the chemicals were purchased from Merck (Johannesburg, South Africa), and were all used without any further purification. Levulinic acid (98 %), methanesulfonic acid (95 %), γ-valerolactone (98 %), formic acid (95 %), triethylamine (95 %), sulfuric acid (95 %), ethyl acetate (95 %), 1-butyl-3-methylimidazolium hydrogen sulphate (≥95 %), sulfuric acid (95 %), tosylic acid (98.5 %), 1-ethyl-3-methylimidazolium tosylate (≥98 %), butanol (≥99.4 %), ethanol (≥99.8 %), and methanol (99.8 %).

3.3.2.2 Effect of temperature, time, and catalyst loading on GVL production from commercial LA using MsOH

To determine the optimum conditions for GVL production from commercial LA, the minimum and maximum of the investigated reaction conditions were used (Table 3.3). A set of experiments (table 4.8) were generated using the BBD. A constant mass of 1.0 g of commercial LA was added to a 100 ml stainless steel reactor (Parr Instruments Company, Moline, IL, USA) with 10 ml of water, 700 µl of formic acid and 220 µl of triethylamine. A predetermined catalyst loading of MsOH (table 4.8) was added to the reaction vessel. The mixture was stirred at 200 rpm and the duration of the reaction was measured when the set temperature was reached. At the end of the reaction, the heat supply was quickly removed, and the reactor vessel was inserted in a cold-water bath to rapidly cool the reaction to room temperature. The liquid component of the cooled reaction mixture was extracted with 40 ml of ethyl acetate; the solvent was removed by vacuum. The products were stored in a refrigerator at 4 °C before high-performance liquid chromatography (HPLC) (Shimadzu, Japan) analysis. The procedure for the HPLC analysis is detailed later.

Table 3.3 Investigated levels for the three parameters: temperature, time, and catalyst loading using BBD

Factors	**Range and level**		
	-1	0	+1
Time (h)	2	6	10
Temperature (°C)	25	112.5	200
Catalyst loading (g)	0.5	2.75	5

3.3.2.3 Effect of catalysts on GVL Yield

The effect of catalysts on GVL yield was studied by using the optimum condition for the GVL production from commercial LA using MsOH. The following catalysts were used: tosylic acid [TsOH], 1-butyl-3-methylimidazolium hydrogen sulphate [BMim][HSO_4],1-ethyl-3-methylimidazolium tosylate [EMim][OTs], and sulfuric acid [H_2SO_4].

3.3.2.4 Effect of solvent on the production of GVL

The following solvents: water (H_2O), methanol (CH_3OH), ethanol (C_2H_5OH), ethanol and water (C_2H_5OH and H_2O), and butanol ($C_4H_{10}O$) were used for GVL production from commercial LA in the solvent optimization reactions using the conditions optimized for the catalyst MsOH.

3.3.2.5 Hydrogenation of LA derived from DSB into GVL

The LA derived from DSB was used to produce GVL using the optimized conditions obtained from the optimization study where a commercial sample of LA was used.

3.3.2.6 GVL analysis using high performance liquid chromatography

The qualitative and quantitative analysis of LA and GVL was carried out using HPLC (Shimadzu, Japan) equipped with an ultraviolet detector at 210 nm fitted with an Aminex HPX 87 H column (Bio-Rad, Hercules, CA, USA) at a flow rate of 0.5 ml/min with a column temperature of 50 °C and mobile phase of aqueous sulfuric acid (0.005 M). Using a syringe, 1 ml samples and standards were filtered over a 0.45-micron filter to prevent any solids from entering the HPLC column. Standards were dissolved in distilled water. The concentration of LA and GVL was calculated using standard calibration curves. The retention time of LA and GVL is 16 and 35 minutes, respectively. The GVL yield (Y_{GVL}), actual yield (Y_{act}), theoretical yield (Y_{th}), LA conversion (X_{LA}), and GVL selectivity (S_{GVL}) were calculated according to Eqs. 3.4-3.8:

$$Y_{GVL}(\%) = \frac{Y_{act}}{Y_{th}} \times 100 \qquad 3.4$$

$$Y_{act} = \frac{GVL\ (g)}{Initial\ feedstock\ (g)} \qquad 3.5$$

$$Y_{th} = n_{LA} \times Mr_{GVL} \qquad 3.6$$

Where n_{LA} is the number of moles of LA and Mr_{GVL} is the molar mass of GVL. LA molar mass is 116.11 g.mol^{-1} and GVL molar mass is 100.12 g.mol^{-1}.

$$X_{LA}\ (\%) = \frac{C_{LA,O} - C_{LA}}{C_{LA,O}}\ \text{x}\ 100 \qquad 3.7$$

Where $C_{LA,O}$ is the initial concentration of LA and C_{LA} is the concentration of LA.

$$S_{GVL}\ (\%) = \frac{Y_{GVL}}{X_{LA}} \times 100 \qquad 3.8$$

3.3.2.7 Experimental design

To determine the optimum reaction conditions of GVL production from LA, RSM was used where BBD was to design the set of experiments in table 4.8.

Five replicates in the central point (time: 6 hours, temperature: 112.5 °C and catalyst loading: 2.75 g) with a total of 17 experiments (table 4.8) were done for the optimization of GVL production from commercial LA. The independent variables were the time (A), temperature (B), and catalyst loading (C). The output variable Y was the yield of GVL (Y_{GVL}).

Design expert statistical 12 software (Stat Ease Inc. Minneapolis, USA) was used to regress and fit the data to a second-order model, as well as, to calculate the analysis of variance (ANOVA). A quadratic method was used to analyse the data. The terms of the model were tested at the 95 % confidence level ($p \leq 0.05$). Five replicates were performed in the central points to estimate random errors.

3.3.3 Diphenolic acid (DPA)

The following materials and methods were used:

3.3.3.1 Materials

All chemicals were purchased from Merck (Johannesburg, South Africa) and were used without any further purification. Levulinic acid (99 %), phenol (95 %), methanesulfonic acid (98 %), p-toluenesulfonic acid monohydrate (≥ 98.5 %), methanol (98 %), acetonitrile (99 %), 1-butyl-3-methylimidazolium hydrogen sulphate (≥ 95 %), 1-ethyl-3-methylimidazolium tosylate (≥ 98 %), sulfuric acid (98 %), and 1-ethyl-3-methylimidazolium hydrogen sulfate (95 %).

3.3.3.2 Optimization of DPA production using MsOH

To determine the optimum reaction conditions for DPA production from commercial LA, the minimum and maximum reaction conditions used are given in table 3.4 and were used in the BBD to derive the set of experiments (Table 4.10). A constant mass of 5.0 g of commercial LA, 15 g of phenol (LA: phenol ratio of 1:3), and a predetermined amount of MsOH catalyst (Table 4.10) was placed in a PTF liner and inserted into a 100 mL Parr batch reactor (Parr Instruments Company, Moline, IL, USA). The reaction time and temperature were varied for each experiment according to table 4.10. The reaction mixture was stirred at 200 rpm, and the duration of the reaction was measured from the time the set temperature was reached. At the end of the reaction, the heat supply was quickly removed, and the reactor vessel was inserted into a cold-water bath (5 °C) to cool the vessel and the reaction to room temperature. A sample of 20 mL of methanol was added to the cooled mixture, and the reaction product was stored at 4 °C.

Table 3.4 Investigated minimum and maximum reaction parameters for LA conversion into DPA using BBD

Factors	**Range and Level**		
	-1	0	+1
Time (h)	2	6	10
Temperature (°C)	25	75	125
Catalyst loading (g)	1	5.5	10

3.3.3.3 Effect of the catalyst on the production of DPA

The optimized reaction conditions obtained using methanesulfonic acid and the commercial LA were used for four other catalysts: tosylic acid (TsOH), 1-butyl-3-methylimidazolium hydrogen sulphate [BMim][HSO_4], 1-ethyl-3-methylimidazolium tosylate [EMim][OTs], and sulfuric acid [H_2SO_4].

3.3.3.4 Effect of LA to phenol ratio on DPA production

To determine the effect of the LA to phenol ratio on the DPA production, the ratio of commercial LA and phenol was varied based on the optimized reaction conditions. The ratio of 1:3 was used as a control. The investigated ratios of commercial LA to phenol were 1:4, 1:5, 2:3, 2:4, and 2:5.

3.3.3.5 Condensation reaction of LA derived from DSB into DPA

The LA derived from DSB was used to produce DPA using the optimized conditions, replacing the commercial LA.

3.3.3.6 Product analysis

(I) DPA characterization by HPLC

The concentration of DSB derived LA and DPA were analysed by a high-performance liquid chromatograph (HPLC) (Shimadzu, Kyoto, Japan) equipped with a C18 column (150 x 4.6 mm) at a flow rate of 1.0 mL/min with a column temperature of 40 °C and using an ultraviolet (UV) detector at 270 nm. The mobile phase was water and acetonitrile (40%). Using a syringe, 1 mL of samples and standards were filtered over a 0.45-micron filter to prevent any solids to enter the HPLC column and then injected into the HPLC system for analysis. The total retention time was 20 min. Both samples and standards were dissolved in methanol. The concentration of DPA was calculated using a standard calibration curve. The retention time of p,p'- DPA, o,p'- DPA, and LA were 5, 7, and 10 min, respectively.

The DPA yield (Y_{DPA}), combination of the two isomers (p,p'-DPA and o,p'-DPA), actual yield (Y_{act}), theoretical yield (Y_{th}), LA conversion (X_{LA}), and DPA selectivity (S_{DPA}) were calculated from Eqs. 3.9-3.13:

$$Y_{DPA}(\%) = \frac{Y_{act}}{Y_{th}} \times 100 \tag{3.9}$$

$$Y_{act} = \frac{DPA\ experimental\ mass\ (g)}{Mass\ of\ initial\ feedstock\ (g)} \tag{3.10}$$

$$Y_{th} = n_{LA} \times Mr_{DPA} \tag{3.11}$$

$$X_{LA}\ (\%) = \frac{C_{LA,O} - C_{LA}}{C_{LA,O}} \times 100 \tag{3.12}$$

$$s_{p,p'-DPA\ or\ o,p'-DPA}(\%) = \frac{n_{p,p'-DPA}\ Or\ n_{o,p'-DPA}}{(n_{p,p'-DPA} + n_{o,p'-DPA})} \times 100 \tag{3.13}$$

where n_{LA} is the number of moles of LA, Mr_{DPA} is the molar mass of DPA,LA molar mass is 116.11 $g.mol^{-1}$, and DPA molar mass is 286.33 $g.mol^{-1}$, $C_{LA,O}$ is the initial concentration of LA, C_{LA} is the concentration of LA, S is the selectivity (%), and $n_{p,p'-DPA}$ or $n_{o,p'-DPA}$ is the number of moles of p,p'-DPA or o,p'-DPA.

Chapter 4: Results and Discussion

4.1 Chemical composition of DSB

The chemical composition of DSB together with the standard deviation of each compound is shown in table 4.1. The moisture content of DSB was found to be 60.6 %. The standard deviation was calculated from duplicate results. The resultant solid residue was analysed to determine the amount of glucan used for LA production. The glucan conversion to glucose was 85 % (based on the initial glucan value of 43.6 % in table 4.1).

Table 4.1 Compositional analysis of DSB (dry basis)

Compounds	Values (%)
Sugar polymers	
Glucan	43.6 ± 0.3
Xylan	22.4 ± 2.1
Arabinan	2.1 ± 0.5
Lignin	
Klason lignin	21.1 ± 1.5
Acid-soluble lignin	2.0 ± 0.1
Ash	5.0 ± 0.9
Residue	3.8 ± 0.0

Section A: Optimization of LA production from DSB catalyzed with ILs.

The results are shown below for the two investigated ILs used to catalyze the reaction of levulinic acid from DSB:

4.2 LA optimization catalyzed by [BMMim][BF_4]

4.3 LA optimization catalyzed by [EMim][HSO_4]

4.2 LA optimization catalyzed by [BMMim][BF_4]

In this work, the IL [BMMim][BF_4] was investigated for the production of LA from DSB. [BMMim][BF_4] is a combination of an alkylated imidazolium cation $[BMMim]^+$ and tetrafluoroborate anion $[BF_4]^-$. Imidazolium based ILs have been shown to effectively dissolve cellulose [176, 177] and the $[BF_4]^-$ anion, derived from fluoroboric acid (a strong acid), can catalyse the conversion of cellulose to LA.

The optimum condition for LA production was a temperature of 100 °C, a duration of 7 h, and 4 g of catalyst loading (IL), which yielded 44.8 % of LA (table 4.2). The maximum LA yield from the Biofine process is 80 % [160], which is higher by 35.2 % when compared to the LA yield obtained in this work (44.8 %). Although the Biofine process yields higher LA, the corrosive sulfuric acid used in the process adds to the cost for the reactor equipment replacement and sulfuric acid cannot be recycled. In our previous work, we used sulfuric acid and MsOH as catalysts [2, 10] where the pH of the sample was < 1. The pH of all the samples in this study ranged from 2.1-2.7.

Table 4.2 The investigated reaction conditions, experimental data and results (response)

	A	B	C	Response
Run	**Temperature (°C)**	**Time (h)**	**Catalyst loading (g)**	**LA yield (%)**
1	100	2	1	11.2
2	100	2	2.5	15.9
3	100	2	4	20.6
4	100	7	1	22.6
5	100	7	2.5	30.8
6	**100**	**7**	**4**	**44.8**
7	100	12	1	18.6
8	100	12	2.5	19.4
9	100	12	4	29.3

10	160	2	1	12.2
11	160	2	2.5	13.6
12	160	2	4	14.6
13	160	7	1	22.4
14	160	7	2.5	19.4
15	160	7	4	25.4
16	160	12	1	17.2
17	160	12	2.5	14.5
18	160	12	4	20.8
19	220	2	1	11.8
20	220	2	2.5	4.9
21	220	2	4	7.1
22	220	7	1	20.8
23	220	7	2.5	14.2
24	220	7	4	16.7
25	220	12	1	14.3
26	220	12	2.5	8.1
27	220	12	4	10.9

4.2.1 Effect of temperature, time and catalysts loading on LA yield

Figure 4.1 (a) illustrates the relationship between temperature and time in the production of LA from DSB using [BMMim][BF_4]. It shows that the moderate conditions favour a higher yield of LA. Increasing both temperature and time above the optimum condition will favour low LA yield (Table 4) and unwanted by-products such as humins are produced. Figure 4.1 (b) shows the RSM plot for LA yield for time and catalyst loading. It shows that the moderate duration of the reaction and higher amount of IL favours a high LA yield. Having a moderate duration of the reaction as the optimum is an advantage because a shorter duration of the reaction means less energy will be used for the reaction whereas higher catalyst loading than the maximum catalyst loading is a disadvantage since IL are known to be expensive.

The use of less IL in a reaction means less production cost although no experiment was done with a catalyst loading greater than the optimum catalyst loading to determine if increasing the catalyst loading will increase or decrease the LA yield. The model (Eq. 4.1) predicted 4 g as the optimum catalyst loading even when looking outside the investigated minimum and maximum reaction conditions. Figure 4.1 (c) illustrates the interaction between catalyst loading and time, moderate time and higher catalyst loading favour the maximum LA yield. Cellulose and hemicellulose are densely packed by layers of lignin that protect cellulose and hemicellulose against hydrolysis. Hence, breaking the lignin layers to expose cellulose and hemicellulose increases the biomass surface area, removes hemicellulose, and subsequent hydrolysis of the cellulose requires a strong catalyst [178]. Also mild conditions of temperature and time proves that harsh reaction conditions favours low LA yield and facilitate the formation of humins and other unwanted compounds.

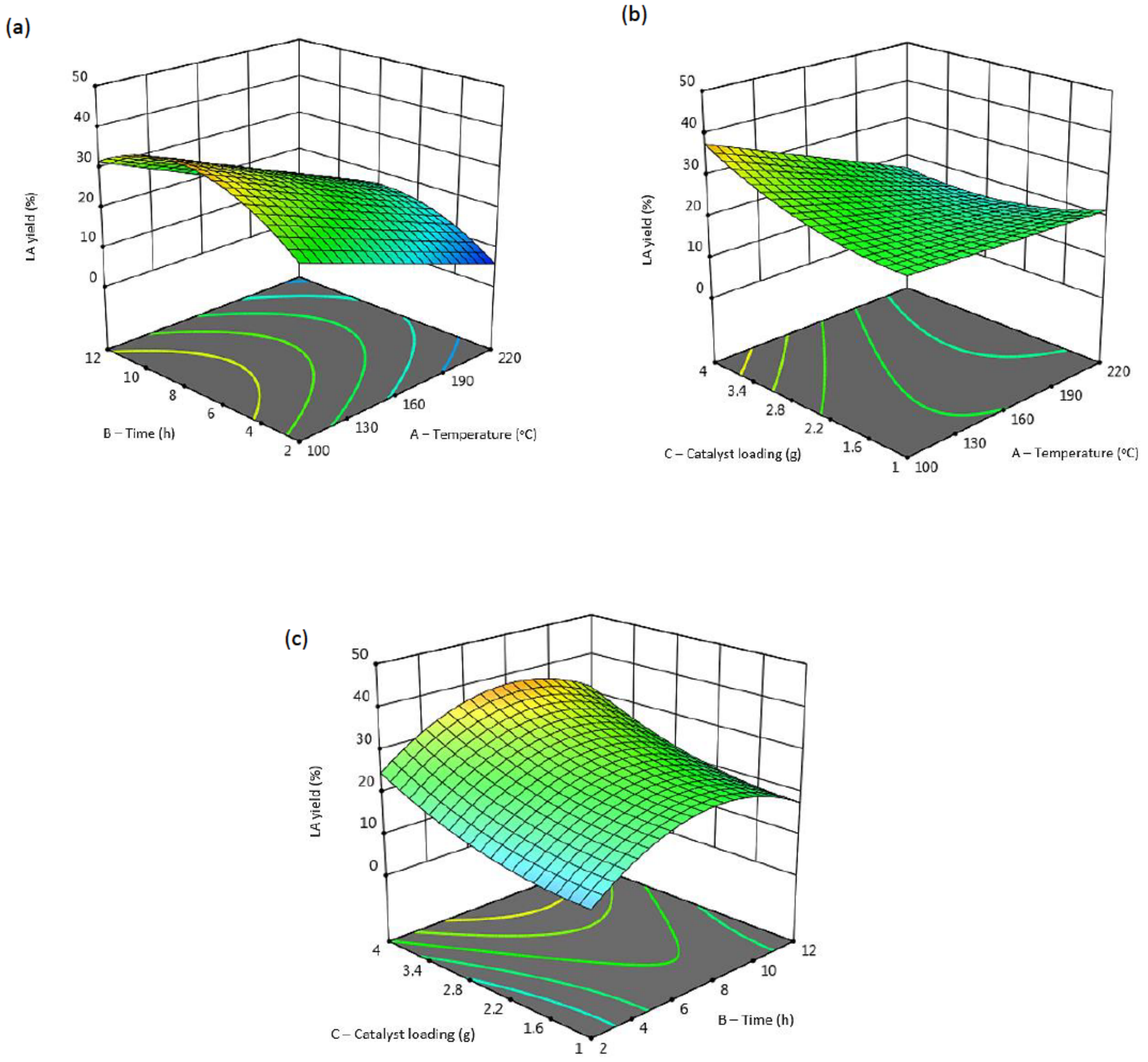


Figure 4.1 RSM plot for LA yield illustrating the interactions between two variables while one variable is kept constant. The three variables investigated in this work are time (2-12 h), temperature (100-220 ºC), and catalyst loading (1-4 g): (a) time vs temperature, (b) catalyst loading vs temperature and (c) catalyst loading vs time.

4.2.2 Response surface methodology model for LA production from DSB

The polynomial regression model for LA production from DSB is given in Eq. 4.1, where Y is the LA yield (dependent variable).

$$
\begin{aligned}
Y = {} & +21.83 - 5.77\,A + 2.29\,B + 2.14\,C \\
& -0.8452\,AB - 4.51\,AC + 0.3249\,BC \\
& +0.0691\,A^2 - 9.34\,B^2 + 3.29\,C^2
\end{aligned}
\qquad 4.1
$$

The optimized conditions were used to calculate the theoretical yield of LA which was 62.1 %. This value was closer to the LA yield from the Biofine process (70-80 %) [160]. Analysis of variance (ANOVA) in table 4.3 was used to determine the contribution of each model term to the overall response. A good model is identified by the significance of the regression model and individual model coefficients. The regression, correlation coefficient (R^2) measures how well the estimated model fits the experimental data. R^2 must be close to 1 for the model to be significant. In this study, the R^2 value was found to be 0.9291 at the 95 % significance level specifying that 92.91 % of the variability in the responses can be explained by the model and that 7.1 % of the total variability was not explained in the regression model. The high value of R^2 indicates a good estimate of the response within the process conditions range from the model [179].

Probability, P-values or F-values with 95% confidence level was used to determine the significance of the model and model terms. Table 4.3 shows the ANOVA parameters for the production of LA from bagasse generated from Eq. 4.1. The larger F-value and the smaller 'P' value ($P\text{-value} > F$), shows the significance of the model [180, 181]. The model F-value of 24.75 implies the model is significant, there is only a 0.01 % chance that an F-value this large could occur due to noise. P-values less than 0.0500 indicate model terms are significant. In this work, the P-value of the model is 0.0001 which is less than 0.0500 indicating that the model is significant. In this case, A, B, C, AC, B^2, C^2 are significant model terms.

Table 4.3 ANOVA for the response surface quadratic model for LA production.

Source	**Sum of squares**	**Degree of freedom**	**Mean square**	**F-value**	**P-value**
LA (R^2 = 0.9291)					
Model	1619.13	9	179.90	24.75	< 0.0001

A-Temperature	598.79	1	598.79	82.37	< 0.0001
B-Time	94.50	1	94.50	13.00	0.0022
C-Ionic liquid loading	82.74	1	82.74	11.38	0.0036
AB	8.57	1	8.57	1.18	0.2927
AC	244.41	1	244.41	33.62	< 0.0001
BC	1.27	1	1.27	0.1743	0.6816
A^2	0.0287	1	0.0287	0.0039	0.9507
B^2	523.92	1	523.92	72.07	< 0.0001
C^2	64.90	1	64.90	8.93	0.0083
Residual	123.59	17	7.27		
Total	1742.71	26			

The parity plot shown in figure 4.2 indicated a satisfactory correlation between the experimental and predicted values of LA produced from DSB using [BMMim][BF_4]. The parity plot determines the reliability of the model, it illustrated that the predicted LA yield by the model is similar to the experimental LA yield. The points in the graph are close to the straight line indicating that the model is able to predict the LA yield and this makes the model to be significant.

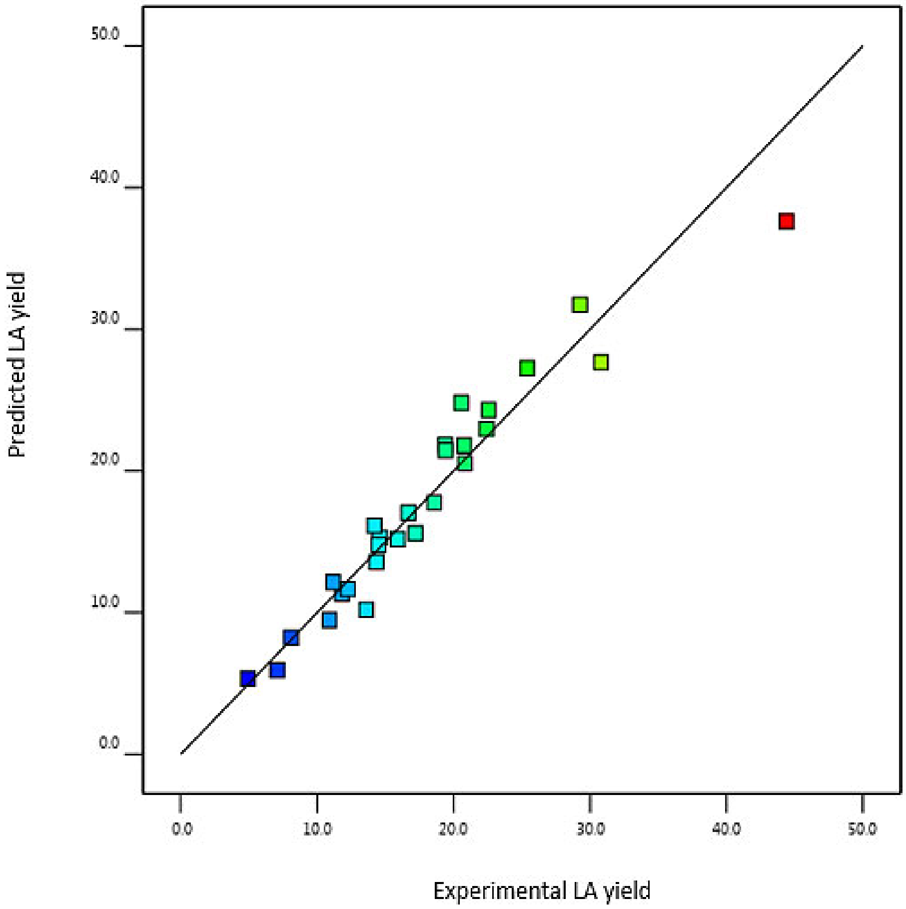


Figure 4.2 Parity plot for the production of LA from DSB compares the LA yield predicted by the model with LA yield obtained experimentally

The pareto chart in figure 4.3 illustrate that the temperature (A) is the most influential factor towards LA formation compared with all the other investigated factors followed by time (B) and catalyst loading (C), determined by their highest LA estimate coffiecients and the P-values in table 4.3 are in agreement with the pareto chart results.

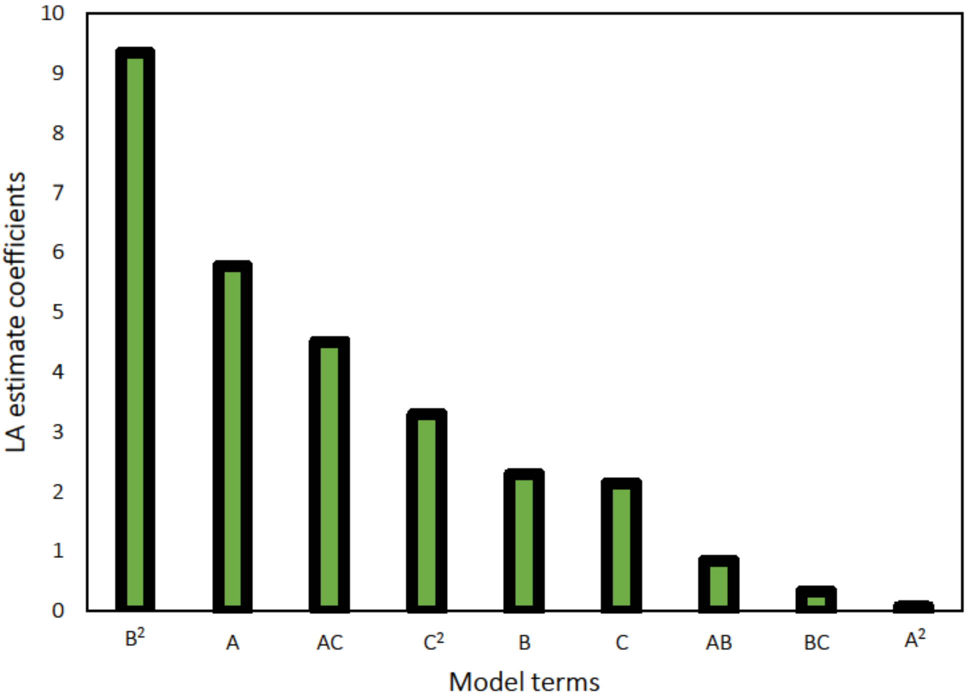


Figure 4.3 Pareto chart of the model terms for LA production which indicate the model term that has more effect on LA yield. Model terms are the investigated variables (temperature (A), time (B), and catalyst loading (C))

4.2.3 Effect of pure glucose and fructose as a starting material for the production of LA

The concentration of LA produced from pure fructose and glucose is 68.4% and 51.8 % respectively, which is higher than the maximum LA yield of 44.8 % produced from DSB. This may be due to the processing difficulties related to the formation of intractable materials encountered with lignocellulosic material [182]. Bagasse contains ash which is basic therefore it neutralizes the hydrolysis reaction that occurs during the production of LA [15]. The use of sugars for the production of LA reduces the number of processing stages thus high LA yield is achieved and it also prevents the undesired products that are formed when DSB is utilized.

4.2.4 Effect of the solvent in the production of LA from DSB

In this study two types of solvents were used to study the effect of solvents in the production of LA from DSB, namely, polar protic (water and/or ethanol) and polar aprotic (dimethyl sulfoxide (DMSO) and methyl isobutyl ketone (MIBK)). Polar protic solvents are defined as solvents that have a proton that can be donated whereas polar aprotic solvents are solvents that do not have a proton to donate in a reaction [183].

Figure 4.4 illustrates that the polar aprotic solvents produced higher LA yield when compared to polar protic solvents [148]. The factors that play an important role when choosing a solvent include selectivity, LA yield, the environmental impact of the solvent, mobility, acute toxicity for humans, chronic toxicity for humans, acute toxicity for aquatic organisms, persistency in the environment, and bioaccumulation [147]. Qi *et al*. [128] reported that although water is an environmentally friendly solvent it ionization can promote the formation of formic acid and humins which decreases the levulinic acid yield. Water was used as a controlled solvent since it is the preferred solvent because it is environment friendly and easily available. But in this work, MIBK was the best solvent for the LA production which is due to its high equilibrium distribution coefficient for LA conversion [1] thus higher amount of LA is produced.

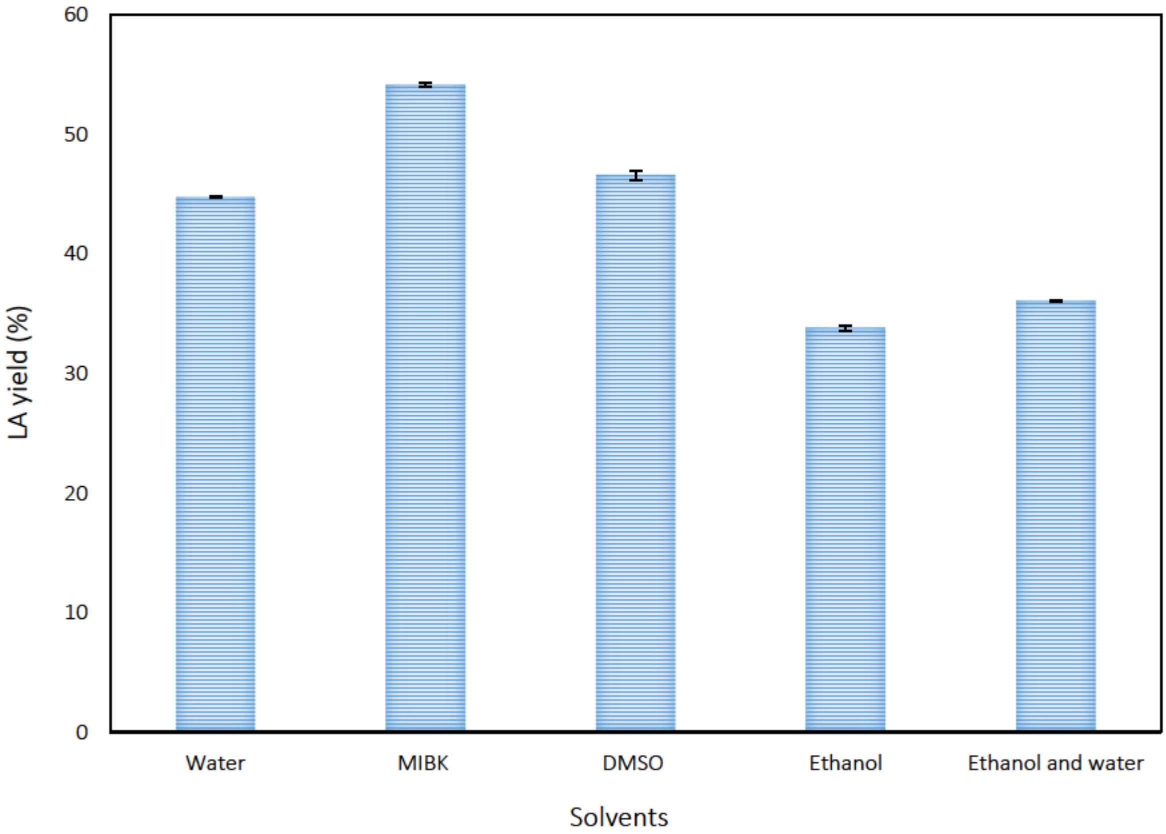


Figure 4.4 Effect of solvent on the LA yield at the optimized conditions: 100 °C, 7 h, and 4 g [BMMim][BF_4] using DSB

4.2.5 Reusability of [BMMim][BF$_4$] for the production of LA from DSB

The two important properties of a catalyst are reusability and activity. In this study, the catalyst [BMMim][BF$_4$] was tested for reusability in the production of LA from DSB. The results showed that from the maximum LA yield (44.8 %) after recycling the IL four times, there was a 9 % loss in the maximum LA yield. These results indicated that this catalyst [BMMim][BF$_4$] can be used up to four times.

4.3 LA optimization catalysed by [EMim][HSO$_4$]

A Brønsted acidic ionic liquid (BAIL): 1-ethyl-3-methylimidazolium hydrogen sulfate ([EMim][HSO$_4$]) was chosen to catalyze the conversion of LA from DSB because the imidazolium cation can effectively dissolve biomass [184-186] and the anion, ([HSO$_4$]$^-$) has the ability to facilitate hydrolysis of the biomass [187].

4.3.1 RSM study of LA production from DSB catalyzed with [EMim][HSO$_4$]

Model Analysis

BBD was employed to analyze the interaction between the responses and variables. Table 4.4 lists the design of the experimental data and the results for LA yield from DSB, where temperature (A), reaction time (B) and ionic liquid loading (C) were the input variables and the LA yield was the response.

Table 4.4 Experimental data set for DSB conversion to LA and LA yield

	A	**B**	**C**	**Response**
Run	**Temperature (°C)**	**Duration (h)**	**Ionic liquid loading (g)**	**LA yield (%)**
1	100	2	1	8.6
2	100	2	2.5	22.7
3	100	2	4	39.6
4	100	7	1	9.9
5	100	7	2.5	22.5
6	**100**	**7**	**4**	**54.6**
7	100	12	1	16.9
8	100	12	2.5	17.4
9	100	12	4	31.4

10	160	2	1	8.6
11	160	2	2.5	21.6
12	160	2	4	34.5
13	160	7	1	7.3
14	160	7	2.5	17.8
15	160	7	4	35.3
16	160	12	1	2.4
17	160	12	2.5	5.3
18	160	12	4	18.7
19	220	2	1	1.8
20	220	2	2.5	4.8
21	220	2	4	6.8
22	220	7	1	2.2
23	220	7	2.5	4.1
24	220	7	4	1.9
25	220	12	1	1.7
26	220	12	2.5	6.6
27	220	12	4	6.6

The proposed model for the response/dependant variable (Y) which is the LA yield produced from DSB is given in Eq. 4.2:

$$\begin{aligned} Y = &+ 17.31 - 10.59\,A - 7.35\,B + 14.32\,C \\ &+ 1.77AB - 11.25AC - 2.40\,BC \\ &- 3.77A^2 - 3.6\,B^2 + 4.23\,C^2 \end{aligned} \tag{4.2}$$

In this study, the R^2 value was found to be 0.9974 (table 4.5), at the 95 % significance level specifying that 99.74 % of the variability in the responses can be explained by the model and that 0.26 % of the total variability was not explained in the regression model. The high F-value of 70.10 indicates that the model is significant. Therefore, the model is able to estimate the LA yield when the variables are adjusted.

Table 4.5 ANOVA for the response surface methodology results

Source	**Sum of Squares**	**DF**	**Mean Square**	**F-value**	**P-value**
LA (R^2 = 0.9974)					
Model	4948.03	22	224.91	70.10	0.0004
A - Temperature	403.65	1	403.65	125.80	0.0004
B – Time	194.48	1	194.48	60.61	0.0015
C - Catalyst loading	738.45	1	738.45	230.15	0.0001
AB	12.60	1	12.60	3.93	0.1186
AC	506.25	1	506.25	157.78	0.0002
BC	23.04	1	23.04	7.18	0.0552
A^2	17.03	1	17.03	5.31	0.0826
B^2	15.70	1	15.70	4.89	0.0914
C^2	21.51	1	21.51	6.70	0.0608
Residual	12.83	4	3.21		
Total	4960.86	26			

The reliability of the developed model shown in the parity plot (figure 4.5), compares the predicted and observed LA yield from the DSB conversion experiments, most points lie near the straight line, indicating that the quadratic model developed for DSB conversion to LA is significant.

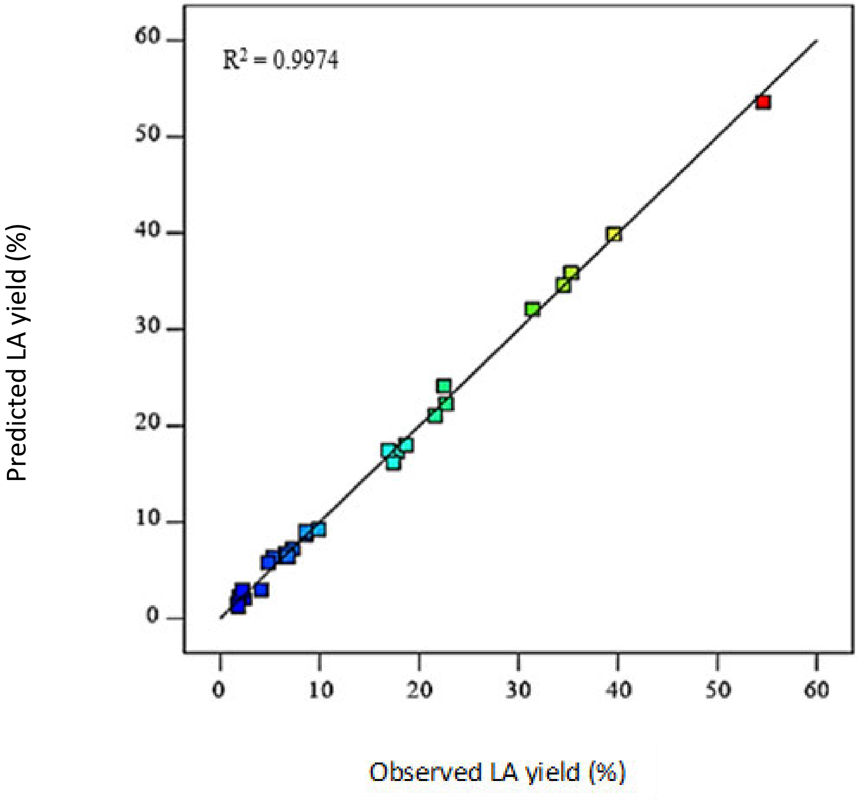


Figure 4.5 Parity plot of LA yield

The significance of the process variables namely, linear (A, B, C), quadratic (A^2, B^2, C^2) and interaction (AB, BC, AC) terms are revealed in the pareto chart (figure 4.6). Figure 4.6 shows the effect of the input variables (temperature, time or ionic liquid loading) and their influence on the response (LA yield). A P-value smaller than 0.05 indicates that the variable/s is more significant towards the response [186]. The pareto chart (figure 4.6) revealed that temperature (A), ionic liquid loading (C), both temperature and ionic liquid loading (AC) and time (B) were the most significant model terms that influenced the LA yield (table 4.5). The model terms AB and BC (P-value = 0.1186 and 0.0552) have insignificant effects on LA yield. All quadratic terms (A^2, B^2, and C^2) are insignificant for LA yield indicating that all the model terms reached their optimum and there is no need to increase each model term [146].

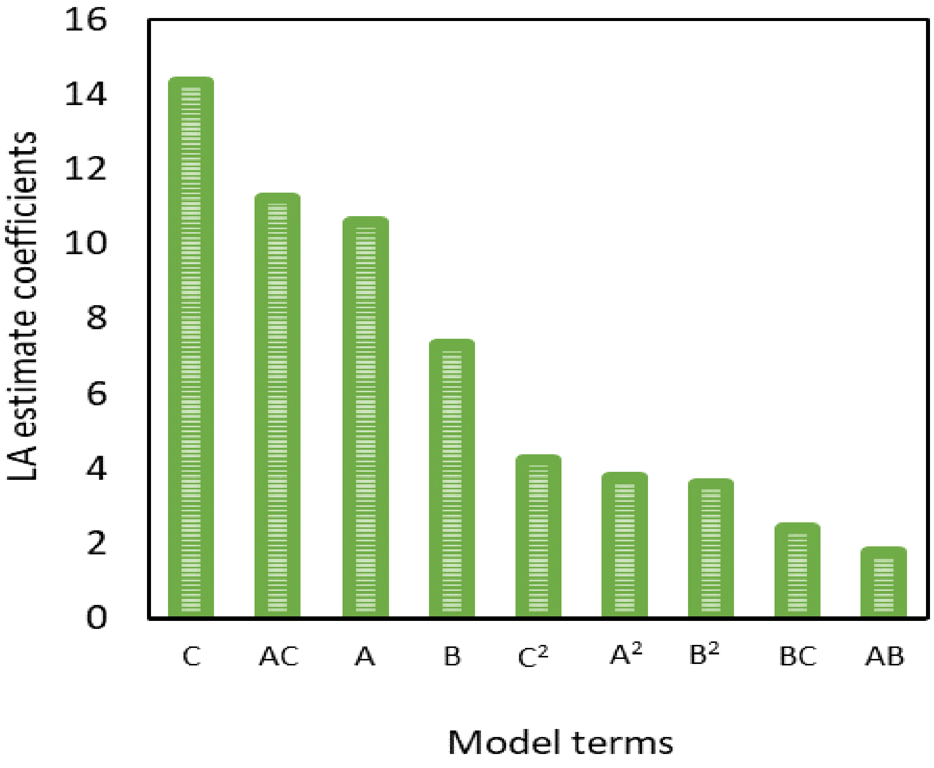


Figure 4.6 Pareto chart for the LA yield using the model

4.3.2 LA yield three-dimensional (3D) response surface and contour plots

The 3D response surface and contour plots show the interactions between the response and the variables. Each plot consists of two variables and their effect on LA yield (figure 4.7 i-iii). Figure 4.7 (i) illustrates the interactions between temperature and reaction time, where low temperature and short reaction time favours high LA yield. At a temperature of 100 ^{o}C and a reaction time of 7 h, a maximum LA yield (54.6 %) was achieved. The LA yield decreased (6.6 %) at the maximum temperature of 220 ^{o}C and the maximum duration of 12 h. When the temperature exceeded 100 ^{o}C, more unfavourable by-products including humins were produced which resulted in a decrease in the LA yield. Ramli and Amin. [107] used 1-sulfonic acid-3-methylimidazolium tetrachloroferrate and oil palm fronds to produce LA, at the temperature above the optimum (150 ^{o}C), resulted in the formation of humins and a decrease in LA yield. Peng et al. [137] also observed that high temperature favours more production of humins.

The 3D response surface and contour plots in figure 4.7 (ii) show less significant interactions between reaction time and IL loading. It also shows that LA yield increases with increasing IL loading at a shorter reaction time. The reaction time of 7 h and IL loading of 4 g yielded a maximum LA yield of 54.6 %. Increasing reaction time above 7 h decreased the LA yield and this may be due to humin formation, caused by the sugars (glucose, fructose, and xylose) [107].

The interaction of ILs loading and temperature is shown in figure 4.7 (iii), LA yield increased with increasing ILs loading at low temperatures. The maximum value of IL loading (4 g) is the optimum. After determining the optimum conditions for LA production, lower temperatures (75 and 50 ^{o}C) less than the optimum temperature of 100 ^{o}C was tested to determine whether LA yield will increase or decrease. It was found that LA yield decrease as the temperature decreases which confirmed 100 ^{o}C as the optimum temperature for the LA production from DSB using [EMim][HSO_4].

According to the RSM, all the three variables optimized in this work are significant although ionic liquid loading is the most influential and the reaction time is the least influential towards the LA yield. The optimum conditions for this study are a temperature of 100 ^{o}C, a 4 g of IL loading and a reaction time of 7 h. No formation of humins was observed in the optimum conditions. Sun et al. [142] produced 63 % of LA from cellulose using 1-(3-propylsulfonic acid)-3- methylimidazolium phosphotungstis acid in the presence of water and MIBK which is 8.4 % higher than this study. This may be due to the presence of two acids (in both the cation and anion of the ionic liquid) and there was no interference by hemicellulose and lignin since LA was produced directly from cellulose. Amarasekara and Wiredu. [146] achieved 29.6 % less LA yield of this study using 1-(1-propylsulfonic acid)-3-methylimidazolium chloride with water and ethanol as solvents. Shen et al. [27], produced 39.4 % of LA using 1-(4-butyl-sulfonic acid)-3-methylimidazolium hydrogen sulphate in the presence of water, which is less by 15.2 % compared to the results of this study.

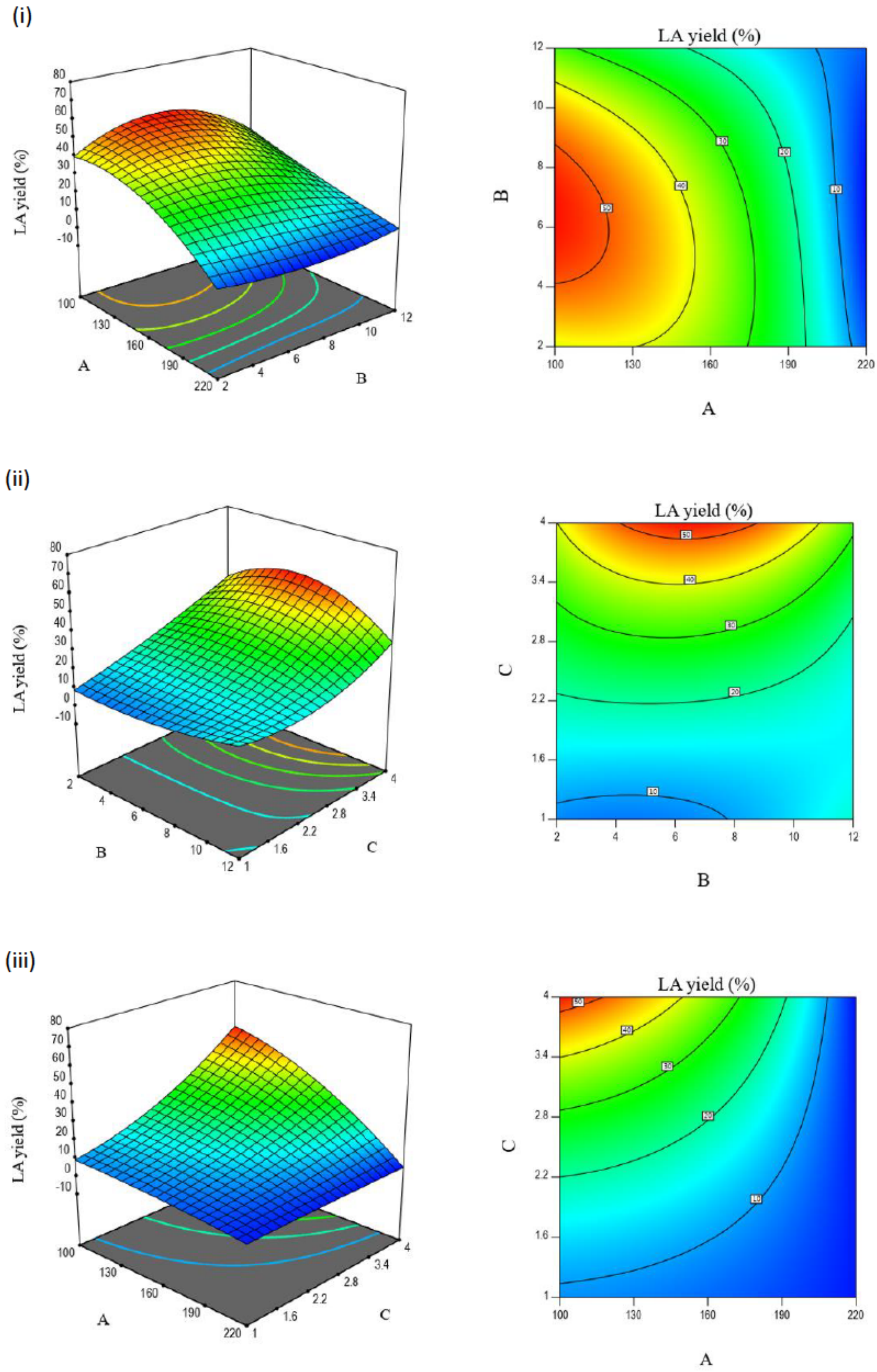

(i)
LA yield (%)
80
70
60
50
40
30
20
10
0
-10
100
130
160
190
220
A
2
4
6
8
10
12
B
LA yield (%)
12
10
8
6
4
2
B
100
130
160
190
220
A
50
40
30
20
10
(ii)
LA yield (%)
80
70
60
50
40
30
20
10
0
-10
2
4
6
8
10
12
B
1
1.6
2.2
2.8
3.4
4
C
LA yield (%)
4
3.4
2.8
2.2
1.6
1
C
2
4
6
8
10
12
B
50
40
30
20
10
(iii)
LA yield (%)
80
70
60
50
40
30
20
10
0
-10
100
130
160
190
220
A
1
1.6
2.2
2.8
3.4
4
C
LA yield (%)
4
3.4
2.8
2.2
1.6
1
C
100
130
160
190
220
A
50
40
30
20
10

Figure 4.7 3D Response surface and conto 1 contour plots for LA yield (i) temperature (A) and reaction time (B) (ii) reaction time (B) and IL loading (C) and (iii) temperature (A) and IL loading (C)

4.3.3 Solvent effect on the production of LA from DSB using [EMim][HSO_4]

Figure 4.8 illustrates the yield of LA when different solvents were used for the production of LA using the optimum conditions which were determined when using water as the solvent (control). MIBK yielded 62 % of LA being the highest of all the four solvents used in this study. Nhien et al. [1] reported on a solvent case study for production of LA from lignocellulosic biomass, using furfural, MIBK, octanol for extraction of LA, and formic acid (FA). The MIBK solvent extracted more LA compared to the other two solvents. Sun et al. [142] reported a 63 % LA yield using water and MIBK to hydrolyse cellulose since MIBK enhances the conversion of cellulose [188]. It was observed that DMSO and MIBK were added to the bagasse it immediately dissolved the bagasse unlike other solvents used in this work. Also, even after the reaction, the bagasse becomes fibreless in appearance when compared to when water, ethanol and water/ethanol are used.

The first reaction step in the production of LA from bagasse is the dissolution process of cellulose from bagasse. It is therefore a very important step and a solvent that is capable of dissolving cellulose is advantageous because it translates into more cellulose to produce a higher LA yield. DMSO yielded 45.5 % of LA. The addition of DMSO has been used to reduce the viscosity of the ionic liquid, as well as, act as a potential stabilizer for HMF and to prevent the formation of humins. However, the addition of DMSO has a negative impact on the LA yield [189]. Ethanol yielded the least LA (42.4 %) but when water and ethanol were used in equal amounts, the LA yield increased by 9.7 % (52.1 %) which shows that water under acidic conditions is significant for the hydrolysis of cellulose, as it forms H_3O^+ that attacks the (1-4)-glycosidic bond [190] increasing the LA yield.

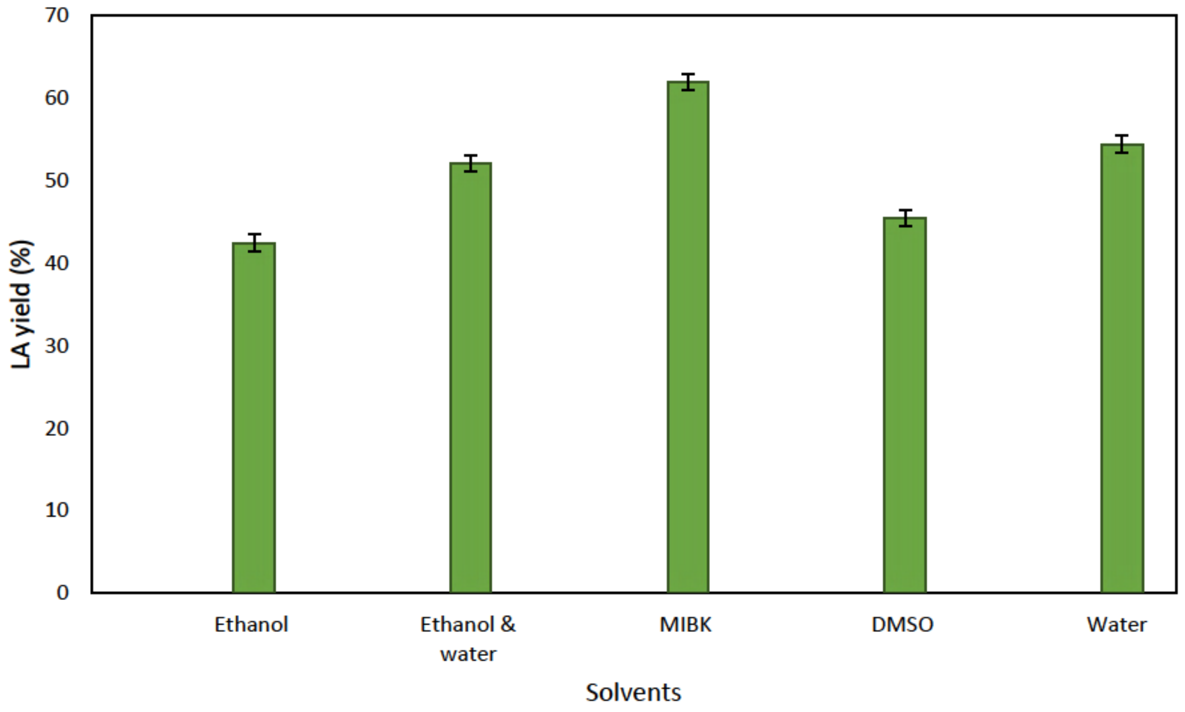


Figure 4.8 Solvent optimization for the production of LA using [EMim][HSO_4]

4.3.4 Reusability of [EMim][HSO_4] for LA production

Ionic liquids are expensive [191], therefore, testing its reusability is a very important step. The reusability test results (figure 4.9) show a small change in the IL activity for the five runs using the recycled IL. The decrease in the LA yield after the 5th run was ± 15 %.

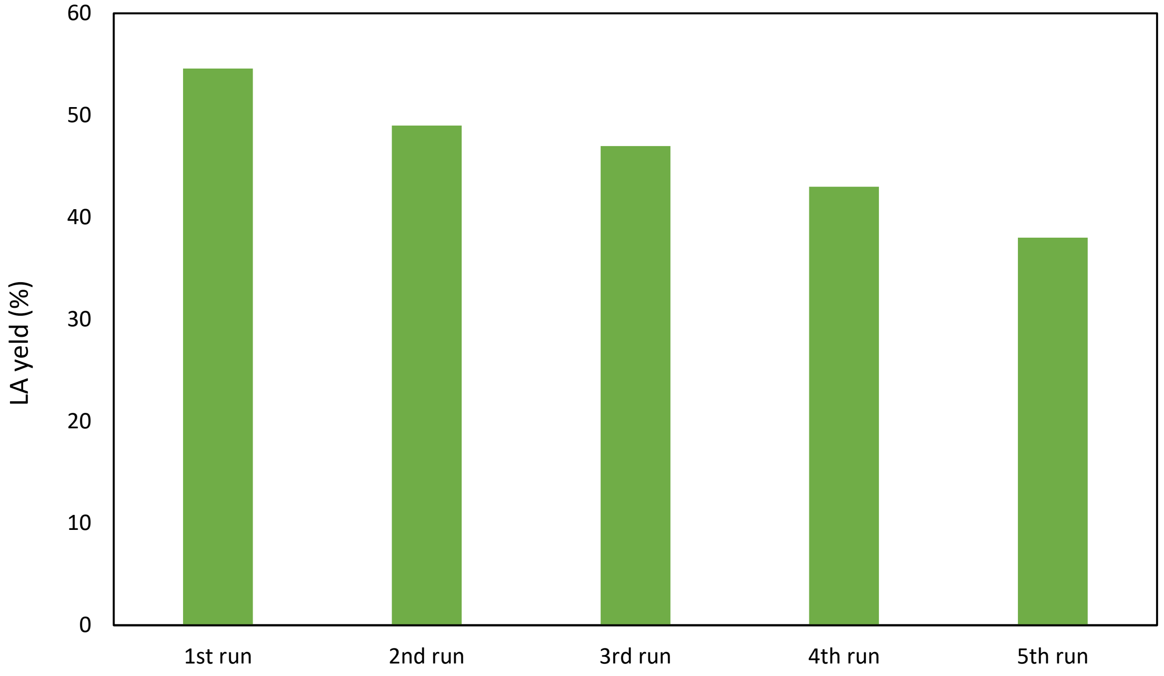


Figure 4.9 Reusability tests for [EMim][HSO_4] using the optimized conditions (a temperature of 100 °C, reaction time of 7 h and ionic liquid loading of 4 g)

4.3.5 Production of LA from pure glucose and fructose using [EMim][HSO_4]

In this work, LA was also produced directly from pure fructose, using [EMim][HSO_4] and water as the solvent. A yield of 88.9 % of LA was obtained which is 7.9 % higher than the LA yield obtained by Kuster and Van der Baan. [192] using hydrochloric acid. Pure glucose yielded 70.7 % LA when using [EMim][HSO_4] and water as the solvent. Ramli and Amin. [107] produced a maximum amount of 71.7 % of LA from pure glucose using 1-sulfonic acid-3-methyl imidazolium tetrachloroferrate under the following conditions: temperature of 170 °C, a reaction time of 3 h, catalyst loading of 6 g, and glucose loading of 0.2 g. Which is 1 % higher than the LA yield obtained in this study. This is due to the difference in the reaction conditions and IL utilized. The production of LA from sugars is less complicated when compared with producing LA directly from depithed sugarcane bagasse (DSB) and that is due to the complex structure of DSB. The complex structure of DSB requires a strong catalyst to disrupt the hydrogen bonds in the structure and render access to cellulose to form glucose. Unlike pure fructose and glucose, when DSB reacts in the presence of the catalyst and solvent, various side products are generated, which subsequently decreased the LA yield.

4.3.6 Product characterization with FTIR

(I) DSB before and after production of LA

FTIR spectroscopy was performed to detect changes in functional groups and/ molecular conformation that occurred in DSB as a result of LA production. The complex structure of DSB consists of cellulose, hemicellulose and lignin. The FTIR spectra bands for the DSB after LA production showed lower absorption values compared to the untreated DSB, which may be due to the reaction formation of LA (figure 4.10). The band at 897 cm^{-1} represents the glycosidic bond β-(1-4) cellulose. The region between 1200 and 1100 cm^{-1} represent hemicellulose and cellulose, the long peak at about 1035 cm^{-1} is due to C-O stretching and the peak at 1164 cm^{-1} is for the asymmetrical stretching of C-O-C. A peak around 1733 cm^{-1} is for C=O stretching of unconjugated hemicellulose. The fingerprint region ranging from 1830 to 730 cm^{-1} of both spectra is different due to LA formation. The region between 3800-3000 cm^{-1} is for the crystalline structure of cellulose [175].

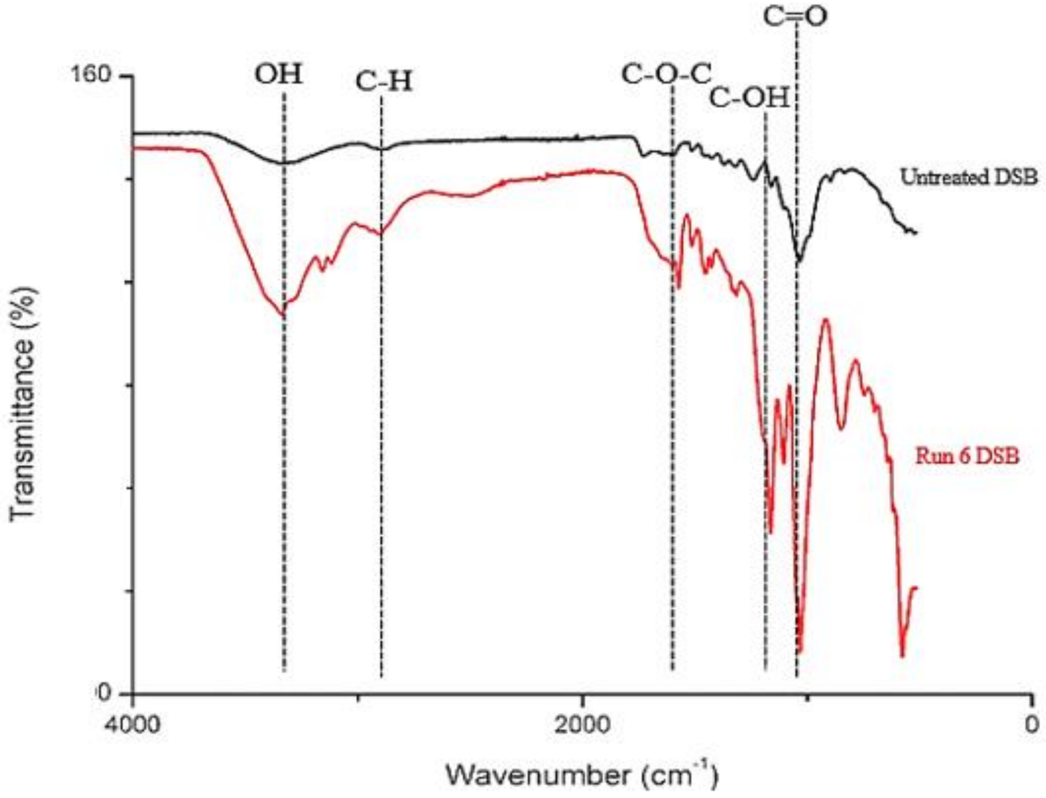


Figure 4.10 FTIR spectra for untreated DSB and optimum run (100 °C, 7 h, and 4 g [EMim][HSO_4] loading)

(II) Characterization of the optimum product

The optimum product (organic layer) was analysed with FTIR to determine the presence of LA (figure 4.11). The peak around 3300-2500 cm^{-1} is for O-H stretch for the carboxylic acid group, the peak in 3000-2850 cm^{-1} is for C-H stretch for alkane group it is very small, impurities may be the reasons the peak is not clear on the spectra, 1760-1690 cm^{-1} C=O stretch for carboxylic acid, the peak at 1715 cm^{-1} is due to C=O stretch for ketone group, the peak at 1370-1350 cm^{-1} is for C-H rock for alkane, the peak at 1320-1000 cm^{-1} is for C-O stretch for carboxylic acid group and the peak at 950-910 cm^{-1} is for O-H bend for a carboxylic acid group. All the functional groups that are present in figure 4.11 are functional groups present in the LA structure indicating the presence of LA in the reaction product.

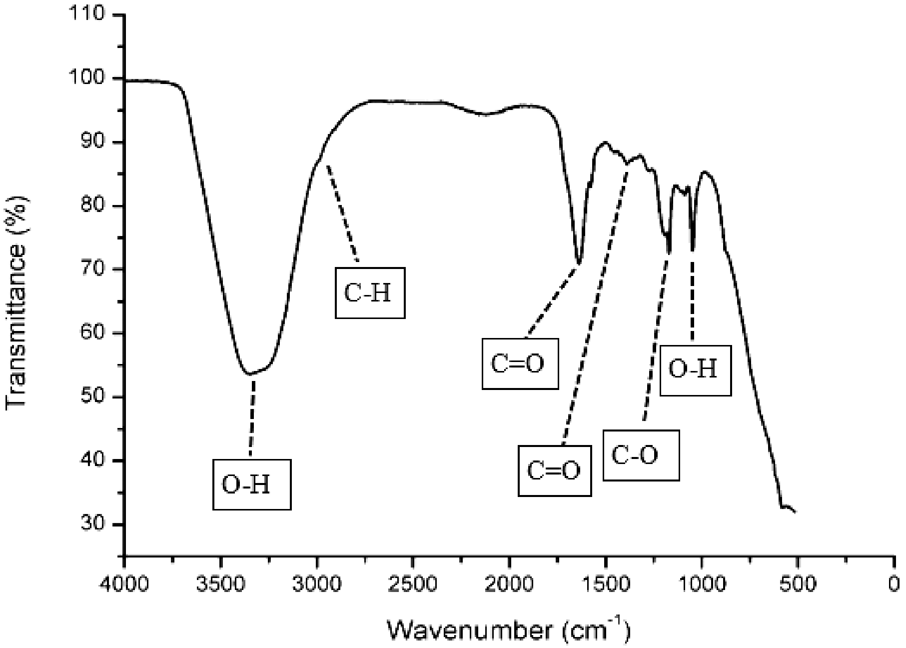


Figure 4.11 FTIR spectra for LA from the optimum run (100 °C, 7h, and 4g [EMim][HSO_4]

4.4 Upscaling the conversion of DSB to LA catalysed with [EMim][HSO_4]

The upscaled LA production from DSB catalyse with [EMim][HSO_4] yielded 55 % which is 0.4 % higher compared to the LA yield produced for the laboratory scale. This shows that there is no significant difference that occurred when the reaction was upscaled and that the optimized parameters can be used to reproduce the laboratory scale results. The only difference that was observed is the amount of water required, the mixture was too thick therefore it required more water to be added for the mixture to be stirred. This shows that a process that requires combining raw biomass with liquid reagents does not scale linearly, i.e. the physical amount of biomass relative to the liquid reagents is far greater in the large-scale process. Ramli and Amin. [107] produced 24.8 % of LA yield from oil palm fronds (OPF) using 1-sulfonic acid-3-methyl imidazolium tetrachloroferrate [SMIM][$FeCl_4$] which is lower than the yield obtained in this work, this may be due to different catalysts used, or different reaction conditions.

Section B: Application of synthesized LA from DSB, three LA derivatives production were optimized with various catalysts, the results are shown below:

4.5 Ethyl levulinate (EL)

4.5.1 Optimization of commercial LA conversion to EL using MsOH

The optimization results for the esterification reaction of commercial LA to EL are shown in table 4.6. The optimum reaction conditions were a reaction time of 5.25 h, a temperature of 90 ^{o}C, and a catalyst loading of 2.75 g (MsOH) which yielded a maximum EL of 92.2 % at a LA conversion of 98 % and EL selectivity of 94 %. MsOH was used in the study because Rackemann et al. [52] showed that MsOH reaches comparable yields as using sulfuric acid or hydrochloric acid and it is less corrosive. The predicted EL yield (92.17 %) was close to the experimental value showing that the model accurately captured the significance of the model terms. The response (EL yield %) in table 4.6 was obtained from HPLC analysis using EL standards in a calibration curve (peak area vs concentration). Table 4.5 also shows high LA conversion and high EL selectivity.

The polynomial regression model for esterification of LA into EL is given in Eq.4.3:

$$\begin{aligned} \text{EL yield (\%)} \ (Y_{EL}) = {} & 92.17 + 0.7938\,A - 3.72\,B - 7.60\,C \\ & 4.54\,AB - 2.38\,AC - 4.33\,BC \\ & 9.06\,A^2 - 9.91\,B^2 - 3.03\,C^2 \end{aligned} \tag{4.3}$$

The equation in terms of coded factors can be used to make predictions about the response for given levels of each factor. The coded equation is useful for identifying the relative impact of the factors by comparing the factor coefficients.

Table 4.6 Optimization reaction factors, a yield of EL (%), commercial LA conversion (%) and EL selectivity (%)

Run	Factor 1	Factor 2	Factor 3	Response	Commercial LA conversion X_{LA} (%)	EL selectivity S_{EL} (%)
	A: Time (h)	**B: Temperature (°C)**	**C: Catalyst loading (g)**	**EL yield (%)**		
1	0.5	120	2.75	75.1	89	84
2	5.25	120	5	62.7	88	71
3	5.25	90	2.75	91.3	97	94
4	**5.25**	**90**	**2.75**	**92.2**	**98**	**94**
5	0.5	60	2.75	72.3	87	83
6	0.5	90	0.5	85.5	91	94
7	5.25	90	2.75	91.1	96	95
8	5.25	60	0.5	82.0	93	88
9	5.25	90	2.75	91.7	96	96
10	5.25	60	5	77.5	88	88
11	0.5	90	5	73.0	79	92
12	10	90	0.5	91.9	98	94
13	5.25	90	2.75	92.0	98	94
14	10	90	5	69.9	80	87
15	10	120	2.75	62.5	73	86
16	10	60	2.75	85.4	90	95
17	5.25	120	0.5	89.6	95	94

Optimum conditions are in bold

The quality and accuracy of the model for the optimization of EL production from commercial LA was determined by the analysis of variance (ANOVA) shown in table 4.7 The coefficient of determination R^2 is 0.9978 which is close to 1.0 indicating good ability of the model to predict the EL yield. The model F-value of 350.36 implies the model is significant, there is only a 0.01% chance that an F-value this large could occur due to noise. P-values less than 0.0500 indicate model terms are significant. In this case A, B, C, AB, AC, BC, A^2, B^2, C^2 are significant model terms. The lack of fit F-value of 3.28 implies the lack of fit is not significant relative to the pure error. There is a 14.04 % chance that a lack of fit F-value this large could occur due to noise. The non-significance of the lack of fit indicates that the model was able to satisfactorily predict the response.

Table 4.7 ANOVA analysis for the quadratic model for EL production

Source	**Sum of Squares**	**df**	**Mean Square**	**F-value**	**P-value**
R^2 = 0.9978					
Model	1629.89	9	181.10	350.36	< 0.0001
A-Time	5.04	1	5.04	9.75	0.0168
B-Temperature	110.63	1	110.63	214.03	< 0.0001
C-Catalyst loading	462.08	1	462.08	893.96	< 0.0001
AB	82.36	1	82.36	159.33	< 0.0001
AC	22.56	1	22.56	43.65	0.0003
BC	74.82	1	74.82	144.75	< 0.0001
A^2	345.94	1	345.94	669.27	< 0.0001
B^2	413.86	1	413.86	800.67	< 0.0001
C^2	38.57	1	38.57	74.63	< 0.0001
Residual	3.62	7	0.5169		
Lack of Fit	2.57	3	0.8577	3.28	0.1404
Pure Error	1.05	4	0.2613		
Corrected Total	1633.51	16			

The parity plot in figure 4.12 illustrates the experimental EL and predicted EL yields. The points are all close or in the straight line of the graph which indicates that the model successfully predicted EL yield.

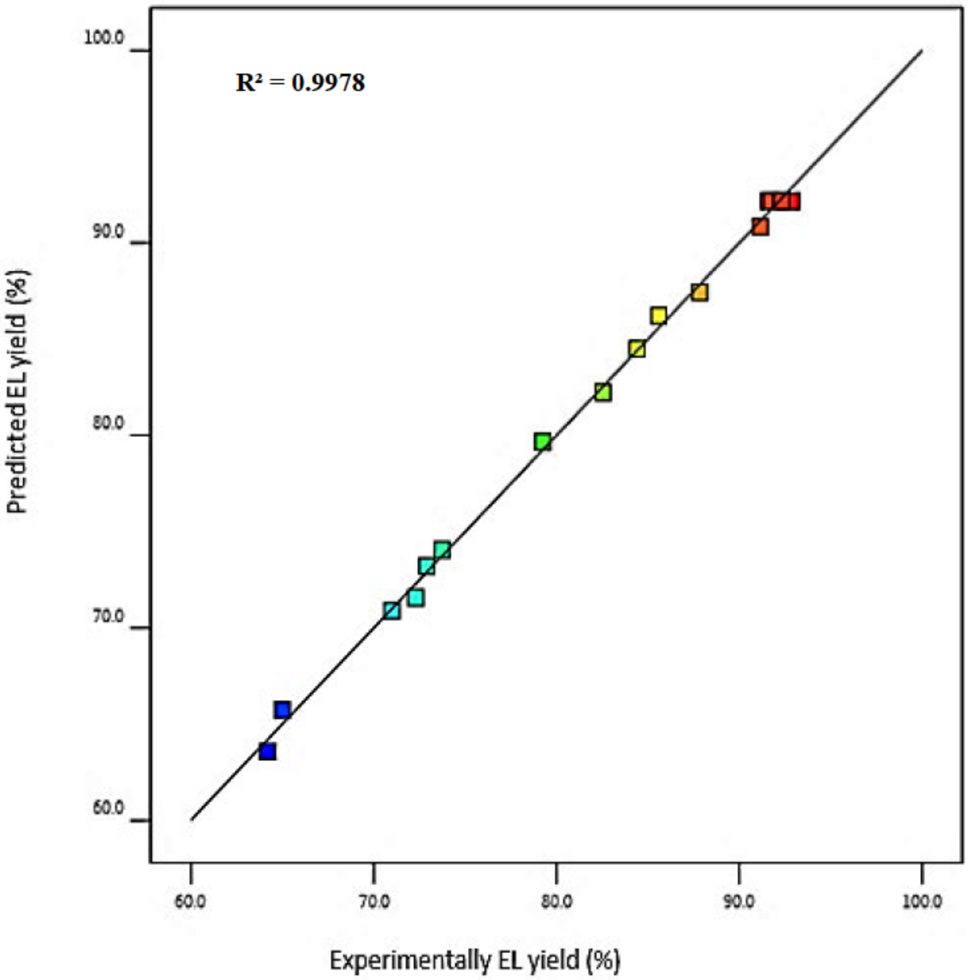


Figure 4.12 Parity plot for the esterification of LA into EL, comparing predicted and experimentally EL yield

In this work, three factors were investigated and the pareto chart (figure 4.13) illustrates which factor has a more significant effect on the EL yield. The significance of linear (A, B, C), quadratic (A^2, B^2, C^2) and interaction (AB, BC, AC) model terms towards EL yield is shown in figure 4.13 where A is the reaction time, B is the temperature, and C is the catalyst loading. Figure 4.13 shows that the quadratic terms of temperature and time are the most significant model terms followed by catalyst loading.

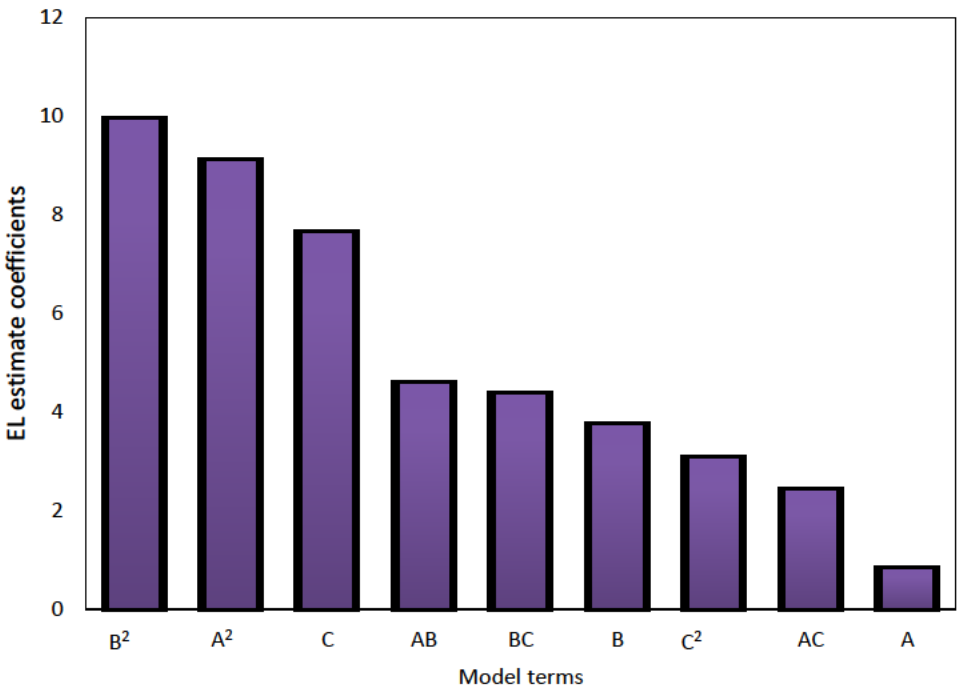


Figure. 4.13 Pareto chart of the model terms for the esterification of LA into EL.

Figure 4.14 a-c illustrates the interaction of two factors with one factor remaining constant. The RSM plots are used to study the effect of two factors at a time on the product yield (EL %). Figure 4.14 a-c shows that both minimum and maximum conditions favour lower EL yield compared to the moderate conditions. All the investigated factors play an important role in the response.

Figure 4.14 (a) shows that lower (60 °C) and higher (120 °C) temperatures lower the EL yield, as well as, shorter (0.5 h) and longer (10 h) reaction times. The results show that both temperature and time have an effect on EL yield.

Figure 4.14 (b) illustrates the RSM plot for the catalyst loading and time. A catalyst loading of 2.75 g and a reaction time of 5.25 h yielded the maximum EL (92.2 %). Figure 4.14 (b) shows that high catalyst loading and long reaction time increase reaction rate thus high EL is obtained.

Figure 4.14 (c) shows the interaction between catalyst loading and temperature where a catalyst loading of 2.75 g at a temperature of 90 °C produced the maximum EL yield (92.2 %). Increasing both parameters from the minimum values (catalyst loading of 0.5 g and temperature of 60 °C) also increases the EL yield although the maximum values (catalyst loading of 05 g and temperature of 120 °C) decreased the EL yield. The investigated factors showed that moderate conditions: temperature of 90 ºC, catalyst loading of 2.75 g and reaction time of 5.25 h gave a maximum EL yield (92.2 %). The moderate conditions increases the reaction rate of the reaction hence high yield was obtained.

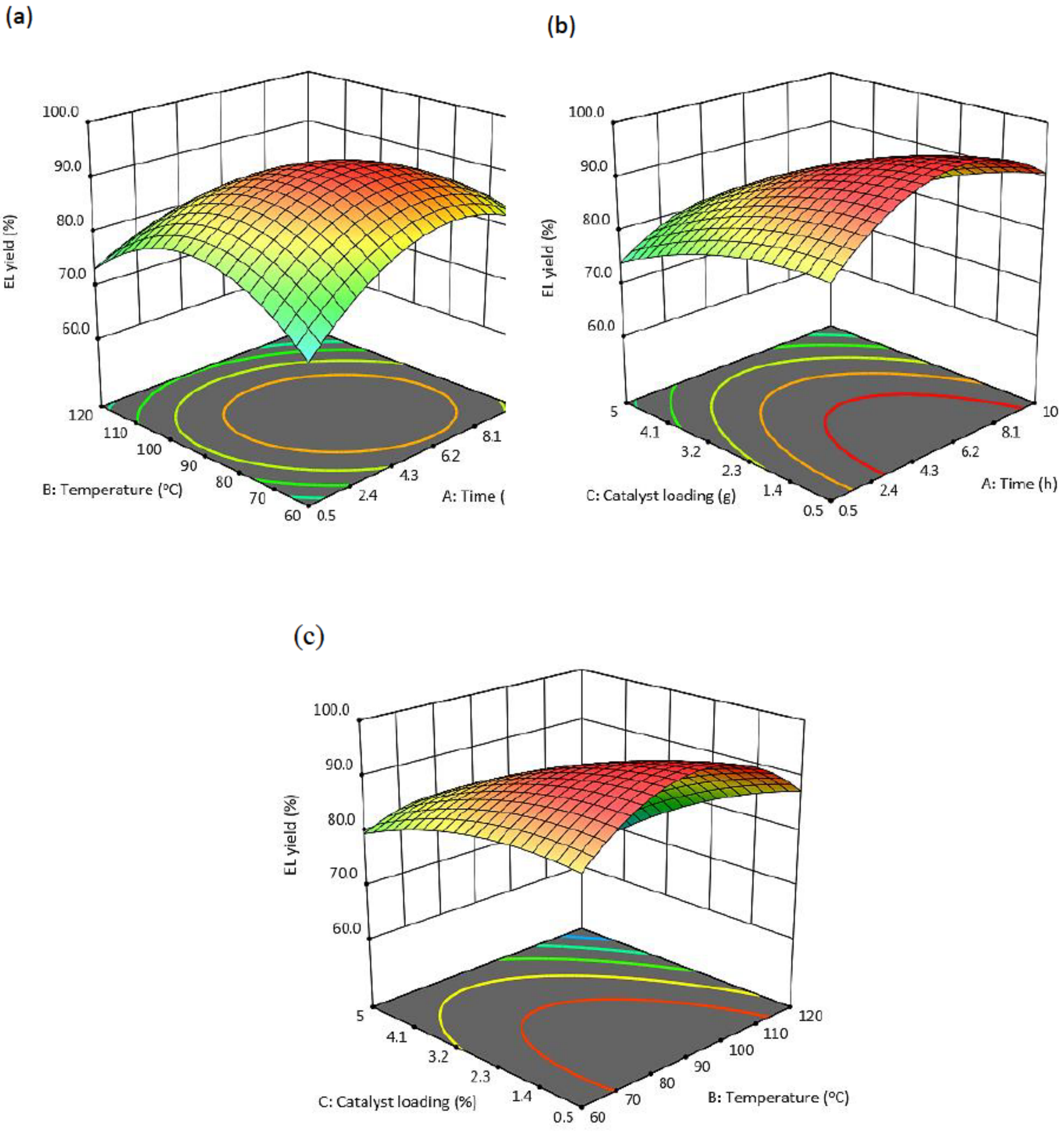


Figure 4.14 RSM plots for the interaction of the investigated factors: (a) temperature vs time (b) catalyst loading vs time (c) catalyst loading vs temperature

4.5.2 FTIR scan of the optimum EL

For the optimization of EL production from LA, 17 experiments were carried out to determine the optimum conditions of the process. The optimum run was then analysed with FTIR, the other 16 runs weren't analysed with FTIR because of the large volume of data. Figure 4.15 illustrate the optimum sample the EL standard that was analysed by FTIR. Ethyl levulinate is an ester and the functional groups of an ester are shown in the FTIR scan. The C-H stretch is at 3000 cm^{-1} (lit 2969 cm^{-1}). The characteristics C=O stretch due to the ester group is at 1700 cm^{-1} (lit 1718 cm^{-1}). The C-O stretch occurs at 1000 cm^{-1} (lit 1029 cm^{-1}). The C-H bending at 1350 cm^{-1} (lit 1366 cm^{-1}) [186]. The peaks for the pure EL (standard) are longer and sharper. The C=O stretch and C-O stretch for the EL standard is more pronounced. The presence of the above functional groups indicates the presence of EL in the optimum sample.

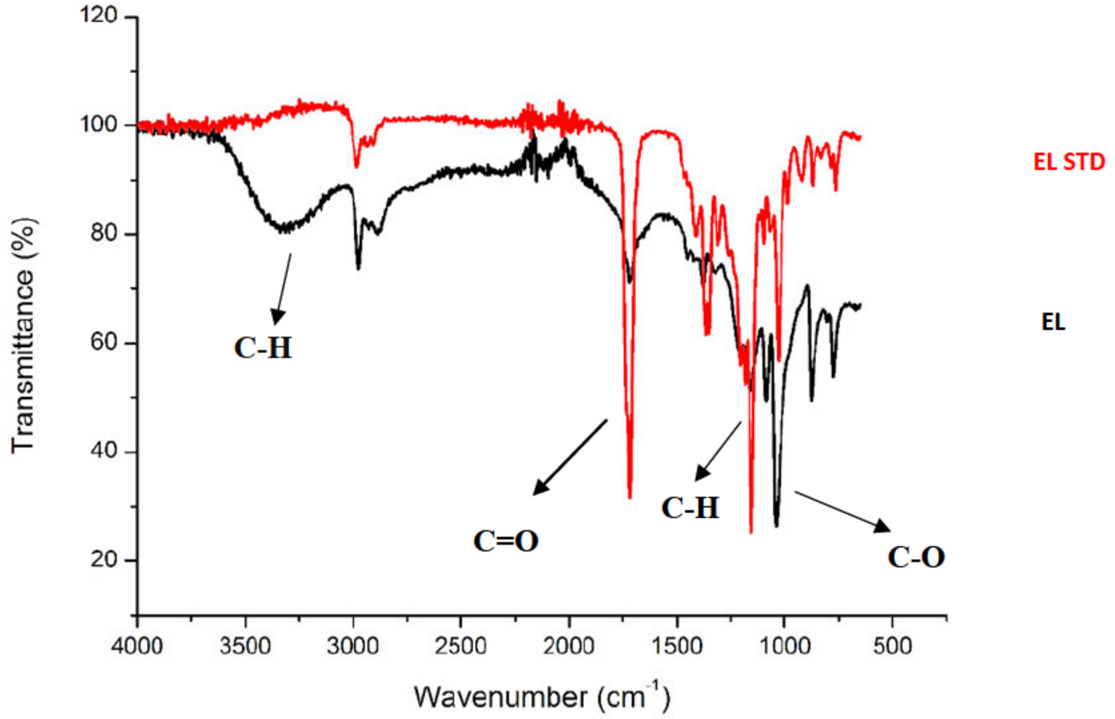


Figure 4. 15 FTIR scan for ethyl levulinate (EL)

4.5.3 Catalyst effect on the conversion of commercial LA to EL

Figure 4.16 illustrates the effect of the catalysts on the production of EL from commercial LA. Sulfuric acid exhibited the highest yield (94 %) followed by MsOH (92.2 %). Sulfuric acid is toxic and corrosive and in the long term more expensive. The reactivity of LA esterification into EL depends on the acidity of the catalyst (acid sites density and accessibility of the acid sites) [193]. In this work, tosylic acid produced 90 % EL. Cirujano et al. [170] produced 99 % of EL from commercial LA using tosylic acid under the following conditions: reaction time of 8 h, the temperature of 78 °C, and ethanol to LA (15:1). This may be due to the milder reaction conditions employed in this work. Of the two ILs: [BMim][HSO_4] and [EMim][OTs] the latter ([EMim][OTs]) gave an EL yield of 78.25 % and since it is recyclable it can be seen as more cost-effective for EL production.

Although lower EL yield was achieved when ILs were used, ILs are known to be environmentally friendly because their evaporation into the atmosphere is low which decreases the contamination of the environment [8, 30]. ILs are nonflammable, thermally and chemically stable, can be recovered, and recycled. Since ILs are less corrosive and reusable, this shows that more EL can be produced using a minimal amount of IL with a lower corresponding cost of reactor equipment maintenance. Amarasekara and Wiredu. [146] produced 19.0 % of EL from cellulose using the IL 1-(1-propylsulfonic)-3-methylimidazolium chloride which is low when compared to EL yield obtained in this work.

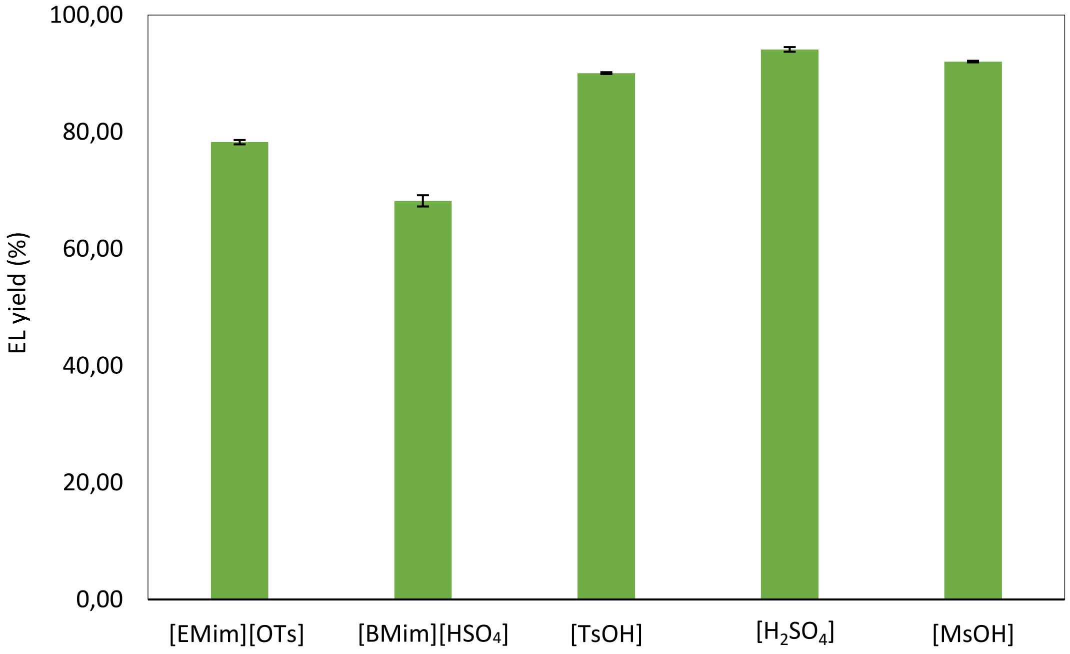


Figure 4.16 Catalyst optimization for EL production from LA

4.5.4 Esterification of commercial LA to levulinic esters using various alcohols

The yield of levulinate esters are shown in table 4.8 Ethanol yielded the highest levulinate ester (ethyl levulinate 92 %) followed by methyl levulinate (90 %). Ramli et al. [194] reported on the production of methyl levulinate (69 %) and butyl levulinate (40 %) using sulfated SiO_2 as a catalyst. When compared to this work, the literature yields are lower, the difference in EL yields may be due to the different catalyst (MsOH) used in this work. Table 4.8 shows that MsOH is a good catalyst to produce levulinate esters. Kalghatgi and Bhanage. [195] produced 89.6 % of butyl levulinate at 90 °C using 1-methyl imidazolium hydrogen sulphate [Mim][HSO_4] compared with 85 % for this work. 2-Propanol produced the lowest yield (70 %) of ester (propyl levulinate), this could possibly be due to the branched structure of the alcohol making esterification difficult. Levulinate esters have been produced from various alcohols namely ethanol, methanol, butanol [196, 197], 2,3-butanediol [198], propanol, 1,2-propanediol, isobutyl alcohol, 2-butyl alcohol, isopropanol [199]. Luan et al. [199] stated that linear carbon chains in alcohol have a positive effect on the production of alkyl esters from LA. But with branched alcohols (2-butyl alcohol and 2-propanol) lower conversion of LA to esters was observed which may be attributed to larger steric hindrance which blocks the carboxylic acid in the esterification reaction [199]. A similar case was observed in this work, LA conversion to esters using branched alcohols was lower than when using the linear chain carbon alcohol equivalent (Table 4.8).

Table 4.8 Esterification of LA to levulinic esters

Solvents	**Levulinate esters yield (%)**	**LA conversion (%)**	**Ester selectivity (%)**
Methanol (CH_4O)	90	95	95
Ethanol (C_2H_6O)	92	96	96
Propanol (C_3H_8O)	88	93	95
Butanol ($C_4H_{10}O$)	85	91	93
2-propanol (C_3H_8O)	70	88	80
2-butanol ($C_4H_{10}O$)	82	90	91

4.5.5 Production of EL from LA derived from DSB

The conversion of DSB to LA was 89 %, DSB derived LA conversion to EL was 75 %, and EL selectivity was 84 %. The EL yield (75%) produced in this study is higher compared to the EL yield (55.2 %) that was produced by Liu et al. [199] when utilizing duckweed (lemna minor) with 0.04 mol/L sulfuric acid in ethanol at 200 ºC in 3 h. The lower EL yield, when compared to this work, may be attributed to the different carbohydrate content in the different biomass utilized, and the higher temperature used by Liu et al. [199]. Which can promote the formation of char and humins when strong acids are used. Also, in this work, the converted LA was first extracted before it was converted to EL. Ramli et al. [107] studied the EL production from an oil palm frond, using 5 g of 1-sulfonic acid-3-methyl imidazolium tetrachloroferrate ([SMIM][$FeCl_4$]) in 30 mL at 78.4 °C for 7 h yielding 20.1 %. The yield obtained by Ramli et al. [107] was also lower than the EL yield obtained in this study. Guan et al. [200] produced EL from wheat straw using sulfonate ILs and obtained a yield of 16.23 % in the liquefied fraction. Amarasekara and Wiredu. [146] used a Bronsted acidic ionic liquid 1-(1-propylsulfonic)-3-methylimidazolium chloride in a one-pot reaction to produce EL from cellulose but obtained a very low yield (15.1 %).

Therefore, LA derived from DSB is a good substrate for EL production. Also, biomass (DSB) valorization can promote an increase in small scale sugarcane farming, lead to a localized biorefinery and a bioeconomy where value chemicals (LA and EL) are produced from waste biomass. The production of chemicals from crude oil refining is environmentally damaging and contributes to global warming effects and the exploitation of waste biomass can mitigate this effect.

4.6 γ-valerolactone (GVL)

4.6.1 Effect of temperature, time, and catalyst loading for GVL production from commercial LA to GVL

The hydrogenation of commercial LA to GVL was optimized using data from table 3.3 and the results are shown in Table 4.9. The optimum conditions are a temperature of 112.5 ^{o}C, a reaction time of 6 h, and a catalyst loading of 2.75 g which yielded a maximum GVL of 78.6 %. Table 4.9 also shows that the hydrogenation of commercial LA to GVL is reproducible since five runs were repeated and their response differed by <1.3 %.

Table 4.9 Investigated reaction parameters with responses for GVL, LA conversions, and GVL selectivity

Run	Factor 1	Factor 2	Factor 3	Response	LA conversion (%)	GVL selectivity (%) (S_{GVL})
	A: Time (h)	**B: Temperature (°C)**	**C: Catalyst loading (g)**	**GVL (%) (Y_{GVL})**		
1	2	112.5	0.5	48.6	66	74
2	6	112.5	2.75	78.1	93	84
3	6	112.5	2.75	78.6	97	81
4	10	112.5	0.5	52.3	75	70
5	6	200	5	49.1	72	68
6	6	112.5	2.75	77.9	96	81
7	10	200	2.75	39.2	57	69
8	6	200	0.5	39.5	54	73
9	10	112.5	5	58.3	72	81
10	6	25	5	58	85	68
11	6	112.5	2.75	78.3	95	82
12	2	25	2.75	46.7	70	70
13	6	25	0.5	48	67	67
14	10	25	2.75	45.9	63	73
15	2	112.5	5	61	87	70
16	6	112.5	2.75	78	98	80
17	2	200	2.75	36.1	59	61

4.6.2 RSM analysis

The polynomial regression model for GVL production from commercial LA is given in Eq. 4.4:

where *A* is the temperature, *B* is the time, and *C* is the catalyst loading.

$$Y\ (\text{GVL yield \%}) = +78.18 + 0.4062\,A - 4.34\,B + 4.75\,C + 0.9625\,AB - 1.60\,AC - 0.1100\,BC - 14.91\,A^2 - 21.30\,B^2 - 8.22\,C^2 \qquad 4.4$$

The optimum experimental GVL yield (78.6 %) is close to the theoretical GVL yield (78.2 %) calculated from Eq. 4.4.

Table 4.10 shows that the quadratic model is significant in determining the response (model p-value < 0.0001). The coefficient of determination (R^2) value is 0.9998 also indicating that the variation around the average could be explained by the model i.e. 99.98 % of the variability in the responses can be explained by the model [201]. The model *F*-value of 4384.69 implies the model is significant. There is only a 0.01 % chance that an *F*-value this large could occur due to noise in the data. $P < 0.0500$ indicates that the model terms are significant at the 95 % confidence level. In this case, A, B, C, AB, AC, A^2, B^2, C^2 are significant model terms. The lack of fit *F*-value of 1.57 implies the lack of fit is not significant relative to the pure error (random error). There is a 32.77 % chance that a lack of fit *F*-value this large could occur due to noise. Non-significant lack of fit means that the model is fit to predict the response.

Table 4.10 ANOVA for the response surface quadratic model for GVL production as a function of time (*A*), temperature (*B*), and catalyst loading (*C*)

Source	**Sum of squares**	**df***	**Mean square**	***F*-value**	***P*-value**
GVL (R^2 = 0.9998)					
Model	3785.69	9	420.63	4384.69	< 0.0001
A	1.32	1	1.32	13.76	0.0076
B	150.60	1	150.60	1569.84	< 0.0001
C	180.12	1	180.12	1877.58	< 0.0001
AB	3.71	1	3.71	38.63	0.0004
AC	10.24	1	10.24	106.74	< 0.0001
BC	0.0484	1	0.0484	0.5045	0.5005
A^2	936.51	1	936.51	9762.16	< 0.0001
B^2	1910.95	1	1910.95	19919.77	< 0.0001
C^2	284.24	1	284.24	2962.92	< 0.0001

Residual	0.6715	7	0.0959		
Lack of fit	0.3635	3	0.1212	1.57	0.3277
Pure error	0.3080	4	0.0770		
Cor total	3786.36	16			

*Degrees of freedom

The parity plot is used to determine the reliability of the model. The parity plot of GVL yield is shown in figure 4.17 where the predicted GVL yield is compared with the experimental (observed) GVL yield. The points in the graph are in a straight line indicating that the model is significant and can predict GVL yields accurately.

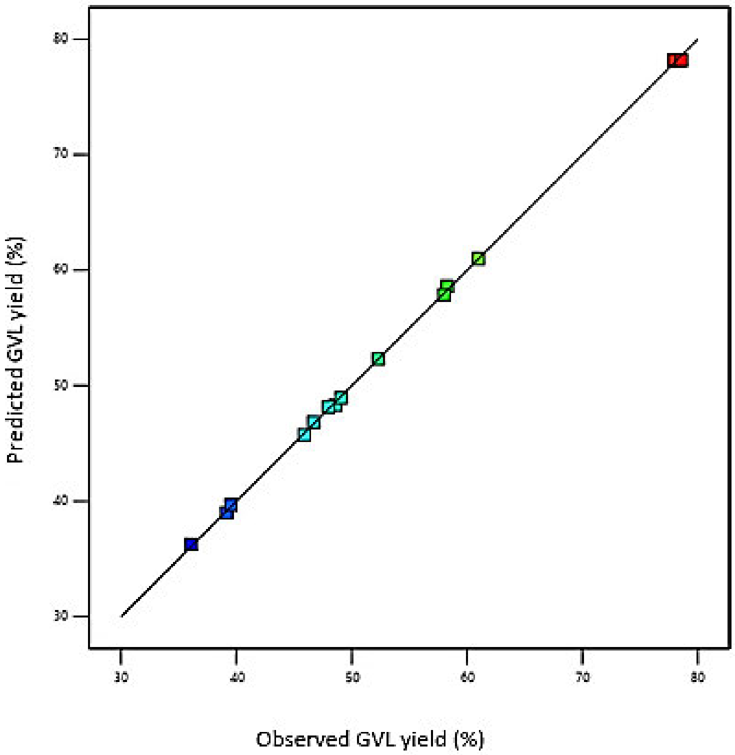


Figure 4.17 GVL parity plot that compares the predicted GVL yield with experimental GVL yield

The pareto chart illustrates which of the investigated parameters have a greater influence on GVL yield. Figure 4.18 shows that temperature (B) had the greatest effect, compared to time (A) and catalyst loading (C). The *P* values in table 4 shows that all the investigated parameters are significant, but the interaction of temperature and catalyst loading (BC) has minimal effect on GVL yield.

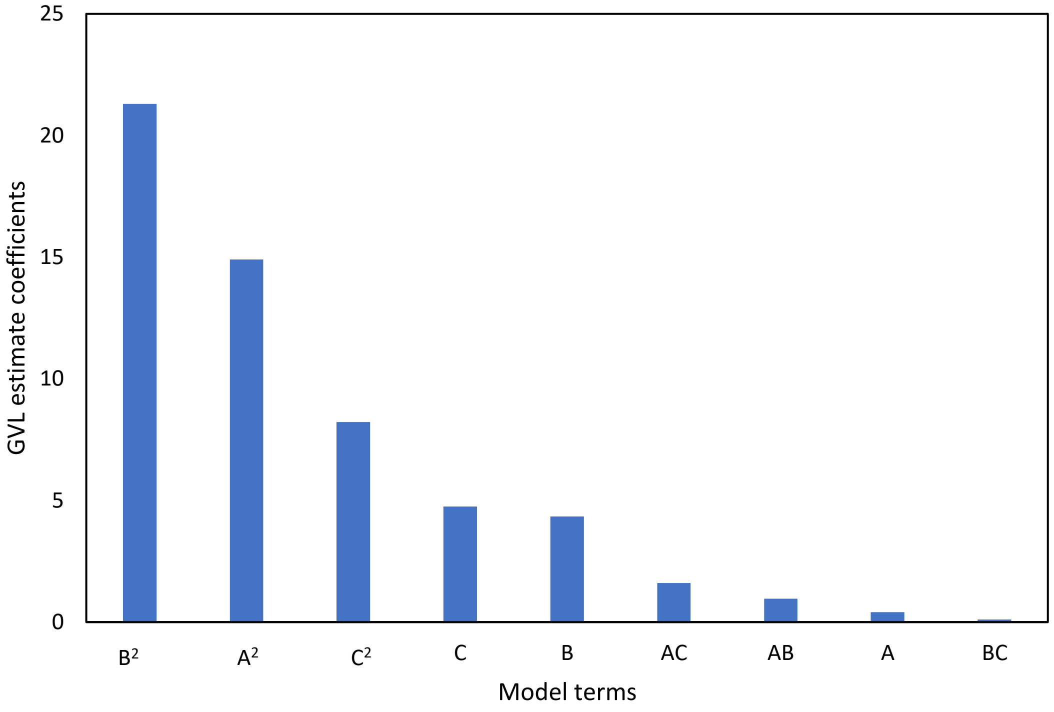
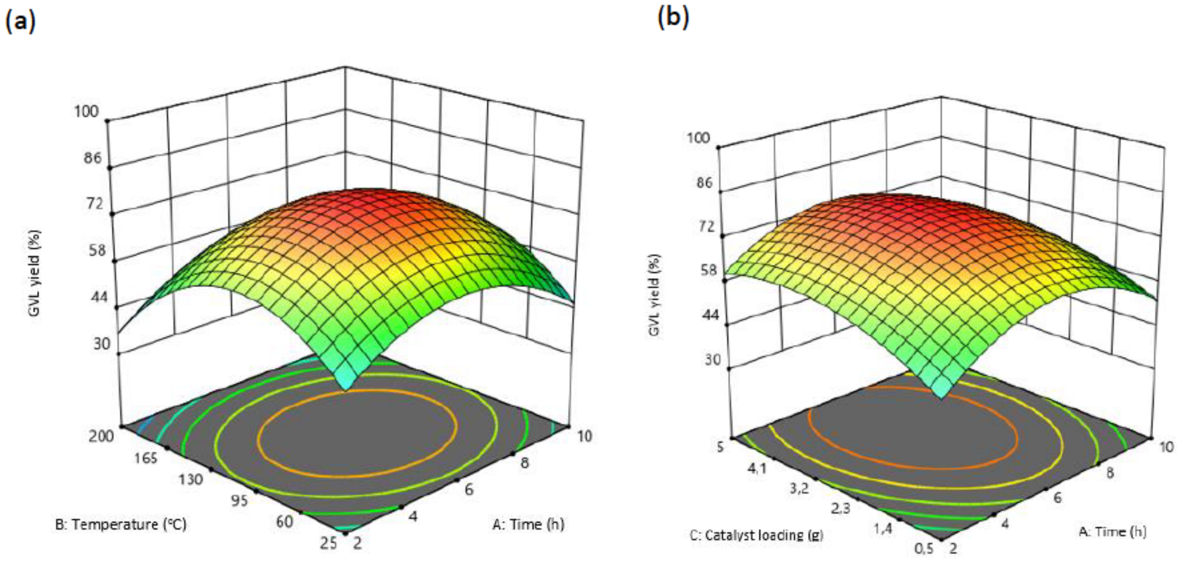


Figure 4.18 GVL pareto chart of the model terms which illustrate the terms that have more effect on the GVL yield. Investigated model terms are temperature (A), time (B), and catalyst loading (C)

The response surface and contour plots (figure 4.19 a-c) illustrate the interaction of the investigated factors (time, temperature, and catalyst loading) to produce GVL from commercial LA. Figure 4.19 a) indicates that both temperature and time are significant to GVL yield. The minimum temperature (25 ^{o}C) and time (2 h) yielded a low GVL yield (46.7 %). Increasing the temperature to 112.5 ^{o}C and time to 6 h resulted in maximum GVL yield (78.6 %), however increasing the temperature and reaction time to 200 ^{o}C and 10 h, respectively resulted in a marked decrease in GVL yield (39.2 %). Therefore, a temperature of 112.5 ^{o}C and a time of 6 h are the optimum conditions for GVL production from LA using MsOH as the catalyst.

Figure 4.19 b illustrates the interaction of catalyst loading and time on GVL yield. Increasing the catalyst loading and time from 0.5 to 2.75 g and 2 h to 6 h increases the GVL yield. A catalyst loading of 2.75 g and time of 6 h yielded a higher GVL yield ranging from 77.9 to 78.6 %. Increasing the time to 10 h with a catalyst loading of 2.75 g results in lower GVL yields (39.2 to 45.9 %) whereas increasing the catalyst loading from 2.75 g to 5 g for a reaction time of 10 h results in an increased GVL (49.1 to 58.3 %) yield. In general, increasing the catalyst loading and time is supposed to increase the rate of reaction thereby increasing the product yield but that is not the case in this work. This may be due to the production of by-products (1,4-pentanediol and 4-hydroxypentanoic acid (4-HPA)) [202]. Even if the maximum reaction conditions produced the highest yield, increasing both time and catalyst loading means the production process of GVL will be expensive because it will require more energy and more catalyst.

The relationship of catalyst loading and temperature on the reaction is shown in figure 4.19 c, where a catalyst loading of 2.75 g and a temperature of 112.5 ℃ produced the maximum GVL yield (78.6 %). Figure 4.19 indicates that moderate reaction conditions favour a high yield of GVL whereas the minimum and maximum factors lower the GVL yield. All the factors play an important role in the production of GVL, which was confirmed by ANOVA (table 4.9). The optimized conditions are a: temperature of 112.5 ℃, time of 6 h, and catalyst loading of 2.75 g yielding 78.6 % GVL.



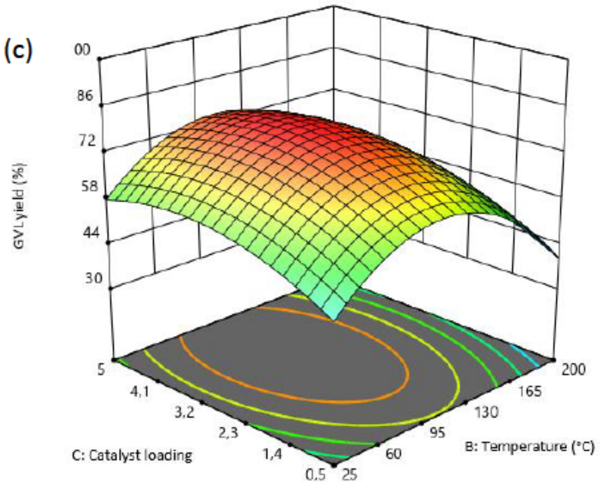


Figure 4.19 Response surface and contour plots for the interaction of the investigated factors: (*a*) temperature vs time (*b*) catalyst loading vs time (*c*) catalyst loading vs temperature

Singh et al. [203] used Ni/NiO catalyst to produce GVL from commercial LA which showed a high conversion of > 90% and high selectivity of > 90%, the LA conversion obtained in this study is higher by 7% whereas the GVL selectivity is low by 9 % the difference is due to the different catalysts used.

4.6.3 Effect of catalysts on GVL yield

Figure 4.20 illustrates the effect of the catalysts on the production of GVL. Various catalysts: tosylic acid [TsOH], 1-butyl-3-methylimidazolium hydrogen sulphate [BMim][HSO_4], 1-ethyl-3-methylimidazolium tosylate [EMim][OTs], sulfuric acid [H_2SO_4] and methanesulfonic acid [MsOH] were used to study the catalysts' effect on the production of GVL from commercial LA. The maximum GVL yield was for sulfuric acid (80.9 %) followed by methanesulfonic acid (78.6 %) and tosylic acid (71.4 %). Although mineral acids usually produce high yields their disadvantages include high cost of neutralization, separation, purification steps, and corrosiveness that needs special materials of construction. It is necessary to separate the mineral acid from the reaction products because it negatively affects downstream processes [161, 204]. Two ILs (1-butyl-3-methylimidazolium hydrogen sulphate and 1-ethyl-3-methylimidazolium tosylate) were used to catalyse the conversion of LA to GVL, which yielded 65.1 % and 58.6 % of GVL, respectively. These results illustrate that ILs can catalyze the conversion of LA to GVL in the presence of formic acid and triethylamine. The advantages of ILs over minerals acids are their: negligible vapour pressure, non-flammability, thermal and chemical stability, recoverability, and recyclability [53, 54]. Therefore, the ILs are preferred as catalysts for GVL production from LA although [BMim][HSO_4] yielded 15.8 % less when compared to [H_2SO_4].

Sanchis et al. [205] used a synthesized nickel catalyst which presented a relatively high yield and selectivity to GVL (up to 40 % and > 98%, respectively) in the hydrogenation of LA, the maximum GVL yield obtained in this work is higher however the nickel catalyst is highly selective compared to MsOH. López-Aguado et al. [206] reported on GVL production, where high LA conversion (> 95%) and GVL yield (> 90%) were achieved however the duration of the reaction was too long (20 days) at 170 ºC using Zr–Al-beta zeolite catalyst. Jori and Jadhav. [207] produced GVL from biomass-derived levulinic acid using 150 wt % of catalyst (hafnium based carbonaceous (Hf@$CCSO_3H$)) at 200 °C for 24 h in isopropanol solvent as a hydrogen donor. 100 % conversion of LA was achieved with a high yield of 96 % with more than 99 % selectivity of GVL. This is higher compared to the maximum yield obtained in this study which is due to the different catalysts used, the catalyst used seem to be more effective under harsh conditions which are opposite of the catalyst used in this study.

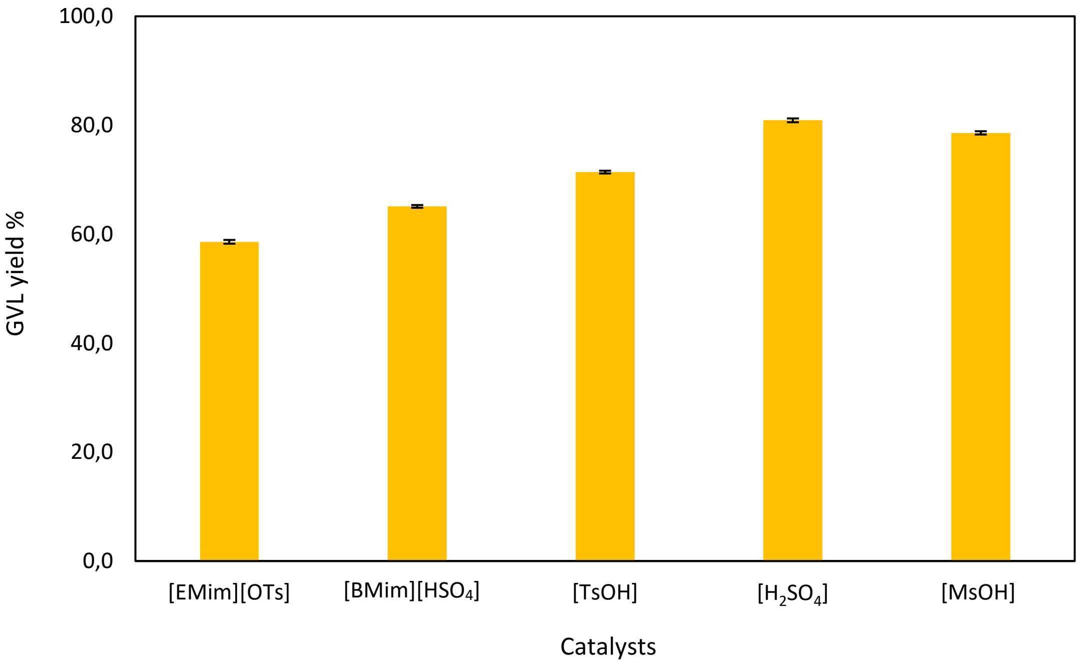


Figure 4.20 Effect of catalysts on GVL production from LA.

4.6.4. Effect of solvent on the production of GVL

There are different types of solvents that have been used for GVL production namely water, ethanol, dichloromethane, and water, 1,4-dioxane, and methanol [208]. Also, alcohols have been used as an H-donor for the hydrogenation of GVL production [208]. Therefore, in this work, various solvents are studied to observe their effect on the GVL yield. The effect of the solvent in the hydrogenation of commercial LA to GVL using MsOH is shown in figure 4.21. The following solvents were used: water (H_2O), methanol (CH_3OH), ethanol (C_2H_5OH), ethanol and water (C_2H_5OH and H_2O), and butanol ($C_4H_{10}O$). Water is the best solvent for GVL production (78.6 %). Water is also a preferred solvent because of its chemical and physical properties which makes water to be non-toxic to human and aquatic organisms, easily available, and environmentally friendly [10, 147]. Ethanol also had a similar effect to water for the conversion process (76.5 %). The ethanol and water mixture gave a lower yield of GVL (61 %). This could be due to the intermolecular hydrogen bonding occurring between water and ethanol molecules preventing the conversion of LA to GVL. Polar mixed solvents do not increase the GVL conversion.

To ensure a high degree of LA conversion, solvents such as alcohols (methanol, ethanol, butanol), or water are used [209, 210]. Hengst et al. [211] reported LA conversion of 75–100% when various alcohols were used for GVL production with Ni/Al_2O_3 catalyst. When water was used, the LA conversions were low with 2% compared to alcohols, even though similar reaction conditions (150 °C, 10 bar H_2, 6 h) were used however the GVL selectivity of water was the highest (100 %). The outcome of this study is the opposite of Hengst et al. [211] since when water was used the LA conversion was 97 % and GVL selectivity was 81 % which were higher compared to alcohols (LA conversion, 85-95 % and GVL selectivity, 60-80 %) this is due to the different conditions and catalysts used. Fu et al. [144] attained higher LA conversion (100%) and GVL selectivity (99.2%) by employing dioxane as the solvent under milder reaction conditions (180 °C, 2 h), even though the LA conversion and GVL selectivity are higher but the CHEM21 solvent selection guide which ranks solvents according to the severity of safety (S), heath (H) and environmental (E) hazards state dioxane as not recommended due to its toxicity [212].

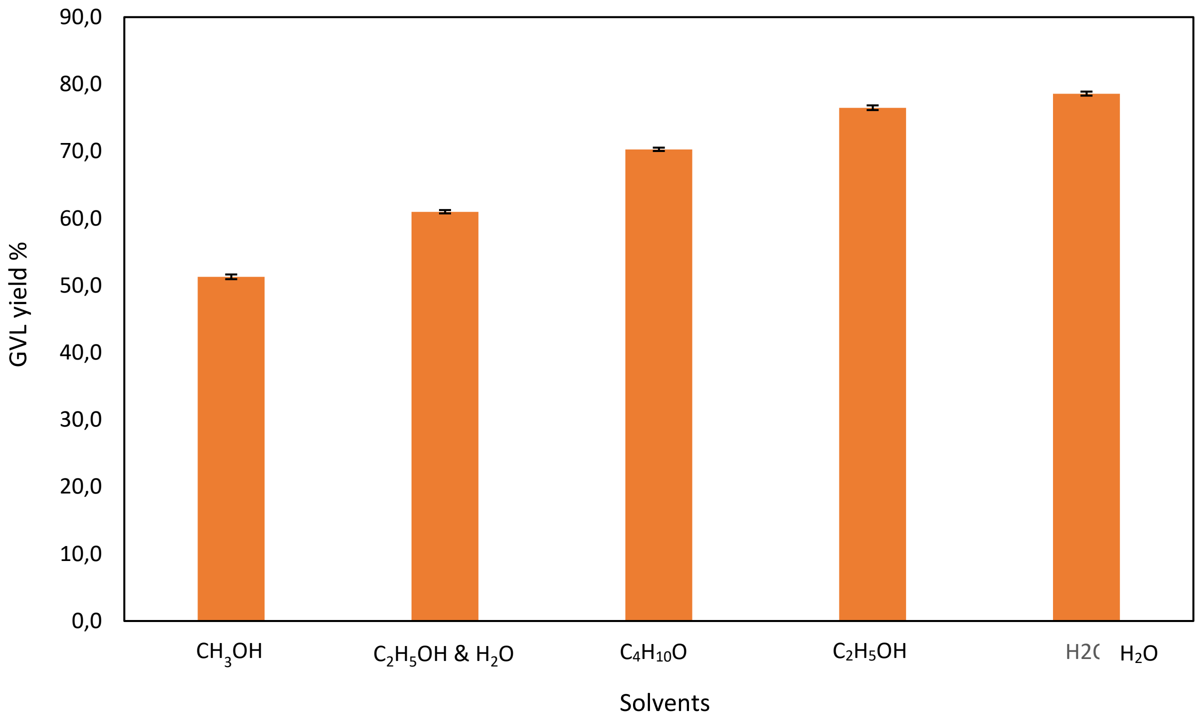


Figure 4.21 Effect of solvents on the GVL production from commercial LA

4.6.5 Hydrogenation of LA derived from DSB into GVL

The use of LA derived from DSB with the optimized conditions for the commercial LA conversion to GVL of 6 h, 112.5 °C, and 2.75 g of MsOH yielded a GVL of 77.6 %, LA conversion of 95 %, and 82 % of GVL selectivity. The GVL yield obtained from DSB derived LA is 1.0 % less compared to the GVL yield produced from commercial LA. The difference may be due to impurities in the LA derived from DSB, but the difference is minor. Thus, LA derived from DSB is a promising reactant for GVL production. Barla et al. [213] used cobalt-based catalyst for the hydrogenation of biomass-derived LA to GVL which resulted in a 99 % conversion of LA and 80% selectivity of GVL, although the catalyst used is different however the LA conversion difference is 4 % and GVL selectivity is 2 % which is less, this shows that MsOH can replace metal catalysts and that LA derived from DSB can be used as a starting material for GVL production.

4.7 Diphenolic acid (DPA)

4.7.1 Optimization of DPA production from commercial LA using MsOH

Table 4.11 lists the DPA yield (%), commercial LA conversion (%), and *p,p'*-DPA/*o,p'*-DPA selectivity (%). The optimum reaction conditions were 6 h (time), 75 °C (temperature), and 5.5 g (catalyst loading), yielding 65.8% of DPA. In table 4.11 (run 12) where the lowest % LA conversion occurred (46%) the factors that had the least effect were temperature (75 ^{o}C) and catalyst loading (10 g) and the factor that had the greatest effect was a time (2 h). For run 4 with the same temperature and loading but a different time (10 h), the LA conversion was 90%, so the variable time could give a difference as large as 44% in the % conversion of LA which is significant. A similar trend can be observed for % DPA conversion (runs 1 and 6) where % DPA produced increased from 21.1 % to 32 %, respectively when time increased from 2 h to 10 h. The reproducibility was high because 5 experiments (2, 8, 10, 14, and 16) using the same reaction conditions had a response difference within +/- 2 %. The optimum conditions favour higher selectivity of the p,p'-DPA isomer.

Table 4.11 Experimental Conditions, DPA Yield, LA Conversion (%), *p,p'*-DPA/*o,p'*-DPA Selectivity (%)

Experiment No.	**Factor 1**	**Factor 2**	**Factor 3**	**Response**	**LA conversion X_{LA} (%)**	***p,p'*-DPA selectivity S_{DPA} (%)**	***o,p'*-DPA selectivity S_{DPA} (%)**
	A: Time (h)	**B: Temperature (°C)**	**C: Catalyst loading (g)**	**DPA yield Y_{DPA} (%)**			
1	2	75	1	21.1	70	74.1	26.0
2	**6**	**75**	**5.5**	**65.8**	**90**	**55.5**	**44.5**
3	6	125	1	38.8	89	61.2	38.8
4	10	75	10	46.9	90	51.2	48.8
5	10	25	5.5	44.2	78	59.1	40.9
6	10	75	1	32	75	54.9	45.1
7	2	125	5.5	46.7	88	57.9	42.1

8	6	75	5.5	64.8	87	57.5	42.5
9	10	125	5.5	61.4	89	51.0	49.0
10	6	75	5.5	65.1	88	58.8	41.2
11	6	25	1	30.9	68	60.2	39.8
12	2	75	10	27.2	46	88.0	12.0
13	2	25	5.5	28.9	78	67.5	32.5
14	6	75	5.5	64.5	87	55.3	44.7
15	6	125	10	58.6	70	57.5	42.5
16	6	75	5.5	64.9	89	55.8	44.2
17	6	25	10	34.6	69	57.5	42.5

Eq. 4.5 has the coded factors for the parameters and was used to make predictions about the response for given levels of each factor. By default, the high levels of the factors are coded as +1 and the low levels are coded as -1. The coded equation is useful for identifying the relative impact of the factors by comparing the factor coefficients.

$$\begin{aligned}\text{DPA yield (\%)} = {} & 65.02 + 7.57\,A + 8.36\,B + 5.56\,C \\ & 0.1500\,AB + 2.20\,AC - 4.03\,BC \\ & 14.32\,A^2 - 5.40\,B^2 - 18.90\,C^2 \end{aligned} \qquad 4.5$$

Table 4.12 displays the ANOVA for DPA yield. The model F-value of 1063.01 implies the model is significant. There is only a 0.01% chance that an F-value this large could occur due to noise. P-values less than 0.0500 indicate model terms are significant. In this case A, B, C, AC, BC, A^2, B^2, and C^2 are significant model terms. The lack of fit F-value of 2.85 implies that the model is fit to predict the DPA yield. The coefficient of determination (R^2) is 0.9993 which is close to one indicating that the model is significant.

Table 4.12 ANOVA for the RSM Results

Source	**Sum of Squares**	**Df**	**Mean Square**	**F-value**	**P-value**
R^2 = 0.9993					
Model	4066.71	9	451.86	1063.01	< 0.0001
A-Time	459.04	1	459.04	1079.92	< 0.0001
B-Temperature	559.45	1	559.45	1316.13	< 0.0001
C- Catalyst loading	247.53	1	247.53	582.33	< 0.0001
AB	0.0900	1	0.0900	0.2117	0.6594
AC	19.36	1	19.36	45.55	0.0003
BC	64.80	1	64.80	152.45	< 0.0001
A^2	863.72	1	863.72	2031.95	< 0.0001
B^2	122.67	1	122.67	288.58	< 0.0001
C^2	1503.64	1	1503.64	3537.39	< 0.0001
Residual	2.98	7	0.4251		
Lack of Fit	2.03	3	0.6758	2.85	0.1687
Pure Error	0.9480	4	0.2370		
Corrected Total	4069.68	16			

The parity plot in figure 4.22 illustrates the comparison between experimental and predicted DPA yield. There is excellent agreement between the experimental and predicted responses.

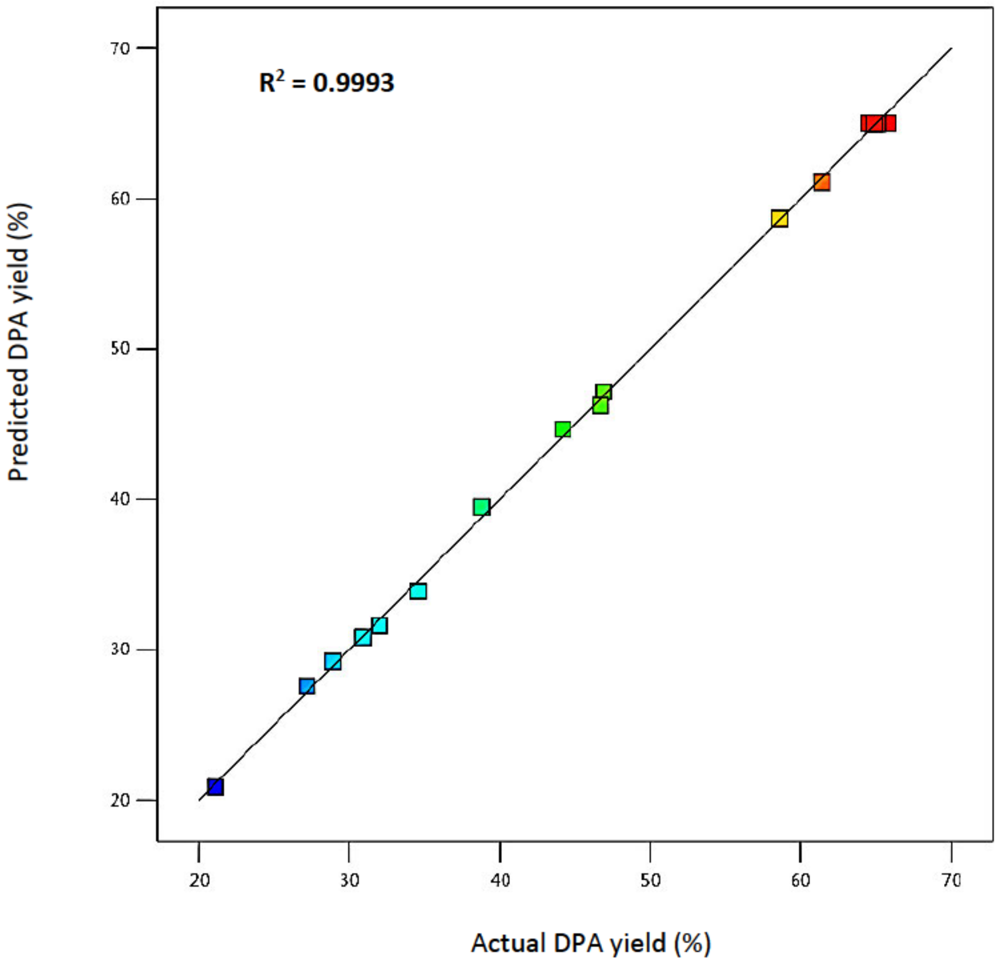


Figure 4.22 DPA parity plot which compares the predicted DPA yield with the experimental DPA yield

The pareto chart in figure 4.23 illustrates which factors have a high impact on the DPA yield. According to figure 4.23, the factors that have a high impact on DPA yield are temperature (B) followed by time (A), and catalyst loading (C).

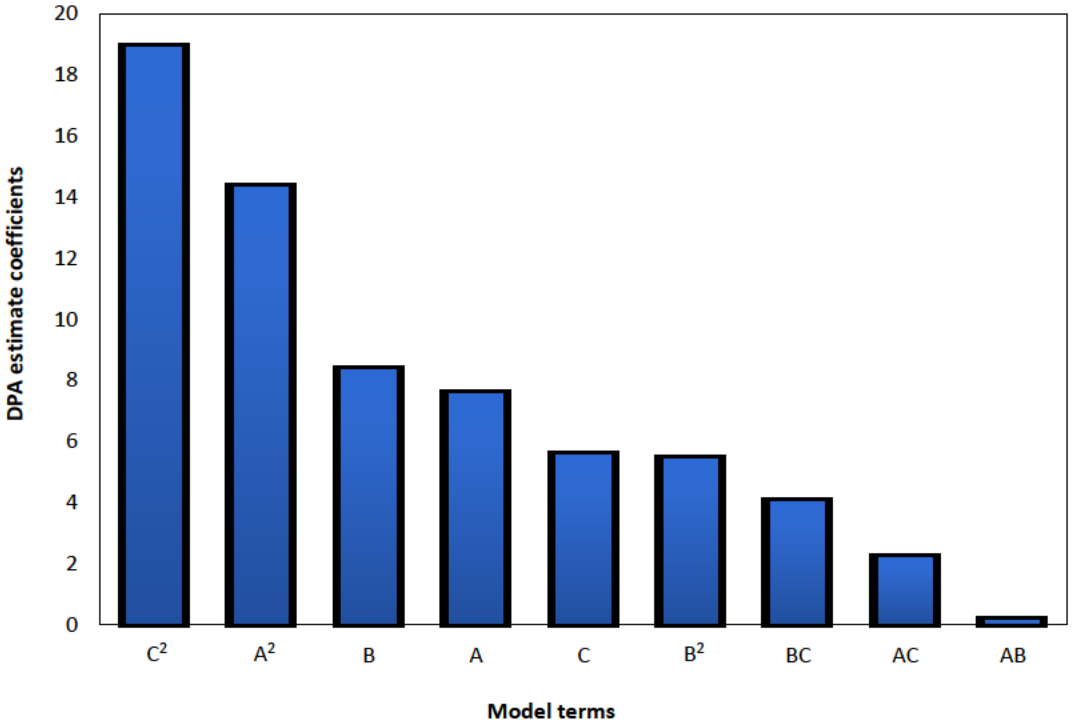
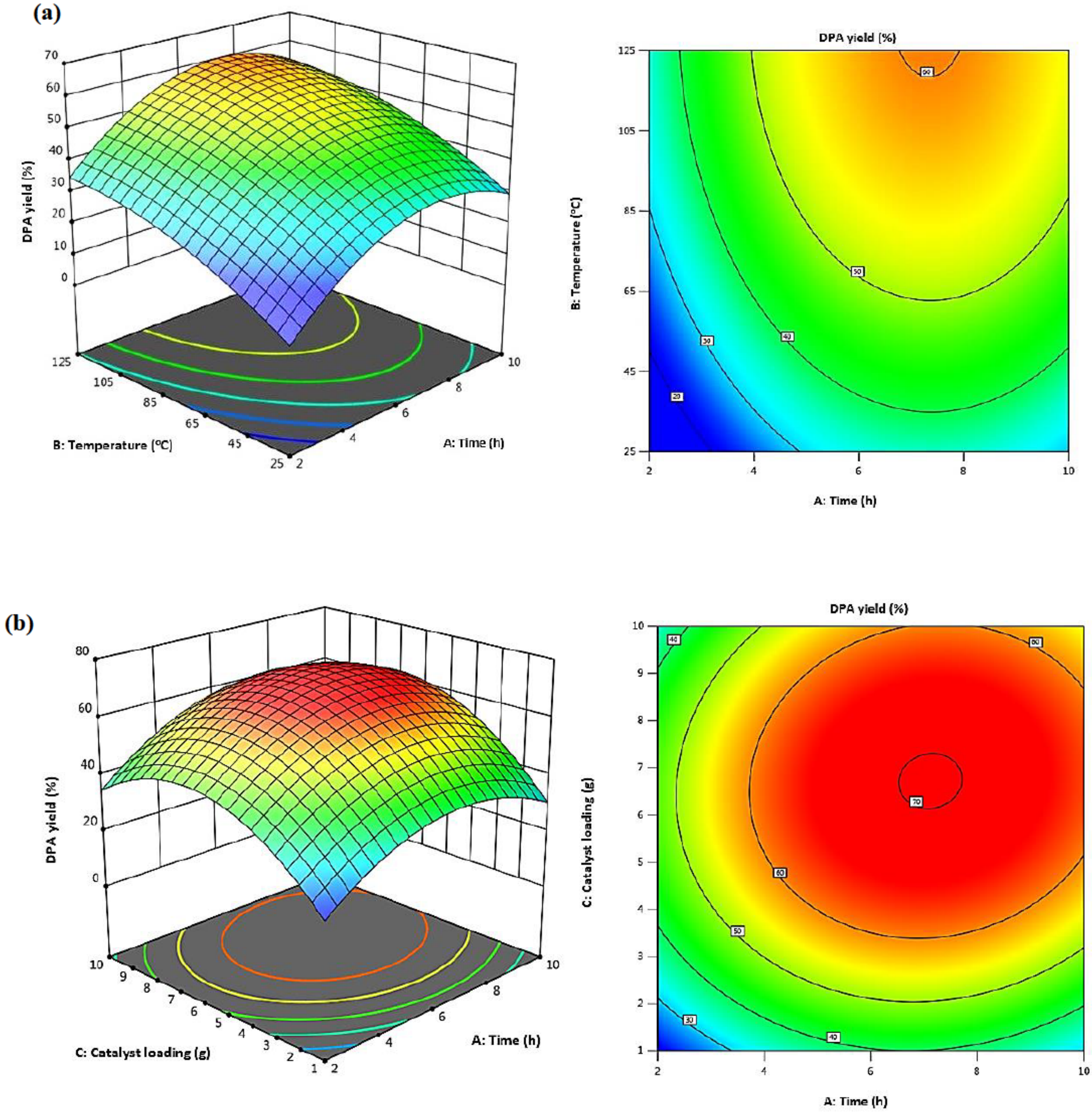


Figure 4.23 Pareto chart for DPA yield, which determines the most influential model term on DPA production

To study the interaction of the investigated factors in the production of DPA, RSM was used. The 3D response surface and contour plots are shown in figure 4.24 a-c where two factors and the response were evaluated while one factor remained at the optimum condition. Figure 4.24 illustrates the interaction between temperature and reaction time, the investigated range of temperature (25 to 125 °C) and 2 to 10 h for the reaction time. The temperature of 75 °C and the reaction time of 6 h yielded maximum DPA. Figure 4.26 a shows that the minimum and maximum temperature, and time yield lower DPA, whereas the moderate conditions favour the maximum production of DPA. Figure 4.24 b illustrates the interaction between catalyst loading and time, the reaction was carried out at 1 to 10 g and 2 to 10 h. The DPA yield increased with increasing catalyst loading and time.

Figure 4.24 b shows that a catalyst loading of 5.5 g and a reaction time of 6 h yielded maximum DPA yield. Figure 4.24 c shows the interaction between catalyst loading and temperature that shows increasing the catalyst loading from 1 to 5.5 g increased the DPA yield. Increasing the catalyst loading to 10 g decreased the DPA yield. The optimum conditions were temperature of 75 °C, time of 6 h, and catalyst loading of 5.5 g yielding 65.8% of DPA. From figure 4.24 a-c it is observed that less catalyst results in lower yield. This is possibly due to a lower overall reaction rate. Higher catalyst loadings coupled with longer reaction times result in lower yields, which could be due to degradation of the catalyst due to prolonged reaction times. Higher temperatures did not have a huge impact on the yield, but higher temperatures coupled with a higher catalyst loading reduced the yield. In summary, higher catalyst loading had a negative impact on the yield.



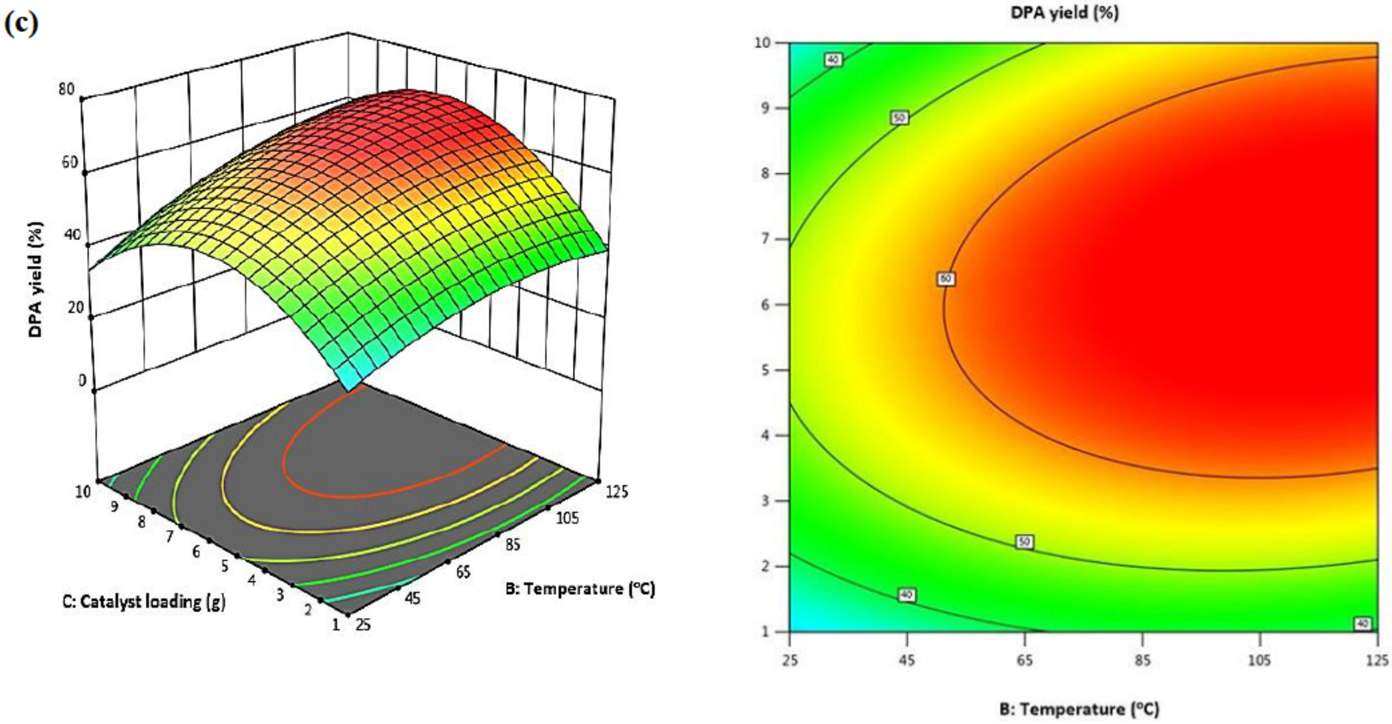


Figure 4.24 3D response surface and contour plots for the interaction of the investigated factors (a) temperature *vs*. time, (b) catalyst loading *vs*. time, and (c) catalyst loading *vs*. temperature

4.7.2 DPA FTIR characterization

The FTIR characterization of optimized DPA obtained from commercial LA is illustrated in figure 4.25 compared with a standard sample of DPA. The absorbance bands associated with the functional groups of DPA are observed in figure 4.27 by wavenumbers: carboxylic acid, COOH (1741 cm^{-1}), alkane, CH_3 (2862 to 2882 cm^{-1}) and CH_2 (2843 to 2863 cm^{-1}), hydroxyphenyl, OH (3650 to 3590 cm^{-1}). The above functional groups indicate the presence of DPA in the analysed reaction product. The FTIR scans of both DPA and DPA standard possess the same functional groups however the shape of the peaks are not similar this may be caused by the different production processes of DPA or that the DPA produced in this study was analysed in a reaction product therefore it was not purified.

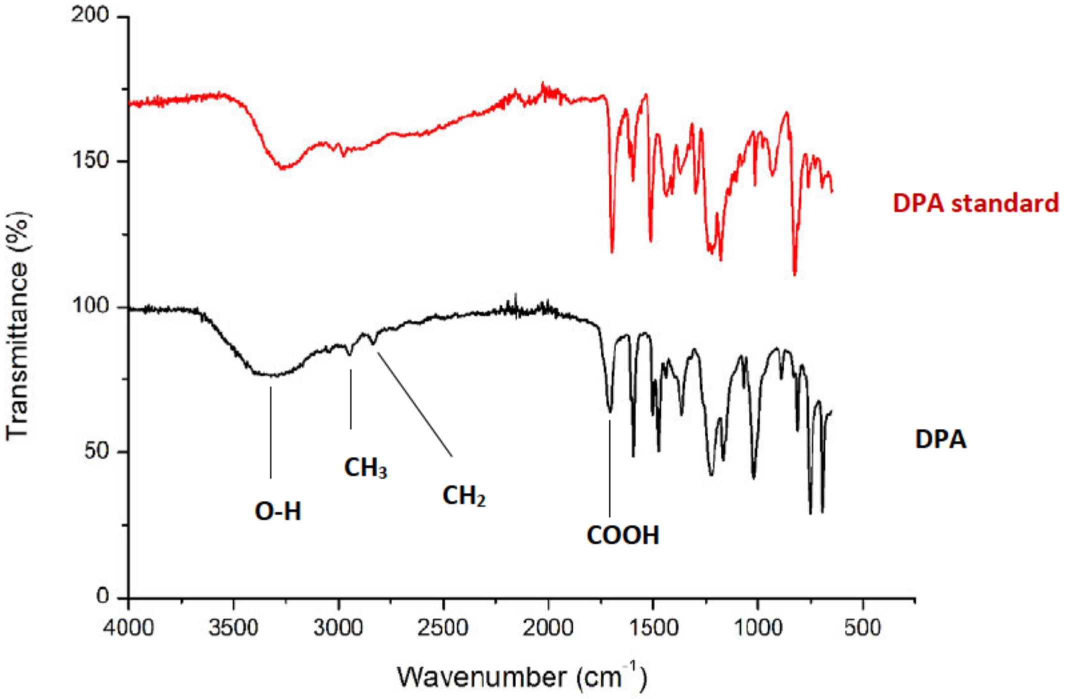


Figure 4.25 FTIR scan of DPA standard vs DPA produced from commercial LA

4.7.3 Effect of the Catalysts on the Production of DPA

Figure 4.26 shows the effect of catalysts on DPA yield. The evaluation of the effect of catalysts in the condensation reaction of DPA was carried out using tosylic acid [TsOH], 1-butyl-3-methylimidazolium hydrogen sulphate [BMim][HSO$_4$], 1-ethyl-3-methylimidazolium tosylate [EMim][OTs], sulfuric acid [H$_2$SO$_4$], and methanesulfonic acid [MsOH]. Where sulfuric acid yielded the maximum DPA yield of 74.0%. ILs also showed high catalytic activity especially [BMim][HSO$_4$] with a DPA yield of 68.2% followed by [EMim][OTs] with a DPA yield of 59.3%, which is an advantage because ILs are environmentally friendly compared with sulfuric acid.

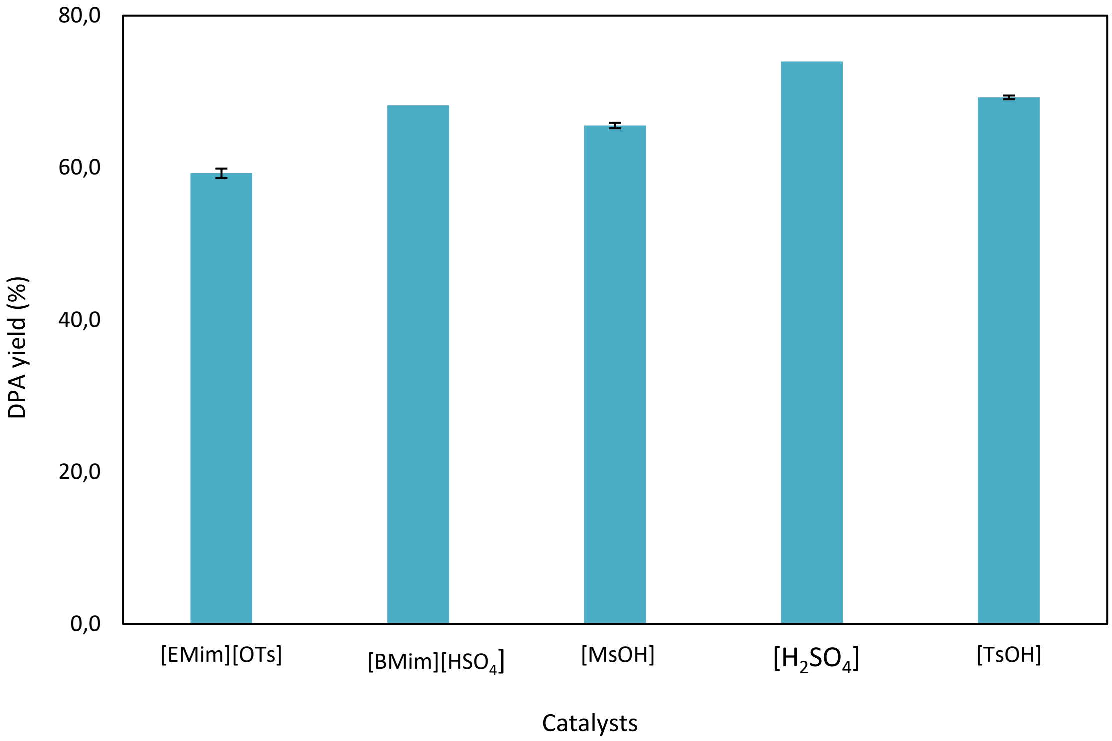


Figure 4.26 Effect of catalysts on the condensation reaction of DPA

4.7.4 Effect of the ratio of LA to phenol on the production of DPA

The effect of commercial LA to phenol ratio was studied by using the optimum values and only varying the commercial LA to phenol ratio. The following ratios (LA: phenol) were used: 1:4, 2:3, 2:4, 1:5, and 2:5. The results in figure 4.27 illustrate that increasing both LA and phenol increased the DPA yield. The 2:5 ratio yielded the highest DPA of 86.35%, which is higher compared with the DPA yield obtained when using the control ratio (1:3). Utilizing a higher ratio means more reactants are needed for the maximum DPA production, which will result in higher production costs.

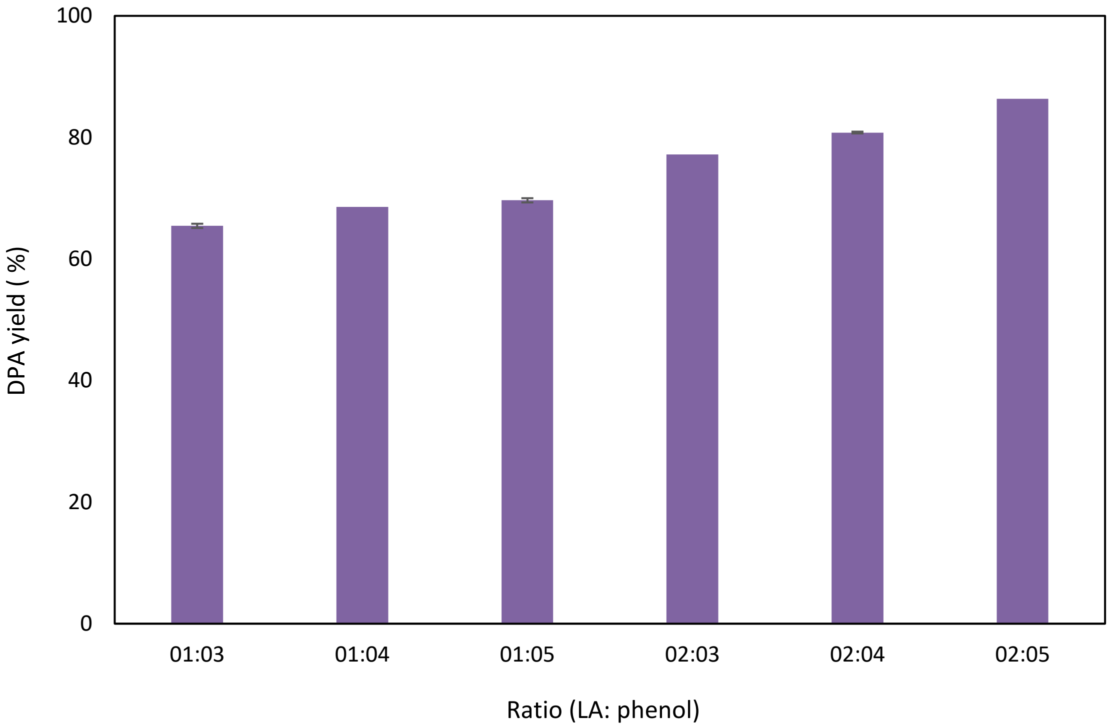


Figure 4.27 Effect of LA: phenol ratio on DPA production

4.7.5 Condensation reaction of LA derived from DSB into DPA

The use of LA derived from DSB with the optimized conditions of 6 h, 75 °C, and 5.5 g of MsOH yielded a DPA of 64.5%. This is comparable to that obtained from commercial LA. Thus, LA derived from DSB is a promising reactant for DPA production.

Conclusion and Recommendations

Two ILs ([BMMim][BF_4] and [EMim][HSO_4]) were used in this work for the production of LA from DSB. From the first IL [BMMim][BF_4] it was found that the optimum condition for the production of LA from DSB was 100 °C, 7 h, and a catalyst loading of 4 g which yielded 44.8 %. One of the limitations of the commercial process used for LA production from biomass is the formation of humins which was not formed in this study for the optimum condition. The type of solvent has an impact on the LA yield since different LA yield was achieved when using different solvents with the same reaction conditions. MIBK resulted in a higher LA yield when compared to all other solvents. The advantage of using [BMMim][BF_4] catalyst over sulfuric acid is that it is easily recovered, and it can be reused up to four times without losing its activity. The pH of the samples of this study was not as acidic as it is when using sulfuric acid as a catalyst and it was not corrosive to the reactor. Although this study has overcome some of the Biofine process limitations such as the formation of humins, cumbersome acid recovery and extensive water usage it has also one limitation which is the separation and purification of LA.

For the second IL [EMim][HSO_4] the analysis of the study illustrated that the optimum LA yield of 54.6 % was obtained at the temperature of 100°C, a reaction time of 7 h, and IL [EMim][HSO_4] loading of 4.0 g in water. When MIBK was utilized it increased the LA yield to 62 % but water is the preferred solvent for the LA production from DSB using [EMim][HSO_4] because of environmental issues. The [EMim][HSO_4] reusability test demonstrated that [EMim][HSO_4] can be used more than four times without the LA yield decreasing rapidly. The utilization of [EMim][HSO_4] was able to overcome the Biofine process limitations, which include the formation of humin, extensive use of water, catalyst recovery and inefficient separation.

Comparing both the ILs used in study reveals that both of these ILs were able to overcome some limitations of Biofine process. Another advantage of these ILs is that the mixture products pH is higher compared to the pH of the mixture product that results when the LA production was catalysed by sulfuric acid. High acidity damages the laboratory equipment (reactor). Another advantage is that these catalysts are reusable which closes the gap about the high cost of ILs compared to mineral acids and the high yield gap between the LA yield obtained from Biofine process which ranges from 70-80 mol% which is higher compared to the yield obtained in this study. The maximum LA yield of these ILs differ for about 10 % which is due to the anion of the IL, where $[HSO_4]^-$ is more reactive than $[BF_4]$. Hence the rate of reaction increases forming a high yield of LA. Because of the above reasons, $[EMim][HSO_4]$ is recommended for the LA production from DSB.

Since LA is highly reactive it produces various chemicals hence it is called a platform chemical. The next step was to upscale the LA production from 100 mL – 1L to get enough LA for the LA derivatives experiments. The upscaling production showed that more solvent was required to make the mixture steerable because using the ratio 1:10 resulted to in a thick mixture that could not be stirred.

The fourth step was to produce the LA derivatives. To save the synthesized LA, the optimization of the three LA derivatives was done with commercial LA, and the optimum conditions were further used for the LA derivative production from the LA derived from DSB. All the LA derivatives were catalysed by MsOH because it is highly reactive and environmentally friendly, other catalysts were tested to observe their effect on the LA derivatives yield.

The first LA derivative studied was EL. From the RSM studies for the optimization of EL production from LA, the optimum conditions were a reaction time of 5.25 h, a temperature of 90 ^{o}C, and a catalyst loading of 2,75 g which yielded 92.2 % of EL. The high LA conversion (98 %) and EL selectivity (94 %) showed that MsOH was highly efficient in converting LA to EL. The study of the effects of different catalysts showed that MsOH produced higher EL from LA when compared to the ionic liquids, which may be due to the high acidity. Esterification of LA to levulinic esters using various alcohols illustrated that ethanol yielded the maximum levulinate ester. Which confirm that long carbon chain in alcohols increases the product yield compared to branched alcohols. The esterification of DSB derived LA into EL using MsOH yielded 75 % EL, LA conversion of 89 % and EL selectivity of 84 %.

The second LA derivative was GVL, the optimization study of LA conversion to GVL showed that time, temperature, and catalyst loading have a significant effect on the GVL yield. IL: 1-butyl-3-methylimidazolium hydrogen sulphate produced a relatively high GVL yield (65.1 %) and could be considered for environmentally green technologies. Sulfuric acid yielded the highest GVL, but it is toxic and corrosive. Water produced the highest GVL yield and the mixed solvent of water and ethanol yielded the second-lowest GVL yield. The GVL yield produced from DSB derived LA is 77.6 % which is 1.0 % less compared to the GVL produced from the commercial sample of LA. LA derived from DSB is a promising replacement of non-biomass derived LA.

The last LA derivative that was studied in this work is DPA. The optimum conditions were 75 °C, a reaction time of 6 h, and 5.5 g of MsOH, which yielded a maximum DPA yield of 65.8 %. The response surface methodology and BBD were used to optimize the DPA production from LA, where the ANOVA and parity plot indicated that the resultant quadratic response model was significant and that it can predict the DPA yield. The pareto chart also reveals that temperature is the most influential factor towards DPA yield. The catalysts imparted different activities to the reaction system; different DPA yields were obtained. In general, acids yield high DPA compared with ionic liquids. However, 1-butyl-3-methylimidazolium hydrogen sulphate [BMim][HSO_4] yielded higher DPA than the control catalyst MsOH. The advantage of ILs is that they can be re-used. The effect of the ratio of LA to phenol also showed that adding more phenol increased the DPA yield, which is also a disadvantage because a high volume of phenol will contribute to a higher cost for the production of DPA. LA derived in this work from DSB produced 64.5% of DPA.

Limitations

Unavailability of a 50 L reactor, with separation and purification system, to study the impact the upscaling of that size will have on the production process of LA.

Recommendation

For future studies, DSB loading could also be included in the investigated parameters to study the impact it will have on the LA yield. Exploring varies purification system for the LA production then study 50 L upscale production and economy feasibility of the study. These may lead to commercialization of biomass value-added company.

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