

Catalytic Condensation of Depithed Sugarcane Bagasse Derived Levulinic Acid into Diphenolic Acid

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Levulinic acid (LA) is a platform chemical that can be produced from biomass. Diphenolic acid (DPA) is a derivative of LA with the 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 (MsOH). The optimized reaction parameters were time (6 h), temperature (75 °C), and catalyst loading (5.5 g), yielding 65.8% DPA at 90% LA conversion. The response surface methodology (RSM) 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 to 68% of DPA, MsOH produced 65.6% of DPA, and sulfuric acid produced the maximum DPA of 74%. The study of LA: phenol ratio revealed that more reactants (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.

Keywords: Condensation; Levulinic acid; Diphenolic acid; Depithed sugarcane bagasse; Methanesulfonic acid

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INTRODUCTION

The biorefinery concept, whereby biomass waste can be used to synthesize valuable chemicals, has received enormous attention over the years because of the depletion of fossil fuels and the negative climate change effects associated with the latter. Sugarcane (*Saccharum officinarum*) is a major crop in Africa, South America, and Asia, containing sucrose stored in the stalk (Chambon *et al.* 2018). When the sugarcane stalks are mixed with water and crushed to make sugar, the solid residue that results is called sugarcane bagasse (SB), which consists of hemicellulose (25.63 wt%), lignin (30.36 wt%), and cellulose (39.53 wt%) (Zhao *et al.* 2002). Even though sugarcane bagasse is used to power sugar mills, as well as in paper and tissue production, there is still excess of SB. As one of the largest agro-industrial processes in the world, it is estimated that over 500 million wet tons (~ 250 million dry tons) of sugarcane bagasse are produced annually (Chambon *et al.* 2018). The excess bagasse may be used to produce chemicals. When the pith is removed from SB, the resulting SB is called depithed sugarcane bagasse (DSB) (Mthembu *et al.* 2020). When original bagasse (mill-run bagasse) was compared with the depithed sugarcane bagasse (Mkhize *et al.* 2016), it was discovered that DSB is easier to handle, and it contains slightly more glucose. Hence, DSB was used in this study. Levulinic acid

(LA) has been identified as one of the sugar-derived platform chemicals that can be produced from lignocellulosic biomass through hydrolysis or dehydration of hexose sugars (Bozell *et al.* 2000; Cha and Hanna 2002; Chen *et al.* 2011; Yan *et al.* 2013; Yan and Chen 2013).

Diphenolic acid (4,4-bis(4-hydroxyphenyl)pentanoic acid or 4,4-bisphenoxy pentanoic acid or 4-(bis(hydroxyphenyl))pentanoic acid) is a derivative of LA that is prepared by the condensation reaction of LA with phenol (Hayes *et al.* 2006). DPA has wide practical uses and extensive application value in the synthesis of polymeride (Kitano *et al.* 1976), which is a feedstock for the production of water-soluble resins that are used in industrial Millipore and oil filter papers (Kitano *et al.* 1976; Zhang *et al.* 2012; Mthembu 2016). DPA is also a widely used chemical intermediate in paints (Holmen and Olander 1977), protective and decorative coatings (Blegen 1982), lubricants (Chafetz *et al.* 1995), cosmetics, surfactants, plasticizers and polymers (Bozell and Petersen 2000), and textile chemicals (Liu *et al.* 2012; Shen *et al.* 2014; Zuñiga *et al.* 2017). DPA is a structural analog of bisphenol A (BPA) and 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 (Yu *et al.* 2008; Ertl *et al.* 2014).

The traditional reaction for DPA production is the condensation reaction of phenol with LA in the presence of a catalyst, usually hydrochloric acid (HCl) or sulfuric acid (H₂SO₄) (Liu *et al.* 2013; Ertl *et al.* 2014). However, most mineral acids are toxic and corrosive, produce various unnecessary side-products that are difficult to separate from the reaction media, and result in expensive waste treatment (Yu *et al.* 2008; Shen *et al.* 2014). Therefore, solid catalysts have been used as a replacement for mineral acids (Guo *et al.* 2007; Li *et al.* 2009). Even though greener solid catalysts have been used for the condensation of LA into DPA, there are some drawbacks, which include low catalytic active sites and high susceptibility to leaching (Shen *et al.* 2014).

To overcome some of the shortcomings of mineral acids and solids catalyst, ionic liquids (ILs) have been used as a catalyst for DPA production (Shen *et al.* 2014). ILs are considered as green solvents/catalysts due to their low vapor pressure, high thermal stability, and low flammability (Zhang *et al.* 2015). The added advantage of using the IL over the acid, besides the high yield, is that it can be recycled and is non-volatile. Liu *et al.* (2013) used thiol-containing acid ILs for DPA production, which resulted in a high DPA yield (>90 %); however, there is a limitation that is associated with high cost of the ILs. Other disadvantages of using ILs include long reaction time (24 h) to achieve high DPA yield (Shen *et al.* 2014) and the long reaction time implies higher energy usage. There is a need for a green catalyst for DPA production from LA.

In this work, DPA production was optimized using commercial LA and methanesulfonic acid as the control catalyst. Response surface methodology (RSM) was used to optimize this study. A Box-Behnken design (BBD) was used to produce a set of experiments for the optimisation process. Various other catalysts, namely tosylic acid [TsOH], 1-butyl-3-methylimidazolium hydrogen sulphate [BMim][HSO₄], 1-ethyl-3-methylimidazolium tosylate [EMim][OTs], and sulfuric acid [H₂SO₄] were used to determine the effect of the catalysts for DPA production from commercial LA. The optimization parameters were time, temperature, and catalyst loading. The optimized reaction conditions were used to produce DPA from LA derived from DSB. Figure 1 illustrates the production of DPA, including the formation of the two isomers (p,p' and o,p')

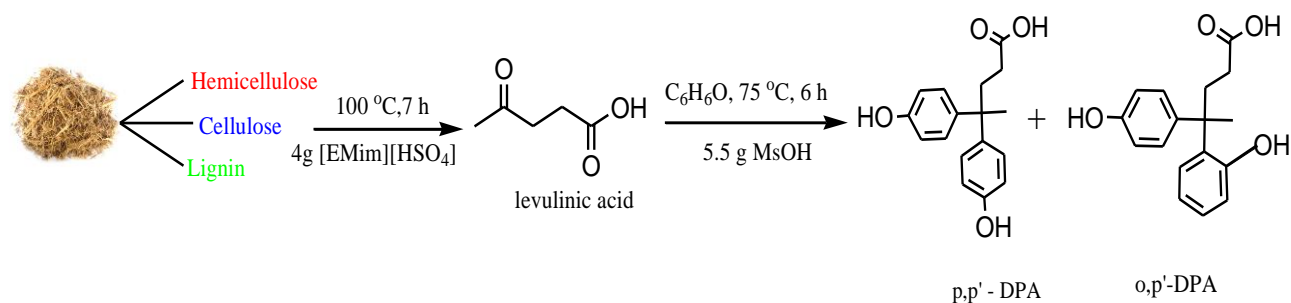


Fig. 1. DPA (p,p' and o,p') production from LA and phenol in the presence of a catalyst

EXPERIMENTAL

Materials

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

Methods

Compositional analysis of DSB

The DSB was dried in an oven (Scientific, South Africa) at 105 °C for 24 h, milled using a Pulverisette 16 (Fritsch, Germany), and sieved to 40-mesh particle size. The procedure used for compositional analysis of DSB is explained in our previous study (Mkhize *et al.* 2016).

Optimization of DPA production using methanesulfonic acid (MsOH)

To determine the optimum reaction conditions for DPA production from commercial LA, the minimum and maximum reaction conditions are given in Table 1 and were used in the BBD to derive the set of experiments (Table 2). 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 2) were placed in a PTF liner and inserted into a 100 mL Parr batch reactor (Parr Instruments Company, Moline, IL, USA).

Table 1. 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

The reaction time and temperature were varied for each experiment according to Table 2. 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.

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][HSO₄], 1-ethyl-3-methylimidazolium tosylate [EMim][OTs], and sulfuric acid [H₂SO₄].

Effect of LA to phenol ratio on DPA production

To determine the effect of 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.

DSB Conversion to DPA

Conversion of DSB to LA

The procedure for the production of LA from DSB was similar to that used in a previous study (Mthembu *et al.* 2020). For this study, the production was upscaled from the ratio 1:4, *i.e.*, 1 g of bagasse and 4 g of 1-ethyl-3-methylimidazolium hydrogen sulfate [EMim][HSO₄] to 100 g of bagasse and 400 g of [EMim][HSO₄]. The reaction was carried out in a round bottom flask immersed in an oil bath for 7 h at 100 °C.

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.

Product Analysis

HPLC characterization

The concentration of DSB derived LA and DPA were analysed by high performance liquid chromatography (HPLC) (Shimadzu, Kyoto, Japan) equipped with a C18 column (150 x 4.6 mm) at 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.

Equations

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. 1 through 5,

$$Y_{DPA}(\%) = \frac{Y_{act}}{Y_{th}} \times 100 \quad (1)$$

$$Y_{act} = \frac{DPA \text{ experimental mass (g)}}{Mass \text{ of initial feedstock (g)}} \quad (2)$$

$$Y_{th} = n_{LA} \times Mr_{DPA} \quad (3)$$

$$X_{LA}(\%) = \frac{C_{LA,O} - C_{LA}}{C_{LA,O}} \times 100 \quad (4)$$

$$S_{p,p'-DPA \text{ or } o,p'-DPA}(\%) = \frac{n_{p,p'-DPA} \text{ Or } n_{o,p'-DPA}}{(n_{p,p'-DPA} + n_{o,p'-DPA})} \times 100 \quad (5)$$

where n_{LA} is the number of moles of LA, Mr_{DPA} is the molar mass of DPA, LA molar mass is $116.11 \text{ g}\cdot\text{mol}^{-1}$, and DPA molar mass is $286.33 \text{ g}\cdot\text{mol}^{-1}$, $C_{LA,O}$ 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.

RESULTS AND DISCUSSION

DSB Compositional Analysis

The compositional analysis of DSB revealed that DSB consists of about 44% cellulose, 21% hemicellulose, and 25% lignin. The compositional analysis of DSB in this work was within the range of the literature values: 40 to 44% cellulose, 26 to 29% hemicellulose, and 22 to 30% lignin (Chandel *et al.* 2014; Chambon *et al.* 2018).

Optimization of DPA Production from Commercial LA using MsOH

Table 2 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 2 (run 12), where the lowest % LA conversion occurred (46%), the factors that had the least effect were temperature (75 °C) and catalyst loading (10 g), and the factor that had the greatest effect was 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 percent DPA conversion (runs 1 and 6), where the percentage of 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 2. 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} (%)	<i>p,p'</i> -DPA selectivity S_{DPA} (%)	<i>o,p'</i> -DPA selectivity S_{DPA} (%)
	A: Time (h)	B: Temperature (°C)	C: Catalyst load (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

Equation 6 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.

$$\begin{aligned} \text{DPA yield (\%)} = & 65.02 + 7.57 A + 8.36 B + 5.56 C \\ & 0.1500 AB + 2.20 AC - 4.03 BC \\ & 14.32 A^2 - 5.40 B^2 - 18.90 C^2 \end{aligned} \quad (6)$$

Table 3. ANOVA for the Response Surface Methodology 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			

Table 3 displays the ANOVA for DPA yield. The model F-value of 1063.01 implies that 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, A², B², and C² 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 (R²) is 0.9993 which is close to one indicating that the model is significant.

The parity plot in Fig. 2 compared the experimental and predicted DPA yield. There is excellent agreement between the experimental and predicted responses.

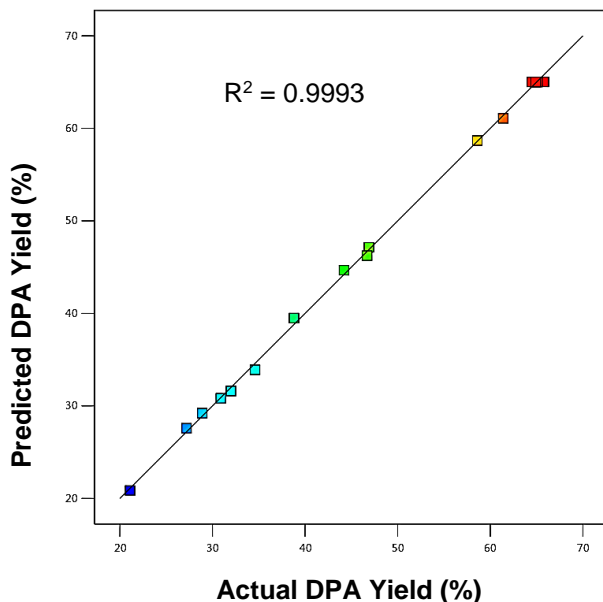


Fig. 2. DPA parity plot which compares the predicted DPA yield with the experimental DPA yield

The Pareto chart in Fig. 3 illustrates which factors have a high impact on the DPA yield. According to Fig. 3 the factors that have a high impact on DPA yield are temperature (B) followed by time (A), and catalyst loading (C).

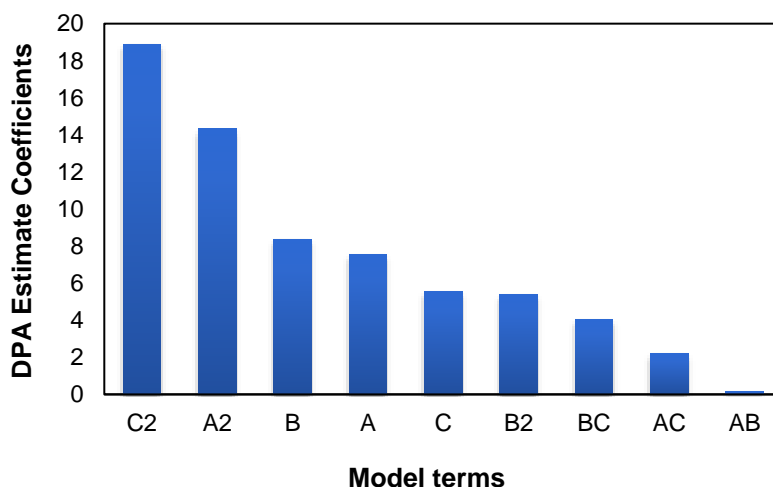


Fig. 3. Pareto chart for DPA yield, determining the most influential model term on DPA production

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 Fig. 4 a-c, where two factors and the response were evaluated while one factor remained at the optimum condition.

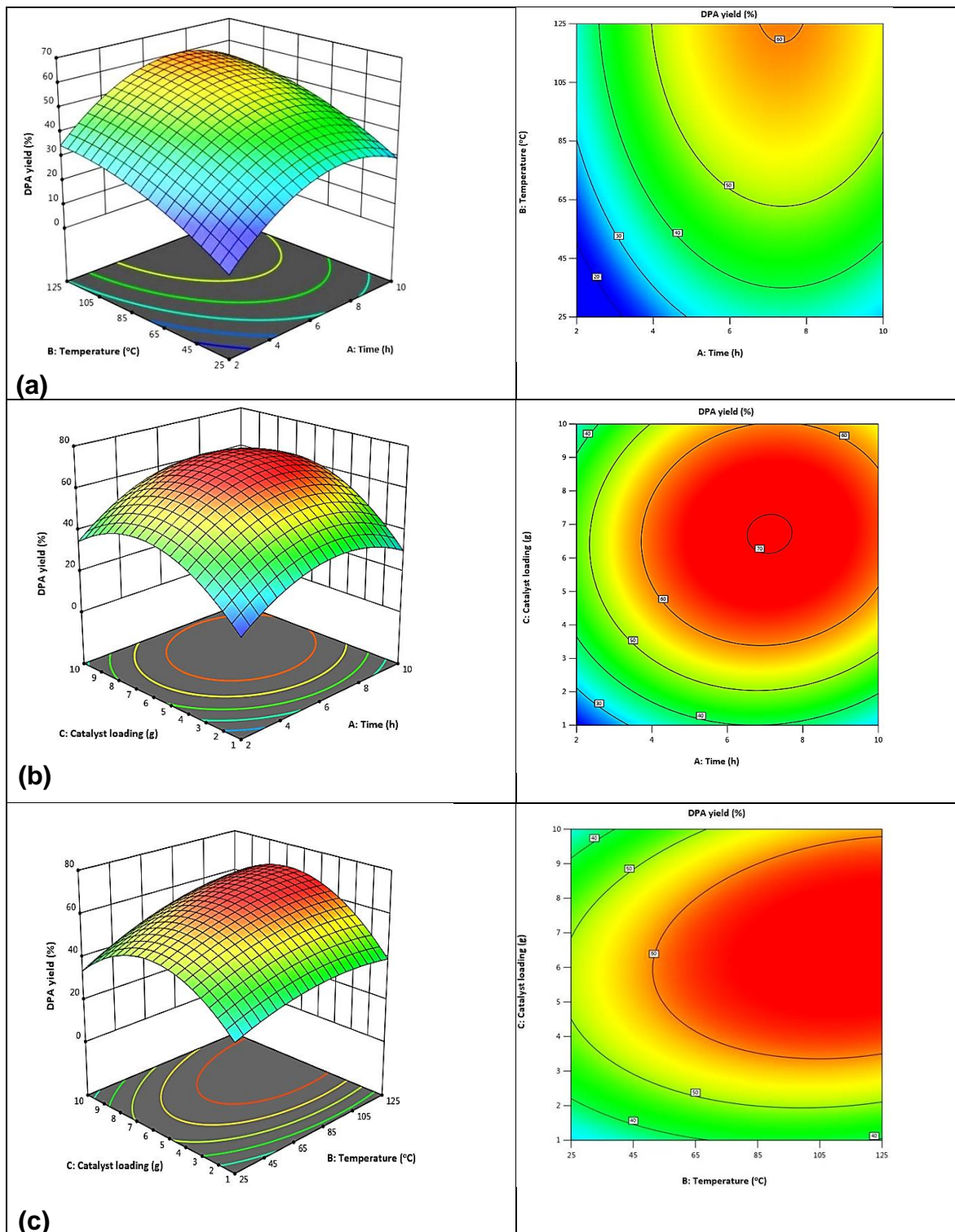


Fig. 4. 3D response surface and contour plots for the interaction of the investigated factors (a) temperature vs. time, (b) catalyst loading vs. time, and (c) catalyst loading vs. temperature

Figure 4a 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 4a shows that the minimum and maximum of temperature, and time yields lower DPA, whereas the moderate conditions favour the maximum production of DPA. Figure 4b 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 4b shows that a catalyst loading of 5.5 g and a reaction time of 6 h yielded maximum DPA yield. Figure 4c 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 Fig. 4 a-c it is observed that less catalyst resulted in lower yield. This was possibly due to lower overall reaction rate. Higher catalyst loadings coupled with longer reaction times results 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.

DPA FTIR Characterization

The FTIR characterization of optimized DPA obtained from commercial LA is illustrated in Fig. 5 compared with a standard sample of DPA.

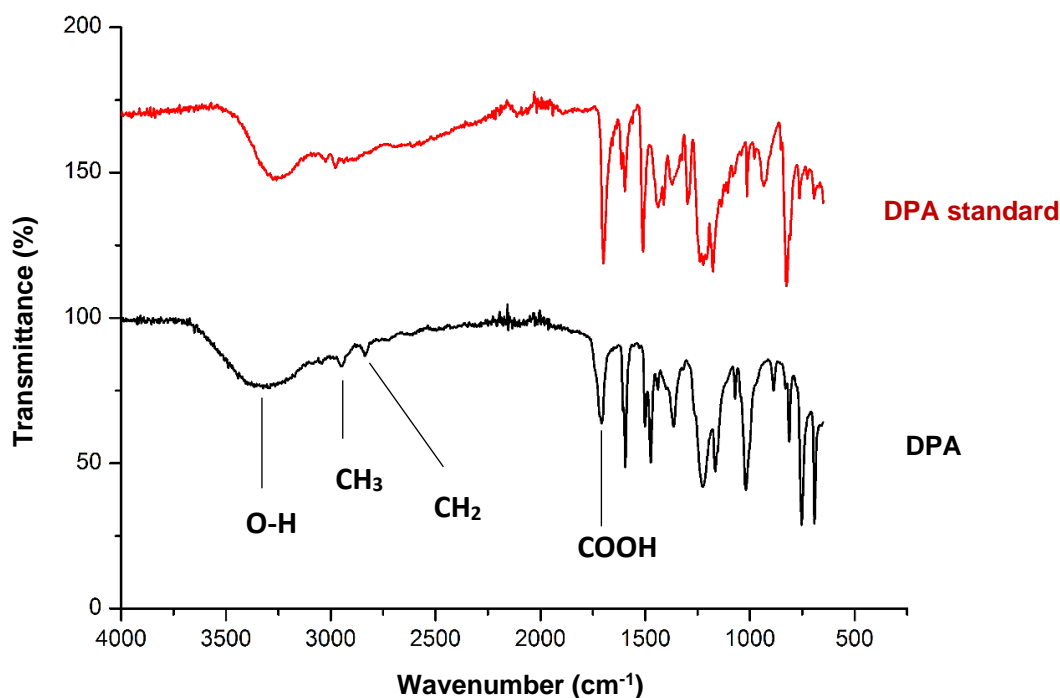


Fig. 5. FTIR scan of DPA standard vs DPA produced from commercial LA (this study)

The absorbance bands associated with the functional groups of DPA are observed in Fig. 5 by wavenumbers: carboxylic acid, COOH (1741 cm^{-1}), alkane, CH₃ ($2862\text{ to }2882\text{ cm}^{-1}$), CH₂ ($2843\text{ to }2863\text{ cm}^{-1}$), and hydroxyphenyl, OH ($3650\text{ to }3590\text{ cm}^{-1}$). The above functional groups indicate the presence of DPA in the analysed reaction product. The FTIR scans of both DPA and DPA standard include same functional groups; however, the shape of the peaks are not similar. This may be caused by the different production process of DPA or that the DPA produced in this study was analysed in a reaction product therefore it was not purified.

Effect of the Catalysts on the Production of DPA

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][HSO₄], 1-ethyl-3-methylimidazolium tosylate [EMim][OTs], sulfuric acid [H₂SO₄], and methanesulfonic acid [MsOH]. Sulfuric acid yielded the maximum DPA yield of 74.0%. ILs also showed high catalytic activity especially [BMim][HSO₄] 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.

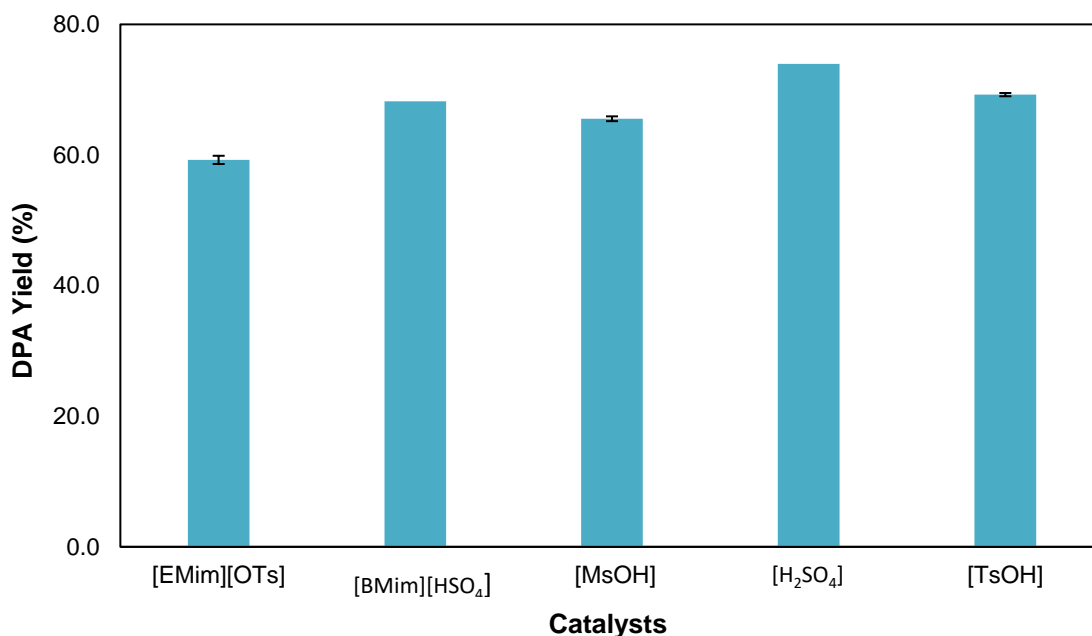


Fig. 6. Effect of catalysts on the condensation reaction of DPA

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 Fig. 7 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 higher ratio means more reactants are needed for the maximum DPA production, which will result in higher production cost.

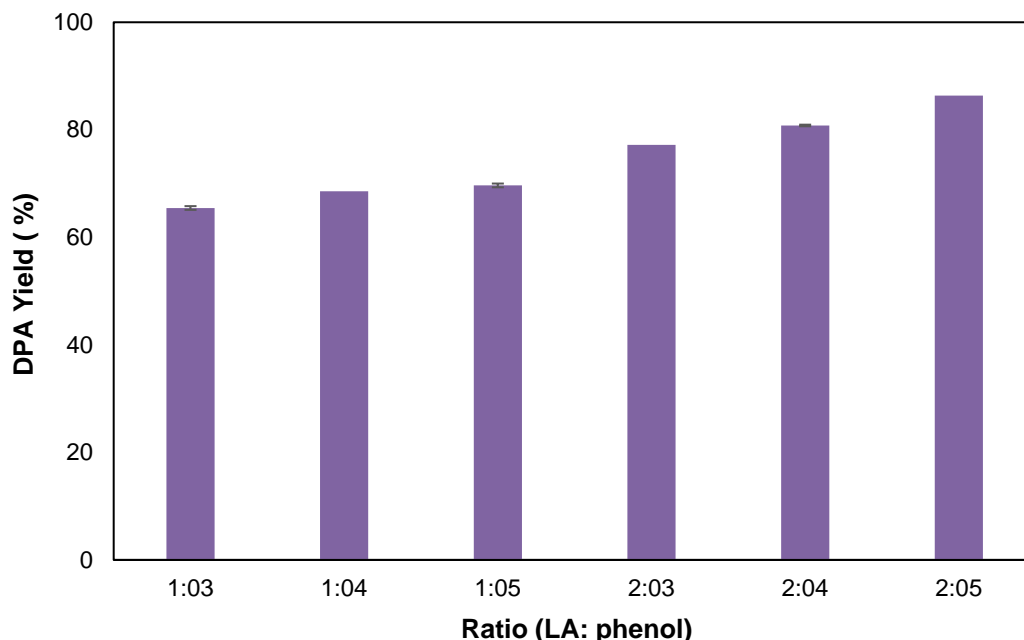


Fig. 7. Effect of LA: phenol ratio on DPA production

DSB Derived LA Conversion to DPA

LA production from DSB

The LA yield obtained in this work was 55%, which is 0.4% higher than the smaller scale production of LA from DSB (Mthembu *et al.* 2020). This shows that there is no significant difference in LA yield when the reaction was upscaled.

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.

CONCLUSIONS

1. The production of diphenolic acid (DPA) from levulinic acid (LA) was optimized using methanesulfonic acid as a catalyst and commercial LA as the feedstock. The investigated factors were temperature, time, and catalyst loading. The optimum conditions were 75 °C, a reaction time of 6 h, and 5.5 g of MSA, which yielded a maximum DPA yield of 65.8 %.
2. The response surface methodology and Box-Behnken design 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 revealed that temperature was the most influential factor towards DPA yield.

3. 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][HSO₄] yielded higher DPA than the control catalyst MsOH. The advantage of ILs is that they can be re-used.
4. The effect of ratio of LA to phenol also showed that adding more phenol increased the DPA yield. This can be regarded as a disadvantage because a high volume of phenol will contribute to higher cost for the production of DPA. LA derived in this work from DSB produced 64.5% of DPA.

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