UJPICR Volume 1 Number 2 : December, 2021
UMYU Journal of Pure and Industrial Chemical Research
Volume1 No. 2 December, 2021.
ISSN: **2814 – 1628**

STUDY ON THE EFFECTS OF REACTIONS VARIABLES ON LEVULINIC ACID PRODUCTION USING TAGUCHI METHOD OF DESIGN OF EXPERIMENT

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ABSTRACT

The study on the effects of reactions variables on levulinic acid production was carried out using Taguchi method of design of experiment. The production of LA was carried out in a 50 cm^3 Teflon lined stainless steel batch reactor and extracted from the aqueous mixture using ethyl acetate. The production process was optimized using a Taguchi method of design of experiment, with optimum yield of 74.54 % at reaction variables of a temperature of 180 °C, for 3.5 H and acid concentration 0.3 M. The FTIR spectrum of the produced LA showed absorption at about 1705.13 cm^{-1} and 3039.91 cm^{-1} indicating the conjugated carbonyl and the hydroxyl of carboxylic acid functional group. It was recommended that high yields of LA can be achieved across a range of optimization variables as long as two out of the three conditions are met: high acid catalyst concentration, long reaction time or high temperature within the range tested, as LA is relatively stable once formed. Finally, the results revealed that groundnut shell could be a potential substrate for levulinic acid production.

Keywords: Levulinic acid, Taguchi, Factorial design, Reaction variables

1. INTRODUCTION

Levulinic acid (LA) also known as 4-oxopentanoic acid or 4-ketopentanoic acid is a linear C_5-alkyl carbon chain. It is a widely used industrial chemical that consist of a carbonyl, carboxyl group and α-H in its inner structure (Figure 1).

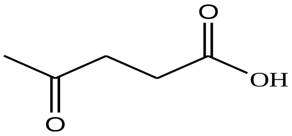

Figure 1: The Molecular Structure of Levulinic Acid

Levulinic acid is a non-volatile acid [1], with a molecular weight of 116 g/mol and exist as a yellow crystalline solid. It is soluble in water and other polar organic solvent. It has boiling and melting points of 275 °C and 33 °C respectively [2].

Lignocellulosic biomass is the most abundant biomass in the world which can be converted into various valuable platform compounds such as furfural, lactic acid, formic acid and levulinic acid by biorefinery processes [3]. LA has wide applications in industry and agriculture to produce a variety of products such as plasticizer, oil additives and fragrances [4]. The production of LA has been investigated from a variety of sources of LA feedstock such as sugars, cellulose, chitin and raw lignocellulosic biomass by homogeneous or heterogeneous catalysts [5].

In terms of starting materials used for LA production, monosaccharides such as glucose and fructose can give high LA yields [6]. The high cost of sugars restricts their application in LA production. Therefore, the production of LA from cellulose and in particular, from raw and waste biomass is preferred due to their abundance and low cost. When cellulose or raw lignocellulosic biomass are used as starting materials, LA is usually produced by the acid-catalyzed conversion of cellulose, following a reaction pathway in which cellulose is hydrolyzed into glucose via enzymatic or acid-catalysis methods and the generated glucose is dehydrated to 5-hydroxymethylfurfural (HMF), followed by a rehydration step converting HMF to LA, (Figure 2). [3].

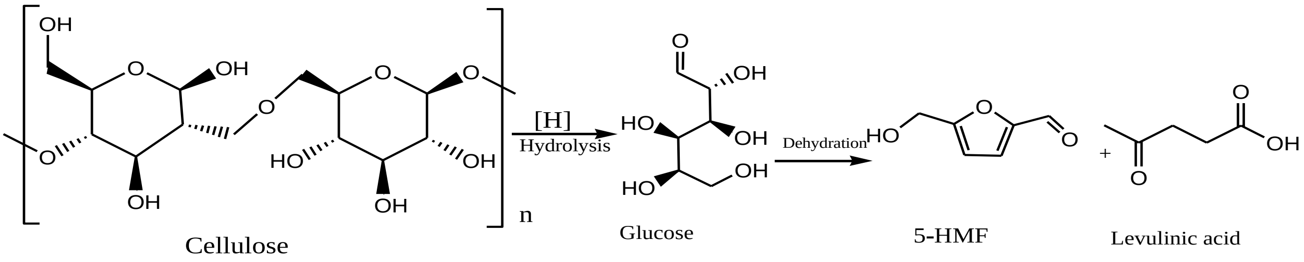

Figure 2: Reaction pathway for the acid-catalyzed conversion of cellulose to levulinic Acid

The objective–of this research were to study the effects of reaction variables (acid concentration, temperature, and reaction time) using Taguchi method of design of experiment via simultaneous hydrolysis and dehydration.

2. Experimental procedure

2.1 Sample Collection and Preparations

Groundnut shells were collected from the processing sites at Adarawa village behind Usmanu Danfodiyo University, Sokoto stadium. The sample was identified as groundnut shell (*Arachis hypogaea* shell) at the Department of Crop Science, Faculty of Agriculture, Usmanu Danfodiyo University, Sokoto The shells were crushed, milled and sieved. Particles that passed through the 40 mm mesh sieve were retained and stored in a plastic container until required for LA production and analysis.

2.2 Extraction of Cellulose from the Groundnut Shell

The methods described by [7] and [8] was adopted for the extraction of cellulose from dried sample as follows:

(a) Acid Treatment

The dried groundnut shell (3.0 g) was pre-treated with 30 cm^3 of 12 M hydrochloric acid solution for 30 minutes in an autoclave reactor at 121 ^oC. The content was cooled to ambient temperature, then filtered.

(b) Alkali Treatment

The oven dried substrate (2.0 g) from acid pre-treatment was further treated with 20 cm^3 0.06 M sodium hydroxide solution for 15 minutes in an autoclave reactor at 121 ^oC to remove lignin. The solution was cooled, filtered, washed to a neutral pH and oven dried overnight at a temperature of 50 ^oC.

2.2.1 Test for Cellulose

The method described by [9] was adopted with modification. 0.5 g Cellulose powder was placed on a watch glass, and dispersed in a drop of iodinated zinc chloride solution and the color change was observed. The color change from white to violet blue is indicative of cellulose.

2.2.2 Test for Lignin (Wiesner Test)

The oven dried substrate (1.0 g) from alkali pre-treatment was dispersed with few drops of dilute hydrochloric acid on a glass slide. Two drops of benzene-1,3,5-triol (phloroglucinol) were added and the slide was slowly heated over a Bunsen burner, until the liquid content has evaporated. The slide was then examined under a light microscope MBL2000.

2.3 Levulinic Acid Production

Production of LA was carried out in a 50 cm^3 Teflon lined stainless steel reactor. About 2 g of the treated sample of groundnut shell was placed in 20 cm^3 of 0.2 M HCl aqueous solution and loaded into the reactor. The reactor was closed and immersed in a paraffin oil bath. Subsequently, the reactor was magnetically stirred at 1000 rpm and heated to 180 ^oC using a hot plate magnetic stirrer for 3.5 hours. The internal temperature of the reactor was determined by a thermocouple. The reaction was quenched using cold water and a liquid sample was obtained after filtration [10]. The percentage yield of LA was calculated using equation 1.

$$\%\text{Yield Levulinic Acid} = \frac{\text{Mass of levulinic Acid produced(g)}}{\text{Mass of cellulose utilized (g)}}\ x100 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \ (1)$$

2,4 Characterization of Levulinic Acid Produced

The FT-IR analysis was carried out at the National Research Institute for Chemical Technology, Zaria using Shimadzu-8400s and MB-3000 Fourier transform infrared spectrophotometer. The transmission rate was set at the range of 4000 – 750 cm^{-1} at a resolution of 2.0 cm^{-1}. A drop of the sample was placed between two plates of potassium bromide (KBr) cells and squeezed to remove any trapped. A thin film was formed between the plates to allow light to pass through the sample. The plates were placed in the sample holder and positioned in the standard sample compartment of the spectrophotometer and the spectral data was obtained.

2.5 Taguchi Orthogonal Array Design of Experiment

The study on the effects of levulinic acid production was conducted using Minitab 17 statistical software, the effect of temperature, time and acid concentration on LA yield was investigated using Taguchi orthogonal array design. Parameters that were used for this study are given in Table 1. After inserting the three parameters a set of experiments Table 2 shows the experiments that needed to be done to measure the amount of LA produced

Table 1: Experimental Range and Levels of Independent Variables

Parameter	Minimum	Maximum
Temperature	160 °C	220 °C
Reaction Time	2.0 Hours	3.5 Hours
Acid Conc.	0.2 M	0.35 M

The ranges of the variables were chosen based on information from a previous study [10]. The effects of temperature, time and acid concentration that affect the hydrolysis and dehydration stage were optimized. A range of temperature (160 – 220^{o}C), residence time (2.0 – 3.5 hours) and acid concentrations (0.2 – 0.35 M) were selected as independent process variables. 16 treatments were run in a random order to minimize the effect of any unexplained variability in the observed responses. The response measured were the yields of levulinic acid.

Table 2: Taguchi Orthogonal Array Design for Levulinic Acid Production.

Run.	TEMP.(^{o}C)	TIME (Hours)	HCl $_{(aq)}$ (M).
1	160	2.0	0.20
2	160	2.5	0.25
3	160	3.0	0.30
4	160	3.5	0.35
5	180	2.0	0.25
6	180	2.5	0.20
7	180	3.0	0.35
8	180	3.5	0.30
9	200	2.0	0.30
10	200	2.5	0.35
11	200	3.0	0.20
12	200	3.5	0.25
13	220	2.0	0.35
14	220	2.5	0.30
15	220	3.0	0.25
16	220	3.5	0.20

3. Results and Discussion

The cellulose extracted from groundnut shell has a violet blue coloration indicating the presence of cellulose and absence of red colour indicating the absence of lignin in the cellulose powder extracted [9]. Table 3 shows the results obtained for LA production using a Taguchi Orthogonal Array Experimental Design. The study was carried out based on the three factors variables (reaction temperature, reaction time and acid concentrations) which are in four different levels of the experimental runs. Experimental run number 8 it was showed that the acid hydrolysis of treated groundnut shell with 0.30 M at 180 °C, for 3.5 hours gave the highest yield of 74.54 % LA compared with other parameter The results agreed with the findings of [11] who reported similar range of values.

Table 3: Taguchi Orthogonal Array Experimental Design and LA Yield

Run.	TEMP. (^{o}C)	TIME(H)	HCl $_{(aq)}$ (M).	LA YIELD (%)
1	160	2.0	0.20	33.56
2	160	2.5	0.25	46.25
3	160	3.0	0.30	31.45
4	160	3.5	0.35	40.10
5	180	2.0	0.25	52.74
6	180	2.5	0.20	60.37
7	180	3.0	0.35	63.42
8	180	3.5	0.30	74.54
9	200	2.0	0.30	28.32
10	200	2.5	0.35	31.46
11	200	3.0	0.20	26.32
12	200	3.5	0.25	41.65
13	220	2.0	0.35	17.48
14	220	2.5	0.30	25.20
15	220	3.0	0.25	33.25
16	220	3.5	0.20	29.62

The Main Effect plot for Signal to noise (S/N) ratios (Figure 4) using Taguchi method, has shown that high yield of levulinic acid was achieved at experimental run number 8.

The increased of reaction temperature to 200 °C shows a decrease in LA yield with increasing reaction time. The model equations are given below.

Regression Equation:

% YIELD LA = 40.98 + 1.86 Reaction Temperature, ^{0}C_160
+ 21.78 Reaction Temperature, ^{0}C_180- 9.05 Reaction Temperature, ^{0}C_200
- 14.60 Reaction Temperature, ^{0}C_220 - 7.96 Time, Hours_2.0 - 0.16 Reaction
Time Hours_2.5 + 2.63 Reaction Time, Hours_3.0 + 5.49 Reaction Time Hours_3.5 -
3.52 Acid Concentration, M_0.20 + 2.49 Acid Concentration, M_0.25
+ 3.89 Acid Concentration, M_0.30 - 2.87 Acid Concentration, M_0.35

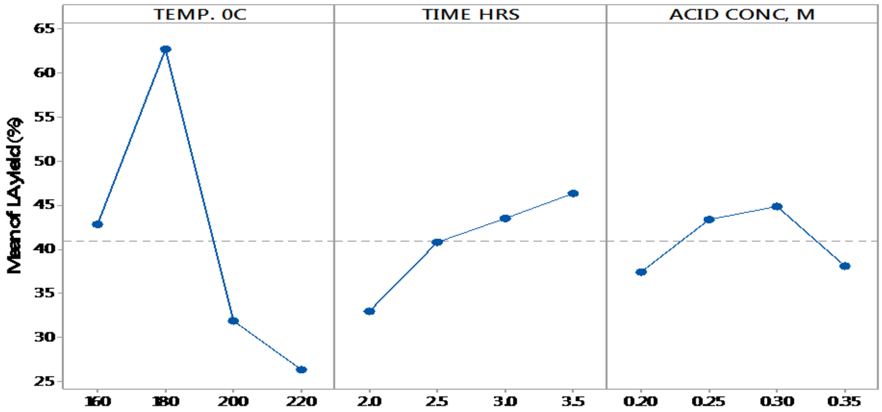

Figure 3: Main Effect Plot of S/N ration of LA yield

The general linear model shows that the response variables (reaction temperature, reaction time and acid catalyst concentrations) are statistically significant.

Table 4: Analysis of variance and Model Summary

Source	DF	Adj. SS	Adj. MS	F-Value	P-Value
TEMP. (^{o}C)	3	3091.5	1030.48	46.62	0.000
Time (HRS)	3	401.8	133.93	6.06	0.030
Acid Conc. (Mol/dm^3)	3	167.8	55.93	2.53	0.015
Error	6	132.6	22.10		
Total	15	3793.7	R-sq.	R-sq. (adj.)	R-sq. (pred.)
			97.50 %	91.26%	75.14 %

The Analysis of Variance (Table 4) gives, for each term in the model, the degrees of freedom the adjusted (partial) sums of squares (Adj SS), the adjusted means squares (Adj MS), the F-statistic from the adjusted means squares, and its p-value. The adjusted sums of squares are the sums of squares given that all other terms are in the model. These values do not depend upon the model order. The 'P' values for all the factors used are less than the 0.05 this indicated that all the terms are statistically significant. The correlation coefficient (R^2) of the analysis was found to be 97.50 % which shows that the variables are significant and they fit the model.

3.1 Identification of Levulinic Acid

Table 5 shows the FTIR absorptions bands for the produced levulinic acid and their standard ranges of absorptions and Figure 3 shows the FT-IR Spectrum of LA produced from Groundnut shell.

TABLE 5: FT-IR Absorption Bands of Levulinic Acid Produced and Standard Range

Standard Range of Values (cm^{-1})	Frequency (cm^{-1})	Bond	Intensity	Functional group
3300-2500 (m)	3039.91 (m and b)	O-H stretch	40.38	Hydroxyl
3000 –2850 (m)	2939.61 (m)	C-H stretch	42.46	C-H (Alkane)
1760 –1690 (s)	1705.13 (s)	C=O stretch	30.15	C=O (Ketone)
1760 –1690 (m)	1751.42 (w)	C=O stretch	83.25	C=O (Acid)
1320-1000 (s)	1226.77(m)	C-O stretch	61.98	C-O

Where (*m*) – medium peak, (*s*) -sharp peak, (*w*) – weak peak and (*b*) broad peak

The important vibrations of LA observed from the FTIR spectrum were O-H (3039.91 cm^{-1}) which is broad and intense stretching for carboxylic group, a very strong absorption at 1705.13 cm^{-1} which corresponds to absorption due to a carbonyl (C=O) carbon of a ketone. The stretching frequency at 1751.42 cm^{-1} is due to the carbonyl carbon of carboxylic group. C-H (2939.61 cm^{-1}) stretching for alkane were observed in this spectrum. The sp^2 hybridized C-O vibration stretching for carboxylic group showed absorption around 1226.77 cm^{-1}. Similarly, the broad O-H stretching: both carboxylic acid and alcohol have these broad absorptions but the O-H vibration stretching for carboxyl group absorbs around 2500-3300 cm^{-1} whereas the O-H vibration stretching for alcohols absorbs between 3200-3500 cm^{-1}. These findings were compared with the standard range of absorptions are in agreement with [11].

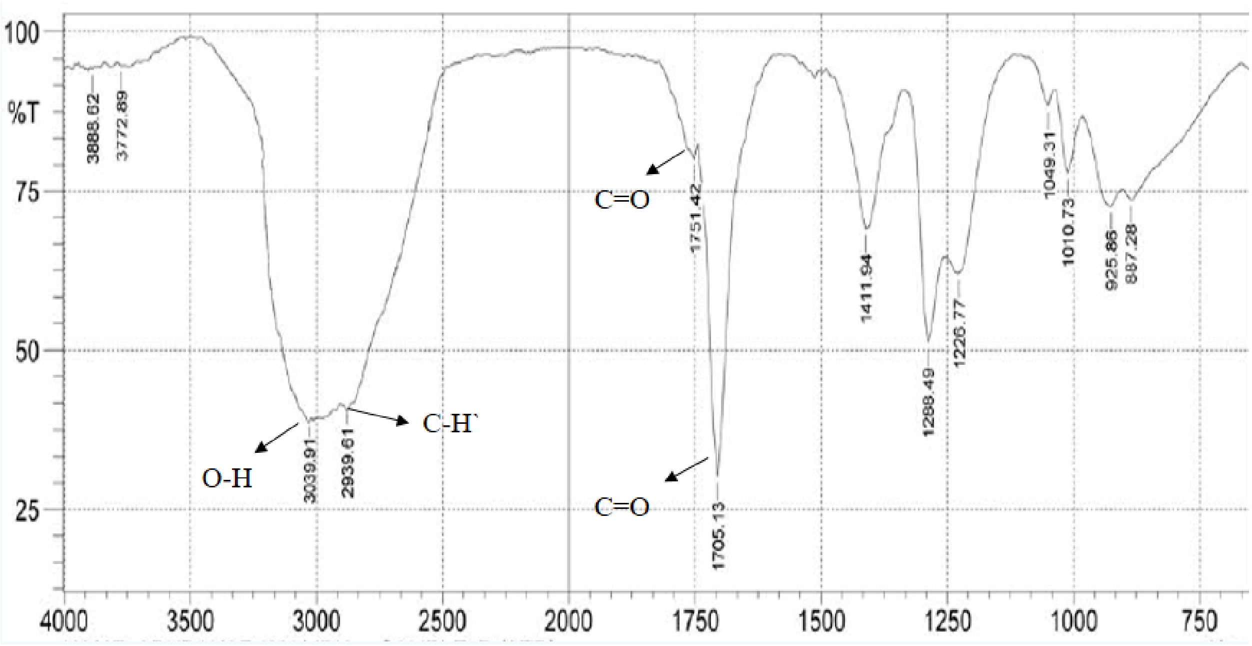

Figure 4: FT-IR Spectrum of LA produced from Groundnut shell

3.2 Effect of Reaction Temperature on the Production of LA

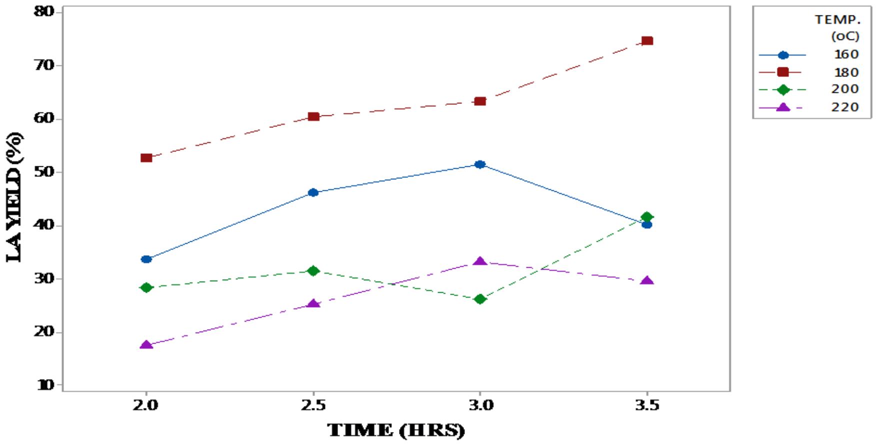

Figure 5: Interaction Plot Showing the Effect of Reaction Temperature (160 – 220 ^{0}C) on the Production of LA.

The influence of the reaction temperature on the production of LA from treated groundnut shell was investigated (Figure 5). When the reaction was conducted at 160 ^{o}C, the LA yield increased slowly with the increase in reaction time. In the catalytic conversion of lignocellulosic biomass, the reaction temperature is an important factor that plays a crucial role in determining the products' distribution [4]. LA is generally produced by the rehydration of 5-hydroxymethylfurfural [12], which is obtained by the dehydration of glucose or fructose by eliminating three water molecules [13]. The hydrolysis of cellulose to glucose is considered to be a key step in the production of LA directly from lignocellulosic biomass [14]. Generally, compared with the hydrolysis of cellulose, the production of levulinic acid needs higher temperatures [5]. Thus, LA yield of 51.45 % was attained in a 3.0 hours' reaction time. When the temperature was increased to 180 ^{o}C the LA yields increased from 51.45 % to 74.74 % between 2.0 to 3.5 hours' respectively. As the reaction temperature increased from 200 ^{o}C to 220 ^{o}C a decreased in LA yield with time was observed. Thus, 180 ^{o}C was considered an optimum temperature for the synthesis of LA from groundnut shell.

3.3 Effect of Acid Concentration on the Production of LA

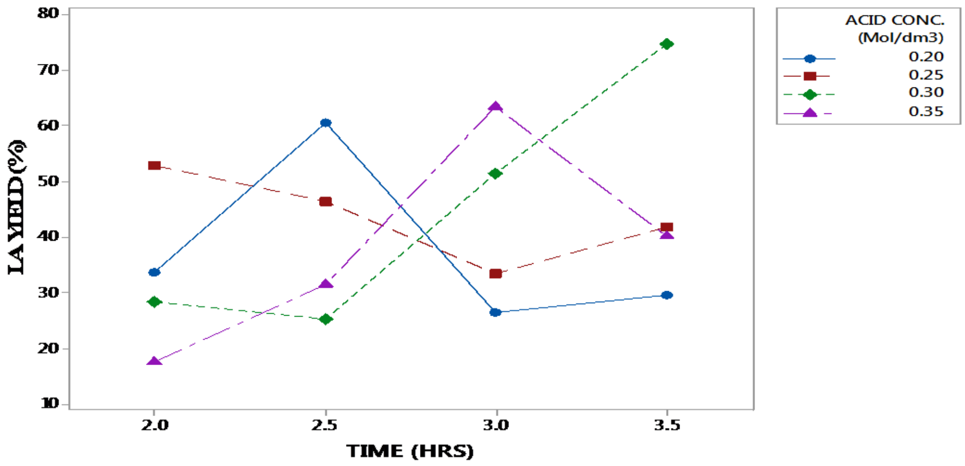

Figure 6: Interaction Plot Showing the Effect of Acid Concentration (0.20 – 0.35 M) on the Production of LA.

The effect of the acid concentration on the catalytic synthesis of LA from the pre-treated groundnut shell was investigated (Figure 6). When the reaction was performed in 0.2 M HCl aqueous solution, the LA yield increased rapidly with the prolonged reaction time. LA yield of 60.37 % was achieved in a 2.5 hours' reaction time, which decreased to 26.32 % at 3.0 hours. With increased in HCl concentration, the LA yield significantly increased. A maximum LA yields of 74.54 % at 3.5 hours and 63.42 %at 3.0 hours were obtained for 0.3 M and 0.35 M HCl aqueous solutions, respectively.

4. CONCLUSION

This study illustrated the production of levulinic acid from groundnut shell. However, study of the effect of reaction variables on LA production process was performed using one-stage process. Maximum levulinic acid yield of 74.54 % were obtained at optimum temperature of 180 °C, at 3.5 hours with acid concentration of 0.3 M. From the result obtained, it could be concluded that groundnut shell could be a potential raw material for the production of a bio-based chemical such as levulinic acid. The following conclusions were drawn from the result obtained

i. High yields of levulinic acid can be achieved across a range of reactions variables as long as two out of the three conditions are met: high concentration acid catalyst (0.3 M), long reaction time (3.5 H) or high temperature (180 °C) within the range tested, as levulinic acid is relatively stable once formed. However, increasing the temperature to 200 °C shows a decrease in LA yield with increasing reaction time.

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