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Research paper

Optimization of furfural production from hemicellulose of citrullus colocynthis (melon) seed husk using response surface methodology (RSM)

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Abstract

Global population explosion has led to an increase in demand for chemicals and fuels. Consequently this is accompanied by energy security and environmental challenges such as GHGs emissions. Hence, the need for alternative sources of chemicals from greener sources cannot be overemphasized. Furfural was produced from hemicellulose of citrullus colocynthis (Melon) seed husk (MSH) which involves the simultaneous steps of acid catalyzed hydrolysis/dehydration of the (MSH). A response surface methodology (RSM) was used for furfural production and optimization using MINITAB 17statistical software. Results obtained from RSM for furfural production were analyzed using analysis of variance (ANOVA). A furfural with optimum yield of 75.03% was achieved via degradation of hemicellulose fraction of the MSH at optimized variable conditions of Temperature (220 °C), Acid Concentration (10% H2SO4), and Reaction Time (55 minutes). FT-IR spectrum of the produced furfural showed absorption at 1670cm-1 and 2800cm-1 indicating a conjugated carbonyl functional group and aldehydic hydrogen. The result revealed that the utilization of MSH in furfural production may serve as a viable solution of disposing this agricultural wastes and may address environmental problems associated with fossil fuels when the produced furfural used as a feedstock in industries for biofuels and fine chemicals production.

Keywords: *Furfural; Hemicellulose; Melon Seed Husk; Response Surface Methodology; Optimization.*

1. Introduction

Citrullus colocynthis (melon) is a tropical herbaceous, tendril-bearing, vine plant of the cucurbitaceae family commercially cultivated in various regions in Africa (more especially northern part of Nigeria). It is an essential perennial cash crop cultivated for its fruits and oil-bearing seeds, the fruits are ovoid shaped and weighs an average of 1.5kg. The mesocarp comprises numerous brown colored oval shaped, dorsoventrally flattened seeds enclosed in a brittle cortex. The seeds contain a white, soft textured oil-rich kernel that is typically deshelled for processing into melon seed oil (MSO) [1]. The cultivation and extraction of vegetable oil from melon seeds generates large quantities of lignocelluloses waste known as Melon Seed Husk (MSH). With the growing culinary and medicinal importance of melon seeds, it is estimated that the cultivation and extraction of Melon Seed Oil will result in increased waste over the coming years [2]. This will present further waste disposal and management challenges for the communities reliant on the crop for livelihood. In addition, current strategies for the disposal and management of agricultural wastes such as melon seed husk are considered inefficient, unsustainable, and environmentally hazardous [3].

The exploitation of biomass for energy and biochemical production has been recognized as a viable option for adding value to lignocelluloses agricultural residue such as corn Stover, wheat straw, rice husk/straw, and millet husk [4]. Therefore, an alternative, albeit potentially more efficient waste disposal strategy involves the utilization of Melon Seed Husk as a feedstock for clean energy fuels and power generation. This can be achieved by converting hemicelluloses of citrullus colocynthis (Melon) seed husk (MSH) to furfural which are found in the hemicelluloses of agricultural waste. However, this will serve as an alternative for feedstock of transportation fuels from fossil fuels, potentially mitigate the uncontrolled emission of greenhouse gases (GHGs) and Open-air burning, landfilling and reduce the associated costs of managing solid wastes [5].

Biomass, a renewable non fossil carbon energy source, is regarded as an ideal alternative to traditional fossil resources because it is environmentally friendly and abundant. In recent decades, great interest has been devoted to the production of biofuels and biochemical using non-edible lignocellulosic biomass, which is abundant in agricultural residues and waste streams [6].

The use of lignocellulosic biomass avoids the food-versus-fuel debate and can potentially significantly reduce CO_2 emissions. It is one of the most promising options for the green and sustainable production of fuels and chemicals. Lignocellulosic biomass mainly contains cellulose, hemi- cellulose, and lignin, which constitute 40−50%, 25−35%, and 15−20% of lignocellulose respectively [6].

Xylans, one of the types of hemicelluloses present in abundance in lignocellulosic, are composed mainly by pentose and generally are the major constituents of hemicelluloses in grasses and woods. Lately, studies focusing in the conversion of xylans to bioenergy, chemicals and biomaterials have received a lot of attention in the context of bio refineries. Among the products which can be obtained from pentose, there is furfural, which is a promising alternative, since it is a versatile compound that can be used in the synthesis of several important chemicals, such as furan and furfural alcohol, and it is vastly used in several applications in refining oil, plastics production, pharmaceutical and agrochemical industries [7]

Furfural is a liquid chemical that is sourced from renewable resources; it is created from hemicelluloses components (pentosans) of vegetable matter. It is also the only compound of the furan series being directly obtained from biomass (e.g. Melon Seed Husk) at industrial scale. Furfural production is generally carried out by hydrolysis of hemicelluloses-derived pentosans into monomeric pentose, and their subsequent acid-catalyzed dehydration. It is an important organic chemical, produced from agro industrial wastes and residues containing carbohydrates known as pentosans [8].

As no commercial synthetic routes have been found so far, all furfural manufacturing activity is based on pentosans containing residues that are obtained from the processing of various agricultural and forest products. In commercial terms the most important intermediate derived from furfural is furfuryl alcohol. The chemical formula for furfural is $C_5H_4O_2$, in structure it is a heterocyclic compound consisting of a furan ring (four carbon atoms and an oxygen atom) plus an aldehyde group. Chemically, furfural participates in the same kinds of reactions as aldehyde and other aromatic compounds. Indicating its diminished aromaticity relative to benzene, furfural is readily hydrogenated to the corresponding tetrahydrofuran derivatives.

This compound can be prepared from lignocellulosic and easily separated from the aqueous phase due to its low solubility in water, stability in acid and alkaline conditions, low toxicity, easy recycling and environmentally friendly characteristics, because it is a product from green chemistry [9].

The pentosans fraction of lignocelluloses is converted into monosaccharide by acid hydrolysis. Then further dehydration reactions of pentoses yield furfural. Pentosan ($C_5H_8O_4$) fraction of melon seed husk is converted into pentose $(C_5H_{12}O_5)n$ which is then cyclohydrated to furfural ($C_5H_4O_2$) using dehydration method. Dilute sulphuric acid is used for this purpose. Furfural formed is recovered using distillation and separation [10].

Aiming to optimize furfural production processes, several studies have been done by involving the use of new types of catalysts in monophasic and biphasic reaction systems.

Besides improving reaction system, it has been studied the use of catalysts which do no harm so much the environment as the mineral acids.

In order to replace the use of mineral acids in furfural production, in recent years, many acid solid catalysts were developed and applied successfully in the reaction for furfural preparation. One of the problems about using solid catalysts is when the reaction solvent is too polar and highly protic, as water for example, because only a few acid solids can keep the desired acidity due to interactions between solvent-surface by solvation [9]

Sokoto et al., (2018) investigated the furfural production from millet husk via simultaneous hydrolysis and dehydration processes. Effect of reaction variables such as temperature (120–200°C), resident time (15–45 min), and acid concentration (5–10%) was studied using central composite design. Furfural yield (71.55%) was achieved at 184°C, 39 min, and 9% acid concentration. FT-IR spectrum of the produced furfural showed absorption at 1,697 and 2,880 cm^{-1} indicating a conjugated carbonyl functional group and aldehydic hydrogen.

Li (2016) investigated the effect hemicelluloses characteristics of corn stalk in alkaline medium for furfural production. It was found that a higher amount of xylose, lower number of branches, higher polydispersity and crystallinity of hemicelluloses contributed for furfural production.

Several works were reported by the literature on the optimization of furfural production from lignocellulosic biomass, such as Millet husk [11]. To the best of our knowledge there is no published information in literature on the on the optimization of furfural production from Hemicelluloses of Citrullus Colocynthis L. (Melon) Seed Husk using response surface methodology, therefore this research intend to optimized Furfural production obtained from Hemicelluloses of Citrullus Colocynthis L.(Melon) Seed Husk using Response surface methodology.

2. Materials and methods

2.1. Chemicals

The chemicals used are Sulphuric acid (97%, BDH), Sodium Chloride (99%,LOBA) , Sodium Sulphate (99.0%,LABTECH).

2.2. Sample collection and treatment

The Melon seed husk was obtained from locally melon seed processing centre in Nguru local government area of Yobe State, Nigeria. The collected sample was dried under the sun in a dry place, ground, and sieved then stored in a dry place.

2.3. Instrumentation

2.3.1. FT-IR analysis of furfural produced

The produced furfural was analyzed using Carry630 Model FT-IR Spectroscopy. The transmission rate was set at the range of 4000-650 cm^{-1} at a resolution of 4 cm^{-1}. A drop of the sample was placed on a thin film positioned in the standard sample compartment of the FT-IR and the spectral data was obtained.

2.4. Methods

2.4.1. Experimental design

Response Surface (Central Composite Design) statistical experiment design was used to design the furfural production experiment and the optimization design. Three independent variables namely Temperature (° C), Time (Mins), and Acid Concentration (%) were selected for the investigation. Table 1 shows the lower and upper levels of the factors employed based on literature survey. [11]; [12].

Table 1: Process Variables and their Levels used in the Central Composite Design

Independent Variables	Symbols	Level of Variable Low(-)	High(+)
Temperature (° C)	A	150	220
Time (Mins)	B	25	55
Acid Concentration (%)	C	5	10

The experiment was design using MINITAB 17 statistical software and the data collected from the experiments was analyzed using same software at $\alpha = 0.05$ (95% confidence level).

2.4.2. Description of the experimental runs for furfural production

The method described by Sokoto et al., (2018) was adopted for the synthesis of furfural. Each trial involved dried samples (5.0g) of melon seed husk and sodium chloride (NaCl) (5.0g) were mixed in a clean beaker. The mixture was placed into a borosilicate glass tube reactor (250cm^3) and dilute sulphuric acid (H_2SO_4) (50cm^3 of 10%, 8%, 7% or 5%) as in the design matrix was added into the glass tube. The reactor was placed upright inside furnace and connected to water condenser. The Distillation process was carried out according to the chosen variables of sulphuric acid concentration (%), temperature (^{O} C) and time (mins) as in the design matrix respectively.

The organic portion of the distillate was extracted with dichloromethane using separating funnel and sodium sulphate (0.2g) was added to remove any trace water in the distillate. The solvent used was removed using rotary evaporator at 40ºC. And the resultant solution was analyzed by FT-IR spectroscopy.

To obtain furfural yield, the weight of furfural obtained from each run was normalized to the weight of the sample of melon seed husk (equation (1)). [11]; [12].

$$\%\text{FurfuralYield} = \frac{\text{Weight of Furfural formed(g)}}{\text{Dry weight of substrate utilized(g)}} \text{ x100} \tag{1}$$

2.4.3. Data analysis

The furfural yields obtained from the experiments conducted were analyzed on MINITAB 17 Statistical Software to estimate the main and interaction effects on the reaction variables (temperature, time and acid concentration) on the furfural yield. The percentage furfural yield was fitted with a full quadratic polynomial model using regression analysis (equation (2)). The fitness of the model was evaluated by the coefficient of determination (R^2) and the effects of terms were evaluated using analysis of variance (ANOVA) at 95% confidence level.

$$Y = b_0 + b_1X_1 + b_2X^2_2 + b_3X_1X_2 \tag{2}$$

Where, b_0, b_1, b_2, b_3, are intercept, linear, quadratic, and interaction coefficients respectively.

Contour plots were developed using the fitted quadratic polynomial equation, holding one of the independent variables at a constant value and changing the other variables. Optimizer on the MINITAB 17 was used to optimize the factors and the optimal level obtained was experimentally validated [12].

2.4.4. Optimization and validation of the furfural yield

Optimization of the furfural yield was carried out using response optimizer in MINITAB 17 statistical software. Three independent variables namely Temperature, Time and Acid Concentration that affect the furfural were optimized in this study to determine the experimental condition that is best for maximization of furfural yield. Further experimental study was carried for Validation on the reliability of the conditions predicted by the response surface optimizer.

3. Result and discussion

3.1. Effect of the process variables on the furfural yield

The experiments were performed on furfural production from melon seed husk. Table 1 above shows the experimental conditions applied for each treatment condition. 20 runs of experiment and their results were obtained (Table 2). At experimental conditions the value of furfural yields varies from 18.72% to 72.86%

Table 2: Central Composite Design for the Furfural Production

Run	Temp.(ºC)	Time (Min)	Acid Conc. (%)	Furfural Yield (%)
1	150	25	5	18.72
2	220	25	5	29.64
3	150	55	5	58.40
4	220	55	5	47.12
5	150	25	10	38.00
6	220	25	10	66.13
7	150	55	10	37.61
8	220	55	10	72.86
9	183	40	8	43.72

10	187	40	8	50.40
11	185	39	8	40.06
12	185	41	8	38.02
13	185	40	7	54.42
14	185	40	8	56.30
15	185	40	8	54.70
16	185	40	8	59.66
17	185	40	8	53.08
18	185	40	8	56.66
19	185	40	8	55.46
20	185	40	8	50.92

The ANOVA analysis results (Table 3) of the model F-value for furfural yield indicates that the model is significant. The significant of the models are confirmed by relatively higher Fischer's 'F-statistics' value and lower value of probability ('P' value) [13]. The results of analysis of variance (ANOVA) in fitting the results (Table 3) into equation (2) reveal that with exception of square terms and interaction of Temperature and Time all other linear and interaction terms of the process variables are all statistically significant ($p< 0.05$, at $\alpha = 0.05$), although with the "lack of fit" (F-value = 7.00) and (p-value = 0.026) implies that the lack of fit of the data is significant ($p <0.05$). The high coefficient variation (R^2 = 87.28%) show that the model adequately accounts for the empirical relationship between the furfural yield and the process variables.

Table 3: Results of Analysis of Variance (ANOVA) for Furfural Yield (%)

Source	DF	Adj SS	Adj MS	F- Value	P-Value
Model	9	2713.92	301.547	8.31	0.001
Linear	3	1465.51	488.502	13.46	0.001
Temp.,(^{o} C)	1	501.40	501.403	13.82	0.004
Time (mins)	1	502.10	502.403	13.84	0.004
Acid Conc. (%)	1	462.00	462.004	12.73	0.005
Square	3	389.30	129.768	3.58	0.055
Temp.,(^{o} C)* Temp.,(^{o} C)	1	0.03	0.029	0.00	0.064
Time (mins)* Time (mins)	1	197.68	197.684	5.45	0.978
Acid Conc. (%)*Acid Conc. (%)	1	201.84	201.840	5.56	0.042
2-Way Interaction	3	859.11	286.369	7.89	0.040
Temp.,(^{o} C)*Time (mins)	1	28.43	28.426	0.78	0.005
Temp.,(^{o} C)*Acid Conc. (%)	1	507.85	507.848	14.00	0.397
Time (mins)*Acid Conc. (%)	1	322.83	322.834	8.90	0.004
Error	10	362.81	36.281		
Lack-of-Fit	5	317.74	63.548	7.05	0.026
Pure Error	5	45.07	9.013		
Total	19	3076.73			

DF= degree of freedom, Adj SS= adjusted sum of squares, Adj MS= adjusted mean squares, F-Value = F-statistic value.

Table 4: Model Summary

Model Summary			
S	R-sq	R-sq(adj)	R-sq(pred)
5.71011	87.28%	79.86%	17.31%

Regression analyses of the results (Table 4) further shows that with the exception of square term of temperature and interaction term of Temperature and time all other linear and square terms of the process variables are statistically significant ($p < 0.05$). On the other hand, all the interactions terms are also statistically significant. Thus, on eliminating the insignificant terms from the model the new regression model (equation (3)) with seven significant terms is slightly better than previous model (adjusted R^2 = 79.86% compared to 77.60%) (Table 4) with 9 terms.

Table 5: Results of Regression Analysis Showing the Estimated Coefficients of the Model and Their Significance

Term	Effect	Coef	SE Coef	T- Value	P-Value	Significance
Constant		51.12	1.74	29.39	0.000	S
Temp.,(^{o} C)	15.83	7.91	2.13	3.72	0.004	S
Time (mins)	15.84	7.92	2.13	3.72	0.005	S
Acid Conc. (%)	15.19	7.60	2.13	3.57	0.978	Ns
Temp.,(^{o} C)*Temp.,(^{o} C)	-78	-39	1391	-0.03	0.042	S
Time(mins)* Time(mins)	-6494	-3247	1391	-2.33	0.042	S
Acid Conc. (%)*Acid Conc. (%)	6562	3281	1391	2.36	0.040	S
Temp.,(^{o} C)*Time (mins)	-3.77	-1.88	2.13	-0.89	0.397	Ns
Temp., (^{o} C)*Acid Conc. (%)	15.94	7.97	2.13	3.74	0.004	S
Time (mins)*Acid Conc. (%)	-12.70	-6.35	2.13	-2.98	0.014	S

S=statistically significant, and ns= statistically not significant, Coeff= regression equation coefficient, SE Coeff= Standard error for coefficients, T-value = t-statistics value.

The four-in-one residual plots (Figure 1) show that the basic requirements of the regression analysis have been met: the residuals are randomly and normally distributed. Because of the apparent skewness of the residuals from the histogram, the normality distribution was confirmed with test for normality (Figure 2) (p = 0.392, ($P>0.05$) Anderson-Darling statistic = 0.369):

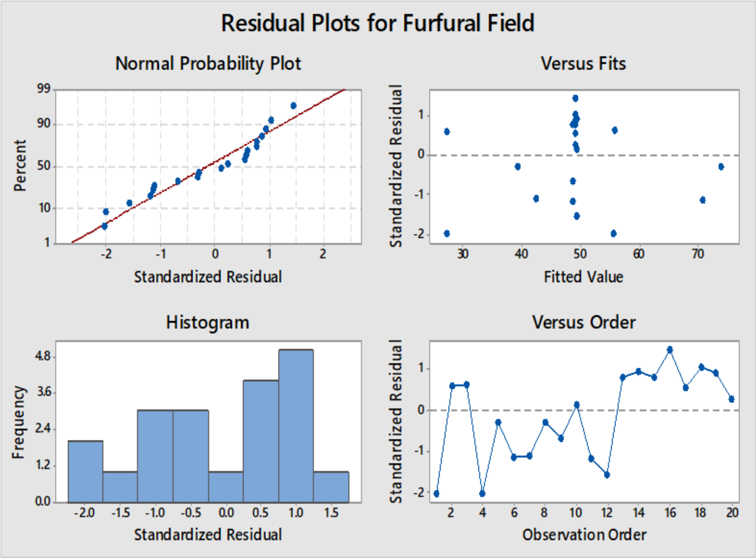

Fig. 1: Four-in-One Residual Plots for Furfural Yield (%).

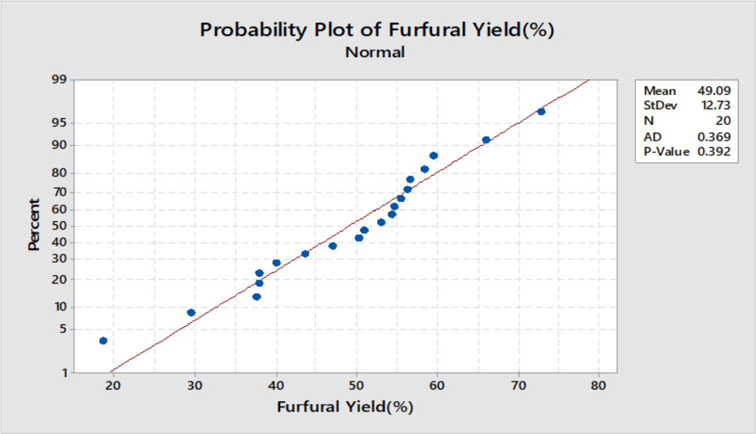

Fig. 2: Probability Plot for Normality Test.

Regression Equation
FurfuralYield(%)=6108- 0.1938 Temp.,(^{O}C)+ 1163 Time(mins) 7823 Acid Conc.(%)-
14.52 Time(mins)*Time(mins)+ 522 Acid Conc.(%)*Acid Conc.(%)+ 0.03863 Temp.,(^{O}C)*Acid Conc.(%) -
0.1694 Time(mins)*Acid Conc.(%) (3)

Figure 3-5 are contour plot describing the relationship between any two of the process variables as they affect the furfural yield while holding the other variable constant.

The furfural yield increased with increasing Acid concentration and reaction Time. At a lower Acid concentration and reaction time (<6%, <30 minutes), the furfural yield was <30%. Highest yields (>70%) are only obtained at Acid concentration >9% and reaction Time 55 minutes. (Fig 3)

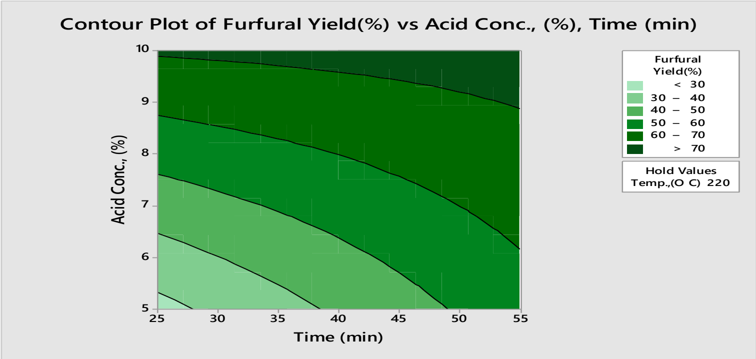

Fig. 3: Contour Plot Showing the Combined Effect of Acid Concentration and Reaction Time on Furfural Yield with the Reaction Temperature Held Constant.

Acid Concentration and Temperature also interact positively to influence the furfural yield (Fig 4). When Acid Concentration is >9% and the Temperature is < 160 ^{O} C, the furfural yields is <45%. Maximum yields of the furfural (>70%) are obtained when the distillation process conducted at Acid Concentration (>9%) and Temperature (>210 ^{O}C) (Fig. 4).

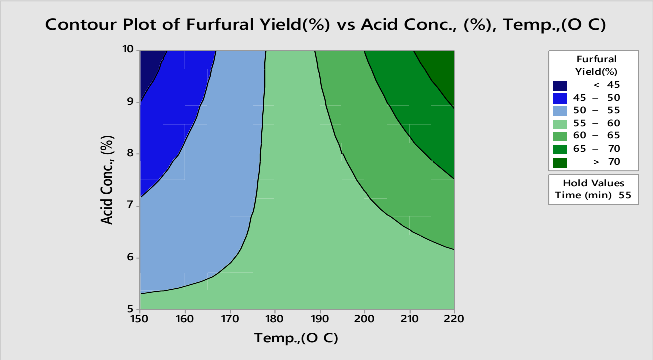

Fig. 4: Contour Plot Showing the Combined Effect of Acid Concentration and Reaction Temperature on Furfural Yield with the Reaction Time Held Constant.

Fig 5 shows the combined effect of the reaction time and temperature on the furfural yield. When the reaction time is <35 minutes and Temperature <160 ^{O}C the furfural yield is <40%. The yield increases with an increase in both variables such that, with the reaction performed with Acid Concentration 10%, yields of >70% can only be obtained when the reaction Time is 55 minutes and Temperature is >210 ^{O}C (Fig 5).

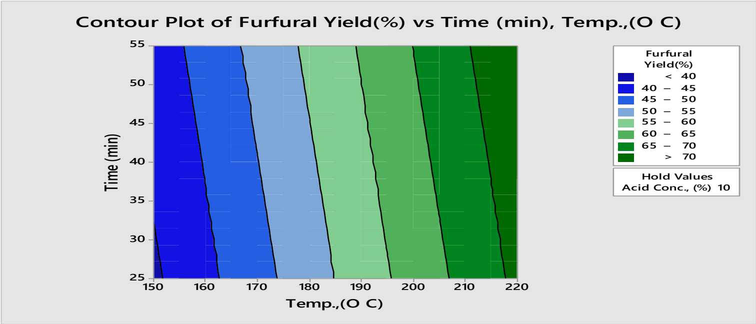

Fig. 5: Contour Plots Showing the Combined Effect of Reaction Time and Reaction Temperature on Furfural Yield with the Acid Concentration Held Constant.

3.2. Response optimization and validation

Table 6 shows the predicted results for an optimal solution obtained from the optimization. The solution predicted a maximum furfural yield of 74.14% and desirability of 1 with optimal process conditions of temperature, time and Acid concentration of 220 ^{O} C, 55 minutes and 10% respectively.

Furfural yield of 75.03% was obtained from validation experiment carried out at the levels of the process variables predicted in solution 1.it was observed that the optimizer predicted and experimental validated results were 74.14 and 75.03% respectively which indicates a relative deviation of 0.89% between experimental validated result and model predicted result. Since the result of the validation result showed agreement with predicted value, the model is reliable [12]. Thus, it can be suggested that the optimization model is reliable and may therefore be more attractive for larger scale furfural production from melon seed husk via acid catalysed hydrolysis/dehydration using Distillation process. Sokoto et al., (2018) reported a maximum yield of 71.55% from millet husk at 184^{O}C for 39 minutes reaction time, 9% acid concentration. Their result is slightly lower yield compare to current work but, it was achieved at lower temperature, time and acid concentration.

Table 6: Predicted Result of Optimization and Validation of Melon Seed Husk Furfural Yield

	Temp., (^{O}C)	Time (mins)	Acid Conc., (%)	Furfural Yield (%)	Desirability
Solution 1	220	55	10	74.1401	1

3.3. Furfural identification

The produced furfural identity was evaluated using Carry630 Fourier Transform Infra-red (FT-IR). The FT-IR spectrum (Figure 6) shows a very strong absorption at 1670 cm^{-1}. This absorption shows a very significant functional group which corresponds to absorption of conjugated carbonyl (C=O). The C=O absorption wave number slightly lower than usual (i.e 1740-1720 cm-1) absorption of aldehyde due to internal hydrogen bonding which occurs in conjugated unsaturated aldehydes, and conjugation lower the vibrational frequency of carbonyl compounds. The absence of peak at 1725 cm^{-1} indicates strongly the presence of aldehydes not ketone group [10]. The presence of the aldehyde group was proven with the existence of two weak absorption observed at 2850 cm^{-1} and 2800 cm^{-1} which indicates moderate intense stretching of aldehydic C-H which is attributable to Fermi resonance between the fundamental aldehydic C-H stretching and the first overtone of the aldehydic C-H bending vibration it appears at 1,370 cm^{-1} in the spectrum, these bands are frequently observed for aldehyde group.. In addition, Strong peaks indicated from 1570 cm^{-1} to 1470 cm^{-1} are inactive of stretching of C=C from aromatic ring. Aromatic =C-H bending out of plane peaks was observed from 900 to 750. Two strong peaks at 1,160 cm^{-1} and 1,200 cm^{-1} indicated C-O stretching vibration. This IR spectrum was compared with the furfural IR spectrum published by Garba et al., (2019), Ameh et al., (2016), and Ong and Sashikala (2007) and it suits that spectrum.

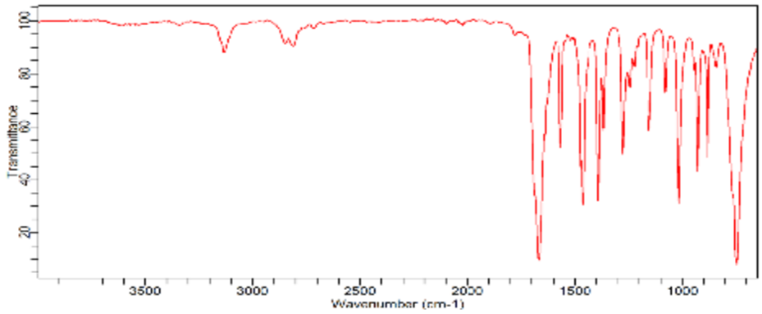

Fig. 6: FT-IR Spectrum of Furfural Produced.

4. Conclusion

Furfural was produced from Hemicellulose of melon seed husk. A central composite design was used for the optimization of the process conditions. The pathway involved the simultaneous steps of melon seed husks hydrolysis/dehydration. Data obtained from the response surface methodology (RSM) for furfural production were analyzed using Analysis of variance (ANOVA). The optimum furfural yield of 75.03% was achieved via degradation of hemicellulose fraction of the citrullus colocynthis (melon) seed husk at optimized process condition of temperature, time and acid concentration of 220 ^{O} C, 55 minutes and 10% respectively. The outcomes showed that using melon seed husk as a feedstock for the synthesis of furfural, which may be used to make fine chemicals and biofuels, may be a practical way to dispose these agricultural wastes and subsequently addresses environmental issues related to greenhouse gases emission results from open air burning of the wastes and usage of fossil fuels.

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