

Application of Response Surface Design to Optimize the Production of Bioethanol from Lignocellulosic Biomass (*Maize cob*)

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Abstract: Another sustainable energy source with many uses is bioethanol. The investigation of diluted H₂SO₄ hydrolysis (0.25 M to 2 M) was initially conducted in this context of producing bioethanol from maize cob using a magnetic stirrer at varied temperatures (40 to 100°C) and reaction times (60 to 105 min) with the purpose of optimizing the processes. According to the findings, a low glucose output was seen at low acid concentrations of 0.25 M and 0.5 M, increasing gradually at 1 M and 2 M. At a high temperature of 90°C, a significant glucose yield was seen, with the glucose yield decreasing as the reaction time increased past 90 minutes. The outcome additionally demonstrated that yeast affected the glucose yield during fermentation. After fermentation, bioethanol was later recovered by distillation at 78.9°C. Bioethanol characterization showed that kinematic octane rating was 117, cloud point was -11, pour point was -13, flash point was 16.5, and specific gravity was 0.781. The empirical model obtained showed that reaction time, catalyst concentration and reaction temperature are the most important variables that influence the process.

Keywords: Bioethanol, *Maize cob*, Fermentation, Optimizing

1. Introduction

Meeting the rising need for energy for transportation, heating, industrial processes, and to supply raw materials for industries in a sustainable manner is one of society's biggest issues in the twenty-first century [1]. Furthermore, society is under pressure to find an alternative fuel source due to concerns about the security of the oil supply and the damaging effects of fossil fuels on the environment, particularly the global warming that is brought on by an increase in greenhouse gases (GHG) in the atmosphere that is primarily the result of human activity since the beginning of the industrial revolution [2]. Because it is an environmentally beneficial energy source and keeps the amount of carbon dioxide constant, biomass has gained attention as a substitute energy source in recent years, constant by the process of photosynthesis in the atmosphere. The photosynthetic process absorbs the carbon dioxide released during the combustion of

biomass [3]. One such alternative fuel that could reduce greenhouse gas emissions while complementing fossil fuels is biofuels, which may be because they include oxygen molecules that promote more efficient and thorough burning [4].

In terms of volume and market value during the past few decades, bioethanol has been the most popular renewable fuel produced by bio-refineries, making it the most frequently utilized liquid biofuel [5]. The chemical formula of ethanol, or ethyl alcohol, is C₂H₆O. It is a volatile, flammable, colorless liquid with a faintly distinguishing odor. It can be made in one of two ways: either by a petrochemical process, such as the hydrolysis of ethylene during the refinement of petroleum [6]. The second method of producing ethanol involves either using cellulosic feedstock, such as paper, cardboard, wood, and other fibrous plant material derived from agricultural feedstock, or fermentation of sugars such as sugar cane juice, sugar beet juice, molasses,

and starch-based materials such as maize, wheat, potato, cassava, and many others [7].

In respect of this, the new global economy attention has been drawn to the transfer of crude oil-based refinery to biomass-based bio refinery [8]. This came as a result of the expected environmental damages like global warming, acid rain and urban smog. These problems have tempted the public to reduce the carbon emissions and shift toward utilizing a variety of renewable energy resources such as; solar, wind, biofuel, etc. that are less environmentally harmful. The sustainability of bioethanol made it the most promising alternative biofuel that can play an important role in addressing such environmental problems caused by fossil fuels. Similarly, recent developments in the production of bioethanol have attracted strong scientific interest which focuses on the development of several raw materials in a sustainable way for bioethanol production which will serve as an alternative transportation fuel to petroleum fuel been non-renewable [9].

2. Methods

2.1. Experimental Design

The response surface (Central Composite) statistical experimental design and the statistical software MINITAB 17 were used to produce the optimization. Reaction duration, temperature, and acid concentration were chosen as the three independent variables for the study. Table 1 displays the lower and upper bounds of the factors that were used. Each run was completely randomized, resulting in a total of 20 runs. Table 2.

Table 1. Optimization Processes Variables.

Factor	Lower Level	Upper Level
Acid Concentration (M)	0.25	2.00
Temperature (°C)	40.0	100
Time (min)	60.0	105

Table 2. Experimental Design Matrix for Hydrolysis.

Experimental Runs	Concentration (M)	Time (min)	Temperature (°C)
1	0.25	75	60
2	0.50	105	40
3	1.00	75	60
4	0.25	105	80
5	1.00	60	40
6	0.50	75	60
7	0.50	105	100
8	1.00	90	80
9	0.25	60	40
10	1.00	105	100
11	2.00	105	100
12	1.00	90	100
13	2.00	105	90
14	0.50	60	40
15	2.00	90	80
16	2.00	60	40
17	2.00	75	40
18	0.25	105	100
19	0.50	90	80
20	0.25	90	80

2.2. Fuel Properties of Bioethanol

2.2.1. Pour and Cloud Point

A cylindrical tube was filled with precisely 10 ml of the sample, the machine was turned on, and the temperature was allowed to drop to -15°C (i.e., real time temperature) for an hour. The samples were placed in a testing chamber (cold bath), which contained a solvent that acted as a cooling solvent and was primarily ethanol. Tests start at -15°C. In the vertical position, the tube was firmly fastened. In order to verify for its liquidity, the pour point was determined in accordance with ASTM D97-02 through chilling at the required temperature and intervals of 3°C. The pour point, or lowest temperature at which liquid can flow, was observed (ASTM D97-02). A thermometer was dipped into the tube and used to record the sample's temperature after it had been allowed to continue cooling for around 40 minutes and turned hazy (ASTM D2500-05).

2.2.2. Flash Point

A test cup was filled with exactly 70 ml of the sample, which was then heated steadily while being swirled at a set rate. A fire was lit to test the cup's opening at certain temperature intervals, causing a steam sample to momentarily catch fire and spread to the liquid's lowest temperature. This was noted as the flash point for air pressure that is normal (ASTM D92).

2.2.3. Octane Rating

A precise 10 ml of the sample was put into a 25 mm cylindrical cupboard to the mark and put into the knob of the cabinet where testing started. The apparatus (Cadonhair KD-R3039) was turned on, ethanol was selected, and the testing started and was recorded (ASTM D2700-18).

3. Results

Table 3. Experimental Design Matrix and Results (glucose yield) from the Experimental Runs.

Run Order	Concentration (M)	Time (min)	Temperature (°C)	Glucose Yield g/g
1	0.25	75	60	0.000178
2	0.500 0.50	105	40	0.000194
3	1	75	60	0.000285
4	0.25	105	80	0.000216
5	1	60	40	0.000251
6	0.5	75	60	0.000267
7	0.5	105	100	0.000321
8	1	90	80	0.00038
9	0.25	60	40	0.000141
10	1	105	100	0.000465
11	2	105	100	0.000348
12	1	90	100	0.00033
13	2	105	90	0.000397
14	0.5	60	40	0.000226
15	2	90	80	0.000429
16	2	60	40	0.00038
17	2	75	40	0.00033
18	0.25	105	100	0.00034
19	0.5	90	80	0.000287
20	0.25	90	80	0.000209

Table 4. Result of Analysis of Variance (ANOVA) for Glucose Yield (%).

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Model	9	0.000000	0.000000	6.60	0.003
Linear	3	0.000000	0.000000	6.88	0.009
Conc	1	0.000000	0.000000	11.73	0.006
Time	1	0.000000	0.000000	0.05	0.883
Temp	1	0.000000	0.000000	0.21	0.657
Square	3	0.000000	0.000000	1.55	0.263
Conc*Conc	1	0.000000	0.000000	4.58	0.058
Time*Time	1	0.000000	0.000000	0.02	0.904
Temp*Temp	1	0.000000	0.000000	0.51	0.490
2-way interaction	3	0.000000	0.000000	1.47	0.282
Conc*Conc	1	0.000000	0.000000	0.00	0.992
Time*Time	1	0.000000	0.000000	0.13	0.724
Temp*Temp	1	0.000000	0.000000	0.03	0.867
Error	10	0.000000	0.000000		
Total	20	0.000000	0.000000		

DF = degree of freedom, Adj SS = adjusted sum of squares, Adj MS = adjusted mean squares, F = F-statistics, P = p-value, and S = statistically significant.

3.1. Analysis of Variance

3.1.1. Model

These tests whether the terms in the model have any effect on the response. For regression model to be significant ($P < 0.05$). The P-value observed was ($P = 0.003$) which is a clear indication that, at least one of the terms in the model has an impact on the mean response. Model is further broken into different orders of terms in the model namely; linear, square, and interaction effect.

3.1.2. Linear Effect

For concentration ($P=0.006$) is less than 0.05. Therefore, conc has linear effect on the model whereas P-value for time ($P=0.833$) and temp ($P=0.657$) both are greater than ($P < 0.05$) which shows that time and temp has no linear effect on the model.

3.1.3. Squared Effects

Squared terms are used to evaluate whether or not there is curvature in the response surface. The p-value of 0.263 for the squared effects is more than 0.05. Therefore, there is no significant evidence of a quadratic effect. The individual p-values for conc*conc time*time and temp*temp and are 0.058, 0.904, 0.490 respectively, indicating that the relationships between time and yield and temperature and yield does not follows a curved line.

3.1.4. Interaction Effects

The p-value of 0.282 for the Time by Temperature

interaction is less than 0.05. Therefore, there is a significant interaction effect. That is, the effect of time on reaction yield depends on the temperature.

3.2. Model Summary

S, R^2 adjusted, R^2 , and R^2 predicted are measures of how well the model fits the data. These values can help you select the model with the best fit.

S; is measured in the units of the response variable and represents the standard distance that data values fall from the regression line. For a given study, the better the equation predicts the response, the lower S is.

R^2 ; describes the amount of variation in the observed response values that is explained by the predictor (s). R^2 always increases with additional predictors.

R^2 adjusted; is a modified R^2 that has been adjusted for the number of terms in the model. If you include unnecessary terms, R^2 can be artificially high. Unlike R^2 adjusted R^2 may get smaller when you add terms to the model. Use R^2 adjusted to compare models with different numbers of predictors.

R^2 predicted; is a measure of how well the model predicts the response for new observations. Large differences between Predicted R^2 and the other two R^2 statistics can indicate that the model is overfit. An overfit model does not predict new observations nearly as well as the model fits the existing data. Predicted R^2 is more useful than adjusted R^2 for comparing models because it is calculated with observations not included in the model calculation.

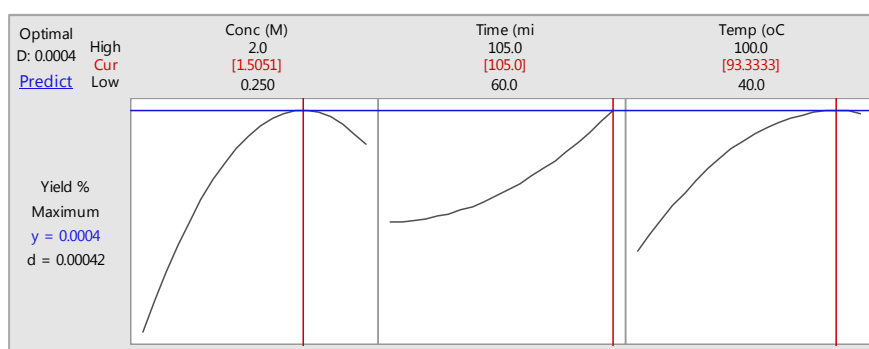
For the acid hydrolysis data, 85.60% of the variation in yield is explained by model, the predicted R is 0.00%, and the adjusted R is 72.63%. The lower R^2 may indicate that the model is overfit and suggests that the model will not predict new observations nearly as well as it fits the existing data.

Table 5. Result of summary of the model used for ANOVA.

S	R^2	R^2 (adj)	R^2 (pred)
0.0000462	85.60%	72.63%	0.00%

3.3. Optimization Plot

Based on the glucose yield obtained from hydrolysis runs, Minitab 17 Statistical Software was used to predict the optimum conditions; acid concentration, time and temperature for obtaining optimum glucose yield as shown in figure 1 below.

**Figure 1.** Optimization Plot.

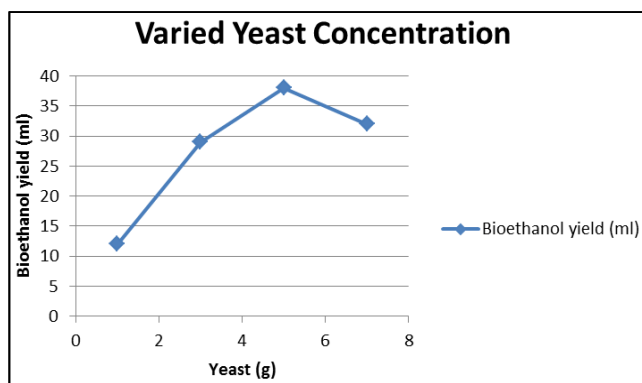


Figure 2. Effect of Yeast on Bioethanol Yield.

Table 6. Fuel Properties of Bioethanol from *Maize cob*.

Parameter	Unit	Bioethanol	ASTM Standard
Flash Point	°C	16.50	16.50 - 16.70
Octane Rating	°C	117	96 above
Pour Point	°C	-13	-5.0
Cloud Point	°C	-11	-23

4. Discussion

4.1. Optimization Plot

The goal of the optimization plot was to identify the ideal process parameters (acid concentration, duration, and temperature) that would result in the highest possible glucose production [10]. The optimum conditions for the procedure were found to be 93°C, 105 min, and 1.5 M, respectively, with a predicted glucose yield of 0.000420 percent. Further experimental research was conducted in order to validate the forecast and confirm the validity of the condition indicated. It was noted that the experimental validation result was 0.000422, whereas the optimizer projected 0.000420 percent glucose yield. The model is trustworthy because the outcome of the validation experiment revealed agreement with the expected value.

4.2. Effect of Yeast on Bioethanol Yield

We noticed how yeast affected the amount of ethanol produced from the hydrolyzed *Maize cob*. The production of bioethanol gradually grew as the yeast concentration rose from 1 g to 5 g; however, at 7 g yeast concentration, the yield of ethanol decreased to 32 ml.

4.3. Fuel Properties of Bioethanol

4.3.1. Flash Point

One of the many factors that must be taken into account when determining a substance's overall flammability is flash point is the lowest temperature at which an ignition source will cause a substance to ignite [11]. The result 16.50°C shows that the experimental bioethanol's flash point is within the ASTM E100 standard (range 16.50-16.70). A gasoline with a higher flash point is safer to handle, store, and transport even under mild temperature conditions.

4.3.2. Pour Point and Cloud Point

Pour point is a quality of a liquid that, due to a high paraffin content, causes it to lose its flow characteristics at low temperatures and becoming semi-solid [12]. The outcome demonstrated that the experimental bioethanol has an excellent pour point value of -13°C, which is over the ASTM limit for E100 (-5.0°C), clearly demonstrating that it is free from fatty acids and suitable for usage in polar regions where the air pressure is below -13°C. The lowest temperature below which a cloud of wax crystals occurs in the fuel while it is cool was measured for cloud point, just like pour point. The experimental bioethanol's cloud point was found to be -11°C, which is below the ASTM standard, according to the results table (-23°C). The likelihood of solidified waxes present increases with a fuel's lower cloud point and pour point, which may thicken the fuel and clog filters and injectors in engines [13].

4.3.3. Octane Rating

The antiknock qualities of a liquid fuel are quantified by the octane rating. In other words, it a measurement of the fuel's ability to ignite. It will be more suited as gasoline if the octane number is greater [14]. The octane rating for experimental bioethanol was reported, and it is completely consistent with the ASTM E100 standard for bioethanol (96 above). The higher reported octane value was expected since ethanol was thought to have a high octane number globally, which makes it acceptable for combining with other petroleum products to improve car engine performance and lower fuel costs. According to the Alternative Fuel Data Center [15]. Ethanol with a high octane rating is thought to have a high heat of evaporation and high flammability temperature, which positively affects engine performance and raises the compression ratio [16].

5. Conclusion

Application of the response surface methodology to the synthesis of bioethanol from corn cobs was effective. The second-order polynomial's high regression coefficients demonstrated how well the model fit the experimental data. The ANOVA suggested that the main important factors influencing the yield of bioethanol are the molar ratio of acid to ethanol, reaction temperature, and reaction duration. It was found that the ideal process conditions were 100°C, 105 minutes, and 1.00 M for the catalyst concentration, temperature, and reaction time, respectively.

References

- [1] Saeed, A. F. Ni, Y. (2011). Chitosan as a Flocculant for Pre-Hydrolysis Liquor of Kraft-Based Dissolving Pulp Production Process. *Carbohydrate Polymer*, 86, 1630-1636.
- [2] Naik, S. N. Goud, V. V. Rout, P. K. (2010). Production of First and Second Generation Biofuel a Comprehensive Review. *Renewable and Sustainable Energy*. 14 (2), 578-597.

- [3] Farrell, A. E. Plevin, R. J. Jones, A. D. O'hare, M. and Kammen, D. (2006) Ethanol can Contribute to Energy and Developmental Goals. *Science* 311 (5769), 506-508.
- [4] Sivakumar, G. V. D. Xu, J. Burner, J. O. Ge, X. and Weathers, P. J. (2010). Bioethanol and Biodiesel: Alternative Liquid Fuels for Future Generation. *Engineering and Life Science*, 8-18.
- [5] Dufey, A. (2006). Biofuel Production Trade and Sustainable Development Emerging Issues. Environmental Economic Program Sustainable Markets Discussion Paper No. 2. *International Institution for Environment and Development (IIED), London*.
- [6] Balata M. Balata, H. and Cahide, O. Z. (2007). Global Bio-Fuel Processing and Production Trends. *Energy Explore Exploit*, 195-218.
- [7] Demirbas, A. (2005). Bioethanol from Cellulosic Materials: a Renewable Motor Fuel from Biomass. *Energy sources*, 27 (4), 327-337.
- [8] Alvira, P. Tomas-pejo, E. Ballestores, M. and Negro, M. (2010) Pretreatment Technologies for an Efficient Bioethanol Process Based on Enzymatic Hydrolysis a Review. *Bioresource Technology*. 101 (13), 4851-4861.
- [9] Banerjee, S. M. Sen. L. Giri, D. Satpute, T. Chakrabarti, R. A. Pandey (2010). Commercializing Lignocellulosic Bioethanol Technology Bottleneck, Biofuels, Bio Products and Bio Refining *Biotechnology*, 77-93.
- [10] Gurgel (2012). Dilute Acid Hydrolysis of Sugarcane Bagasse at High Temperature: a Kinetic Study of Cellulose Saccharification and Glucose Decomposition. Part 1: Sulfuric Acid as the Catalyst. *Industrial and Engineering Chemistry Research*, 51 (3), 1173-1185.
- [11] Adeeyo, O. A. Ayeni, A. O. Oladimeji, T. E. Oresgun, O. M. (2015) Acid Hydrolysis of Lignocellulosic Content of Sawdust to Fermentable Sugars for Ethanol Production. *International Journal of Scientific and Engineering Research*, 3-6.
- [12] Ajani, A. O. Agarry, S. E. and Agbede, O. O. (2012). A comparative Kinetic Study of Acidic Hydrolysis of Waste Cellulose from Agricultural Derived Biomass. *Journal of Nigerian Society of Chemical Engineers*, 27 (1), 166-134.
- [13] Shen, J. F. P. Soleimani, P. Ni, Y. (2012). Lime Treatment of Pre-hydrolysis Liquor from Kraft-Based Dissolving Pulp Production Process Industries. *Engineering and Chemistry Research*, 51, 662-667.
- [14] Silvia, M. R. Jose, M. Campos, M. and Jose, L. G. (2013) Sustainable Energy and Chemistry Group (EQS), *Institute of Catalysis Petroleoquímica, CSIC, Marie Curie, Canto Blanco, 28049 Madrid, Spain*, <http://www.icp.csic.es/eqsgroup/>
- [15] Alternative fuel Data center (AFDC) (1997). Replacement Fuel and Alternative Fuel Vehicle Technical and Policy Analysis, an Overview and Summary. *The United State Department of Energy*.
- [16] Galazka, J. M. Tian, C. Beeson, W. T. Martinez, B. Glass, N. I. and Cate, J. H. (2010). Cellodextrin Transport in Yeast for Improved Biofuel Production. *Science*, 330 (6000), 84-86.