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**Research Paper**

# Process Optimization of Biogas Synthesis from Tannery Effluent for Advance Reactor Performance Using Reaction Models

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***ABSTRACT***
*The leather sector across the globe has tremendous potential towards economic growth and development and it is in-fact the major foreign exchange earner for most countries especially in Africa such as Ethiopia, Uganda, Kenya and even Nigeria. As good as that sounds, the process of its conversion generates huge amount of waste and possess serious challenge managing it. In this research, optimum operational conditions were computed for anaerobic digester design for the synthesis of biogas. Design Expert 6.o software as well as analytical variance ANOVA were adopted to ascertain the best operational conditions in terms of factors such as; temperature, pH, hydraulic retention time, Carbon/Nitrogen ratio and mixing ratio were considered for 15 runs. The synthesized biogas yields ranged from 25.88 to 84.76 % with the lowest yield at run 2 and highest yield at run 12. The C/N ratio and pH affected the model negatively, while mixing ratio, temperature and retention time had positive effect on the model. Also, the ratio/statistical significant difference between the minimum and maximum was 3.49. Hence, there was no need for transformation associated with reaction variations greater than 10. The biogas developed can be used for domestic and industrial heating processes as well as generate electricity. Also, the by-product (digestate) of the synthesis can be used as bio-fertilizers in agriculture. Biogas is an alternative source of energy also known as renewable energy developed to checkmate the hazards of fossil fuel energy such as environmental pollution and global warming responsible for climatic changes. It is recommended that active inoculum be introduced in the digestion process to improve the C/N ratio as well as the biogas yield.*
***Keywords:*** *tannery effluent, biogas, digester, renewable energy,*

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## I. INTRODUCTION

Tanning is a process of conversion of raw hides and skins from animals, reptiles, fishes, birds and so on into leather used for clothing, furniture, mats, upholstery and a variety of finished leather goods. Huge amount of waste as solid, effluent/liquid and gases are generated in the process. In the conversion of a ton of hides to leather only about 20 – 25% is converted to leather and about 35 $m^3$wastewater/effluent is produced consisting of high concentration of salts, chromium, ammonia, dye, chemical solvents and sludge from the raw hides and skins (Sandeep et. al., 2010 cited by Onukak, 2015). These wastes are often disposed illegally into landfills, incinerated or discharged into nearby water bodies or lands and of serious health and environmental concern. Leather trade have high economic value globally and it is the highest income earning revenue in Nigeria next to oil and gas (Nimerbeh,2014). The leather industry has the capacity of employing directly or indirectly across the leather value chain about 2.5M youth and women (Ajibade, 2018). Hence, it is highly essentially to research on possible measures on process environmental pollution control as well as enhancing the economic viability of this valuable commodity. One of such ways by this research is the synthesis of biogas from the tannery effluent. Tannery effluent is as characterized in table 1.

**Table 1**: Physicochemical Properties of Tannery Effluent

| Parameters | Effluent | Standard (WHO, 2002) |
|---|---|---|
| BOD (mg/l) | 4464 | 30 |
| COD (mg/l) | 12840 | 250 |
| TDS (mg/l) | 21300 | 2100 |
| TSS (mg/l) | 1250 | 600 |
| DO (mg/l) | 2.72 | 4.5 |
| EC (µS/cm) | 42500 | 1200 |
| pH | 8.3 | 5.5 - 9 |
| $Cl^-$ (mg/l) | 13.8 | 1000 |
| Bb | 17.1 | 5 |
| Cr (mg/l) | 10.348 | 2 |
| Zn (mg/l) | 1.5241 | 1 |
| Ni (mg/l) | 0.1513 | 3 |
| Na (mg/l) | 12006 | Nm |
| Pb (mg/l) | 0.1818 | 0.1 |
| Fe (mg/l) | 14.675 | 10 |
| Cu (mg/l) | 0.4112 | 0.1 |
| Cd (mg/l) | 0.0046 | 2 |

**Legend**: BOD- Biological Oxygen Demand, COD- Chemical Oxygen Demand, TDS- Total Dissolve Solid, TSS- Total Suspended Solid, DO- Dissolve Oxygen, EC- Electrical Conductivity
**Source**: Jahan, et. al., 2014

Biogas is an aspect of renewable energy generated from organic domestic/municipal, agricultural and industrial composites/waste. It involves the synthesis of such waste mostly under anaerobic conditions in digesters taking cognizance of parameters such as temperatures, pH, carbon/nitrogen ratio, hydraulic retention time, mixing ratio of the waste and microbial activities. The composition of the bio-gas, is about 70% methane ($CH_4$) and 29% carbon dioxide ($CO_2$) with insignificant traces of oxygen ($O_2$) and hydrogen, carbon monoxide (CO), nitrogen ($N_2$) and sulphide ($H_2S$) (Ijaz, M. et. al., 2020, John, 2012, Deublein and Sternhauser, 2008 cited by Nuhu et. al., 2013). Methane gas is a good source of energy for combustion both for domestic and industrial heating and electricity generation. The energy is sustainable, economic and environmentally friendly compared to energy from fossil fuels. Also, the byproduct(digestate) can be used as bio-fertilizers in agriculture.

Digesters are bioreactors designed and produced for effective biological reactions cultured either by aerobic or anaerobic conditions for microbial/enzymic immobilization. It is usually constructed with steel/ferroconcrete for retention heat, kept air tight and water proof. The major component of the biogas plant includes; reactor, gas holder, gas cleansing, heating system and power plant. They are often built in a cone shape and placed partly underground to ensure an oxygen free setting. The addition of inoculum increase the volume of biogas generated. The reactor must meet certain operating conditions necessary for optimal performance (Yusuf et. al., 2003). Such operating conditions include; temperature, pH, agitation, biochemical kinetics, aeration, concentration of microbes, rheology, form of feeding, carbon/nitrogen ratio, hydraulic retention and mixing ratio amongst others (Leonardo et. al., 2019). This research employs the design expert software as well as analysis of variance (ANOVA) in verifying the process variables necessary for optimization of the biogas synthesis from tannery effluent. Experimental models are use in correspondent to sets of controllable variables and for continuous variables, linear, factorial and quadratic models are used;

1. Linear model $Y = \beta 0 + \beta 1 X1 + \beta 2 X2 + \varepsilon$
2. Factorial model $Y = \beta 0 + \beta 1 X1 + \beta 2 X2 + \beta 12 X1 X2 + \varepsilon$
3. Quadratic model $Y = \beta 0 + \beta 1 X1 + \beta 2 X2 + \beta 12 X1 X2 + \beta 11 X21 + \beta 22 X22 + \varepsilon$

Interpretation of the terms follows as;
$\varepsilon$ – interception (common to all), $\beta iXi$– linear term (concurrent i.e. main effect), $\beta ijXiXj$ representing two factors interaction i.e. varying a parameter at the expense of another (control), $\beta iiXi2$ – quadratic term i.e. creating a curvature in the effect of a control response.
(Wu and Hamada, 2000 as cited by Nuhu et. al., 2013)).

## II. METHODOLOGY

ANOVA is generally employed to ascertain statistically the substantial differences in sets of reaction parameters usually determine by the F ratio. The F ratio is the ratio between sum of squares between and within samples. By this analysis, a significant difference occurs when the variation between samples between exceeds the variation between samples within, the set is then selected from different populations.

Model 1 and 2 were adopted for this study for the following parameters; temperature (A), pH (B), mixing ratio (C), carbon to nitrogen ratio (D), retention time (E) and corresponding biogas yield were investing for each set.

Design Expert 6.0 software allow for 15 experimental setups and according to the 2nd principle, each parameter/factor was varied at two levels (high and low), Table 2. The software generates model equations by contrast average of the design experiments thus interpreting the biogas yield.

$$Y = f\ (A, B, C, D, E) \quad (1)$$

$$Y=\alpha A + \beta B + yC + \mu D + \vartheta E + \partial AB + \text{Ø}CE + \eth AD + \mathcal{E}BD + \text{Ɣ}DE + \lambda CD + \Theta ABC + \text{Ɣ}ACD + \S BCD + \vartheta ABD + \beta ABCD \quad (2)$$

## III. RESULTS AND DISCUSSION

**Table 2**: Low and high values for the operating factors.

| Factor | Name | Units | Type | Low actual | High actual | Low coded | High coded |
|---|---|---|---|---|---|---|---|
| A | Temperature | °C | Numeric | 15 | 40 | -1 | 1 |
| B | pH | - | Numeric | 6.5 | 7.5 | -1 | 1 |
| C | Mixing ratio | %w/v | Numeric | 5 | 10 | -1 | 1 |
| D | C/N ratio | - | Numeric | 20 | 30 | -1 | 1 |
| E | Retention time | days | Numeric | 1 | 30 | -1 | 1 |

The result of the 15 experimental runs is shown in Table 3. The resultant yields ranges from 25.88 to 84.76 % and the ratio/statistically significant difference between the minimum and maximum is 3.49. Hence, there is no need for transformation associated with reactions variations greater than 10.

**Table 3**: The 15 Experimental Setup Result

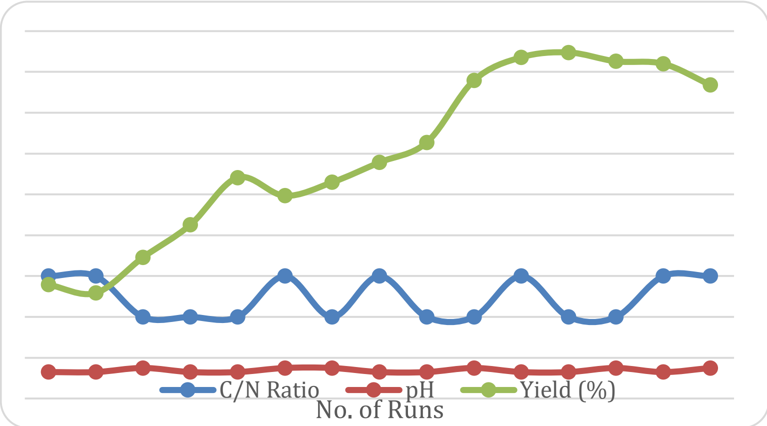
| Run | Standard | Temperature (°C) | pH | Mixing ratio (%w/v) | C/N | Time (days) | Yield (%) |
|---|---|---|---|---|---|---|---|
| 1 | 27 | 40 | 6.5 | 10 | 30 | 2 | 27.92 |
| 2 | 18 | 15 | 6.5 | 5 | 30 | 4 | 25.88 |
| 3 | 32 | 40 | 7.5 | 10 | 20 | 6 | 34.59 |
| 4 | 11 | 40 | 6.5 | 10 | 20 | 8 | 42.54 |
| 5 | 55 | 40 | 6.5 | 5 | 20 | 10 | 54.12 |
| 6 | 57 | 15 | 7.5 | 10 | 30 | 12 | 49.68 |
| 7 | 29 | 15 | 7.5 | 10 | 20 | 14 | 52.97 |
| 8 | 62 | 15 | 6.5 | 10 | 30 | 16 | 57.85 |
| 9 | 3 | 40 | 6.5 | 5 | 20 | 18 | 62.74 |
| 10 | 61 | 40 | 7.5 | 10 | 20 | 20 | 77.92 |
| 11 | 59 | 40 | 6.5 | 10 | 30 | 22 | 83.58 |
| 12 | 64 | 40 | 6.5 | 10 | 20 | 24 | 84.76 |
| 13 | 5 | 15 | 7.5 | 5 | 20 | 26 | 82. 59 |
| 14 | 2 | 15 | 6.5 | 5 | 30 | 28 | 81.99 |
| 15 | 24 | 40 | 7.5 | 5 | 30 | 30 | 76.79 |

**Table 4**: Model Effect Contributions

| Term Intercept | Standard Effect | Sum of Square | % Contribution |
|---|---|---|---|
| A | 9.24 | 0.980E+03 | 6.86 |
| B | -18.5 | 5.572E+03 | 27.20 |
| C | 21.79 | 7.781E+03 | 38.41 |
| D | -0.69 | 1.240E+03 | 6.24 |
| E | 4.97 | 0.485E+03 | 2.15 |
| AC | 3.97 | 2.314E+02 | 1.11 |
| BC | -4.12 | 2.843E+02 | 0.98 |
| BD | 3.05 | 1.937E+02 | 1.04 |
| CD | -3.75 | 2.141 E+02 | 1.15 |

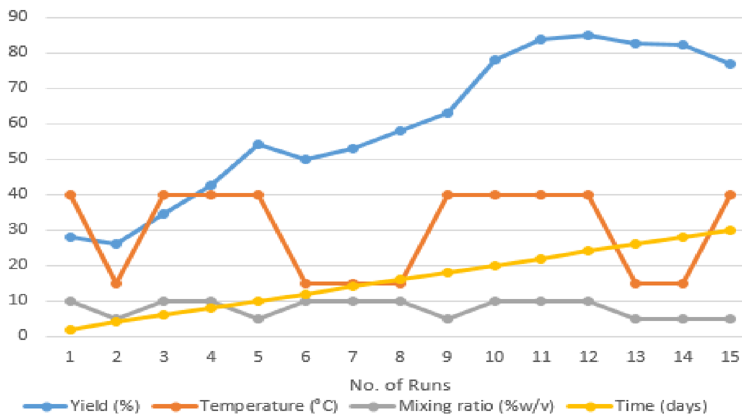
Legend: AC – combine effect of temperature and mixing ratio, BC – combine effect of pH and mixing ratio, BD – combine effect of pH and C/N ratio, CD – combine effect of mixing ratio and C/N ratio.

The contributions of the selected parameters for the model are shown in Table 4. The mixing ratio had the most significant effect of 38.41 % subsequently followed by pH value of 27.20 % and the least value of 2.15 % was observed in retention time. For the interaction effect, the highest value was observed for combine mixing ratio and C/N ratio (1.15%) and then the least value was shown in combination effect of pH and mixing ratio (0.98 %).




**Graph 1**: Demonstration of the effect of pH and C/N Ratio on yield.

Apparently, for the main effects, pH and C/N ratio affected the model negatively while mixing ratio, temperature and retention time had positive effect on the model as shown in graph 1 & 2. For the interaction effects CD and BC affected the model negatively while AC and BD had positive effect on the model.




**Graph 2**: Demonstration of the effect of temperature, mixing ratio and retention time on yield

**Table 5**: ANOVA Factorial Model

| Source | Sum of Squares | DF | Mean Square | F Value | Prob > F | Remark |
|---|---|---|---|---|---|---|
| Model | 18916.23 | 9 | 1763.10 | 98.48 | <0.0001 | Highly significant |
| A | 1451.21 | 1 | 1485.85 | 73.63 | < 0.0001 | Highly significant |
| B | 5048.17 | 1 | 5876.58 | 282.67 | < 0.0001 | Highly significant |
| C | 6754.58 | 1 | 7905.43 | 384.26 | < 0.0001 | Highly significant |
| D | 1028.76 | 1 | 1265.79 | 68.91 | < 0.0001 | Highly significant |
| E | 389.42 | 1 | 427.67 | 21.43 | < 0.0001 | Highly significant |
| AC | 2864.05 | 1 | 276.46 | 13.03 | 0.0006 | Significant |
| BC | 317.65 | 1 | 323.72 | 14.00 | 0.0002 | Significant |
| BD | 241.02 | 1 | 238.03 | 10.13 | 0.0012 | Significant |
| CD | 259.85 | 1 | 261.44 | 10.81 | 0.0008 | Significant |

A factor is significant if it's value (F value) is 98.5as indicated in Table 5. The probability factor value (prob>F) >0.05 also implies the model is significant. In this instance, there is only 0.01% chance than the model F value; noise interference could be responsible for this alteration. Hence, A, B, C, D, E, AC, BC, BD and CD are significant model terms.

**Table 6**: Model R Square Values

| | |
|---|---|
| Mean | 49.58 |
| Standard Deviation | 5.02 |
| Coefficient of Variance | 8.59 |
| R-Squared | 1.3330 |
| R-Squared | 0.8523 |
| R-Squared | 0.8894 |

From Table 6, the values of the R-square are 1.3330, 0.8523 and 0.8894 for mean, standard deviation and coefficient of variance corresponding to standards. Retention time was not involved interaction with other significant factors as it is considered as the intercept;

The Model equation for Table 5 was given as;

Y= αA + βB + yC + μD + ϑE + ∂AB + ØCE + ðAD + ƐBD + ɣDE + ƛCD (3)

The coefficients from Table 4 were substituted for the generalized model equation that described the biogas yield as a function of the design variables.

Y= 49.6 + 5.62A + 9.91B – 19.4C + 22.6D – 0.764E +3.94CE + 4.22BD – 4.13DE – 4.54CD (4)

## IV. CONCLUSION AND RECOMMENDATION

Biogas as a renewable energy is sustainable, economically viable and environmentally friendly. In this study, more value has been added to leather by converting tannery effluents to biogas via the process of Optimum Design Parameter Determination for Biogas Digester. Hence, the maximum yield of 84.76% were obtained from run 12 and the variables considered as the optimum design parameters. This saves time and resources in carrying out multiple failed reactions and design models. It is recommended that active inoculum be introduced in the reaction process to improve the C/N ratio as well as the biogas yield.

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