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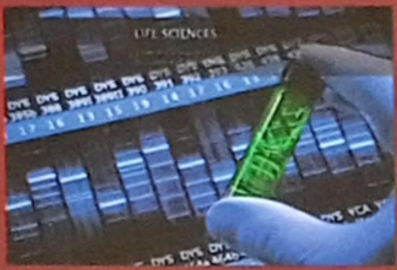

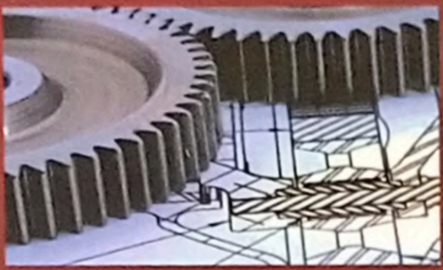

NIGERIA JOURNAL OF ENGINEERING AND APPLIED SCIENCES (NJEAS)

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School of Engineering and Engineering Technology,
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E-mail: njeas@futminna.edu.ng, Website: njeas.futminna.edu.ng

CONTENTS

Modeling and Optimization of Biogas Production from Anaerobic Digestion of Agricultural Waste: A Factorial Design Analysis

Mohammed Alhassan [1*], Abubakar Garba Isah[2] Jibrin Mohammed Jibrin[3]and Mohammed Umar Garba[4],
[1-4]Department of Chemical Engineering , Federal University of Technology , Minna , Niger State, Nigeria
E-mail: moh.alhass@futminna.edu.ng,

Abstract
The aim of this study was to investigate the optimal conditions for biogas production from anaerobic digestion of agricultural waste (namely cow dung, chicken waste and saw dust) using full factorial design of experiments to study the effect of four factors: concentration (A), feed type (B), seeding (C) and time (D) on biogas produced after 28 days of anaerobic digestion. Main effects and interaction effects of these factors were analyzed using statistical techniques. The experimental results showed that the linear model terms of concentration, feed type, seeding and time had significant effect on yield with ($p < 0.05$). However, there was interactive effect between these variables ($p < 0.05$), though, concentration and time show no interaction ($p > 0.05$). The full model equation developed for biogas production is: $Y = K - 11.5842A + 19.9868D$ constant K for biogas production with seeding = 930.877 for cow dung, 1483.28 for chicken waste and 555.692 for sawdust respectively. While K for biogas production without seeding = 351.309 for cow dung, 903.717 for chicken waste and -23.8759 for sawdust respectively. The highest amount of biogas produced was 1973.33mL at optimum conditions of 20% concentration, chicken waste, seeding and retention time of 28 days.

Keywords: Agricultural Waste, Anaerobic Digestion, Modelling, Optimization, Biogas, Full Factorial Design.

Introduction

Today, the issues of global warming and climate change are strongly receiving public attention and have become a major environmental concern both at national and international level. The increasing concentration of atmospheric greenhouse gases as a result of culpable human activities represents the major cause for this problem (Alhassan et al., 2016). The most important Greenhouse gases from such activities are carbon dioxide, methane, nitrous oxide, and fluorinated gases such as sulfur hexafluoride and hydro fluorocarbon (US EPA, 2007). The atmospheric concentration of such gases importantly influences the earth's climate and cause global warming. In the context of global warming, carbon dioxide gas currently gains more public attention than other greenhouse gases. However, it is important to also consider other gases. One of these is methane (CH_4) gas which is produced under anaerobic conditions during degradation of organic materials by certain micro-organisms. The major biological sources of methane include natural wetlands, rice paddies, landfills, ruminants, termites, river beds, and lakes (Steven, 2007). Methane is an important greenhouse gas with the ability of global warming 25 times greater than that of carbon dioxide (IPCC, 2007). It is estimated that more than 60% of the global methane release is connected to human activities. Methane emission accounts for 16% of all global greenhouse gas emissions and the current value of global average atmospheric methane concentration is about 1720 ppbv (parts per billion by volume) which is more than double of the concentration during the pre-industrial period 800 ppbv (Mosier et al., 1998). Methane is therefore important greenhouse gas, which needs a serious consideration. With regard to source, agriculture appears to be the major contributor of atmospheric methane. Worldwide, 35% of greenhouse gas emission is from agriculture (IPCC, 1996). According to Mosier *et al.* (1998) as cited by Olesen *et al.*, (2006) agriculture is a responsible sector for 50% of anthropogenic emission of methane. The major sources of agriculture methane are enteric fermentation and rice paddies.

The rate of energy consumption and waste generation in developing countries necessitates the adoption of technologies that promote renewable energy and the conversion of waste into viable commodity. The biogas technology is one of such systems and has been found to be cost effective and environmentally sound (Brown, 2003). Biogas is a clean, environmental friendly and renewable form of energy generated when micro-organisms degrade organic materials in an oxygen free environment. The formation of biogas can occur either in natural environment or controlled conditions in constructed biogas plants, so called anaerobic degradation (AD). Swamps, marshes, river beds, rumen of herbivore animal are some of the areas where biogas is formed naturally (Marchaim, 1992). The same microbial activities are achieved in both natural and controlled conditions. The feedstock for biogas production in constructed plants is more or less any organic fractions from household organic waste to dedicated energy crops like maize (Lantz *et al.,* 2007). The potential feedstock for the production of biogas include; municipal solid waste, industrial organic waste, garden waste, agricultural waste (manure and crop residue), energy crops, cellulose rich biomass, algae and seaweed (water based), by-products of ethanol and bio diesel production (Lantz *et al.,* 2007; Demetriades, 2008; Börjesson and Mattiasson, 2007; SGC, 2007). Several researchers (Adelekan and Bamgboye, 2009; Adeyosoye *et al.*, 2010, Ofoefule, *et al.* 2011) have reported production of biogas from different substrate such as cassava peels, sweet potato peel, wild cocoyam peel, poultry dropping, maize comb, rice husks and various bulk organic wastes in Nigeria. The country's biogas potential has been estimated at 6.8 million m^3 per day from animal waste, while from municipal solid waste it was estimated at 1.77 million cubic tonnes per year for biogas Production (Mshandete and Parawira, 2009). Biogas production may therefore be a profitable means of reducing the country's energy crisis and waste generation. The Energy crisis in Nigeria started far back the 1970s after the advent of the oil boom, since then there has been growing national concern for sustained shortage in energy supply (GueguimKana *et al.,* 2012 Yadolka, 2004). Many scholars (Preston and Murgueitio, 1992; Mattocks, 1984, Feigelson and Babu, 1992) have also envisaged this problem around the globe. In the United States of America for instance, several million gallons of fuel is consumed on daily basis for transportation and other activities to meet their daily needs (Habmigern, 2003). These fuels are obtained from non-renewable sources which are unsustainable due to their impacts on the environment. Sustainability is a current global trend which addresses issues concerning environmental impacts. It first came into play at the World Commission on Environment and Development (Brundtland,1985; Lele, 1991). It was defined as development that meets the needs of the present generation without compromising the ability of future generations to meet their needs (Brundtland, 1985; Lele, 1991)

Materials and methods

The experiments were carried out on batch laboratory scale reactor (1L Tin Digesters). The batch 1 experiment consists of three digesters and was run in triplicate for each of the digester. These digesters were closed with their lids. A puncture hole was bored in the middle of each lid and a rubber tube of 12 mm diameter was inserted through it, sealed and fixed with araldite. The lid of each digester was further made air tight by melting candle wax all round the edges which on cooling, sealed it up and making it air tight (completely anaerobic). Each digester was connected via a rubber tube, to a 1000 cm^3 cylinder. Organic materials or biomasses used were Cow dung, Chicken waste and Sawdust. Digester A_1 was charged with 100 g of cow dung and was diluted with 400 mL of water giving the ratio of 1: 4 and concentration of 20% as sample A_1. Digester A_2 was charged with 100g of cow dung and was diluted with 300 mL of water giving the ratio of 1:3 and concentration of 25% as sample A_2. Digester A_3 was charged with 100 g of cow dung and was diluted with 100 mL of water giving the ratio of 1:1 and concentration of 50% as sample A_3. Each of the three sub-digester was run in triplicate making a total of 9 digesters for batch A. The same procedure was repeated for digester B. Digester B_1 was charged with 100 g of Chicken waste and was diluted with 400 mL of water giving the ratio of 1: 4 and concentration of 20% as sample B_1. Digester B_2 was charged with 100g of chicken waste and was diluted with 300 mL of water giving the ratio of 1:3 and concentration of 25% as sample B_2. Digester B_3 was charged with 100g of chicken waste and was diluted with 100 mL of water giving the ratio of 1:1 and concentration of 50% as sample B_3. Another digester C_1 was charged with 100 g of saw dust and was diluted with 400 mL of water giving the ratio of 1: 4 and concentration of 20% as sample C_1. Digester C_2 was charged with 100 g of saw dust and was diluted with 300 mL of water giving the ratio of 1: 3 and concentration of 25% as sample C_2. Digester C_3 was charged with 100 g of saw dust and was diluted with 100 mL of water giving the ratio of 1:1 and concentration of 50% as sample C_3. This procedure was triplicated for both sub-digester B and C making a total of 27 digesters for batch1 experiment. The same procedure was repeated and 5g of yeast was added to the substrate as seeding for each of the sub-digester A, B and C making a total of 27 digesters for batch 2 experiments. The overall experiment comprised of 54 runs. The solution was thoroughly mixed to ensure the formation of homogenous mixtures. Each digester was connected via a rubber tube, to a 1000 cm^3 cylinder which was filled with water, inverted and immersed in a trough containing water. Anaerobic fermentation was carried out at an ambient temperature (30-36°C) for a period of twenty eight days. The effective volume of the reactor was maintained at 0.75 L. Biogas production from the reactors was monitored daily by water displacement method. The volume of water displaced from the digester was equivalent to the volume of gas generated. The reactor was mixed manually by means of shaking and swirling twice daily during the period of fermentation. This aids the discharge of the gas in the digester in to the cylinder and also prevents scum formation. The readings were taken every day at 12:00 pm.

Design of Experiment

Minitab16, statistical software was used for the design of experiment and simulation of the results. Design of experiment (DOE) is a well-accepted statistical technique able to design and optimize the experimental process that involves choosing the optimal experimental design and estimate the effect of the several variables independently and also the interactions simultaneously. In a full factorial experiment, responses are measured at all combinations of the experimental factor levels. Each combination of factor levels represents the conditions at which a response measure will be taken. Each experimental condition is called a "run" and each measures an observation. A factorial design of experiments was applied to find out the effect of concentration, feed type, seeding and time on biogas production. The effect of selected factors was studied by means of a full factorial design. The levels of the factors were selected based on the result of preliminary experiments conducted in Table 1.

Results and discussion

Analysis of variance (ANOVA) was used for analysis of regression coefficient, prediction equations, factorial plots (main and interaction effects, surface plot, contour plot, interval plot and residual plots) and case statistics. Regression first-order polynomial models were developed to describe the relationship between selected factors and the response (Y). The general form of mathematical model used is given in equation (1) (Sajeena *et al.*, 2014).

$$Y = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_{12} X_1 X_2 \quad (1)$$

where: Y is the response, X_1 and X_2 are the independent variables, β_0 is the intercept of the model, β_1 and β_2 are the linear coefficients in the regression models and β_{12} is the interaction coefficient between factors.

Table 1: Un coded Values of Independent Variables and Experimental Ranges

Factor	Name	Unit	Type	Level		
				1	2	3
A	Concentration	%	Numeric	20	25	50
B	Feed type	Nil	Text	Cow dung	Chicken waste	Saw dust
C	Seeding	Nil	Text	Yes	No	
D	Time	Day	Numeric	14	21	28

Table 2: Estimated regression coefficients for production rate

Term	Coef	SE Coef	t	P	Remark
Constant	700.167	74.0913	9.4501	0.000	Very significant
A	-11.584	1.2524	-9.2498	0.000	Significant
B_1	-59.074	23.243	-2.5416	0.0120	Significant
B_2	493.333	23.243	21.225	0.000	Very significant
C	289.784	16.4353	17.6318	0.000	Very significant
D	19.987	2.8756	6.9505	0.000	Very significant

Coef: Coefficient SE Coef: Standard Error of Coefficient t: Student's t- test P: Probability

S = 209.187, PRESS = 7339128, R-Sq = 86.29% R-Sq(adj) = 85.85% , R-Sq(pred) =85.26%

The regression coefficients, standard errors, *t*-test and *P*-values are shown in Table 2. The significance of the regression coefficients was determined by applying a student's *t*-test. The *P* -values were used as a tool to check the significance of each of the effect among the variables. The term is very significant as the value of *t* is higher and the value of *P* is smaller $(p < 0.05)$ (Krishna Prasad and Srivastava, 2009). According to this rule, term A and B_1 were significant whereas term B_2, C, and D were very significant.

For biogas generated with seeding:

Yield for cow dung (Y) = 700.167 + B_1 + C + A + D (2)

Y = 930.877 - 11.5842A + 19.9868D (3)

Yield for chicken waste(Y) = 700.167 + B_2 + C + A + D (4)

Y = 1483.28 - 11.5842A+ 19.9868 D (5)

Yield for sawdust(Y) = 700.167 –B_1 –B_2 + C + A +D (6)

Y = 555.692 - 11.5842A+ 19.9868D (7)

For biogas generated without seeding

Yield for cow dung(Y) = 700.167 + B_1 - C + A + D (8)

Y = 351.309 - 11.5842A + 19.9868D (9)

Yield for chicken waste(Y) = 700.167 + B_2 - C + A + D (10)

Y = 903.717 - 11.5842A + 19.9868D (11)

Yield for sawdust(Y) = 700.167 –B_1 –B_2 - C + A +D (12)

Y = -23.8759 - 11.5842A+ 19.9868D (13)

From equation 2-13, a reduced model equation was developed for biogas production.as follows;

Production = K – 11.5842A + 19.9868D (14)

The constant K for biogas production with seeding was 930.877 for cow dung, 1483.28 for chicken waste and 555.692 for sawdust respectively. While K for biogas production without seeding was 351.309

for cow dung, 903.717 for chicken waste and -23.8759 for sawdust respectively.

The R-sq (adj) of 85.85% explains that about 85.85% of the variable in the response could be captured and explained by the model. The Predicted Residual Sum of Squares (PRESS) is a measure of how well the model fitted each point in the design. The smaller the PRESS statistics, the better would be the model fitting the data points (Box *et al.,* 2005). Here the value of PRESS found from the model summary as 7339128.

Table 3: Analysis of Variance for Y(mL) from full model(coded units)

Source	DF	Seq SS	Sum of squares Adj SS	Mean square adj MS	F	P
Regression	5	42976157	42976157	8595231	196.42	0.0000000
A	1	3744023	3744023	3744023	85.559	0.0000000
B	2	23514226	23514226	11757113	268.68	0.0000000
C	1	13603908	13603908	13603908	310.880	0.0000000
D	1	2114001	2114001	2114001	48.310	0.0000000
Error	156	6826455	6826455	43759		
Lack of Fit	48	6438222	6438222	134130	37.313	0.0000000
Pure Error	108	388233	388233	3595		
Total	161	49802612				

DF= degree of freedom

The statistical significance of model equations was checked by an F-test (ANOVA). All the corresponding data are shown in Table 3. Moreover the model F value of 196.42 (Table 3) implies the model is highly significant ($p < 0.0001$). ANOVA results, presented in Table 3, showed that the term A, B, C and D have very significant effect ($p < 0.0001$) on the response Y (biogas yield). These findings are consistent with that of Sajeena *et al.*, (2014) who studied the effect of three process variables; initial pH, substrate concentration and TOC on biogas production.

"Lack of Fit F-value" of 37.313 implies the Lack of Fit is very significant ($p<0.0001$) (ASA, 1983). There is only a 0.01% chance that a Lack of Fit F-value" can occur. A large value for this can occur due to noise (Winer *et al,* 1991). For biogas production, the value of adjusted square correlation coefficient, R-Sq (adj) of 85.85% was also very high, which indicated the higher significance of the model. The R-Sq (pred) value of 85.26% showed the reasonable agreement with the "Adj R-Sq" value of85.85%. This indicated a good agreement between the observed and the predicted values (Sajeena *et al.*, 2014).

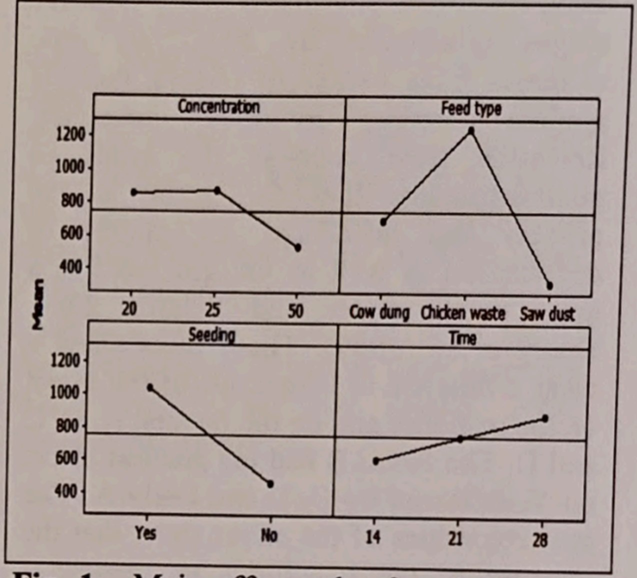

Fig. 1: Main effects plot for Y (Biogas yield)

The main effects plot is used to examine differences between level means for one or more factors. There is a main effect when different levels of a factor affect the response differently. A main effect plot graphs of the response mean for each factor level connected by a line (Montgomery, 2004). From Figure 1, the mean response increase slightly with increase in concentration from 20% to 25%. Further increase in concentration decreases the mean response and this confirms the finding of Hilkiah-Igoni (2008) who showed that when the percentage total solids (PTS) concentration of municipal solid waste in an anaerobic continuous digestion process increases. There is a corresponding geometric increase for biogas produced and at some point in the increase of the TS, no further rise in the volume of the biogas would be obtained. The feed type has the highest effect on the response (biogas yield). The mean response increases mostly with chicken waste followed by cow dung and saw dust (Seadi, *et al.,* 2008). Seeding shows significant effect on the biogas yield as the mean response is higher with seeding (YES) and lower without seeding (NO). This result supports the idea raised by Singh *et al.* (2001) who reported that using microbial Stimulants could improve biogas production by 55%. As time increases from 14days to 28days, there is gradual increase in mean response. Retention time controls the types of microorganisms that can grow in the process and influences the degree of degradation as well as the gas yield to a great extent (Eder and Schulz, 2006; Grady *et al.,* 1999). These plots show a clear difference in magnitude of the effect on the response among the factors: A, B, C and D. The factor B had the greatest effect on Y, followed by C, D and lastly A. The positive values of the effect show that the increase in the magnitude of parameter increases the response Y. Contrary; negative values reveal that the increase in the magnitude of parameter decreases the response Y (Adrian *et al.*, 2013).

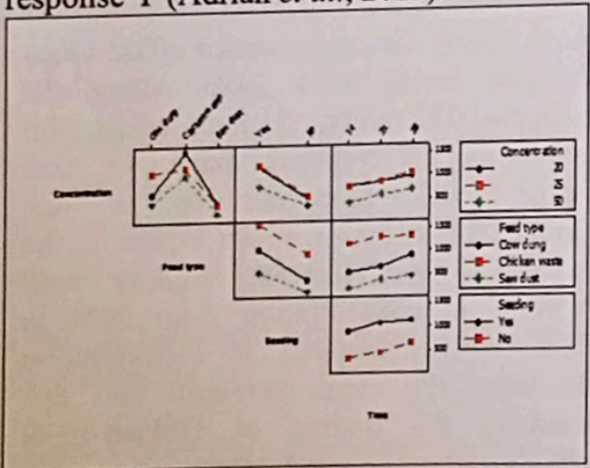

Fig. 2: Interaction effect plot for Y (biogas yield)

Interaction plot

An interaction plot is used to visualize possible interaction when the effect of one factor depends on the level of other factor. An interaction plot displays the levels of one variable on the X-axis and has a separate line for the means of each level of the other variable on the Y-axis. An interaction is effective when the change in the response from low to high levels of a factor is dependent on the level of second factor. Interaction effects represent the combined effects of factors on the dependent measure. When an interaction effect is present, the impact of one factor depends on the level of the other factor. When an interaction is significant, the slope of the two lines should be different and not necessary for the lines to cross or intersect each other within the range of the data. Parallel lines in an interaction plot indicate no interaction (Winer *et al,* 1991). From the Figure 2, Concentration and seeding shows significant interaction. The three lines of mean response of concentration for each level of seeding are not parallel. The three lines of concentration have more mean response for the level of seeding (YES) than without seeding (NO). Concentration and time show no interaction because the mean response for the three lines of concentration for each of the three levels of time is almost parallel. There is interaction between the two factors (feed type and seeding); this is because the lines of mean response of feed type are not parallel indicating that the slopes of the lines are different. There is more mean response of feed type for seeding (YES) than without seeding (Shalini sing *et al.,* 2000). There is interaction between the field type and time because the three lines of mean response of feed type for each of the three levels of time are not parallel. The lines with seeding (YES and NO) show difference in mean response for each of the three levels of time. For this reason, there is interaction between seeding and time (Winer *et al.,* 1991).

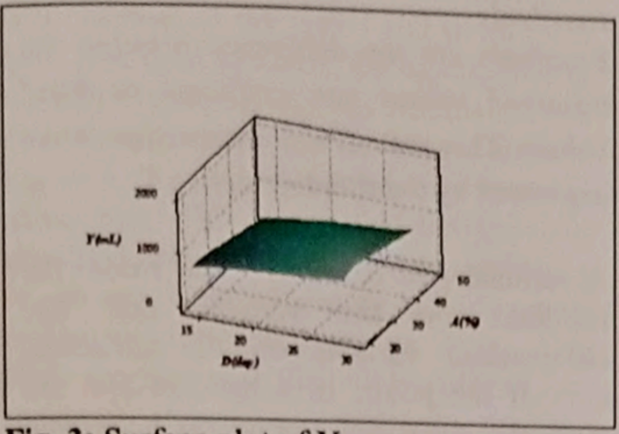

Fig. 3: Surface plot of Y

The Surface plot

The surface plot shows the relationship between three numerical variables. The 3D surface plot for biogas data shows how factor A and D affect the response Y. The surface plot of total biogas yield(Y) produced after 28 days of anaerobic digestion as a function of A and D is shown in Figure 3. The 3D surface plot shows that the maximum total biogas yield, Y (mL) value was found approximately at 25% concentration and at a retention time of 28 days. The minimum total biogas yield value was found at a concentration of 50 % and a retention time of 14 days. This indicates that biogas yield increases with additional increase in concentration (Hilkiah, 2008). Further increase in concentration decreases biogas yield. This also shows that increase in retention time increases biogas yield (Eder and Schulz, 2006; Grady *et al.*, 1999).

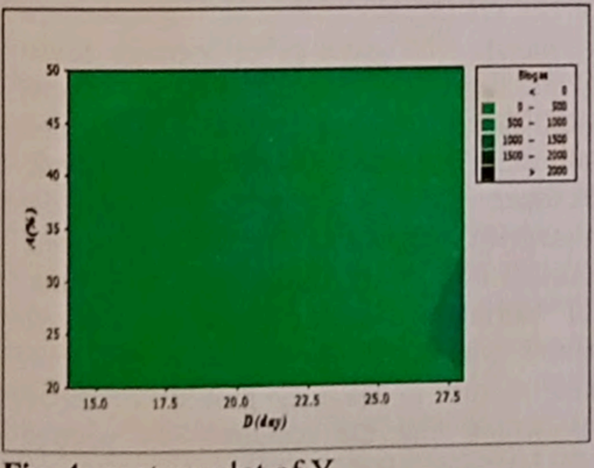

Fig. 4: contour plot of Y

Contour plot

Contour plot is a graphical representation of the relationships among the three numerical variables in two dimensions. Generally, there are two predictors and one response variable. Contour plots are useful for establishing desirable response values and operating conditions.

From Fig. 4, the 3D contour plot shows that the highest total biogas values (1500-2000mL) were found at a concentration of 25% and retention time of 28 days. The lowest total biogas value (0-500mL) was found at a concentration of 50% and a retention time of 14 days. This plot confirms the surface plot of Y in the Fig. 3 that biogas yield increases with additional increases in concentration (Hilkiah-Igoni, 2008). Further increases in concentration decreases biogas yield. This also shows that increases in retention time increases biogas yield (Eder and Schulz, 2006; Grady *et al.*, 1999).

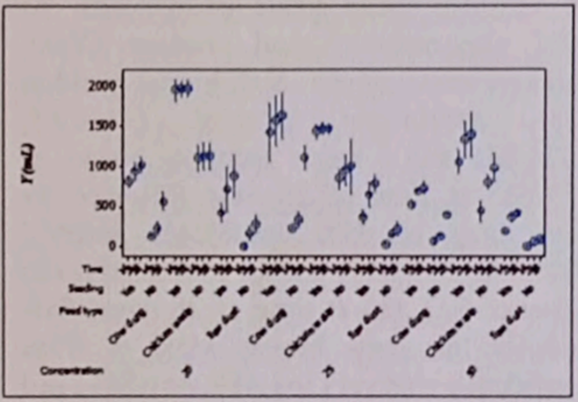

Fig. 5: Interval plot of Y (Biogas) (95% CI for the mean)

Interval plot

Interval plot is a graphical summary of the distribution of a sample that shows the sample's central tendency and variability. The mean value is represented by a circle and the interval is represented by a vertical line with horizontal lines at the upper and lower limits. Interval plots are used to display the sample mean along with a range of likely values for the population mean. Interval plots are especially useful for comparing groups (Montgomery, 2004).

From the Figure 5, the interval plot shows that at 20% concentration and seeding (yes), chicken waste shows the highest biogas yield with an estimated mean values of 1973.33 and 95% confidence interval (1861.32, 2085.35) at time of 21 and 28 days followed by cow dung at 95% confidence interval (918.709, 1117.96) having an estimated mean values of 1018.33. Saw dust shows the least biogas yield at 95% confidence interval (607.739, 1142.26) and mean estimate of 875. At 25% concentration and seeding(yes), cow dung shows higher biogas yield at 95% confidence interval (1345.57,1924.43) and mean estimate value of 1635 at time of 28 days followed by chicken waste at 95% confidence interval (1402.44, 1554.22) and an estimated mean value of 1478.33 at time of 21 and 28 days respectively. Saw dust is the least biogas yield at 95% confidence interval (677.697, 888.970) and an estimate mean value of 783.333. At 50% concentration and seeding (Yes), chicken waste shows high biogas yield at 95% confidence interval (1110.83, 1675.84) and mean estimate value of 1393.33 at time of 28 days followed by cow dung at 95% confidence interval (640.632, 806.034) and an estimated mean value of 723.333 at time of 28 days. Saw dust is the least biogas yield at 95% confidence interval (361.469, 461.864) and mean estimate value of 411.667.

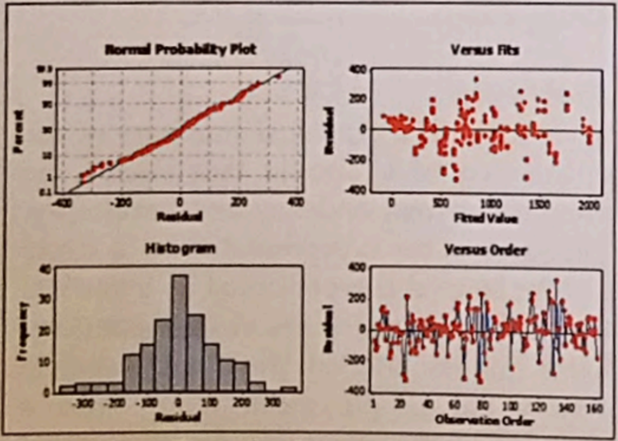

Fig. 6: Four-in-One Residual Plot Residuals

Residuals

Residuals are the difference between the observed values and predicted or fitted values. This part of the observation is not explained by the fitted model.

A residual plot is a graph that shows the residuals on the vertical axis and independent variable on the horizontal axis. If the points in a residual plot are randomly dispersed around the horizontal axis, a linear regression is appropriate for the data. Random patterns indicating a good fit for a linear model.

The normal probability plot is a graphical technique for assessing whether or not a data set is approximately normally distributed. The data are plotted against theoretical normal distribution in such a way that the points approximately on straight line. Departures from this straight line indicate departures from normality for the biogas yield data/ in Fig. 4. Residuals appear to roughly follow a straight line indicating it is normal. This shows no evidence of non normality, outliers, or unidentified variable exists. This result verified the null hypothesis that residuals are normally distributed on a straight line (Feigelson and Babu, 1992).

A histogram is a graphical representation of the distribution of numerical data. It is an estimate of the probability distribution of a continuous variable (quantitative variable). Histogram gives a rough sense of the density of the data. For the biogas yield data, the histogram has a bell shape indicating that the residuals are normal. Because of the appearance of the histogram can change depending on the number of intervals used to group the data, the normal probability plot is used to assess whether the residuals are normal. The normal probability plot in Figure 6 confirmed that the residuals are normal (Feigelson and Babu, 1992).

Residual versus fits plot is a scatter plot with residual on the y axis and fit on the x axis. It is used to verify the assumption or the null hypothesis that the residual have a constant variance. For the biogas data in Figure 6, the errors are randomly scattered about zero. This shows that the residuals are fitted and unbiased. There is evidence of constant variance and no missing terms, outlier or influential points exist. This finding agrees with the null hypothesis that residuals have a constant variance (Minitab User Guide 2, 2000).

Residuals versus order are a scatter plot with residual on the y axis and the order in which the data were collected on the x axis. It is used to verify the assumption that the residual are uncorrelated with each other. It is a way of detecting a particular form of non independence of the error terms, namely serial correlation. It helps to see if there is any correlation between the error terms that are near each other in the sequence. From the residual plot in Figure 6, the residuals appear to be randomly scattered about zero. No evidence exist that the error terms are correlated with one another. Each error is independent of all other errors (Feigelson and Babu, 1992).

Conclusion

The present study focuses on the modelling and optimization of the process parameters such as concentration, feed type, seeding and time for the maximal biogas production .Optimization of those factors was carried out by full factorial design methodology. The factor concentration, feed type, seeding and time had significant individual effects on biogas yield. The interactive effect for all of these factors were found to be significant ($p < 0.05$) except concentration and time which was insignificant ($p > 0.05$).The optimum conditions for maximizing the biogas yield were a substrate concentration of 20% and time of 28 days in which maximum biogas yield of 1811.23mL was obtained. The reduced model equations developed for biogas production with seeding is $Y = K - 11.5842A + 19.9868D$. Where $K = 930.877$ for cow dung, 1483.28 for chicken waste and 555.692 for sawdust. The maximum generation of biogas found experimentally using the optimized condition is 1973.33mL, which is in correlation with the predicted values 1811.23mL. It can be concluded that the factorial design analysis was a useful technique to optimize the biogas yield from the agricultural waste through anaerobic digestion.

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Kinetic Modeling of Rice Husk Components Pyrolysis Based on Independent Parallel Reactions

[1]Garba, M. U[1]., Charlse[1], S. G., Bilyaminu, I[1]., Alhassan, M[1]., Musa U[1]., Isah, A. G
[1]Chemical Engineering Department Federal University of Technology, P. M. B. 65, Minna, Niger State, Nigeria
Email: umar.garba@futminna.edu.ng

Abstract

This study presents the pyrolysis decomposition mechanism of rice husk in nitrogen atmosphere by thermogravimetric analysis (TGA). The thermal decomposition was carried out in three stages: moisture removal (180-200 °C), main devolatilization (200-400 °C) and continuous slight devolatilization (400 °C). The weight loss of rice husk was modeled based on the assumption that lignocellulose components (cellulose, hemicellulose and lignin) undergo pyrolysis independently in parallel first-order reactions. The kinetic parameters of the three lignocellulose components were determined by means of Microsoft Excel Solver tool using least square algorithm. The result of thermal degradation of rice husk samples shows that the model predictions of the cellulose, hemicellulose and lignin components agreed with the experiments. The activation energy and pre-exponential factors of cellulose, hemicellulose and lignin are187kJ/mol and $1.2\times10^{15}\text{min}^{-1}$, 29kJ/mol and $1.6\times10^{7}\text{min}^{-1}$and 90 kJ/mol and $1.8\times10^{1}\text{min}^{-1}$ respectively. The results suggest that thermal decomposition rate of cellulose was found to be higher, whereas that of lignin decomposition rate was lower. The thermal decomposition of hemicellulose decomposition was intermediate.

Keywords: Rice husk, pyrolysis, thermogravimetric analysis, lignocellulose, kinetic model.

Introduction

The depletion of fossil fuel reserves and its associate environmental problems are the major reasons for the shift and focus on sustainable energy resources. Biomass is extensively used as an alternative renewable energy source which is in abundance and in most cases considered to be a waste. It is the world fourth energy resource after oil, natural gas and coal (Vamvuka *et al.*, 2003). Lignocellulose materials are unlike carbonhydrate which belong to food that cannot be digested. The use of lignocellulose biomass as a source of chemical, transportation and energy fuels has been growing at a very rapid rate because lignocellulose biomass does not compete with the food supply chain (Basu, 2006).

Nigeria like many other African countries is blessed with abundant biomass because of its huge agricultural resources and this sector has been reported to provide employment to over 60% of the population. Agricultural activities generate huge waste providing a large potential source of lignocellulosic materials. Among the various lignocellulose species, rice husk has potential for chemical energy. Rice husk is used as a source of energy in rice mill, cooking, furnace and boiler (Garba *et al.*, 2006). In Nigeria, about 664,000tonnes of rice husk is derived from about 3.32 million tons of paddy rice per year (Rainer).

Conversion of lignocellulosic material to efficient fuel remains a burden due to their structural complexity which is responsible for the challenges in separating lignocellulose components.

Thermochemical conversion processes such pyrolysis, combustion, gasification and liquefaction are considered as the alternative means of converting lignocellulose biomass to efficient fuel. However, pyrolysis remains the focal point in all thermochemical conversion processes as in the case of combustion process in which the first step is pyrolysis followed by the reaction of pyrolysis residue with oxygen. The pyrolysis process is the thermal decomposition of biomass in the presence of inert atmosphere to form liquid (bio oil), char (charcoal) and gas. Lignocellulose biomass is composed of hemicellulose, cellulose and lignin (Garba *et al.,* 2012). Experimental results have shown that pyrolysis of organic matter is a complex process involving parallel and series reactions (Garba *et al.,* 2013). The decomposition of biomass has been described by three-component independent reaction, each corresponding to the decomposition of the hemicellulose, cellulose and lignin. The weight loss kinetic model developed for biomass is of two types. The single component overall model (SOM), which considered the biomass as being composed of a single component and uses its char–volatile reaction to describe the weight loss kinetics(Rogers et al., 1980; Cordero et al., 1989; Cordero et al., 1990). The second one is the multi-component overall model (MOM) considering biomass as being composed of hemicellulose, cellulose and lignin (Orfao *et al.,* 1999; Font *et al.,* 19991). In this case, the components are modeled separately and the biomass decomposition is the summation of all the three components. Generally, the weight loss kinetics change as the temperature increases and the weight loss is controlled mainly by cellulose, hemicellulose and lignin. Since the weight loss depends on cellulose, hemicellulose and lignin component, SOM cannot account for the possible change in weight loss kinetics. Contrary, MOM can reveal possible change in weight loss kinetics. Koufopanos *et al.* (1989) developed a modeling approach which described the overall rate of decomposition as a sum of the corresponding rates of the hemicellulose, cellulose and lignin using nonlinear regression method. In a related work, Rao *et al.* (1998) developed a kinetic model in which the pyrolysis of lignocellulose components is described by single reaction first order kinetics. In recent years MOM has been used successfully to describe the weight loss processes of bagasse (Liangfeng *et al.,* 2001;), jatropha residue (Rajeev *et al.,* 2016), switch grass (Vamvuka *et al.,* 2011) and wood pine and cotton stalk (Wang *et al.,* 2012).The result of almost all the previous studies have shown good agreement between experimental and calculated weight loss pattern.

The understanding of biomass pyrolysis is essential for accurate prediction of pyrolysis rates require for optimum design of pyrolyzer. In order to optimize process variable and obtain quality pyrolysis products, there is the need for more profound knowledge of pyrolysis kinetics. In the present work, the pyrolysis of rice husk components is analysed and pyrolysis process is described by independent parallel reactions of first order using nonlinear square methods. The design of equipment for the conversion of biomass through thermochemical processes requires knowledge of pyrolysis kinetic and modeling. Many literatures reported the kinetic investigation however; little knowledge is available on the modeling aspect. Thermogravimetric curves was used to analysis biomass decomposition, the pyrolysis kinetic model of rice husk based on three-component independent parallel first-order reactions was established by non-linear least squares algorithm. The kinetic parameters obtained for rice components were compared with each other and meaningful results achieved were discussed.

Methodology

Proximate and ultimate analysis

The rice husk used in this experiment was collected from Minna, Niger State. The experiments were divided into two steps; the first step was to study the pyrolysis characteristics of rice husk by using proximate, ultimate analysis and thermal decomposition. The second step was to study thepyrolysis kinetics of rice husk. The proximate analysis of the rice husk sample was carried out according to ASTMD 3172 method and ultimate analysis was done according to ASTMD 3176. The thermal degradation was carried out by with the aid of thermogravimetric analysis (TGA). The sample of a ground rice husk was obtained by grinding the rice husk to an average particle size of less than 150 µm. 20 mg of the rice husk sample was used in the experiment. The weight loss of the sample as a function of temperature was measured.

Kinetic modeling of rice husk pyrolysis

The approach by most of these kinetic models simulate the chemical reactions that take place during pyrolysis and the chemical reaction scheme is presented in equation (1).

$$\text{Biomass} \rightarrow \text{volatile} + \text{char} + \text{gas} \qquad (1)$$

The kinetic modeling was performed on the pyrolysis profile provided by TGA. The total mass measured by TGA were assumed to be summation of thepyrolyzable materials such as cellulose, hemicelluloses, lignin, charcoal, and ash (Liangfeng et al., 2011).

$$m = m_p + m_c + m_a$$

where m is the total mass of biomass by TGA, m_p is the mass of pyrolyzable (cellulose, hemicelluloses, lignin components) organic materials, m_c is the mass of produced char, and m_a is the ash mass.

Assuming the ash is ignored, the mass of biomass is a sum of the pyrolyzable organic chemical and the produced charcoal (Liangfeng et al., 2011):

$$m_i = m_{ip} + m_{ic} \text{ for i=1,2,3} \qquad (2)$$

the pyrolyzable organic chemicals are mainly cellulose, hemicelluloses, lignin components.

During the pyrolysis process, the degree of conversion and conversion rate for each component in biomass sample are defined as follows:

$$\alpha_i = \frac{m_{io} - m_{ip}}{m_{ip}} \text{ for i=1,2,3} \qquad (3)$$

Where m_{io} is the intial weight of biomass and α_i is the conversion of each lignocellulose components.

For the three lignocellulose components, the overall conversion rate for each reactioncan be expressed as

$$\frac{dm}{dt} = \sum_1^3 c_i \frac{d\alpha}{dt} \qquad (4)$$

Where c_1, c_2 and c_3 are the partial contributions of the overall weight loss: c_i is defined as

$$c_i = m_{io} - m_{ichar} \qquad (5)$$

The lignicellulose components are presumed to decompose by obeying first-order reaction according to

$$\frac{d\alpha_i}{dt} = k_{i0}.e^{-E_i/RT}(1-\alpha_i) \qquad (6)$$

where E_i, k_{io}, $T$and $R$are the activation energy (kJ/mol), frequency factor (min^{-1}), temperature (K) and respectively.

The nonlinear least square algorithm has been used to identify the kinetic parameters that show the lowest values of the objective function (O.F):

$$O.F = \sum[(\frac{dm}{dt})^{exp} - (\frac{dm}{dt})^{sim.}]^2 \qquad (7)$$

$(dm/dt)^{exp}$ is the experiment DTG curverate of rice husk and $(dm/dt)^{sim.}$ is the simulated DTG curve rate of rice husk.

Kinetic constants from modeling

Equation4 shows the thermal decomposition rates of the rice husk components during the heating process was a function of temperature and degree of conversion. Equation (5) is a nonlinear ordinary first-order differential equation. The degree of conversion is the dependent variable and absolute temperature is the independent variable. Two kinetic constants for each component, pre-exponential factor k_{io} and activation energy E_i, are assumed to be independent of the degree of conversion. The numerical solution could be obtained by solving Equation (6) for the known values of k_{io} and E_i respectively. These constants are determined from the least-square method implemented by the Microsoft Excel Solver tool where the difference between experimental and calculated weight loss were minimized.

Results and Discussion

Characterization of fuel

The proximate and ultimate analysis results are presented in Table 1. The result show that the rice husk was characterized by high volatiles content of about 66% which makes them desirable for a good regulation of gasification processes. The high percentage of ash in rice husk indicates potential slag or foul formation during combustion. However, the content of sulfur is very low, which means that there will be fewer emissions or corrosion whenutilization for power generation (Koufopanos *et al.*, 1989; Rao *et al.*, 1998).

Table 1. Ultimate and proximate analysis of rice husk

Proximate analysis (wt.%)		Ultimate analysis				
Moisture	3.81	C	H	O	N	S
Volatile matter (VM)	66	43.83	6.76	46.07	0.93	0.94
Fixed carbon (FC^{a})	22.01					
Ash	8 .18					

Thermal decomposition characteristic

The thermogram and derivative thermogram (TG/DTG) curves in Fig. 1were obtained for the pyrolysis of the rice husk at a heating rate of 10 °C/min. The TG/DTG curves represent the weight loss of the tested biomass with respect to temperature. The curves are generally divided into three different stages regardless of what biomass sample is tested. The first stage is drying and release of some light volatiles resulting into slight weight loss at temperature below 200 °C as shown in the TG curve. The second stage is the thermal decomposition of hemicellulose, cellulose and lignin where a significant weight loss was observed at a temperature between 200 and 400 °C.In the third stage, the weight loss occurs slowly over wide range of temperature higher than 500 °C mainly due to thermal decomposition of heavy components. In the previous studies (Liangfeng *et al.*, 2011; Vamvuka *et al.*, 20011; Wang *et al.*, 2012), DTG has been reported to qualitatively identifies the components of lignocellulose structures. Generally, hemicellulose decomposition occurs at temperatures between 150 and 350 °C; cellulose decomposition occurs at the temperatures range of 275-350 °C, and lignin is decomposed slowly over a wider temperature range of 250-500 °C (Vamvuka *et al.*, 20011; Wang et al., 2012). The distribution of lignocellulose components in the DTG curve of rice husk is presented in Fig. 1.The DTG curve of rice husk exhibited only one peak. The main peak at temperature of 316 °C stems from cellulose decomposition and its shoulder peak in the DTG curve (which is almost merged to cellulose)is due to hemicellulose decomposition. The curve after the main peak (cellulose) is the decomposition of lignin whose intensity is smaller than that of the hemicellulose and cellulose peaks. It is important to note that one small peaks induced between the temperatures of 800°C and 850°C are due to the fact that rice husk includes another important component which is reactive at a higher temperature .In addition, from DTG curve in Fig. 1 it can be observed that two bumps developed at the temperature between 70 °C and 150°Cas a results of moisture removed from the rice husk.

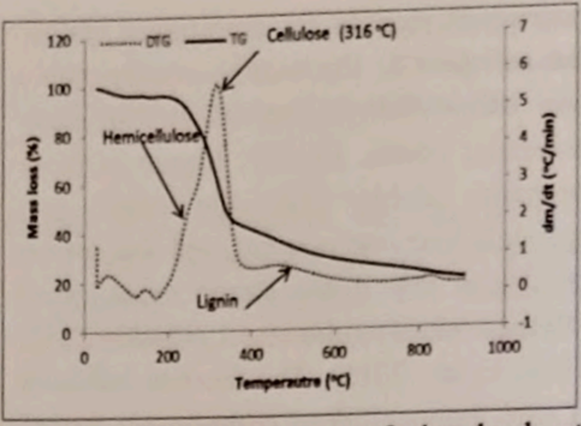

Fig. 1: TG/DTG curves of rice husk at heating rate of 10 °C /min showing the three lignocellulose components.

Kinetics analysis

Figure 2 and 3 shows TG and DTG curve of the modeling for the rice husk. Figure 2 shows that the model simulation gives good prediction compared to the experimental data for the TG curve of rice husk sample. The model simulation of the DTG curve (Fig. 3) also shows good prediction compared to the experimental data. Fig. 4 shows the individual contribution of each lignocellulose to the total decomposition rate. With regard to each lignocellulose biomass component, hemicellulose proved to be least stable lignocellulose component and it decomposes first and fast at low temperature. Lignin is more stable lignocellulose component and decomposition takes place over wider temperature range. Finally, the cellulose decomposition started last and that is the reason why kinetic value has high values (Table 2). Among the lignocellulose component, cellulose shows the maximum total decomposition. Generally, the differences between the thermal behaviours of the lignocellulose components are attributed to their different in the intrinsic chemical structures. Hemicellulose is least thermally stable component due to its amorphous nature and cellulose is the next thermally stable than hemicellulose due its strong intra-molecular bonds. Finally, Lignin is more thermally stable than the other two lignocellulose components and the reason for this is that it has strong cross-linked polymer (Pasangulapati *et al.*, 2012; Xiong *et al.*, 2015). The thermal behavior of each lignocellulose components agreed with other works in the literature (Jeguirim *et al.*, 2001; Vamvuka *et al.*, 2003).

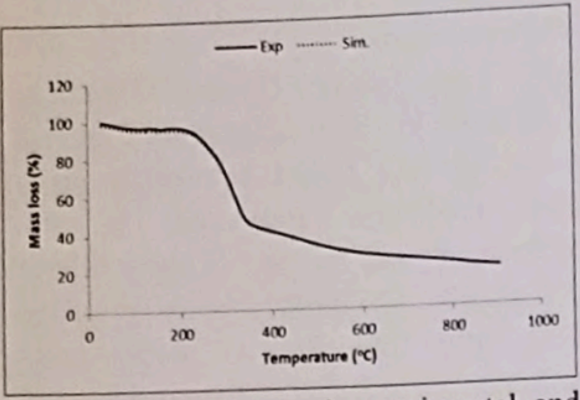

Fig. 2. Comparison of experimental and simulated TG pyrolysis profile of rice husk.

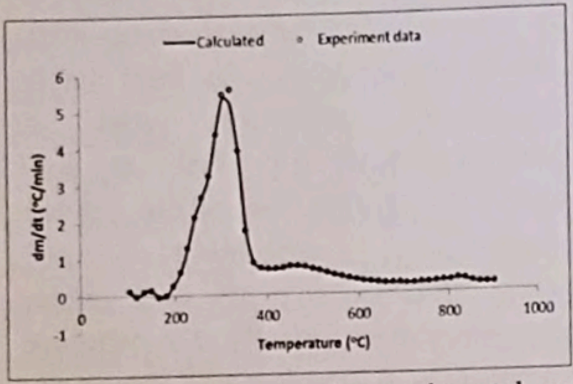

Fig. 3. Comparison of experimental and simulated DTG pyrolysis profile of rice husk.

Kinetic parameters are illustrated in Table 2. In the cellulose decomposition, kinetic constants appeared to have higher values than hemicellulose and lignin. Activation energy is the minimum energy required for each decomposition starts. Subsequently, the higher its value is, the higher is the temperature for the initiation of each decomposition. Cellulose requires more energy compared to the other lignocellulose components because of its strong intra-molecular bonds, which prevent its decomposition in lower temperatures (Xiong *et al.*, 2015). Pre-exponential factor is another important kinetic constant indicates indicate molecular collisions that lead to chemical reaction. A higher value of the pre-exponential factor, the more the molecular collisions that can lead to decomposition.

Lignin shows lowest values of activation energy and pre-exponential factor in Table 2. This fact could be observed from the DTG curves (Fig. 4), where the decomposition is seen to have started at lower temperatures and its decomposition rate was lower, compared to that of the other decomposition reactions. In term of thermal stability, lignin is the most stable component, therefore it is not easily decomposed. The observation made herein have been confirmed by previous studies (Xiong *et al.*, 2015; Jeguirim *et al.*, 2009).

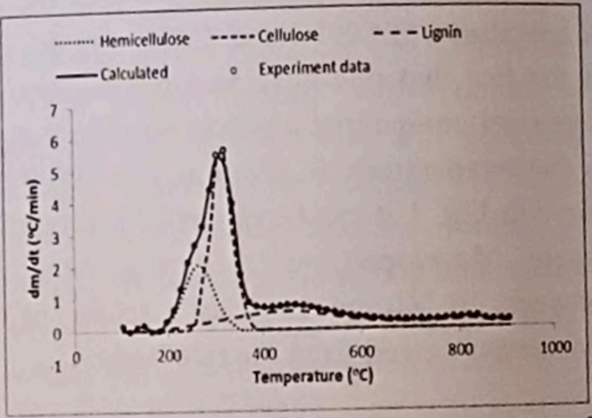

Fig. 4. Comparison of experimental and simulated pyrolysis profile of rice husk and rice husk components.

The calculated pyrolysis kinetic parameters of rice huskare presented in Tables 2. The activation energy of cellulose decomposition is higher (187kJ/mol), whereas that of lignin decomposition lower (29kJ/mol). The activation energy of hemicellulose decomposition is intermediate (90 kJ/mol). The pre-exponential factors of cellulose, hemicellulose and lignin are in the ranges of 1.2×10^{15}, 1.6×10^{7}, $1.8 \times10^{1}\text{min}^{-1}$, respectively.

Table 2. Content of lignocellulose and the kinetic parameters of the pyrolysis process.

Component	Kinetic parameters		
	C(%)	A(min)	E (kJ/mol)
Hemicellulose	26.9	1.6×10^{7}	90
Cellulose	48.9	1.2×10^{15}	187
Lignin	24.2	1.8×10^{1}	29

Conclusions

In this study, the thermal decomposition and pyrolysis kinetics were studied. The thermal decomposition shows that rice husk was divided into moisture removal, main devolatilization and continuous slight devolatilization stages. The mass loss process of rice husk was modeled by assuming cellulose, hemicellulose and lignin undergo pyrolysis independently and in parallel first-order reactions. The kinetic parameters of the three components were determined by means of Microsoft Excel Solver tool using least square algorithm. The simulation rate of thermal decomposition is very close to the experimental data.

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