Effects of Process Parameters on Clay-Catalyzed Rice Husk Hydrolysis

ABSTRACT

Cellulose is a basic ingredient found in rice husk that is used to make second-generation bioethanol. Clay treated with HCl, NaOH, and thermal treatment was used to catalyze the conversion of cellulose from rice husks into reducing sugars. With the use of a clay catalyst, this study attempts to make bioethanol from rice husk. To ascertain the composition of rice husk, proximate analysis and elemental analysis were used to characterize it. The statistical optimization of process conditions was carried out with design expert software using Response Surface Methodology (RSM) based on Central Composite Rotatable Design (CCRD). Proximate analysis result of Eha-Amufu rice husk gave 62.77% as volatile matter content with oxygen content of 63.01% as elemental composition was analyzed. The maximum glucose yield of 22.18%, 20.58%, and 20.02% was realized when hydrolysis of rice husk was carried out with NaOH, thermal, and HCl treated clay, respectively, whereas 3.17%, 3.61%, and 2.92% was realized as the least yield of sugar respectively with varying parameters of NaOH, thermal, and HCl treated clay. The numerical optimization with CCRD to maximize sugar yield gave 19.32% at 53.73 mins for alkaline treated clay and 16.76% at 46.48 mins for acid treated clay. Based on the findings of this research, alkaline treatment of clay for the hydrolysis of rice husk has demonstrated to produce the maximum glucose production when compared to acid and thermal treatment of clay.

INTRODUCTION

The depletion of fossil energy and ecological environments deterioration has posed a challenge that there is need to develop economical, energy-efficient and environmental friendly processes towards achieving sustainable production of fuels and chemicals (Lozano and Lozano, 2018). According to Perlack and Stokes (2011), biomass-based chemicals from lignocellulosic biomass were obvious choice in replacing petroleum feedstock, because they are the most abundant and potentially low-cost commodities from variety of sources including agricultural and forest residues as well as high yield bio-energy crops. Lignocellulosic biomass is any organic matter that is available in a renewable basis which includes energy crops, agricultural residues, aquatic plants, wood and wood residues as well as other waste materials (Maity 2015).

Basically, hydrolysis process could be achieved with two types: acid hydrolysis and enzymatic hydrolysis. In dilute acid hydrolysis as a type of acid hydrolysis, the hemicellulose fraction is depolymerized at lower temperature than the cellulosic fraction (Chandel *et al.*, 2007). The biggest advantage of dilute acid processes is their fast rate of reaction which facilitates continuous processing, whereas the disadvantage is their low sugar yield (Badger, 2002). The primary challenge for dilute acid hydrolysis processes is how to raise glucose yields higher than 70% in an economically viable industrial process while maintaining a high cellulose hydrolysis rate and minimizing glucose decomposition. In concentrated acid hydrolysis, the biomass is impregnated with 70% H_2SO_4 and hydrolyzed by adding water to achieve better yield of fermentable sugars (van Groenestijn, Hazewinkel and Bakker, 2006). According to Chandel *et al*. (2007), heterogeneous catalysts obtained via acid, alkaline, and thermal changes were utilized instead of homogeneous catalysts such as dilute sulfuric acid for rice husk hydrolysis.

Enzymatic hydrolysis is attractive because it produces better yields than acid-catalyzed hydrolysis and enzyme manufacturers have recently reduced costs substantially using modern biotechnology. Enzymes are protein plants that cause or catalyze certain chemical reactions (Badger, 2002). Enzymatic hydrolysis of cellulose is carried out by cellulose enzymes which are highly specific. Reducing sugars, including glucose are the products of this hydrolysis. Its utility costs are lower than acid hydrolysis because it is conducted in mild conditions and does not have a corrosion problem (Duff & Murray, 1996). Enzymatic hydrolysis is impacted by the energy-intensive mixing process. Due to the inefficient mixing, there may be issues with mass and/or heat transfer as well as an uneven distribution of the enzymes, all of which may result in a probable reduction in yield (Kadic and Heindel, 2014).

Clay is a naturally occurring alumino-silicate material formed by weathering of rocks over a long time in the presence of dilute carbonic and other inorganic acids. The major components of clay are alumina and silica tetrahedrons (Al_2O_3 and SiO_2). Clay has found applications in many industrial processes such as catalysis, adsorption and as support materials. The use of clay in heterogeneous catalysis as solid acid catalyst is almost as old as the catalysis concept itself (Arandes *et al*., 2007). Clay catalysts are less expensive, reusable, non-corrosive and have no disposable problems (Prajitha and Pushpaletha, 2017) and thus, the ideal option for rice husk hydrolysis.

Response Surface Methodology (RSM), a collection of statistical and mathematical methods is useful for modeling and analyzing engineering process such as hydrolysis process (Teofilo and Ferreira, 2006). In using this technique, the main objective is to optimize the response surface that is influenced by various process parameters such as time, catalyst and substrate dosage, and catalyst treatment type on hydrolysis of rice husk.
The present study is a ladder towards deriving techniques for utilizing locally available, easily accessible, and cheap raw materials (clays), as well as their application in hydrolyzing rice husks to fermentable simple sugars. Understanding the latter is therefore consistent with the anticipated study outcome of creating a locally available heterogeneous catalyst with potentials for manufacturing bioethanol from lignocelluloses (rice husk).

1. MATERIALS AND METHODS

2.1 Collection of samples and pretreatment

Rice husk sample was collected from Eha-Amufu rice mill, Enugu state Nigeria in a polythene bag. The sample was further dried in an oven at 50^0C for 24 hrs to a 90% dry matter content. The air dried rice husk was placed in tightly sealed plastic bag at room temperature under dry condition ready for analysis. The rice husks were further treated using milling machine and standard sieve plates to obtain a particle size of 60 mesh and then stored in a container at room temperature.

2.2 Characterization of rice husk

2.2.1 Proximate analysis of rice husk

According to ASTM (2003), proximate analysis divides the products into four categories: moisture, volatile matter which consists of gases and vapors pushed off during pyrolysis, fixed carbon that are non-volatile portion of biomass, and ash, the inorganic residue left over after combustion.

2.2.1.1 *Moisture content*

1g of Sample was measured and placed in a petri-dish that had been previously washed, dried and weighed. It was placed in a drying oven at 105°C for 1hr. The petri-dish was left open during the heating process. After heating, the petri-dish was cooled in a desiccator and then weighed. The amount of moisture content present in the sample was determined as:

$$moisture\ content, \% = \frac{(W_1 - W_2)}{W} \times 100 \qquad (1)$$

Where: W_1 = weight (g) of sample and crucible before drying, W_2 = weight (g) of sample and crucible after drying. W = weight (g) of sample

2.2.1.2 *Ash content*

Empty crucible was washed, dried and ignited in a muffle furnace at 600^0C. This was cooled in a dessicator and weighed. 2g of the test specimen was placed in the crucible. The weight of the crucible plus the specimen was determined and placed in an oven at 105^0C for 1hr uncovered. The cover was replaced and cooled in a desiccator and weighed. The cooled specimen was placed in the muffle furnace uncovered and ignited at 600^0C until all the carbon was eliminated. After ignition, it was later placed in a dessicator, cooled and weighed. The heating process was repeated at 30min interval until a constant weight was achieved (ASTM, 2003). The ash content was determined as:

$$ash\ content, \% = \frac{W_2}{W_1} \times 100 \quad (2)$$

Where: W_1 = weight of sample before heating (g), W_2 = weight of ash (g).

2.2.1.3 *Volatile matter content*

The sample was measured and placed in a closed crucible. It was heated up to 900℃ for 7 minutes in a furnace. The crucible was cooled in a desiccator and weighed. The percentage of volatile matter was calculated from the loss in mass of the sample as:

$$volatile\ matter\ content, \% = \frac{(W_1 - W_2)}{W_1} \times 100 \quad (3)$$

Where W_1= weight of sample before heating, W_2= Weight of sample after heating.

2.2.1.3 *Fixed carbon content*

The fixed carbon content was determined by subtracting the sum of percentage compositions of moisture content, volatile matter content, and ash content from 100%.

$$fixed\ carbon, \% = 100 - (moisture,\% + ash,\% + volatile\ matter,\%) \quad (4)$$

Again, other analysis includes the determination of pH, electrical conductivity, bulk density, and particle density.

2.2.2 Elemental analysis of rice husk

The elemental analysis of rice husk was conducted using Elemental analyzer. For every component, five calibration points were calibrated. Samples were run in duplicate and the average values were taken. Nitrogen Content, Percentage of Carbon content, Phosphorus content, and Potassium content were determined in the course of this study.

2.3 Clay Catalyst Preparations

The clay sample was obtained from Ceramics Department of Project Development Institute (PRODA) Enugu State. It was initially sun-dried before being oven-dried overnight at 40^0C. With the help of a scanning electron microscope and energy dispersive X-ray diffraction (SEM/EDX), the chemical composition of each of the three activated clay samples listed below was analyzed. The raw kaolinite clay sample, on the other hand, underwent a mineralogical investigation utilizing X-ray Diffraction (XRD) to identify the mineral phases that were present in it.

2.3.1 Acid activation of clay

10wt% concentration of hydrochloric acid (HCl) was prepared by adding 90ml of deoinized water to approximately 10g of 98% concentrated HCl. The clay sample was activated using this amount of acid. In line with Prajitha and Pushpaletha (2017), which refluxed kaolinite clay samples with sulphuric acid at several concentrations (0.5, 1, 2, 3, 4 and 5N) for 45 minutes at a solid to liquid ratio of 1:4. In this study, a round bottom flask with a condenser and magnetic stirring bar was used to combine 10g of the clay sample with HCl solution. The activation was accomplished by heating the mixture in a magnetic stirrer at 94^0C for varying lengths of time. The time-variant activated samples were centrifuged for 10 minutes at 3000 rpm to filter off the precipitate, which was then cleaned with deionized water. Separation's top, mostly acidic layer was totally washed away. Centrifugation was used three times in succession after each washing. The final samples were put in a petri dish and dried for a while in an oven at 105^0C. A cooling period was given before the analysis.

2.3.2 Alkaline activation of clay

Sodium Hydroxide (NaOH) solution of 10wt% concentration was prepared by adding 10g of NaOH to 90ml of deionised water. This alkaline concentration was used to activate the clay sample. 10g of the clay sample was mixed with NaOH solution in a round bottom flask with condenser and magnetic stirring bar. Alkaline activation was carried out by heating the mixture in a temperature controlled magnetic stirrer at 94^0C for different time intervals (1, 2, 3, and 4hrs). The temperature of the magnetic stirrer should be set at 95^0C, according to Vilcocq *et al*. (2015) recommendation. The time-variant activated samples were centrifuged at 3000 rpm for 10 minutes to filter them, and the precipitate was then cleaned with deionized water. The top, mostly alkaline layer of separation was fully washed off. Three centrifugations were done after each round of washing. The final samples were put in a petri-dish and dried in a 105°C oven for a while. Before the analysis, it was allowed to cool.

2.3.3 Thermal activation of clay

The clay samples were thermally treated in a muffle furnace for four hours at three distinct temperatures: 400^0C, 600^0C, and 900^0C. The surface area of clay particles is increased by heat activation, which is comparable to an appropriate standard of acid activation, and thus increases the catalytic activity of clays (Igbokwe *et al.*, 2011). The muffle furnace's calcined clay samples were taken out and allowed to cool before being stored and prepared for usage.

2.4 Experimental Procedure

Hydrolysis of rice husk

The experiment was performed with 30 mL flask in an oven by mixing rice husk, modified clay catalyst and deionised water at a temperature of ($185\text{-}225^0$C) for 30-90 minutes.

A sample of rice husk, activated clay catalyst, and deionized water was weighed out, placed in a 100 ml flask, sealed, and placed inside an electric oven. To determine its varied effects on the hydrolysis of rice husk, hydrolysis reactions were conducted while taking into account a variety of process parameters, including times, catalyst treatment types, substrate dosages, and catalyst dosages.

Glucose was quantitatively analyzed by 3, 5-dinitrosalicyclic acid (DNS) method and used as standard in this experiment (Marsden, Gray, Quinlan, 1982). The absorbance of each sample in the test-tube was read at 540 nm in an ultraviolet spectrophotometer against the blank sample. The concentration of each substrate was calculated from the standard curve of the known sugar.

2. RESULTS AND DISCUSSION

3.1 Proximate Characterization of Rice Husk

The proximate study of rice husk biomass yielded the results depicted in figure 1: 3.117% moisture, 62.772% volatile matter, 17.78% ash, and 16.329% fixed carbon content. The approach used by Onyelucheya *et al.,* (2017) to get the cellulose content on rice husk resulted in 31.3% cellulose content. Other results from the proximate study included bulk density, particle density, pH, conductivity, and porosity, with values of 0.6937g/ml, 0.5166g/ml, 6.28, 260uscm/cm, and 0.255, respectively.

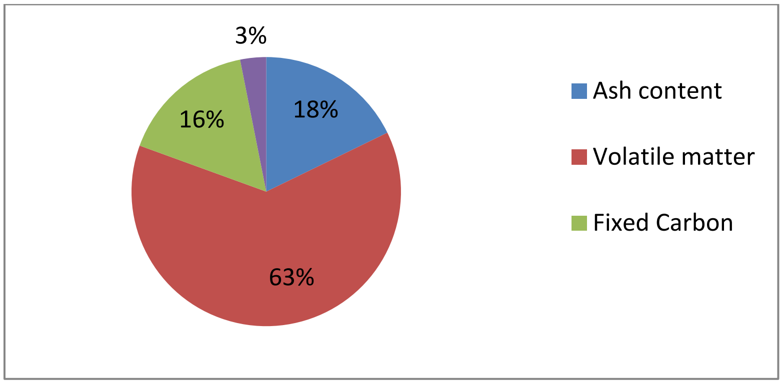


Figure 1: Proximate analysis of rice husk

The elemental composition of rice husk was shown in table 1, with oxygen being the most abundant element and nitrogen being the least.

Table 1: Elemental composition of rice husk before hydrolysis

Components	Composition (%)
Carbon	6.56
Nitrogen	3.85
Oxygen	63.01
Hydrogen	19.24
Sulphur	7.34

3.2 Effect of Process Parameters on Hydrolysis of Rice Husk

3.2.1 Effects of catalyst dosage with clay activated for 1 hour.

Figure 2 depicts the glucose yield from rice husk after a 60-minute hydrolysis reaction time utilizing an hour-long clay activation with 0.1M HCl and 0.1M NaOH. The findings showed that the glucose production increased with increasing catalyst dosages when alkaline catalyzed clays were used. Even though acid-catalyzed clays was employed, their impact on the hydrolysis process was minimal compared to that of alkaline-catalyzed clays. In comparison to other catalyst dosages at the same substrate concentration utilizing both catalyzed clays, the hydrolysis with 0.04g/30ml catalyst dosage and at a temperature of 200^{0}C produced the best glucose yield. The sample of activated clay that contained 0.1M NaOH had the greatest glucose yield value (22.18%). It was found that as catalyst dosages are raised for both acidic and alkaline solutions, above 0.04g/30ml, glucose production begins to decline (Lidstrom *et al*., 2001). Alkaline catalyzed clay's early boost in glucose yield indicates the catalyst's beneficial influence on glucose yield.

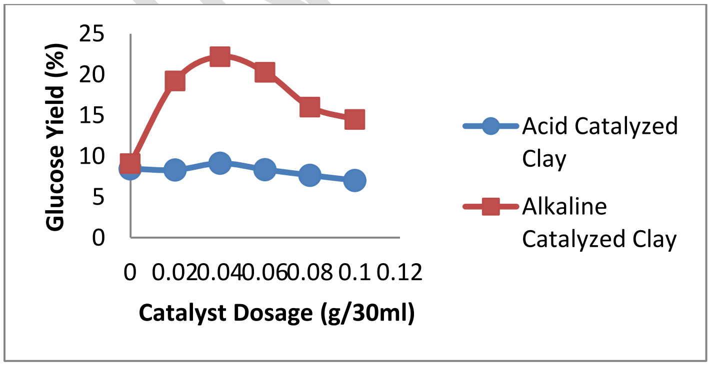


Figure 2: Effect of catalyst dosage on hydrolysis using 1 hr HCl and NaOH activated clays for 60 minutes hydrolysis reaction time.

3.2.2 Effects of catalyst dosage with clay activated for 2 hours.

The glucose yield obtained from rice husk for 60 minutes hydrolysis reaction time using 2 hour clay activated with 0.1M HCl and 0.1M NaOH as shown in figure 3. The hydrolysis with 0.06g/30ml catalyst dosage and at temperature of 200^0C gave the highest glucose yield than other catalyst dosages at same substrate concentration using both catalyzed clays. The maximum glucose yield, 20.32%, was found with a 0.1M NaOH activated clay sample, which was nearly identical to the 20.01% glucose yield from clay that was acid-catalyzed.

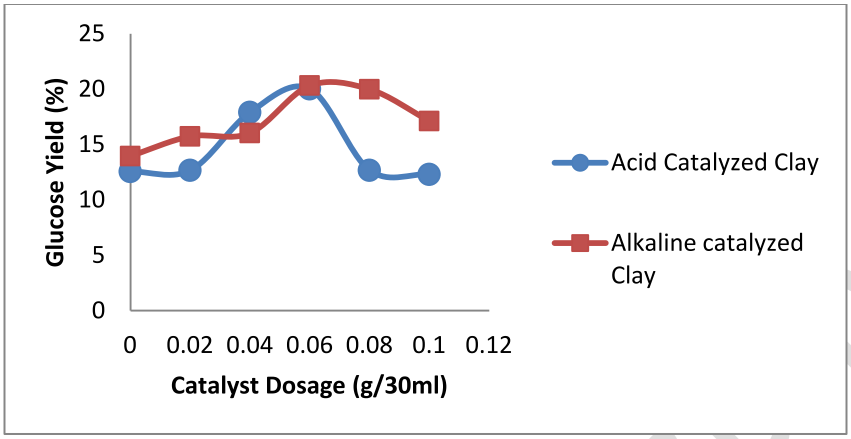


Figure 3: Effect of catalyst dosage on hydrolysis using 2 hr HCl and NaOH activated clays for 60 minutes hydrolysis reaction time

It was found that once catalyst dosages are increased past 0.06g/30ml, glucose yield begins to decrease. According to Dong *et al*. (2020), clays activated with higher acid concentrations produce a higher percentage of simple sugars.

3.2.3 Effect of catalyst dosage with thermally activated clay.

Figure 4 shows the glucose yield from rice husk after 60 minutes of hydrolysis reaction time using thermally catalyzed clays at 400^0C, 600^0C, and 900^0C. In comparison to other catalyst doses at the same substrate dosage, the hydrolysis with 0.06g/30ml catalyst dosage at 200^0C produced the maximum glucose yield. According to Prajitha and Pushpaletha (2017) and Wiyantoko *et al*. (2021), 600^0C thermal activated clay produced the highest glucose yield of 20.58%. For three ranges of catalyzed clays, it was shown that yield decreased with increasing catalyst doses above the catalyst dosage of 0.06g/30ml (Lidstrom *et al*., 2001). At 0.0g/30ml, 0.02g/30ml, and 0.04g/30ml, the glucose production from hydrolysis using 400^0C thermal clay was nearly identical, demonstrating that the catalysts could not function at their best at those reaction conditions without an increase in dosage.

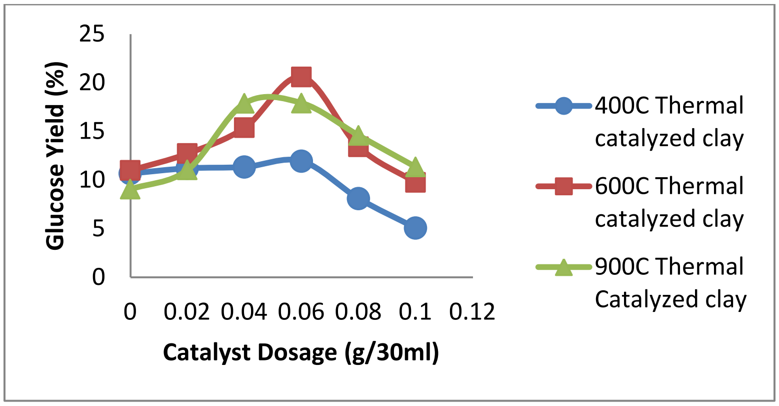


Figure 4: Effect of catalyst dosage on hydrolysis using thermally activated clay at 400^0C, 600^0C, and 900^0C for 60 minutes hydrolysis reaction time

3.2.4. Effect of hydrolysis time with clay activated for 1 hour.

There was an increasing rise in glucose yield when hydrolysis reaction time with NaOH activated clay catalyst was used. Fig 5 gives the range of hydrolysis times with respective glucose yield when NaOH and HCl activated clay catalysts were used. There was steady decline in glucose yield from 30 to 90 minutes hydrolysis time after the quite noticeable increase in glucose yield at 30 minutes when HCl activated clay was used for the hydrolysis of rice husk. At hydrolysis time of 60 minutes and beyond, the glucose production from hydrolysis using both clays demonstrated that the catalysts could not function at their best at those reaction conditions due to degradation of products.

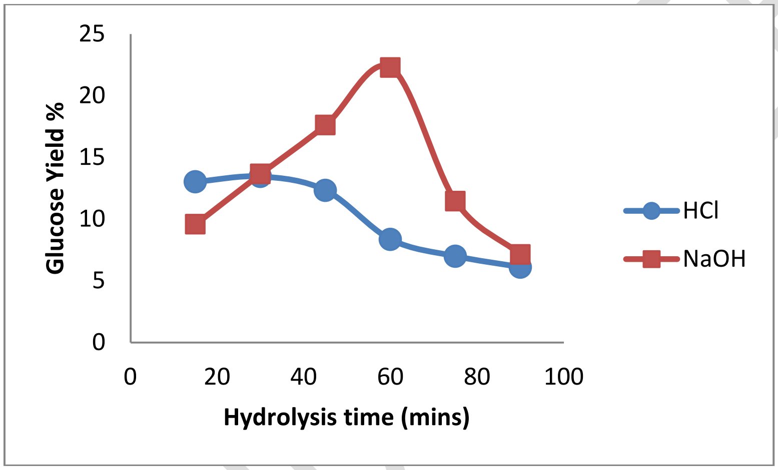


Figure 5: Effect of hydrolysis time on yield of glucose using 1hr HCl and NaOH pretreated clay catalysts

3.2.5 Effect of hydrolysis time with clay activated for 2 hours.

Figure 6 demonstrated the effect of hydrolysis times on glucose yield. Increasing the pretreatment time of clay using HCl and NaOH from one hour pretreatment time in figure 5 to two hours in figure 6 had shown a positive effect of both catalysts between 15 – 60 minutes hydrolysis time. When both clay catalysts were utilised for rice husk hydrolysis, any additional increase in hydrolysis time over 60 minutes resulted in a poor yield of fermentable sugars.

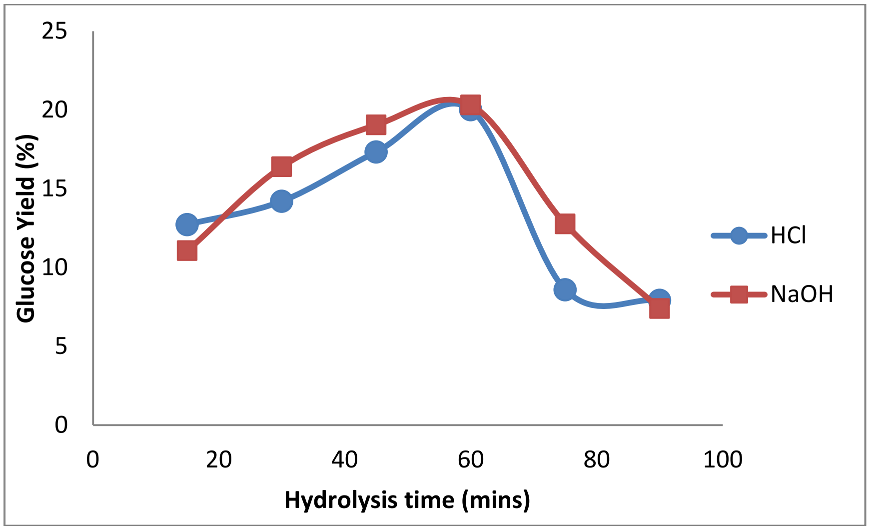


Figure 6: Effect of hydrolysis time on yield of glucose using 2hr HCl and NaOH pretreated clay catalysts

3.2.6. Effect of acid activation time.

Figure 7 illustrates the range of acid activation durations for the five types of clay catalysts: 0, 1, 2, 3, and 4 hours. When the acid activation timeframes for the clay catalyst were taken into account, it was found that the clay catalyst's 2 hour activation time produced the best glucose production during the hydrolysis reaction of 60 minutes when the catalyst dosage was 0.06g/30ml. According to Yang and Wyman (2007), optimizing the acid pretreatment process can increase the hydrolysis of hemicelluloses. Additionally, the lowest glucose yield was produced by clay catalyst types that had not received pretreatment, as seen in Figure 7. The hydrolysis reaction periods for type 0 catalyst were extended from 30 to 90 minutes, however the glucose yield steadily decreased.

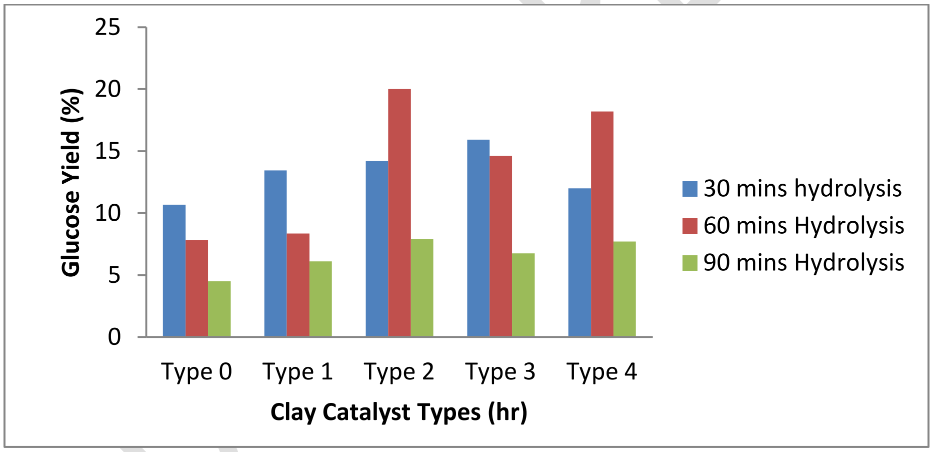


Figure 7: Effect of acid activation times on hydrolysis using 0.06g/30ml catalyst dosage each.

3.2.7. Effect of alkaline activation time.

Different alkaline activation durations were represented by the clay catalyst types in Figure 8. A clay catalyst with a 1-hour activation time produced the maximum glucose production during a 60-minute hydrolysis reaction time when used with a 0.04g/30ml catalyst dosage. According to Wiyantoko *et al*., (2021) and

McMillan (1997), alkaline pretreatment to remove lignin can improve the hydrolysis of hemicelluloses without having a significant impact on other components. Additionally, unpretreated clay catalyst types produced the least amount of glucose, which supports the impact of clay pretreatment on rice husk hydrolysis. There was an improvement in glucose yield even though the hydrolysis reaction time for type 0 catalyst was extended from 30 to 60 minutes. A decrease in glucose yield was caused by further lengthening the hydrolysis reaction time using the same catalyst.

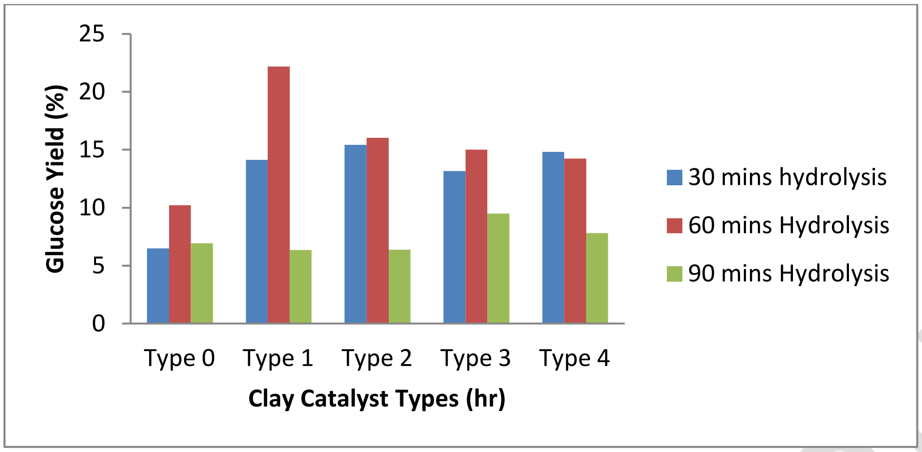


Figure 8: Effect of alkaline activation times on hydrolysis using 0.04g/30ml catalyst dosage each

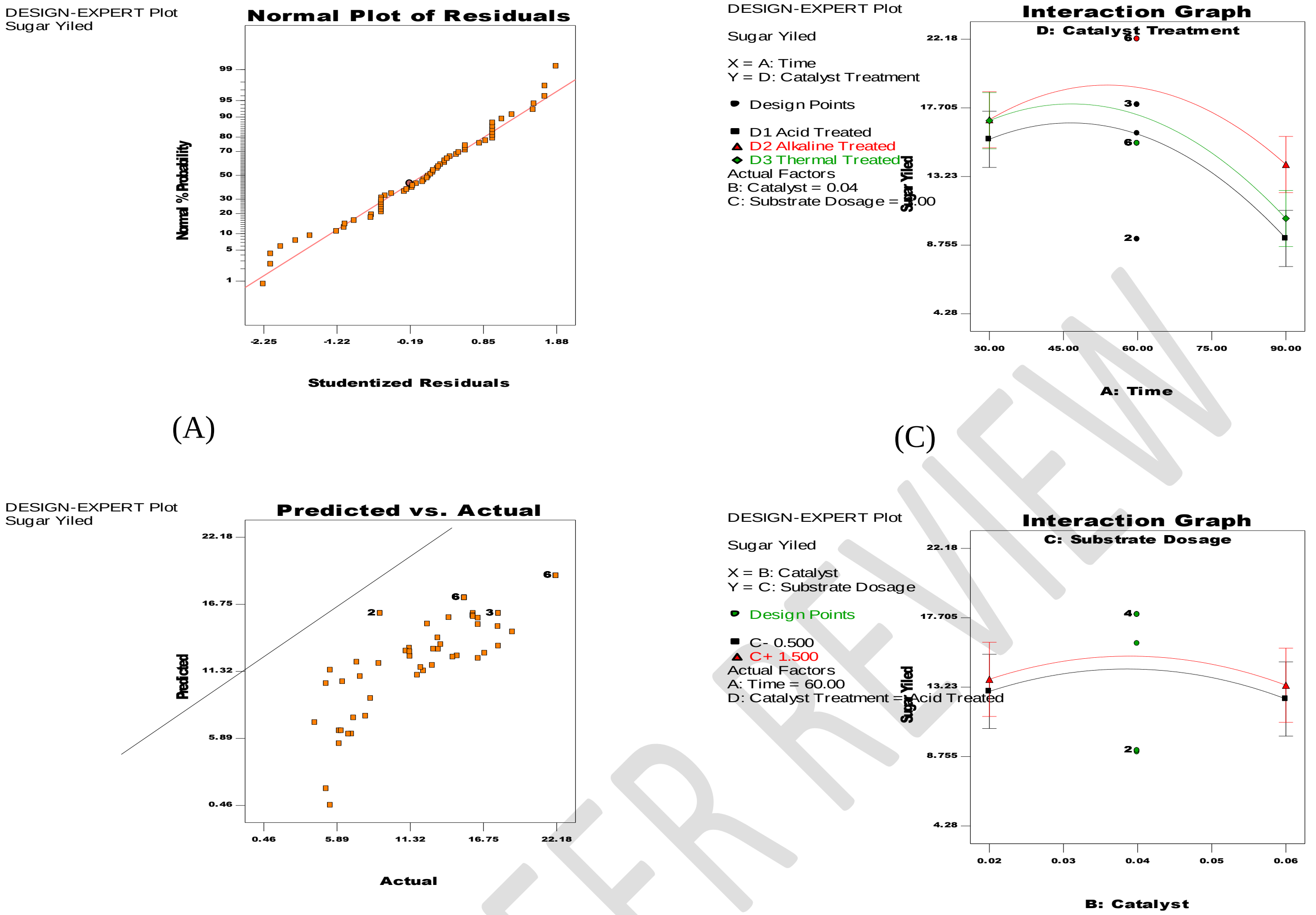
3.3 Optimization of Process Variables

In order to assess the combined impacts of hydrolysis duration, catalyst dosage, substrate dosage, and catalyst treatment type on total reducing sugar yield, Response Surface Methodology based on Central Composite Rotatable Design (CCRD) was utilized. Hydrolysis temperature, pH, acid and alkaline concentration, agitation speed, moisture content, particle size, and other factors could also have an impact on the hydrolysis process. These variables were left out of the experimental plan because Kumar *et al*. (2009) found evidence of their impacts on hydrolysis from earlier studies. So, these factors were left at the optimum points.

Additionally, the mathematical model equation for sugar yields was created using coded variables for each element. Because the coded variable makes the evolution of the model equation easy to express and understand, it was chosen. This outcome also aided to predict the factors that have a favorable and negative impact on the sugar yield. Glucose yield is positively affected by positive coefficients, whilst also negatively affected by negative coefficients. Factors such as A, B, C, and D depict time, catalyst dosage, substrate dosage, and catalyst treatment time respectively. The coded factors B, C, D[2], AC, AD, BC, BD, and CD have positively affected the yield of sugar whereas A, D[1], A^2, B^2, C^2, AB, AD[1], BD[1], and CD[2] had negatively affected the yield of sugar. The basic standard deviation and the approximate degree of freedom used for power calculations as regards clay treatment type were depicted with [1] and [2] respectively. Increasing the effects of factors B, C, D[2], AC, AD, BC, BD, and CD increases the yield proportionally within the specified range. Also, when the effect of factors like A, D[1], A^2, B^2, C^2, AB, AD[1], BD[1], and CD[2] increased, the yield of sugar was decreased. The intercepts for this equation helped to predict the precise results of sugar yield. Based on this, the final mathematical model developed in terms of coded factors is represented in equation (5).

$$\text{Sugar Yield, } Y = 17.43 - 2.63A + 0.529B + 0.35C - 1.44D[1] + 1.61D[2] - 3.57A^2 - 1.68B^2 - 1.18C^2 - 0.143AB + 0.077AC - 0.606AD[1] + 1.17AD[2] + 0.027BC - 0.75BD[1] + 0.38BD[2] + 0.07CD[1] - 0.32CD[2] \tag{5}$$

As part of design for this experiment, figure 9 represents the predicted and actual values, and interaction graphs of substrate and catalyst dosages, time, and catalyst treatment.



(A)

(C)

(B)

(D)

Figure 9: Predicted and Actual plots, and interaction graphs of substrate and catalyst dosages, time, and catalyst treatment

Figure 9 (A & B) show the graph of normal plot of residuals and that of predicted and normal values. The plot on the effects of catalyst treatment type on sugar yield as shown in Figure 9 (C) made it abundantly evident that the sugar yield was greatly improved by an alkaline treated clay catalyst. According to Bayu *et al.*, (2022) research on process optimization for acid hydrolysis using response surface approach, hydrolysis duration is another independent factor that positively influences the hydrolysis of cellulose within a certain range. According to Figure 9 (D), the interaction between catalyst dosage and type of the catalyst treatment had a favorable impact on the yield. Other interactions, such as time with catalyst dose and time with substrate dosage had a favorable impact on the yield of simple sugars up until a certain point, beyond which an increase in time results in a decrease in sugar yield.

3. CONCLUSION

Rice husk can be used as a substrate for the synthesis of bioethanol, according to the results of this study's quantitative and qualitative examination of the hydrolysis of rice husk and fermentation with baker's yeast. Clay, a heterogeneous solid catalyst used to hydrolyze rice husk, was processed using acid, alkaline, and heat methods. While alkaline-treated clay catalyst dosage of 0.04g/30ml produced the maximum output of sugar under the conditions, acid-activated clay catalyst dosage of 0.06g/30ml produced a decent yield of reducing sugar. A decent yield of sugar was produced using thermally activated clay catalyst at a dosage of 0.06g/30ml when treated at 600^0C.

Clays that were activated by acids had a hydrolysis reaction time of 2 hours, but clays that were activated by heat or alkali had a reaction time of 1 hour.

Based on the statistical analysis, the central composite rotatable design-based response surface methodology was found to be an effective tool for determining the crucial elements that controlled the hydrolysis of rice husk as well as their ideal levels.

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