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Optimization of Quicklime (CaO) Production from Calcination of Yandev Limestone

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ABSTRACT
This study presents optimization of quicklime (CaO) production from calcination of Yandev limestone. The limestone sample was collected from the blasted area of Yandev. X-ray Fluorescence spectroscopy was used to determine the chemical compositions of the uncalcined and calcined limestone samples. Isotherms and size analyses of the porous limestone samples were carried out. Quicklime (CaO) was produced from the Yandev limestone by calcination technique. Based on response surface methodology (RSM), central composite design (CCD) tool of Design Expert Software 11 was used to design the experiment. Temperature, particle size and time were the considered factors of the calcination process, while percentage yield was the response. Analysis of the results showed that CaO is the predominant constituent in respect of chemical composition of the limestone sample. Characteristics of the quicklime showed that the calcination improved the quality of the sample in terms of chemical and pore size properties. The percentage CaO increased from 77.9% to 92.7%. Langmuir method of size analysis grossly estimated the surface area, while Density Functional Theory (DFT) method yields reliable surface area and pore volume measurements. The DFT adequately accounted for the effects of microporocity. Quadratic model adequately described the relationship between quicklime yield and calcination factors of temperature, particle size and time. The optimum yield of Yandev quicklime was obtained as 81.05% at temperature of 1000 ^oC, particle size of 90 µm and time of 3 hrs. The generated model should be used to develop chemical plant for limestone calcination process.

KEYWORDS: *Optimization, Quicklime Production, Calcination, Yandev Limestone*

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I. INTRODUCTION

Yandev is one of the Towns in Gboko Local Government Area of Benue State, Nigeria. It is blessed with limestone deposit. According to Ujoh et al (2014), limestone mining and cement production at Yandev started in 1980. From the onset, emphasis has been on processing of the limestone solely on cement production. Its application can be widen with optima processing technique. In other ones, application of limestone can be enhanced through adequate processing techniques. One of the processing techniques that encourage diversification of limestone usage is calcination. Quicklime is produced by burning limestone ($CaCO_3$) in a kiln/furnace at high temperature to yield quicklime (CaO). Calcination is useful for the modification of limestone (García-Labiano et al, 2002; Jiangyin et al, 2005).

Limestone and its derivatives are of great importance in chemical and allied industries (Guemmadi et al, 2009; Akinniyi and Ola, 2016; Ofulume et al, 2017). Variations in physical and chemical properties of limestone deposits necessitate different processing techniques and applications. Limestones that display negative attributes (coarse crystallinity, friability, foliation, excessive calcite veining, microfracturing, highly porous and thin-bedded structure) are prone to decrepitation (Kilic, 2014). Thus, physical properties of limestone rock are vital in determining its texture and applications. Various physical properties of limestone include; hardness, grain size, fracture, streak, porosity, luster, and strength. A high porosity makes for a relatively faster rate of calcination and more reactive quicklime. According to Ofulume et al (2017), crystal structure and physical characteristics of the various limestones determine the quality of the lime product. The texture of the limestone is a factor in the successful calcination of the stone into lumps of lime. Coarse grained limestones are prone to fracturing and crumbling into fines when heated. They can be disintegrated to dust by the heat of the calcination process, a situation dreaded by lime manufacturers. On the other hand, the fine grained limestones can easily be calcined to form lumps of lime because the crystals resist the temperature stress. The Yandev limestone is fine-grained which makes it favourably disposed to calcination into lumps of lime.

In terms of chemical property, calcium carbonate content (% $CaCO_3$) of the limestone ranges from 65.08 to 82.41% (Ofulume et al, 2018). Chemical compositions of limestone determine its reactivity. Chemical reactivity of different limestones shows a large variation due to their differences in crystalline structure and the nature of impurities such as silica, iron, magnesium, manganese, sodium, and potassium (Kilic, 2014). Yang and Yongping (2015) reported that calcination reaction of limestone is always accompanied by sintering of the calcined product. At such, calcination process requires adequate and systematic measures that promote quicklime yield. Limestone application most times requires its calcination in shaft or rotary kilns, where carbonate is thermally decomposed to produce quicklime and CO_2. Okonkwo and Adefila (2013) stated that there are several critical variables that influence calcination operations. The factors that affect the calcination are considered in the design and optimization of the calcination process. The calcination reaction is endothermic (Okonkwo and Adefila, 2013; Kilic, 2014).

II. MATERIALS AND METHOD

2.1 Limestone Preparation and Classification

Limestone sample was collected from the blasted area of Yandev. Method used by Suleiman et al (2013) was adopted in the sample preparation and classification. The sample was washed to remove impurities associated with the limestone crystals. It was sun dried at ambient atmospheric condition for three days. 3000g of the sample was crushed, and ground into powdered form. Crushed sample was classified and re-classified with the aid of the automatic vibrating sieves arranged vertically such in descending order of magnitude and the system set in vibration for 10 minutes.

2.2 Determination of Chemical Composition

X-ray Fluorescence spectroscopy (Supreme 8000, Oxford instrument) was used to determine the chemical compositions of the uncalcined and calcined limestones. Method used by previous works (Ikhane et al, 2009; Nurfatirah et al, 2015) was adopted in this study. The sample was irradiated with high energy x-rays from the controlled x-ray tube. XRF peaks with varying intensities were created and were presented in the spectrum.

2.3 Size Analyses of the Sample

Size analyses of both calcined and uncalcined limestones were carried out. The isotherms and size analyses of the porous uncalcined and calcined limestones were carried out in accordance with standard method (Occelli et al, 2003; Commandre, 2007; Landers et al, 2013; Francisco et al, 2018). Sample size area was grossly estimated by Langmuir method, while density functional theory (DFT) was used to obtain different pore structural morphologies of the samples. DFT accounted for the effects of microporosity and predicted the pore sizes.

2.4 Calcination of the Sample

Quicklime (CaO) was produced from the Yandev limestone by calcination technique. Based on response surface methodology (RSM), central composite design (CCD) tool of Design Expert Software 11 was used to design the experiment. Temperature, particle size and time were the considered factors of the calcination process, while percentage yield was considered as the response. 10g of the limestone sample was weighed into pre-weighed empty crucibles plates. The pre-weighed crucible plate with the limestone was set into laboratory furnace and heated at various temperatures. The sample was removed at various times. It was then allowed to cool for 15 minutes. The weight of the quicklime produced was measured. The experiment was carried out at various particle sizes.

III. RESULTS AND DISCUSSIONS

3.1 Chemical Compositions of the Limestone

The chemical composition of the limestone sample as obtained by the XRF analysis is presented in Table 1. The analytes of Yandev limestone include CaO (77.9%), SiO_2 (13.9%), Al_2SO_3 (3.1%), Fe_2O_3 (2.5%), and traces of SO_3, TiO_2, Mn_2O_3, MgO, K_2O, ZnO, Cl, P_2O_5, Cr_2O_3 and SrO. The concentration by weight of CaO present in Yandev limestone is 77.9%. High presence of CaO, with low contents of Al_2SO_3, Fe_2O_3 and SiO_2, showed that the samples can be used for agricultural purpose. It has been reported that chemical composition of limestone can affect its usage (Bolarinwa and Idakwo, 2013; Kilic, 2014; Ofulume et al, 2018).

Table 1: Chemical Compositions of the Yandev Limestone

Element	Concentration
Na2O	0.000 Wt %
MgO	0.548 Wt %
Al2O3	3.050 Wt %
SiO2	13.864 Wt %
P2O5	0.295 Wt %
SO3	0.764 Wt %
Cl	0.181 Wt %
K2O	0.283 Wt %
CaO	77.917 Wt %
TiO2	0.264 Wt %
Cr2O3	0.005 Wt %
Mn2O3	0.156 Wt %
Fe2O3	2.527 Wt %
ZnO	0.010 Wt %
SrO	0.136 Wt %

3.2 Size Analysis of the Limestone

Size analysis (in terms of surface area, pore volume and pore size data) of the Yandev limestone sample is presented in Table 2. Surface area, pore volume and pore size of each of the samples were revealed. Langmuir methods grossly appraised the surface area, while DFT method produces reliable surface area and pore volume measurements. This observation is in agreement with the finding of previous work (Occelli et al, 2003). The density functional theory (DFT) helps to distinguish between different pore structure morphologies, to account for the effects of microporocity, and to predict the pore sizes (Landers et al, 2013). It is applied for the determination of pore size distribution from adsorption isotherms. DFT cumulative surface area of Yandev limestone is 1.090 x $10^2 m^2$/g. The parameter from the DFT method is important because of its rigorous theoretical fundamentals. It entails the entire region of micro- and mesopores and offers an opportunity of customization to different materials and pore morphologies (Landers et al, 2013). DFT presents the surface roughness as additional structural parameter characterizing the pore wall heterogeneity.

Table 2: Size Analysis of Yandev Limestone

Analysis	Surface Area Data
Langmuir surface area	2.288 X$10^3 m^2$/g
DFT cumulative surface area	1.090 X$10^2 m^2$/g
	Pore Volume Data
DFT method cumulative pore volume	1.314 X$10^{-1} cc$/g
	Pore Size Data
DFT pore Diameter (Mode)	2.647 nm

3.3 RSM Result of the Calcination Process

The RSM result of the calcination of Yandev limestone is presented in Table 3. It showed effects of the interactions among the factors of temperature, particle size and time on the percentage yield of the quicklime (CaO). Low yields were recorded at extreme temperature, particle size and time. This is an indication that at extreme calcination variables, the quality of the CaO is low. The pattern of the data revealed that the peak of the quicklime yield is around the mid-points of the calcination variables (temperature of 1000 ^{0}C, particle size of 90 µm and time of 3 hrs). The quicklime yield decreased with increase in temperature, particle size and time till it got to the peak. This observation is in agreement with previous findings (Rashidi et al, 2012; Suleiman et al, 2013).

Table 3: RSM Result of calcination of Yandev Limestone

Std	Run	Factor 1 A: Temperature (^{0}C)	Factor 2 B: Particle Size (µm)	Factor 3 C: Time (hr)	Response 1 Yield (%)
4	1	1100	100	2	64.7
3	2	900	100	2	68.1
1	3	900	80	2	83.1
11	4	1000	80	3	82.2
18	5	1000	90	3	81.3
12	6	1000	100	3	66.5

14	7	1000	90	4	78.3
16	8	1000	90	3	81.3
10	9	1100	90	3	73.2
19	10	1000	90	3	81.3
2	11	1100	80	2	75.1
13	12	1000	90	2	81.5
17	13	1000	90	3	81.3
5	14	900	80	4	83.2
6	15	1100	80	4	74.2
8	16	1100	100	4	58.3
9	17	900	90	3	81.5
20	18	1000	90	3	81.3
7	19	900	100	4	59.2
15	20	1000	90	3	81.3

3.4 Analysis of Variance

In Table 4, the model F-value of 204.62 implies that the model is significant. There is only a 0.01% chance that an F-value this large could occur due to noise. P-values less than 0.0500 indicate that model terms are significant. In this case A, B, C, AB, BC, A^2, B^2 are significant model terms. The predicted R^2 of 0.9429 is in reasonable agreement with the adjusted R^2 of 0.9897; the difference is less than 0.2. Adequate precision measures the signal to noise ratio. A ratio greater than 4 is desirable (Onukwuli and Omotioma, 2016). The ratio of 44.499 indicates an adequate signal. Thus, the model of the Yandev quicklime yield can be used to navigate the design space. The revealed significant terms indicate that factors of temperature and particle size were responsible for the quadratic nature of the relationship between the yield and the considered factors of the calcination process.

Table 4: ANOVA of the Yandev Quicklime Yield

Source	Sum of Squares	Df	Mean Square	F-value	P-value	
Model	1255.49	9	139.50	204.62	< 0.0001	Significant
A-Temperature	87.62	1	87.62	128.52	< 0.0001	
B-Particle Size	656.10	1	656.10	962.40	< 0.0001	
C-Time	37.25	1	37.25	54.64	< 0.0001	
AB	20.16	1	20.16	29.57	0.0003	
AC	0.2813	1	0.2813	0.4126	0.5351	
BC	26.28	1	26.28	38.55	0.0001	
A^2	30.28	1	30.28	44.41	< 0.0001	
B^2	109.78	1	109.78	161.03	< 0.0001	
C^2	1.62	1	1.62	2.38	0.1539	
Residual	6.82	10	0.6817			
Lack of Fit	6.82	5	1.36			
Pure Error	0.0000	5	0.0000			
Cor Total	1262.31	19				
Std. Dev.	0.8257		R^2			0.9946
Mean	75.84		Adjusted R^2			0.9897
C.V. %	1.09		Predicted R^2			0.9429
			Adeq Precision			44.4986

3.5 Mathematical Model of the Yandev Quicklime Yield

The mathematical model of the quicklime yield in terms of the significant terms is shown in Equation 1. The equation in terms of coded factors can be used to make predictions about the response for given levels of each factor (Omotioma and Onukwuli, 2017). The coded equation is useful for identifying the relative impact of the factors by comparing the factor coefficients. As revealed by the analysis of variance, the model adequately described the relationship between the quicklime yield and the factors of temperature, particle size and time. Thus, the yield is a function of temperature, particle size and time. The positive signs in the model signified synergistic effect, while the negative signs signified antagonistic effect. The model's highest power of at least one of the variables is two, which revealed it as a quadratic equation.

$$\text{Yield} = +\,81.05 - 2.96A - 8.10B - 1.93C + 1.59AB - 1.81BC - 3.32A^2 - 6.32B^2 \qquad (1)$$

3.6 Graphical representations of the Results

Graphical representations of the quicklime yields are presented in Figures (1) – (4). Plot of predicted versus actual yield was used to test the performance of each of the models. The predicted versus actual plot gave linear graph. The graphs (3-D surface plots) showed the relationship between the factors and response of the designed experiment. The 3-D plots revealed the optimum yield with the corresponding optimal factors of temperature, particle size and time. The optimum yield of Yandev quicklime is 81.05% at temperature of 1000 ^{o}C, particle size of 90 μm and time of 3 hrs.

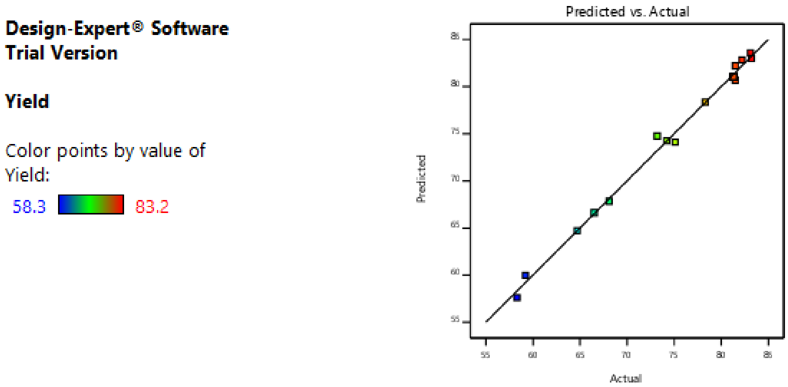

Figure 1: Predicted versus Actual Yield of Yandev Quicklime

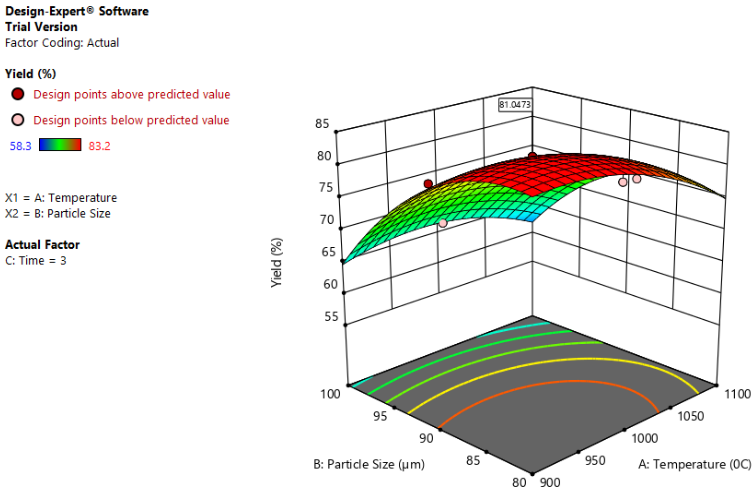

Figure 2: Effects of Temperature and Particle Size on Yandev Quicklime Yield

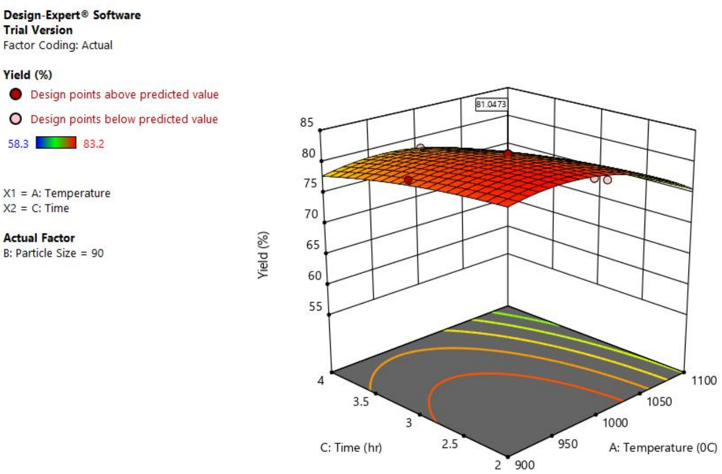

Figure 3: Effects of Temperature and Time on Yandev Quicklime Yield

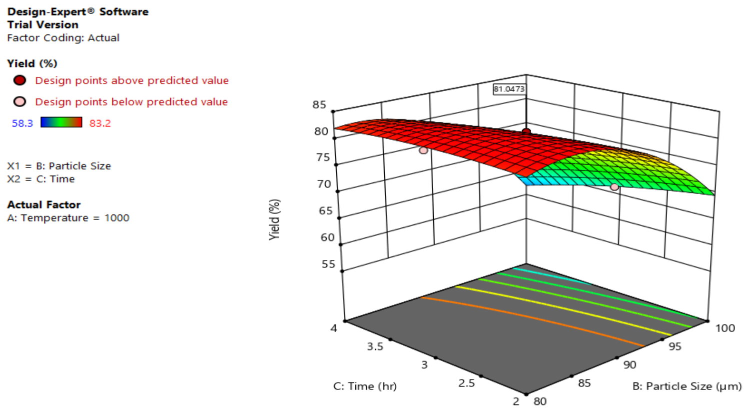

Figure 4: Effects of Particle Size and Time on Yandev Quicklime Yield

3.7 Validation of the Results of the Calcination Process

Data for the validation of the results are presented in Table 5. The experimental result was validated by the determination of percentage deviation of experimental yield from the predicted yield. The percentage deviation is less than 5%, indication that RSM is adequate for the optimization of the calcination process.

Table 5: Validation of the Results of the Calcination Process

Limestone Sample	Temperature (^oC)	Particle Size (μm)	Time (min.)	Experimental Yield (%)	Predicted Yield (%)	Percentage Deviation (%)
Yandev	1000	90	3	83.05	81.05	2.41

3.8 Chemical Compositions of the Quicklime

The analyte concentration of Yandev qucklime is shown in Table 6. The concentrations by weight of CaO present in Yandev quicklime is 92.71%. The weight percent of CaO is more than 90%. The chemical compositions of quicklime determine its reactivity (Ofulume et al, 2018). Comparative analysis of the calcined and uncalcined samples showed great variations in the chemical compositions. The percentage CaO increased from 77.9% to 92.7%. The nature of variation of the chemical compositions of calciend and uncalcined samples is an affirmation that calcination improves the quality of the limestone (Okonkwo and Adefila, 2013; Penuel et al, 2015).

Table 6: Chemical Compositions of Yandev Quicklime

Element	Concentration
Na2O	0.000 Wt %
MgO	0.184 Wt %
Al2O3	0.562 Wt %
SiO2	2.820 Wt %
P2O5	0.081 Wt %
SO3	0.414 Wt %
Cl	0.330 Wt %
K2O	0.239 Wt %
CaO	92.709 Wt %
TiO2	0.178 Wt %
Cr2O3	0.004 Wt %
Mn2O3	0.120 Wt %
Fe2O3	1.585 Wt %
ZnO	0.000 Wt %
SrO	0.774 Wt %

3.9 Size Analysis of the Yandev Quicklime

Surface area, pore volume and pore size data of the Yandev quicklime are displayed in Table 7. Comparing the results of the size analysis, Langmuir methods grossly estimated the surface area, while DFT method provided reliable surface area, pore volume and pore diameter measurements. DFT cumulative surface areas of Yandev quicklime 9.492 x $10^2 m^2$/g. Revealed pore volumes showed that the sample was enhanced by calcination. This observation corroborates with the finding of previous study (Occelli et al, 2003).

Table 7: Size Analysis of the Yandev Quicklime

Analysis	Surface Area Data
Langmuir surface area	1.006 x $10^3 m^2$/g
DFT cumulative surface area	9.492 x $10^2 m^2$/g
	Pore Volume Data
DFT method cumulative pore volume	1.104 x $10^{-1} cc$/g
	Pore Size Data
DFT pore Diameter (Mode)	2.647nm

IV. CONCLUSION

From the analyses of the experimental results, the following conclusions were made:

As obtained by the XRF analysis, CaO is the predominant constituent in respect of chemical composition of the limestone samples. The surface morphologies of the limestone sample showed that the particles are packed together in powdered form with visible pores that will allow passage of fluids.

Langmuir method of size analysis grossly estimated the surface area, while Density Functional Theory (DFT) method yields reliable surface area and pore volume measurements. The DFT adequately accounted for the effects of microporocity.

Quadratic model adequately described the relationship between quicklime yield and calcination factors of temperature, particle size and time. The optimum yield of Yandev quicklime was obtained as 81.05% at temperature of 1000 ^oC, particle size of 90 µm and time of 3 hrs. Characteristics of the quicklime showed that the calcination improved the quality of the sample in terms of chemical and pore size properties. The percentage CaO increased from 77.9% to 92.7%.

The generated model should be used to develop chemical plant for limestone calcination process.

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