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Kinetic Studies of Thermal Decomposition of Periwinkle (*Tympanotonus fuscatus)* Shell

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ABSTRACT

The kinetics of thermal decomposition (calcination) of the periwinkle shell was investigated using the isothermal gravimetric technique in a furnace. To determine the reaction mechanism, all the common models used for solid-state kinetic studies were tested. The kinetic parameters were determined using conventional method (model-fitting) and then the values were compared to those obtained through standard (model-free) method. With regards to the calcination conditions examined in this study, it is shown that the reaction follows the contracting area model (R2). The activation energy (E) of the reaction was 142684.87 J/mol while the frequency factor (A) was 30393.98 min^{-1}. Also, the studies of the effect of temperature and time on the calcination showed that temperature has an exponential relationship with conversion while time has a linear relationship with the conversion. Therefore, the temperature can be said to have more influence than time on the calcination of the periwinkle shell.

1. INTRODUCTION

With the increasing generation of waste due to increasing human population around the world (Hiremath, 2016), recycling has been identified as a major scheme to effectively manage solid wastes and is a field of active research (Jassim, 2017; Abdel-Shafy and Mansour, 2018). Among these wastes are mollusc shells of oyster, cockle, mussel and periwinkle. Due to their significant calcium carbonate ($CaCO_3$) composition, mollusc shells are 'recycled' into a commodity called calcium oxide (CaO) through a process called calcination.

Calcination is an important reaction of $CaCO_3$. It is the industrial process for producing quicklime (calcium oxide). Specifically, it refers to the decomposition of $CaCO_3$ to CaO and carbon (IV) oxide (CO_2) (Commandre´ *et al.,* 2007). Calcination is a kind of process stimulated by heat - called thermal

decomposition reaction. Stanmore and Gilot (2005) reported that the heat energy required for calcination is supplied through the reactor and can be simply represented as shown in Equation 1.

$$CaCO_3(s) \leftrightarrow CaO(s) + CO_2(g) \qquad \Delta H = +182.1\ kJ\ mol^{-1} \tag{1}$$

Kinetic studies enable the determination of kinetic parameters like activation energy (E), pre-exponential factor (A) and mechanism of solid-state reactions (Vyazovkin *et al.,* 2011). The literature review indicates that kinetic study of a thermal decomposition reaction is broadly based on measuring weight loss (gravimetric analysis) isothermally or non-isothermally; then computation of the kinetic parameters using model-fitting or model-free method (Fedunik-Hofman *et al.,* 2019). Isothermal analysis refers to the measurement of weight loss of a specimen to time at a constant temperature while non-isothermal analysis refers to the measurement of weight loss of a specimen measurement to the temperature at constant heating rate.

The model-fitting method requires that the reaction mechanism be known *ab initio* before E can be evaluated. The experimental data are fitted into different reaction models (Khawam and Flanagan, 2006); the model of choice is selected based on the highest correlation coefficient (R^2). Model-free methods do not require fitting the experimental data to a predetermined reaction model before evaluating the E and A (Vyazovkin *et al.,* 2011).

Aside numerous kinetic studies of limestone calcination, calcination studies of oyster, cockle and mussel shells are well reported (Zhong *et al.,* 2012; Mohamad *et al.,* 2016; Barros *et al.,* 2009). Unfortunately, reports on calcination studies concerning periwinkle shell are limited. Specifically, kinetic parameters of periwinkle shell calcination are lacking. Besides, variances in the kinetic behaviour of different $CaCO_3$ sources, inconsistent estimates of the kinetic parameters as well as the effects of reaction parameters require investigating periwinkle shell calcination. Therefore, this work is posed to evaluate the kinetic parameters of periwinkle shell calcination and also study the influence of the reaction variables like temperature, duration time and particle size on periwinkle shell calcination.

2. MATERIALS AND METHODS

2.1. Collection and Preparation of Periwinkle Shell Sample

Collection of the periwinkle shell was done at random from Nembe, Rivers State, Nigeria. Shambhavi IMPEX ball mill was used to crush the shell to open its interior for better washing result. Pipe-borne water was used to wash the shell, to free it from mud, decaying meat and maggots. The cleaned shell was then sun-dried for five days. Grinding followed using the same ball mill. The ground shell was sieved using test sieves and 0.1 mm particle size was stored in ambient conditions for calcination study.

2.2. Calcination Procedure

Calcination was done under ambient conditions similar to an industrial kiln. The works of Okonkwo and Adefila (2012) and Abdulkadir (2016) inspired the set up for undertaking the isothermal gravimetric studies of the calcination. Precisely 30 g of the ground periwinkle shell was placed in a crucible (of average diameter 7.68 cm and depth of 3.6 cm), their masses were measured with weighing balance (GALLENKOMP DT 5000) and then recorded. The sample was placed into the furnace (Carbolite, AAF 11/18) at the set temperature (800 ^oC). Thereafter, it was withdrawn after a period of 30 min and placed in a glass desiccator. The above procedure was repeated for temperatures of 850 ^oC and 900 ^oC (Ar and Dogŭ, 2001; Mohamed *et al.,* 2012; Mohamad *et al.,* 2016). After the sample cooled to ambient temperature, in a desiccator, it was weighed again and the mass recorded. The above procedure was repeated for calcination periods of 45 min

and 60 min. The recorded weight loss measurements were converted to fractional decomposition using Equation 2.

$$\alpha = \frac{M_i - M_t}{M_i - M_f} \tag{2}$$

where Mi is the initial mass of the sample; Mt is the mass of the sample at any time t and M_f is final mass at the end of the reaction (Khawam, 2007).

2.3. Evaluating the Kinetic Parameters

Using the $\alpha - t$ calcination (experiment) data generated at 800 ºC, 850 ºC and 900 ºC, the kinetic parameters were estimated through the conventional method (model-fitting) (Khawam, 2007; Sugiyono, 2012). It involved estimating rate constants (k) of periwinkle shell calcination using Equation 3

$$g(\alpha) = k\, t \tag{3}$$

Where $g(\alpha)$ is the integral form of the reaction mechanism (Khawam, 2007)

As a final step, ln k was plotted against 1/T of the linearised Arrhenius equation (Vyazovkin and Wight, 1998), E and A were both evaluated from the slope and intercept respectively using Equation 4.

$$lnk(T) = lnA - \frac{E}{RT} \tag{4}$$

where *k* is Arrhenius constant, *E* is the activation energy (kJ/mol), A is the frequency factor (min^{-1}), R is the universal gas constant (8.314 kJ/mol K) and T is the absolute temperature (K) (Khawam and Flanagan, 2006).

2.4. Choosing the Reaction Kinetic Model

To determine the calcination mechanism, the values of E evaluated through the conventional method were compared to the one obtained through the standard isoconversional (model-free) method (Khawam, 2007). This approach allows one to select models that might otherwise be indistinguishable based on 'goodness of fit' (R^2) alone. Therefore, the strengths of both model-fitting and model-free methods are used in obtaining the kinetic parameters. Khawam (2007) proposed that both methods can be used in a complementary manner to reach reliable kinetic conclusions.

The standard isoconversional model was obtained by linearising and then rearranging the isothermal rate law

$$g(\alpha) = Ae^{-\frac{E}{RT}}\, t \tag{5}$$

to obtain:

$$-\ln t_\alpha = ln\left(\frac{A}{g(\alpha)}\right)_\alpha - \frac{E_\alpha}{RT_\alpha} \tag{6}$$

The subscript α in Equation 6 emphasizes that at a particular value of α, the plot of $-\ln t$ against $\frac{1}{T}$ produces E from the slope (without considering reaction model); it is according to the isoconversional principle which states that the rate of conversion depends on T at a particular value of α (Vyazovkin and Wight, 1998; Khawam, 2007; Sugiyono, 2012).

The most accurate model is assumed to be the one which produces E value closest to that from the isoconversional analysis (Khawam, 2007). The reaction model was expressed in the form of the rate equation of solid-state reaction kinetics (Equation 7) (Dhyani and Bhaskar, 2018; Fedunik-Hofman *et al.,* 2019)

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \tag{7}$$

Where $\frac{d\alpha}{dt}$ is the rate of the decomposition, $f(\alpha)$ is a function of conversion of the sample describing the reaction mechanism and $k(T)$ is the Arrhenius constant expressed as (Dhyani and Bhaskar, 2018):

$$k(T) = Ae^{-\frac{E}{RT}} \tag{8}$$

Where E is the activation energy (kJ/mol), A is the frequency factor (min^{-1}) and R is the universal gas constant (8.314 kJ/mol K).

3. RESULTS AND DISCUSSION

3.1. Evaluation of the Kinetic Parameters

The results of the kinetic analysis of periwinkle shell calcination using the conventional method are summarised in Tables (1-4). Therein lies the values of E, A and R^2 for each model. As expected, values of A increased with the values of E (Arrhenius relationship).

Table 1: Kinetic parameters from reaction order models

Model (code)	E (J/ mol)	A (min^{-1})	R^2
Zero order (F0/R1)	107034.436	1032.97679	0.9986
First order (F1)	202188.166	49130962.75	0.9822
Second order (F2)	417179.892	1.36134E+18	0.9197
Third order (F3)	728422.796	1.61881E+33	0.8799

Table 2: Kinetic parameters from diffusion models

Model (code)	E (J/ mol)	A (min^{-1})	R^2
1-D Diffusion (D1)	213237.472	49229323.01	0.9977
2-D Diffusion (D2)	258582.028	4279063439	0.9999
3-D Diffusion-Jander (D3)	322832.62	1.44481E+12	0.9928
Ginstling-Brounshtein (D4)	262630.946	1760739979	0.9975

Table 3: Kinetic parameters from geometrical contraction models

Model (code)	E (J/ mol)	A (min^{-1})	R^2
Contracting area (R2)	142684.868	30393.98482	0.9983
Contracting volume (R3)	159038.506	128027.4535	0.994

Table 4: Kinetic parameters from nucleation models

Model (code)	E (J/ mol)	A (min^{-1})	R^2
Power law (P2)	53513.06	4.609410617	0.999
Power law (P3)	35454.22	0.740818	0.9995
Power law (P4)	27003.872	0.316130556	0.9994
Avarami-Erofeyev (A2)	98579.098	754.2319902	0.9839
Avarami-Erofeyev (A3)	64964.7646	20.89479323	0.984

The models showing the goodness of fit that is statistically equivalent to the standard model-free method are shown in Table 5. Based on the complementary approach of Khawam (2007), contracting area (R2) is regarded as the model of choice for describing calcination of the periwinkle shell.

Table 5: Kinetic parameters from models compared to those obtained using standard (model-free) method

Model (code)	E (J/ mol)	A (min^{-1})	R^2
Contracting area (R2)	142684.868	30393.98482	0.9983
Zero order (F0/R1)	107034.436	1032.97679	0.9986
2-D Diffusion (D2)	258582.028	4279063439	0.9999
Power law (P3)	35454.22	0.740818	0.9995
Standard (model – free)	175088.7378	5240880.099	0.9747
Periwinkle shell calcination model	$\frac{d\alpha}{dt} = \left(6.0788 \times 10^4 e^{-\left(\frac{142684.87}{8.3132T}\right)}\right)(1-\alpha)^{1/2}$		

3.2. Effect of Calcination Temperature

The effect of temperature on calcination of the periwinkle shell is shown in Figure 1. As expected, periwinkle shell conversion increases exponentially with increasing temperature. Mohamad *et al.* (2016) reported that increasing calcination temperature increases the kinetic energy of particles which results in the increased decomposition of $CaCO_3$ to CaO. The study agrees with the findings of Ramezani *et al.* (2017).

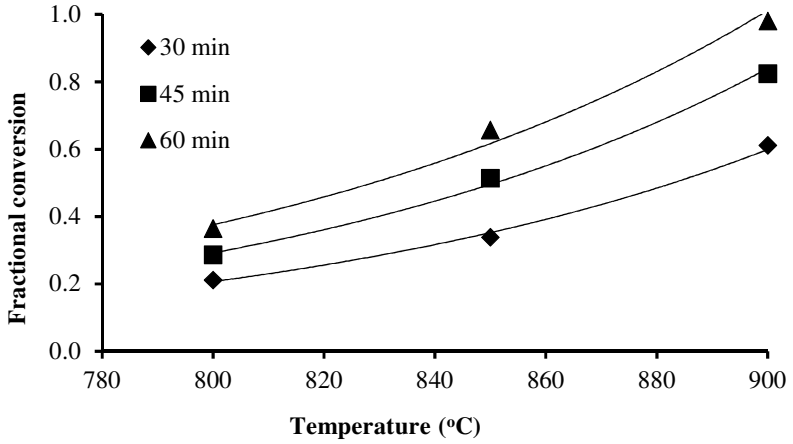

Figure 1: Variation of periwinkle shell conversion with temperature at 30 min, 45 min and 60 min duration of calcination

3.3. Effect of Calcination Time

The influence of time on calcination of the periwinkle shell is presented in Figure 2. For each temperature regime studied, there is a linear increase in conversion of the periwinkle shell with increasing duration of calcination. Increased conversion is because more reactant molecules gain energy for decomposition with the progress of time. Abdulkadir (2016) further explained that for effective calcination, short residence time should be supported with high calcination temperature or vice versa.

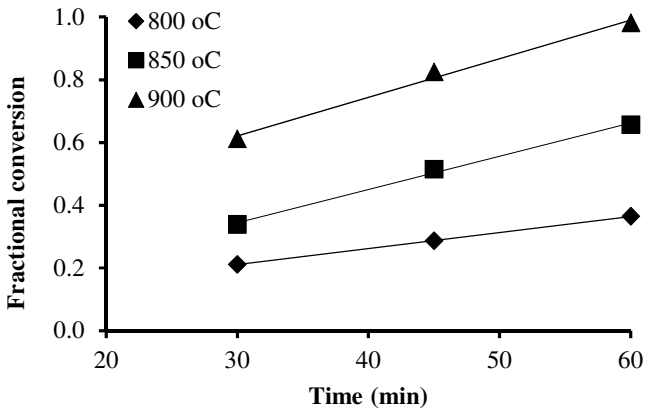

Figure 2: Variation of periwinkle shell conversion with time at 800 ºC, 850 ºC and 900 ºC calcination temperature

4. CONCLUSION

Under the calcination conditions examined in this study, thermal decomposition of periwinkle shell follows the Contracting area (R2) model; and the activation energy (E) of the reaction is 142684.87 J/mol while the frequency factor (A) is 30393.98 min^{-1}.

5. ACKNOWLEDGEMENT

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6. CONFLICT OF INTEREST

There is no conflict of interest associated with this work.

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