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STUDY OF THE PYROLYSIS KINETICS AND ENERGY CONTENT OF ACID WASHED RICE HUSK SAMPLE USING ISOCONVERSIONAL METHODS

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ABSTRACT

The rice husk was characterized by proximate and ultimate analysis. The proximate analysis was determined by moisture, volatile and ash content as 15.48%, 57.28% and 15.35% respectively. Ultimate analysis was determined using the data obtained from proximate analysis to calculate carbon, hydrogen, nitrogen and oxygen percentage as 43.67%, 4.64%, 0.956% and 35.78% respectively. The rice husk pyrolysis was studied by TGA/DTG analysis in a nitrogen atmosphere at flow rate of 60mL/minute, heating from 20.00 °C to 1000.00 °C at three different heating rates: 10, 15 and 20 °C/minute. The devolatilization and decomposition pattern portray by TGA curve for all the samples were almost the same, however, different peak temperatures were shown by DTG curve differently for all the samples at different heating rates. The sample RHC ran at three different heating rates: 10, 15 and 20 °C/minute with peak temperatures of 260.85 °C, 318.14 °C and 358.57 °C respectively. While the acid modified samples RHL and RAA at the same heating rates of 10, 15 and 20 °C/minute with peak temperatures of 402.05 °C, 343.91 °C and 280.76 °C respectively for sample RHL. And 399.34 °C, 325.59 °C and 282.61 °C respectively for sample RAA. Three kinetic models were used in this research, which are known as model fit methods for kinetics. The models are Flynn Wall Ozawa (FWO), Kissinger Akahira Sunose (KAS) and Coats Redfern methods. The KAS and FWO methods were used for the determination of activation energy and C-R method for the reaction mechanisms.

Keywords: Proximate and Ultimte Analysis, Thermogravimetry, Kinetic Model

INTRODUCTION

Agricultural residues, which remain largely unutilized, present a solid waste disposal problem. Among these residues, rice husks, which are created as byproducts of the rice milling process, are generated in large amounts every year, especially in the Asian and Pacific region, and landfilling is becoming an unacceptable solution for rice husks disposal. Therefore, there is a tremendous need for converting rice husks into other forms to bring down the demand for landfill sites. Several technologies have been proposed to solve this problem (Boateng, *et al*., 1992), using rice husks as a source for different industrial processes. Among these technologies, combustion of rice hulls would be the most effective way of solving this disposal problem at present, since the technique for hydrocarbon combustion has been well-developed. Because of their high energy content, rice husks are able to play an important role as an energy source (Hsisheng Teng and Yun-Chou Wei, 1998).

There are several alternative and disposal methods used to investigate the minimization of the wastes and various lignocellulosic biomasses (Guida and Hannioui, 2016). Among these methods, we have thermochemical conversion process which presents several environmental advantages such as the reduction in mass and volume of disposed solids, the reduction in pollutants and the potential for energy recovery (Zhang and Zhang, 2019). Thermochemical conversion such as pyrolysis could be a viable option for environmentally acceptable way to manage waste wood biomass such as sawdust wood (SW) waste, and to manage agricultural biomasse wastes in general (Shahen, and Emam, 2018). Three products are obtained from pyrolysis; bio-oil (condensable volatiles), bio-char (carbonaceous residue) and bio-gas products (non-condensable) (Ortega, Gil and Pérez, 2017). The first product (bio-oil) can be modified to an alternative energy source, or it may be utilized as raw material for petrochemical production. The second product (bio-char) has potential to be applied into the soil for improving N fertilizer use efficiency or can be used as an adsorbent, while for the third product (bio-gas), it could be used as an alternative energy source or to supply heat for driving the pyrolysis (Guida, *et al*., 2019). Since biomass has great potentials for energy purpose and their conversion behaviours can vary depending on the nature and source of row materials, devolatilization reactions are therefore important aspects.

In the next decades, biomass will be the most meaningful renewable energy source as an alternative to fossil fuels (Achinas and Euverink, 2016). Biomass has been recognized as a renewable, inexpensive sustainable feedstock, environmental friendly and received considerable attention from worldwide (Braz and Cmkovic, 2014). The main source of biomass can be divided into three categories, namely agricultural wastes, annual and perennial dry energy grasses, and forestry waste. Due to the extensive agricultural activities in various countries, agricultural wastes contribute significantly to the yearly global yield of biomass (Loow *et al*., 2015).

In the view of the shortage of fossil fuels and with the increasing concerns regarding human impacts on the environment, renewable energy sources and waste materials play an important role as a viable alternative to fossil fuels for both production of chemicals and energy generations (Harjanne and Kohronen, 2019). Waste and particularly agricultural biomass such as rice husk biomass seems to be a realistic alternative power generation leading to technical, economical and environmental benefits (Emel'yanenko, *et al*., 2018). In the international front, several studies and works (Stakiotakis and Vamvuka, 2018) have shown interesting results in the use of rice husk waste to generate products with higher sell and market valuation. There are examples in the field of composite materials (cellulose nanofibers), biofuels (bio-fuels, char and gaseous products), and fertilizers and composting, and among others (Sebay *et al*., 2017).

As the thermal decomposition process influenced by other factors such as temperature, heating rate, moisture, catalyst, particle size, researchers recommend thermal decomposition by thermogravimetric analysis. The thermal characteristics of untreated water washed and acid treated rice husk were explored by thermogravimetric analysis in the present work (Antal and Varhegyi, 1995). The TGA is now used for the kinetic analysis of pretreated biomass sample. In this work, suitable models of Kissinger-Akahira, Flynn-Wall Ozawa and Coats and Redfern are used to predict production of pyrolysis for power plant optimization.

MATERIALS AND METHODS

Materials

The sample of rice husk is from a local rice harvest from Dandume Local Government Area of Katisna State. The sample was washed with tap water to remove debris and dirt and later sun dried in an open air surface. The sample underwent secondary screening to remove unwanted pieces of particles from the feed stream.

Pre-treatment of the Rice Husk.

The rice husk samples were soaked for two weeks prior to devolatilization process and divided into 3 portions RHC, RHL and RAA. RHC was water washed while RHL was HCl (0.1M) acid washed with stirring for 16hours. The acetic acid (1M) washed sample was sample RAA was stirred for 16hours, all the samples were rinsed with deionised water until neutral pH (DeGroot and Shafizadeh, 1984). Finally shade dried and torrefied at 210 ^{o}C for ten minutes. The dried samples were grounded to particle size, and sieved with mesh 2mm and kept in a sample bottle for submission to commercial laboratory.

Proximate Analysis

The methods recommended by the Association of Official Analytical Chemists (AOAC, 1990) was to determine moisture content, volatile matter and ash content of rice husk sample. All analysis were carried out in triplicate and reported as mean standard deviation on dry basis.

Determination of moisture content

About finely powdered air dried sample (1g) was weighed in a crucible. The crucible was placed inside an electric hot air oven, maintained at 105℃. The crucible was allowed to remain in oven for 1 hour and then taken out (with the help of a pair of tongs), cooled in desiccators and weighed. Loss in weight (AOAC, 1990) was reported as moisture (on percentage-basis). (Dara 1999)

Determination of volatile matter

Volatile matter was determined by keeping the dried sample (1g) in a closed crucible at 600℃ for six minutes and then at 900℃ for another six minutes (AOAC, 1990). The difference in the weight due to loss of volatiles was taken as the total volatile matter present in the biomass. Loss in weight was reported as volatile matter on percentage basis.

Determination ash content

The residual coal in the crucible in (2) was then heated without lid in a muffle furnace at 750 ℃ for half hour for (AOAC, 1990). The crucible was then taken out, cooled first in air, then in desiccators and weighed. Heating, cooling and weighing was repeated, till a constant weight was obtained. The residue was reported as ash on percentage-basis.

Determination of Fixed Carbon

The fixed carbon in percentage was calculated by difference, reported by Sanger *et al*., 2011.

Ultimate Analysis of Rice Husk

Calculation of Carbon, hydrogen, oxygen, and nitrogen, of rice husk and its char were found out under the ultimate analysis.

The ultimate analysis is helpful in calculating heat balances in any process in which rice husk is used as fuel. Using the values of proximate analysis, ultimate analysis of rice husk could be done theoretically by using the various formulas according to (Sanger *et al*., 2011) as

Thermogravimetric Analysis (TGA)

Thermogravimetric analysis is one of the most widely used methods for studying biomass decomposition behaviours under different conditions. During the thermogravimetric analysis, loss of biomass sample weight is recorded as a function of conversion parameters including temperature, atmosphere, heating rate, etc. (Thanh Nguyen Cong**,** 2018).

The significance of heating rate in the pyrolysis of cellulose is to find a simple model for the overall weight-loss behaviour of heat-treated cellulose. The pyrolysis of cellulose is controlled mainly by two predominant reactions, presumably dehydration and depolymerisation/cleavage. At low temperature, the rate-determining step is dehydration reaction, while above 240 ^{o}C, depolymerisation/cleavage has the higher reaction rate. Dehydration of the cellulose stabilizes the remaining carbon polymers because the elimination of the hydroxyl groups results in double bonds, conjugated double bonds, and subsequently, in an aromatic structure. The polymeric structure is basically retained and, for low temperatures, weight loss due to volatiles is mainly limited to the evaporation of water. Depolymerization/cleavage at an early stage of pyrolysis without previous dehydration yields small fragments which are often volatile or are likely to be volatilized at higher temperature. From the above hypothesis regarding reaction pathways it can be deduced that either heating at low temperature (low heating rate) or dehydration catalysts can be used to increase the char yield. Since weight loss is connected with char density, porosity and other char properties, the difference in reaction mechanisms of slow and fast pyrolysis should also be reflected in differing char properties. Thus it is expected that physical char properties may change with various heating schemes. The principal objectives are to demonstrate the significance of heating rate in determining the yield and properties of chars formed by pyrolysis of cellulose (Paul and Paul, 1979).

The change in weight measured by TGA is quantitative and no information on the chemistry of evolved gases is obtained. For chemical analysis of vapour products, TGA can be coupled to mass spectrometer (MS) or Fourier transform infrared (FTIR). At each series for increasing temperature. (Thanh Nguyen Cong, 2018). Thermal analyzers that are used for studying thermal decomposition include a high sensitivity balance, a temperature controlled furnace, a unit for evacuation and control of the atmosphere in the furnace, and a control and data recording system.

Results and Discussion

Proximate and Ultimate Analysis

The rice husk sample subjected to different series of pretreatment and characterization to improve the yields which involve physical and chemical treatment. Pretreatment was done to change the structure of biomass. Different series of pretreatment was done like washing, sieving, drying, acid treatment and torrefaction before the feed streams undergo real analysis. The properties of the rice husk sample are listed in the table 1, and table 1 which describe the proximate analysis and ultimate analysis. It was observed that the moisture content of the rice husk is 15.5% approximately. The volatile matter was observed to be 57.3% approximately. Also the ash content was 15.3% approximately and calculated fixed carbon is 11.89%. This shows that report has closeness values with one reported by (Mahir *et al*., 2014), titled: "Analysis of Pyrolysis Kinetics and Energy Content of Agricultural and Forest Waste," which was reported that the moisture content of the rice husk is 8.2%, volatile matter is 51.10%, ash content is 26.30% and fixed carbon is 14.40%. The main difference among the values reported is the moisture content which is almost double due to water treatment and ash content. Also in the ultimate analysis, the report shows that the carbon content is 43.67%, hydrogen content is 4.64%, nitrogen content is 0.96% and oxygen content is 35.83%. This shows that the report has closeness in carbon content by (Mahir *et al.*, 2014) which he reported that the carbon content is 35.60%, hydrogen content is 4.50%, nitrogen content is 0.19%, and oxygen content is 33.40%. This shows that both the two reported work have their closeness values but only nitrogen content due to water treatment. This shows the clear difference which is rendered due to water treatment that washes away many impurities. The result of proximate and ultimate analyses from the determination of moisture, ash and volatile matter content, and elemental composition are given in Table 1 and 2 respectively.

Table 1: Moisture, Volatile Matter and Ash Content of the Rice Husk sample

S/No	Sample	Moisture % ± S.D.	Volatile% ± S.D.	Ash% ± S.D.
1	RHC	15.48 ± 0.51	57.28 ± 1.38	15.35 ± 1.29

Table 2: Ultimate Analysis

S/No	Sample	Element	Percentage (%)
1	RHC	Carbon	43.67
2	RHC	Hydrogen	4.64
3	RHC	Nitrogen	0.956
4	RHC	Oxygen	35.78

Thermogravimetric Analysis (TGA)

In this study pyrolysis of samples (RHC, RHL, and RAA) was performed in a TGA Analyzer at three different heating rates 10, 15, 20 ºC/min from the room temperature to 900 ºC in nitrogen atmosphere. The results of TGA/DTA curves are given in Figs 3.1 – 3.9.

The weight loss curves show similar trend in decrease in weight as the temperature rises at different heating rates. The decomposition process occur at different stages for the different heating rates and initiated at temperature as low as 157 ºC and advances with rise in temperature to 780 ºC at heating rate of 20 ºC/min.

The first stage is the dehydration process followed by the decomposition of organic constituents of cellulose hemicellulose and lignin. The dehydration occurs to remove organic water embedded the structure and the center of the weight loss plateau of the curve is believed to be the end of temperature of water removal (Cai and Lieu, 2007).

There other decomposition process and occur at different temperature zones and vary from one treatment to the other. There are 3 – 5 steps for the processes of samples examined (RHC, RHL, and RAA) and the corresponding temperature ranges are highlighted in Tables 4.1.5.1 – 4.1.5.4 Typical temperature zones are those of the control (RHC) and given as 271 – 330 ºC, 331- 456 ºC and 271 – 894 ºC and corresponds to degradation of hemicellulose, cellulose and lignin (Xu and Chen, 2013).

In the acid washed samples, the temperature ranges for the devolatilization and removal of water given in Tables 4.1.5.1 – 4.1.5.4 suggest that mineral elements like Si and Al that are less soluble than Na, K and Ca require mild acid treatment to weaken the cementations materials (Lei Ding *et al*., 2013). The DTG peaks below 226 ºC are attributed to the release of moisture and volatiles while that between 276 – 360 ºC are associated to hemicellulose degradation. The cellulose decomposes between 360 – 450 ºC while lignin decomposes at much wider range (320 – 700 ºC). The findings corroborated with the reports of Huang *et al*, (2010). In addition the amount of biochar produced from heating of rice sample was highest when HCl acid was used to demineralise the rice husk to suggest that the former is more efficient leading to the conversion of carbonaceous material in the rice risk sample.

The reports from Raveendran *et al*, (1995) on pyrolysis of 12 different biomass feedstock found that demineralization of lignocellulosic material increase the devolatalization rate and initial decomposition temperature while reducing the yield of biochar. This observation is in agreement with what is reported for HCl acid treated samples at low heating rate (10 ºC/min) and acetic acid washed at 15 ºC/min. The biochar yield decreased with increase in heating rates for the control 34.76 – 11.66% and RHL (25.99% - 18.4%) at 10 and 15 ºC/min. respectively while RAA from 16.36% - 18. 16%. In all sample examined biochar is highest in the control at low heating rate.

The decrease or increase biochar yields with change in heating rate are significant in pyrolysis of lignocellulosic materials because, it influence the location and conversion process. In situation where heating rate increase, the pyrolysis temperature (Tm) rises because at longer heating rate, the time to reach equilibrium is short resulting to a maximum rate curve.TGA/DTG Spectra of the Results are as follows:

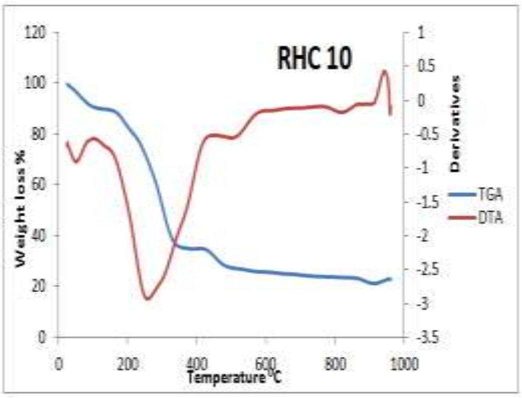

Figure 1: TGA/DTG Spectra of Sample RHC 10 ºC/minute

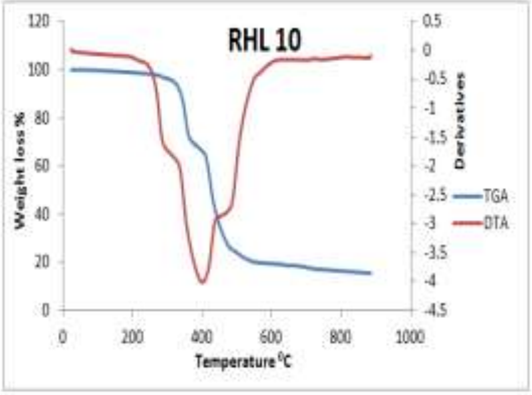

Figure 2: TGA/DTG Spectra of Sample RHL 10 ⁰C/minute

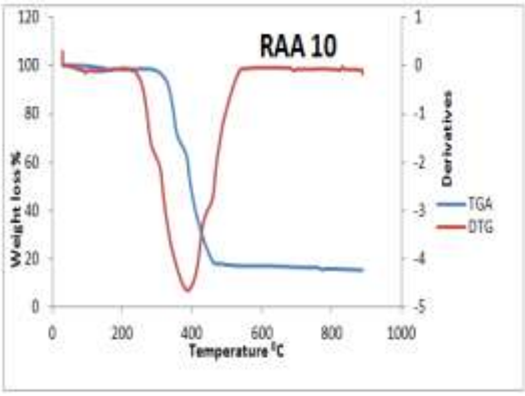

Figure 3: TGA/DTG Spectra of Sample RAA 10 ºC/minute

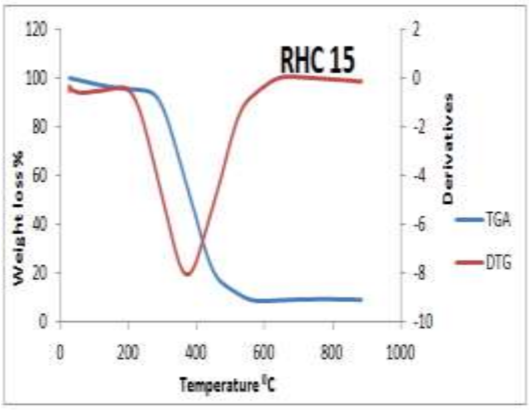

Figure 4: TGA/DTG Spectra of Sample RHC 15 ºC/minute

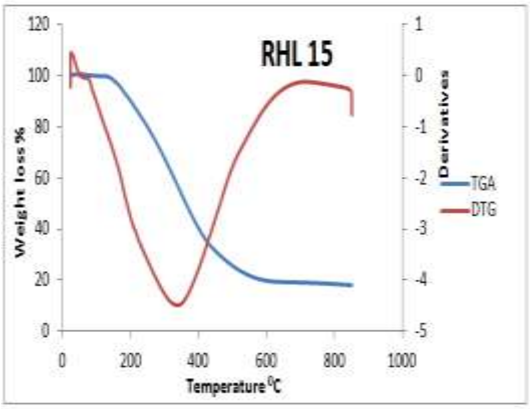

Figure 5: TGA/DTG Spectra of Sample RHL 15 ºC/minute

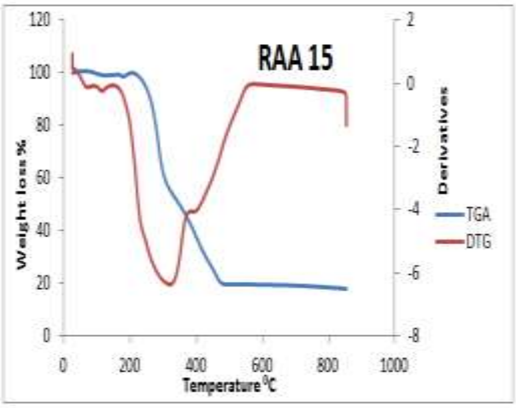

Figure 6: TGA/DTG Spectra of Sample RAA 15 ºC/minute

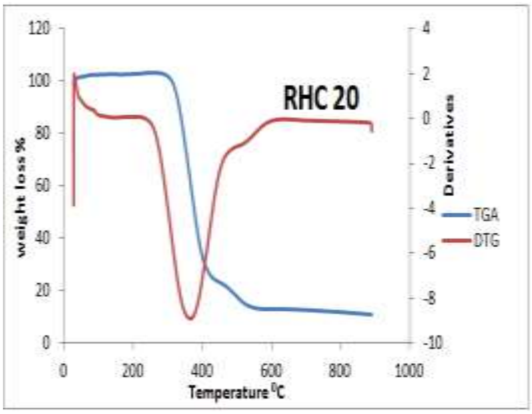

Figure 7: TGA/DTG Spectra of Sample RHC 20 °C/minute

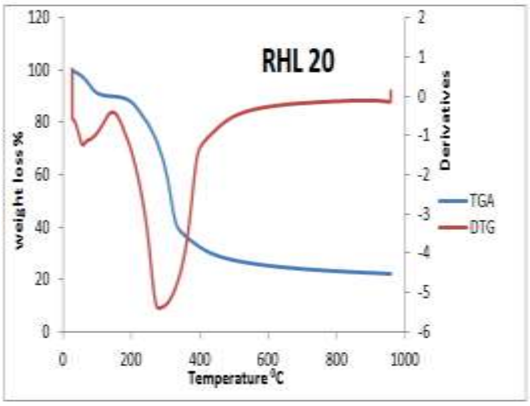

Figure 8: TGA/DTG Spectra of Sample RHL 20 °C/minute

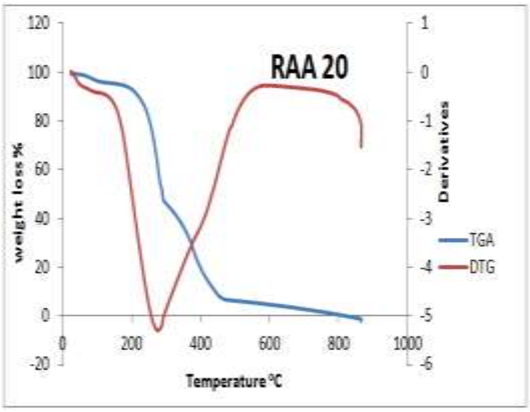

Figure 9: TGA/DTG Spectra of Sample RAA 20 °C/minute

Kinetic Modelling

Kinetic analysis techniques have been classified as either modelfitting (i.e. the identification of a kinetic reaction model) or isoconversional (i.e. model-free) (Guida *et al*., 2016). The latter is preferred by researches for two reasons; (a) model-free kinetics are sufficiently flexible to allow for a change in mechanism during a reaction, and (b) mass loss transfer limitations are reduced by the use of multiple heating rates. In contrast, modelfitting kinetic methods generally involve a single heating rate, which is disadvantageous because the activation energy varies with the heating rate due to mass/energy transfer effects (Mu *et al*., 2015). The kinetic model equations are as follows:

Flynn-Wall-Ozawa method (OFW) (Ozawa,1970)

$$\ln(\beta)=\ln\left(\frac{AE}{Rg(x)}\right)-5.331-1.052\frac{E}{RT_x}$$

....(1)

Thus, the plot *ln β* verus *1/T*, obtained from curves recorded at several heating rates, should be a straight line whose slope can be used to evaluate the activation energy.

Kissinger-Akahira-Sunose method (KAS) (1957 and 2009)

$$\ln\frac{\beta}{T_m^2}=\ln\left(\frac{RA_x}{g(x).E_x}\right)-\frac{E_x}{RT}$$

....(2)

Plotting the left hand side of equation, which includes ln β/T^2 versus 1/T, gives Ea and A from the slope and intercept respectively. The model that gives the best linear fit is selected as the chosen model.

Coats-Redfern Method (CR) (Criado, 2006)

Coats-Redfern method is also an integral method, and it involves the thermal degradation mechanism.

$$\ln\frac{g(x)}{T^2}=\ln\left(\frac{A_xR}{\beta E_x}\right)-\frac{E_x}{RT_x}$$

....(3)

Plotting the left hand side of equation, which includes lng(x)/T^2 versus 1/T, gives the reaction mechanism.

Three models were used in the compiling of the result which are known as model fit methods and are presented in the figure 10 to figure 18. The models are Flynn Wall Ozawa (FWO), Kissinger Akahira Sunose (KAS) and Coats Redfern methods. The KAS and FWO methods were used for the determination of activation energy and C-R method for the reaction mechanisms. Were the RHC samples proceed with mean values of activation energy of Ea 109.74 $kJmol^{-1}$ for the KAS model fit method and Ea 162.37 $kJmoli^{-1}$ for FWO. However, the RHL samples with transition state of activation energy of Ea -72.25 $kJmol^{-1}$ at 0.6 conversions for KAS method and Ea -6.41 $kJmol^{-1}$ for FWO method. Also in RAA samples with transition state of activation energy Ea -93.81 $kJmol^{-1}$ for the KAS method, Ea -82.02 $kJmol^{-1}$ for FWO methods. These values have closeness with those reported by Singh et al, 2020. Where Ea 121.83 kJ/mol for KAS, and 132.98 kJ/mol for FWO. The mechanism of reaction was investigated using Coast and Redfern integral equation to provide the pre exponential factor from ∝ 0.3 – 0.8 and 1st order was used to simulate the process. The values of exponential factor are close for the samples examined and in the range -16.34 to -14.82 min^{-1} to suggest the sensitivity of reaction variables/mode of treatment. However, the value of water leached sample is low compared to demineralized samples to suggest slow reaction rate due is to presence of cementation materials. The values are totally different with those reported by Singh *et al*., 2020, which are ranging from 3.70 x 10^3 to 7.3 x 10^{25} s^{-1} . When R^2 is considered at conversion greater than 0.6, it was low and is the energy to begin the reaction process. It first rises throughout the primary stages, but then decreases as the conversion increase. For R^2 greater than 0.9600 suggest that the model free methods are equal and dependent on the energy of activation (Allen, 2007).

Table 3: Kinetics Parameters using Isoconversional Models of KAS, and FWO for RHC

S/No	α	KAS of 10, 15, 20 °C/minute			FWO of 10, 15, 20 °C/minute		
		EA kJmol^{-1}	A min^{-1}	R^2	EA kJmol^{-1}	A min^{-1}	R^2
1	0.3	176.97	20.08	0.9914	190.34	35.43	0.9884
2	0.4	169.84	19.58	0.9098	184.10	35.14	0.9276
3	0.5	112.24	10.07	0.1507	124.71	25.32	0.1824
4	0.6	172.81	22.31	0.9156	184.10	37.36	0.9276
5	0.7	133.02	15.74	0.9884	145.50	31.02	0.9932
6	0.8	133.02	16.77	0.9884	145.50	32.07	0.9332
Mean		149.64	17.43	0.8241	162.37	32.72	0.8354

Table 4: Kinetics Parameters using Isoconversional Models of KAS, and FWO for RHL

S/No	α	KAS of 10, 15, 20 °C/minute			FWO of 10, 15, 20 °C/minute		
		EA kJmol^{-1}	A min^{-1}	R^2	EA kJmol^{-1}	A min^{-1}	R^2
1	0.3	-109.47	-28.79	0.9936	-97.00	-13.55	0.9932
2	0.4	-92.58	-26.39	0.9738	-82.02	-11.47	0.9732
3	0.5	-80.60	-24.76	0.9543	-70.41	-9.92	0.9499
4	0.6	-72.25	-23.59	0.9405	-61.37	-8.63	0.9276
5	0.7	-74.14	-24.43	0.9800	-6.41	-9.61	0.9787
6	0.8	-61.62	-22.40	0.9882	-52.53	-7.78	0.9820
Mean		-81.78	-25.06	0.9717	-61.57	-10.16	0.9689

Table 5: Kinetics Parameters using Isoconversional Models of KAS, and FWO for RAA

S/No	α	KAS of 10, 15, 20 °C/minute			FWO of 10, 15, 20 °C/minute		
		EA kJmol^{-1}	A min^{-1}	R^2	EA kJmol^{-1}	A min^{-1}	R^2
1	0.3	-78.98	-23.91	0.8280	-68.64	-9.03	0.7921
2	0.4	-93.81	-26.90	0.9764	-82.02	-11.77	0.9732
3	0.5	-80.59	-25.02	0.9543	-70.41	-10.18	0.9499
4	0.6	-71.66	-23.78	0.9499	-61.37	-8.92	0.9276
5	0.7	-67.34	-23.31	0.9915	-58.20	-8.67	0.9932
6	0.8	-62.13	-22.58	0.9979	-52.99	-7.96	0.9991
Mean		-75.75	-24..25	0.9497	-65.61	-9.4212	0.9392

Table 6: Pre-exponential Factor with Changing Heating Rate of Treated Rice Husk Samples using Coats and Redfern Model

Sample	Order of reaction	Pre-exponential Factor of conversions (A min^{-1})					
		0.3	0.4	0.5	0.6	0.7	0.8
RHC	1	-16.14	-15.96	-15.95	-15.55	-15.23	-15.10
RHL	1	-16.21	-16.07	-15.73	-15.52	-15.36	-14.99
RAA	1	-16.38	-16.04	-15.56	-14.76	-15.15	-14.82

Model-Fitting using Kissinger-Akahira-Sunose, Flynn Wall Ozawa and Coats-Redfern Methods

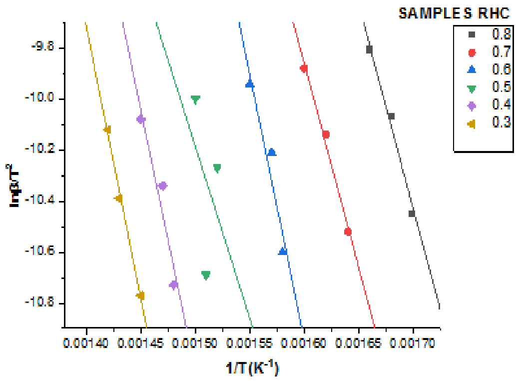

Figure 10: Kissinger Akahira Sunose (KAS) method plot for sample RHC

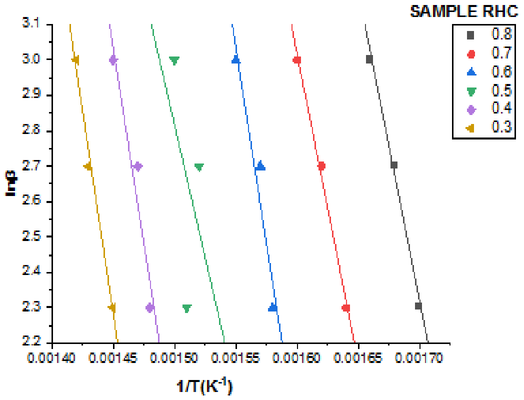

Figure 13: Flynn Wall Ozawa (FWO) method plot for sample RHC

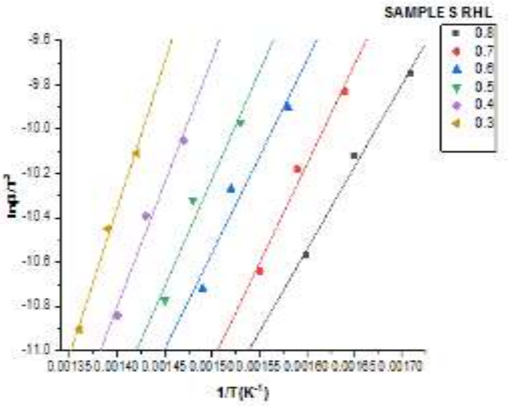

Figure 11: Kissinger Akahira Sunose (KAS) method plot for sample RHL

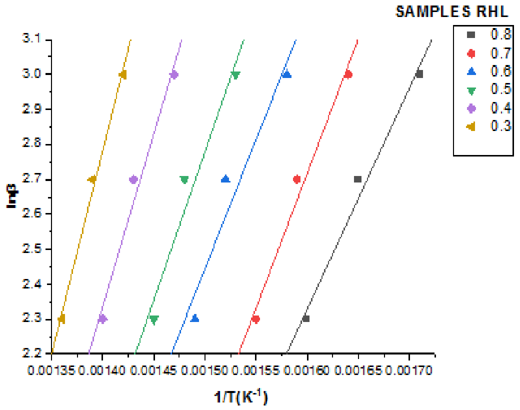

Figure 14: Flynn Wall Ozawa (FWO) method plot for sample RHL

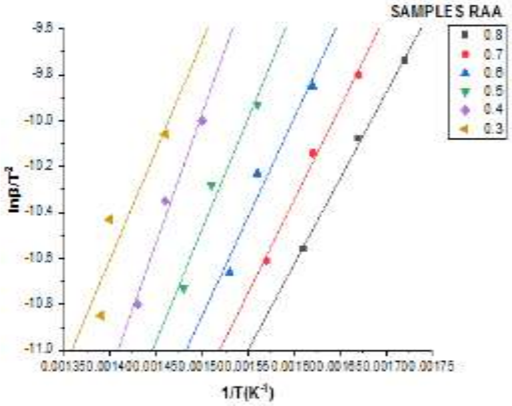

Figure 12: Kissinger Akahira Sunose (KAS) method plot for sample RAA

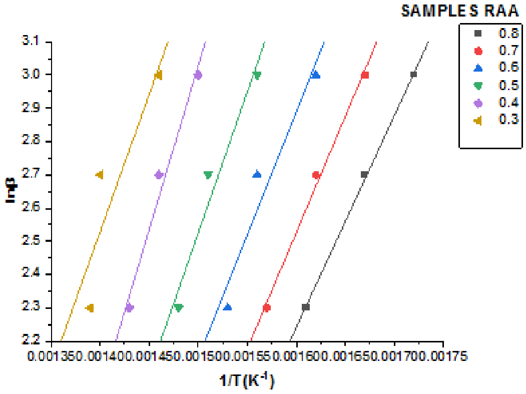

Figure 15: Flynn Wall Ozawa (FWO) method plot for sample RAA

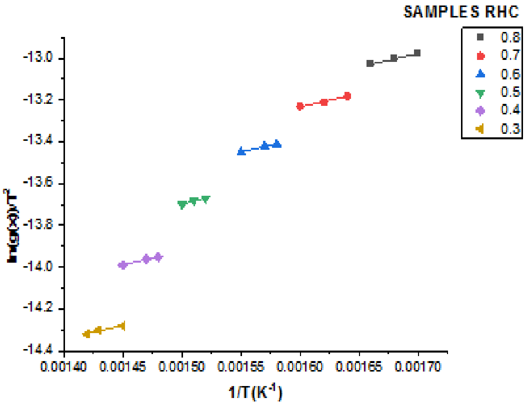

Figure 16: Coats-Redfern (CR) method plot for sample RHC

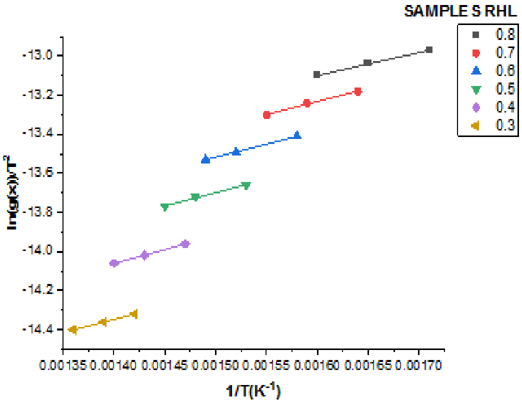

Figure 17: Coats-Redfern (CR) method plot for sample RHL

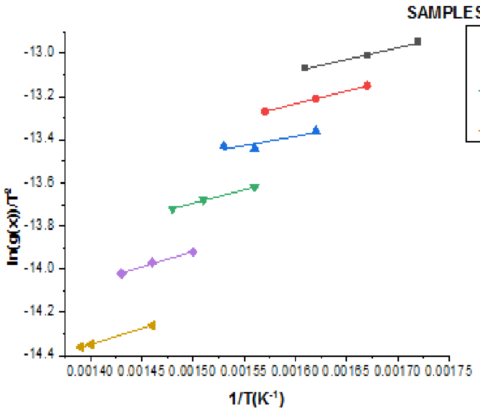

Figure 18: Coats-Redfern (CR) method plot for sample RAA

CONCLUSIONS

In this study, the pyrolysis kinetics of rice husk was carried out by means proximate and ultimate analysis, and thermogravimetric analysis (TGA). It was observed that in proximate analysis, the moisture content of the rice husk is 15.5% approximately. The volatile matter was observed to be 57.3% approximately. Also the ash content was 15.3% approximately and calculated fixed carbon is 11.89%. Also in the ultimate analysis, the report shows that the carbon content is 43.67%, hydrogen content is 4.64%, nitrogen content is 0.96% and oxygen content is 35.83%. In TGA, with the temperature range from 20 °C to 1000 °C at three different heating rates of 10, 15, and 20 °C/min, under the nitrogen atmosphere at flow rate of 60ml/min. The TGA of rice husk of modified and unmodified materials display mostly four peaks which correspond to moisture and volatile evaporation, hemicelluloses, cellulose and lignin. At heating rate of 10 °C/ min, the percentage weight loss of rice husk modified with acetic acid was found to be the highest with no amount of organic matter present. At a heating rate of 15 °C/min, unmodified (water washed) samples had a remarkable percentage weight loss of moisture and volatile content compared to modified samples. The DTG temperature ranges and peaks of the samples are presented in tables and figures, as regards the unmodified (water washed) and modified (acid washed) rice husk samples, the DTG peaks below 200 °C could be related to the released of moisture and volatile matter. The peaks in the range of 200-360 °C could be associated with hemicellulose degradation, the peaks in the range of 360-450 °C could be related to cellulose degradation and the peaks in the range of 450-700 ^{0}C signify lignin degradation. Three models were used in the compiling of the result which are known as model fit methods. The models are Flynn Wall Ozawa (FWO), Kissinger Akahira Sunose (KAS) and Coats Redfern methods. The KAS and FWO methods were used for the determination of activation energy and C-R method for the reaction mechanisms. Were the RHC samples proceed with mean values of activation energy of Ea 149.64 kJmol^{-1} for the KAS model fit method and Ea 162.37 kJmol^{-1} for FWO. However, the RHL samples with transition state of activation energy of Ea -72.25 kJmol^{-1} at 0.6 conversions for KAS method and Ea -6.41 kJmol^{-1} for FWO method. Also in RAA samples with transition state of activation energy Ea -93.81 kJmol^{-1} for the KAS method, Ea -82.02 kJmol^{-1} for FWO methods.

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