A Study of Thermal Stability and Activation Energy on Natural Fibres for Bio Composite Applications

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Abstract— Natural fibres are bio based material, because these offers real alternative to the synthetic fibres and also abundantly available in nature although problem free disposals. The natural fibres are used as reinforcing phase in composite materials. In this project work first chemical treatment of natural fibres with 5% of Naoh solution of certain weight of the fibre are carried out. After chemical treatment the physical properties like density, microscopic structural analysis, water absorption, moisture content and moisture regain, analysis are carried out for fibres like treated and untreated areca, coir, jute and sisal fibres. Further TGA analysis of the fibres carried out to find thermal stability of both treated and untreated fibres. From the TGA analysis, the treated fibres are thermally stable than the untreated fibres. Activation energy of both treated and untreated fibres are calculated by using DTG curves based on non-isothermal model free method (Kissinger method). The activation energy of treated fibres is ranged from 170-260 kJ/mol and of untreated fibre ranged from 105-160kJ/mol. Both physical and thermal analysis of natural fibres is helpful for developing a basic approach to know the thermal decomposition characteristics of these fibres in the bio composites production.

Key words: Kissinger Method, Thermo Gravimetric Analysis, Natural Fibres, Activation Energy, Moisture Content, Moisture Regain

I. INTRODUCTION

Fibres are a rope or string it is in composite material as a component, it is mixed into sheets to make products, such as papers or felt. Fibres are also used to make other materials, generally most of materials made as fibres which is known as the strongest engineering material, for examples carbon fibre and ultra-high molecular weight polyethylene.

Natural fibres are divided into three groups. They are plant fibre, animal fibre and mineral fibre. In these the important natural fibre is plant fibre and it is contain mainly of cellulose, hemicellulose, lignin and pectin. In these cellulose are mainly used in preparation of cloth and paper. These fibre is classified into seed fibre, leaf fibres, stem fibre, fruit fibre, and stalk fibre. Cotton, jute, flax, ramie, sisal, hemp are known as prominent natural fibre.

As the cellulose material offers many potential advantages the availability of inexpensive plant fibres have everywhere in the world has contributed to their use as reinforcement in greener composites. Abundant renewable source, inexpensive, low cost, flexibility during processing, desirable fibre aspect ratio, low density, high specific stiffness and strength bio degradability, reduced wear of the processing machinery ect. For industrial application in several sectors, such as automotive, building, appliance, packaging and bio materials polymer composite based on natural fillers are currently receiving great attention as innovative materials.

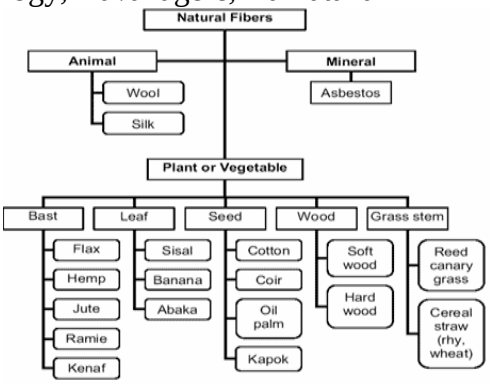


Fig. 1: Classification of the natural fibre on their origin

The use of specific interfacial additives exaggerated interfacial adhesion for composite containing natural fibre can be achieved. Extraction with alcohol, benzene or Noah (delignification, bleaching etc.) are the traditional treatments of natural fibres. Reaction with various reactive monomers, such as acetic anhydride, steric acid, molic anhydride, glycidyl methacrylate, silane and isocynate effective methods of chemical modification of fibres have been developed. By grafting of methyl methacrylate (mma) in to fibres lead to enhanced thermal stability and mechanical properties and to improve the surface adhesion and dispersion of the fibres in composites.

One of the most commonly used method is TGA analysis used for analysis of de volatilisation process, and it gives the evaluation of the weight loss of sample with respect to temperature and time. Solid state kinetic data from TGA can be analysed by various model fitting or model free methods. The model fitting method consist of fitting different models to the data to obtain best statistical fit models through which the kinetic parameters are calculated. But in case of model free methods requires several kinetic curves to perform the analysis without doing assumptions about the reaction function and reaction order. The advantages of this method are its simplicity, and it avoid the risk of selecting the wrong kinetic parameters. So that multiple heating rate method such as the Kissinger method is most commonly used method to find the kinetic parameter. In this method there is no need to find Ea for each conversion value to evaluate kinetic parameter.

II. MATERIAL

Four different natural fibres were used in this study are,

1) Jute fibre from the stem of the plant
2) Sisal fibres obtained from the leaf of the plant
3) Coconut (coir) fibres are collected from the fruit of the plant
4) The areca fibres were obtained from the partial dried areca husk

Fibres were collected from the grower these plants.
Chemical composition of the above fibre

Properties	Coir (%)	Areca (%)	Jute (%)	Sisal (%)
Cellulose content	36-43	-	51-84	60-67
Hemicellulose content	02	64.8	12-20	10-13.9
Lignin content	41-45	13-24.8	5-13	8-12

Table 1: Chemical composition of the natural fibres
Source: Binu haridas et al [8]

III. METHOD

A. *Chemical Modification*

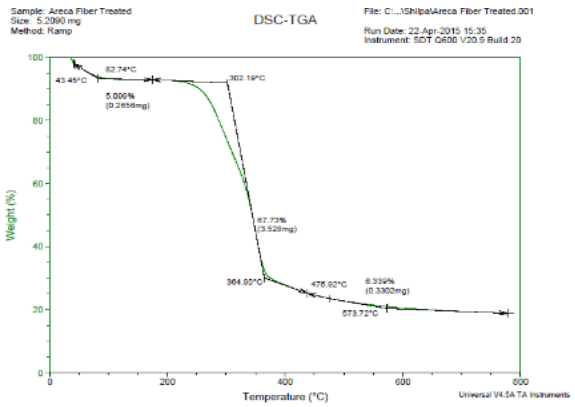
Fibres were modified with the following procedure reported by Binu haridas et al. [8] Fibre was subjected to alkali treatment process because in order to get improved mechanical, thermal and physical characters of the fibres for bio composite applications. In alkali treatment, firstly fibres were prewashed with huge amount of distilled water. In the alkalization process, at 70ºC in hot air oven for 3 hour the fibres of certain weight in a 5% was immersing in Noah aqueous solution. Then for neutralizing, the fibre is removed from the alkali solution and is dipped in 5%of acetic acid. Then it is washed with plenty of distilled water and is dried in an electric oven at a temperature of 100ºC.

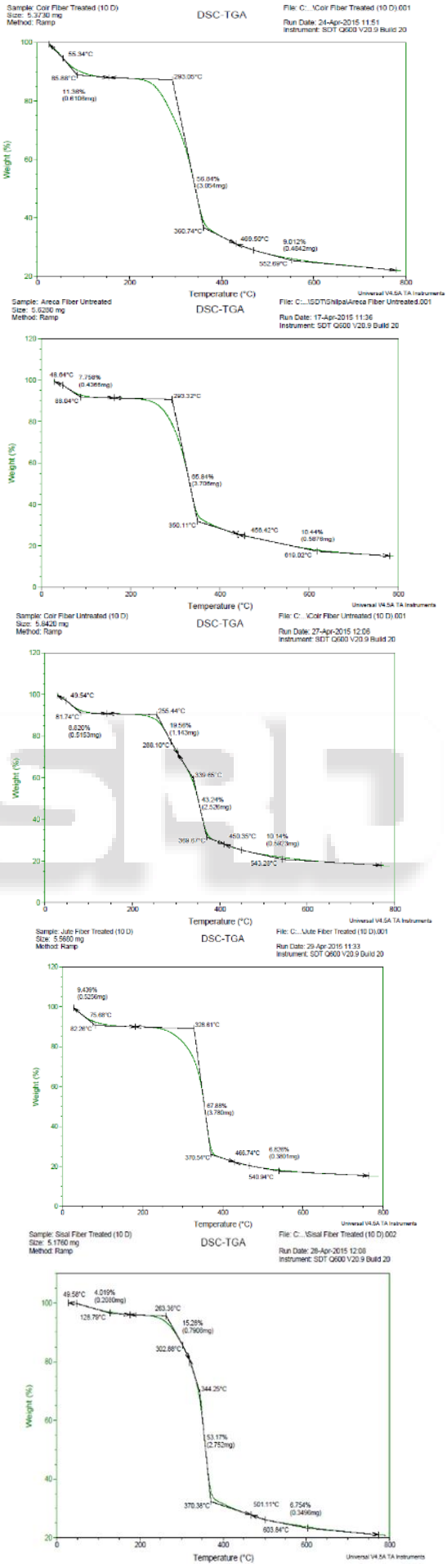
B. *TGA Analysis*

Thermo gravimetric analysis [TGA] was carried out by using thermo gravimetric analyser [SDT Q600, TA instruments]. On the open sample pan, the samples [5 to 10 mg] were evenly and loosely distributed. This sample of small amount was taken in order to ensure the uniformity of temperature of the sample with a good reproducibility. In a high purity nitrogen atmosphere [99.99%] at a flow rate of 100ml/min the temperature was controlled from room temperature (25ºC) to 800ºC at two different heating rates of 10ºC/min and 40ºc/min. due to heat transfer problem higher heating rates were produced too low activation energy. So the heating rate of 10 to 40ºC/min was chosen. Depending upon the previous publications of Anselm Ogah Ogah [2] et al for reproducing results the sample mass, particle size and gas flow rate were fixed. In order to prevent any unwanted oxidative decomposition, nitrogen was used to purge the furnace for 30 min to establish an inert environment before starting each run. Activation energy is calculated by using different heating rates according to iso-conversional model-free method by MS excel software.

IV. RESULT AND DISCUSSION

A. *Thermal Degradation Analysis*





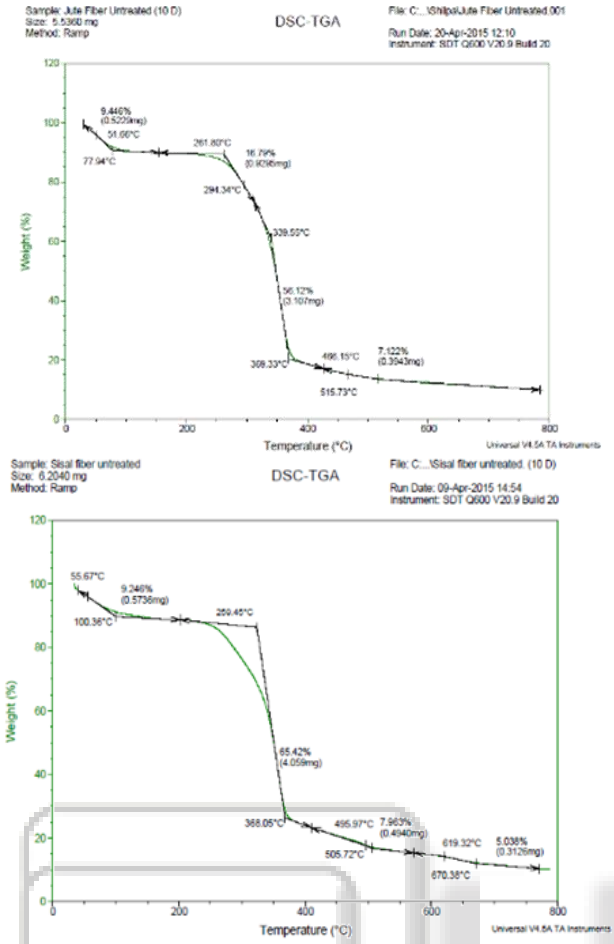


Fig: 4 TGA curves of treated and untreated natural fibres at 10ºC/min heating rate

In a nitrogen atmosphere by using the instrument at 10ºC/min heating rate the treated and untreated natural fibres starting at room temperature at 25ºC to 800ºC the figure shows TGA and DTG curve respectively. The thermal decomposition of plant fibres consists of two or more decomposition steps. Evaporation of moisture is the first stage of decomposition. Three treated fibre the temperature ranged from 40-85ºC, where the temperature ranged from 49-130ºC for treated sisal fibre. For untreated fibres the temperature ranged for 40-90ºC for three fibres and for sisal fibre temperature ranged from 50-100ºC. Through a released of surround water and volatile extractives the weight of the material decreases when the fibre was heated. This phenomenon is common for plant fibres and makes fibres more flexible and easy to collapse as well as improving heat transfer rate (Alwani et al,). Due to hydrophilic nature of plant fibres during drying the structurally surrounded water molecules are resist. For all the treated fibres within the range of 5-10% the weight loss varies. At this stage, for treated jute fibre around 10% the greatest weight loss was observed within the range of 6-12% the moss loss varies for untreated fibre, and around 12% of weight loss for untreated coir fibre. Up to 200ºC the weight loss rate increases gradually and in between 200-400ºC the weight loss more mark able. Whereas coir fibre showed 62.8% respectively. In case of untreated fibres, on reaching 400ºC the moss loss occurs 50-70%. Anslem ogah ogah et al, found similar weight loss when they studied for different agro plant fibres.

The second phase composed of hemicelluloses decomposition at the highest temperature of 302.19ºC and 328.61ºC the treated areca and jute fibres are start to decompose. Comparing to other fibre, around 20% of highest f weight loss was showed by coir fibre. In case of coir and sisal fibre decompositions starts at 250ºC and 260ºC respectively. Comparing to other fibres, at the highest temperature of 261.8ºC the untreated jute fibre start to decompose and around 16.79% it shows highest mass loss. For lower thermal stability the presence of acetyl groups in hemicelluloses may be answerable. Comparing to other chemical compounds the hemicelluloses is degrade more quickly i.e the lignin and cellulose present in fibre. Due cellular break down, as the temperature increased chemical changes took place in the component of hemicelluloses. The result this study was consistent with other previous studies and it has been reported that for untreated fibres the hemicelluloses would decompose within a temperature ranged from 180ºC-300ºC and for treated fibres temperature ranged from 200-350ºC. Cellulose is more thermally stable because of its crystalline nature in which it is bonded together by hydrogen bonds to form microfibrills when it is compared to hemicelluloses and lignin. The fibre sample showed more weight loss of about 30-70% at 350ºC because of decomposition of cellulose and lignin. This stage belongs to the degradation of crystalline cellulose, as the small amount of amorphous cellulose was degraded in the early stage, where the critical temperature for decomposition of crystalline cellulose was found to be 320ºC [Alwani et al.], it was around 350ºC for treated fibres.

Compared to other components the most difficult component to decompose was lignin. For untreated fibre under the whole temperature range up to 700ºC but for the treated fibre the temperature ranged up to 600ºC. According to Yang et al, the decomposition of lignin could start earlier, it decomposes slowly and extended its temperature as high as 900ºC. Under the whole temperature range the decomposition occurs slowly at equilibrium state so the DTG curve of all samples reaches the equilibrium state and therefore, was unidentifiable peaks. Lignin is composed of polysaccharides and heavily cross linked molecules, during thermal degradation making it difficult to decompose. Comparison of onset degradation of all the fibres indicates that, comparing to treated fibres, the untreated fibres start to degrade, indicates that untreated fibres are lesser thermal stability. Degradation at temperature lower than 200ºC would limit the choice of that fibre as reinforcement in polymer composites.

For all treated and untreated fibre types the table shows the thermal degradation data and when degradation starts the decomposition begin temperature, and the decomposition peaks temperatures that appears as shoulders in the TGA and as peaks in the DTG graphs.

Only ash and char were left after 600-700ºC and remaining mass of residue in % shown in table. The difference in the amount of char between the fibres could be depends on the various chemical compositions of the fibre. During pyrolysis higher levels of char is produced by higher the lignin content of natural fibres. Comparing to other fibres the lignin content of coir was significantly more compare to other, so that the char content was the highest in the coir fibre.

Fibre sample		Stability temperature(ºC)	Maximum temperature(ºC)	Final temperature(ºC)	Residue (%)
Areca	Treated	302.19	351.79	375.44	14
	Untreated	293.32	334.10	360.61	19
Coir	Treated	255.44	356.40	383.36	16
	Untreated	230	343.04	372.79	22
Jute	Treated	328.61	357.69	382.49	9
	Untreated	261.80	356.12	383.77	14
Sisal	Treated	263.36	357.48	485.89	12
	Untreated	259.95	356.70	491.55	21

Table 3: Results of TG analysis of untreated and treated plant fibres

B. Activation Energy

The present calculation of activation energy of all the selected treated and untreated fibres by the use of model free method i.e. Kissinger method on the basis of TGA data of all the selected samples, the temperature range in between 250-400ºC. Curves derived from 10 and 40ºC/min heating rates were used for in this analysis. Figure shows the plots for the Kissinger method and table presents the activation energy values of all treated and untreated areca, coir, jute and sisal fibres. Treated coir showed highest activation energy of 257.847 kJ/mol among the studied fibres. The definition of the activation energy is, the energy required to jump the atoms from lower temperature region to higher temperature region, so that the fibre which shows higher activation energy indicates more thermally stable. Because more energy is required for the decomposition process of the fibre. For the calculation of activation energy the peak temperatures are taken from the DTG curves shown below.

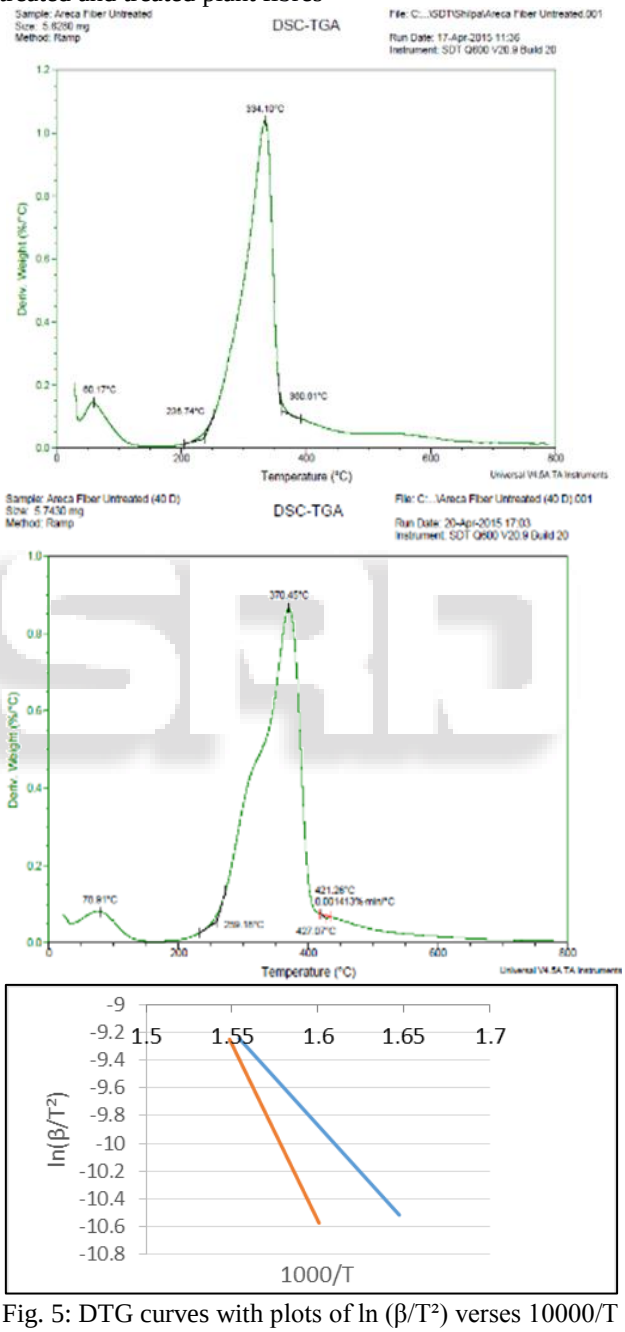
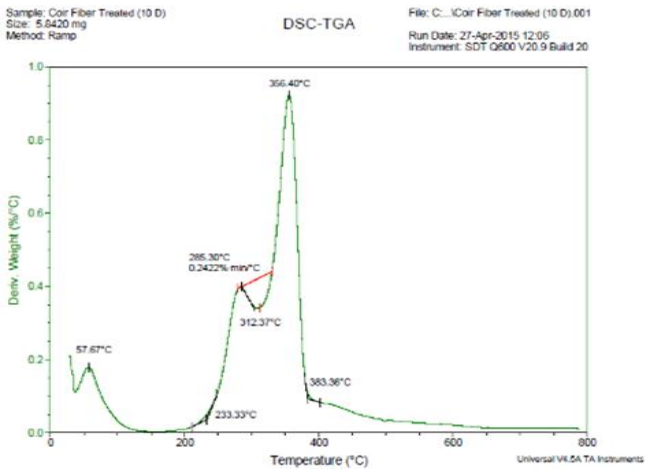
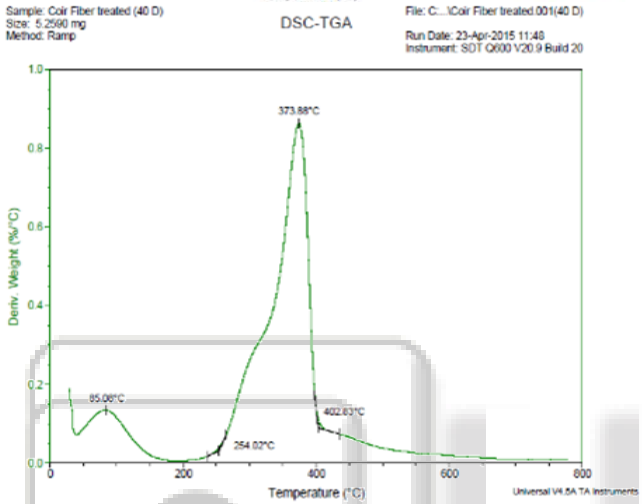
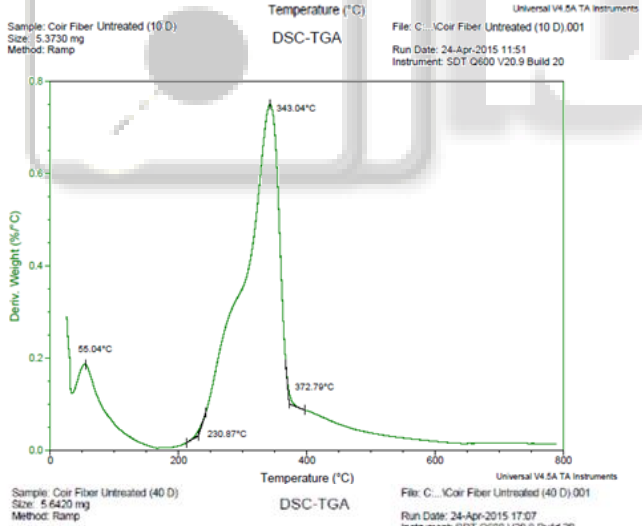
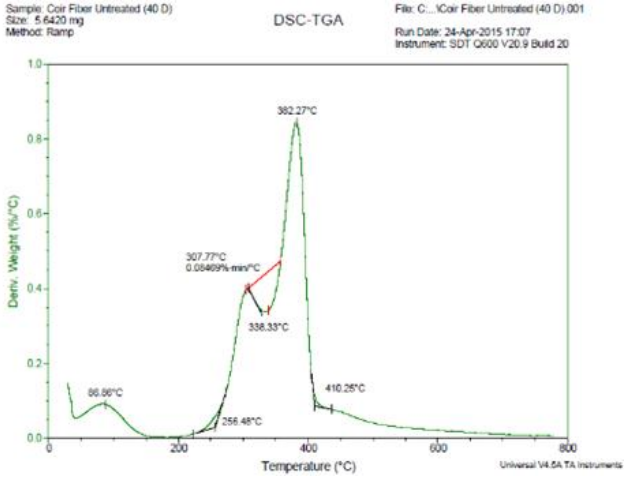


Fig. 5: DTG curves with plots of ln (β/T²) verses 10000/T for treated and untreated areca fibre in Kissinger method
The activation energy obtained are 210.88 and 113.47 kJ/mol for treated and untreated areca fibre respectively shown in table









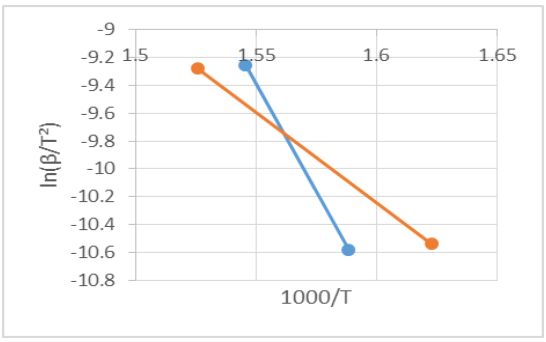
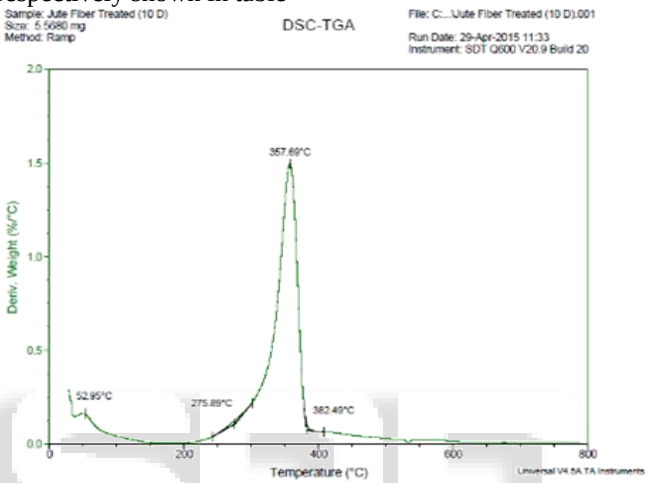
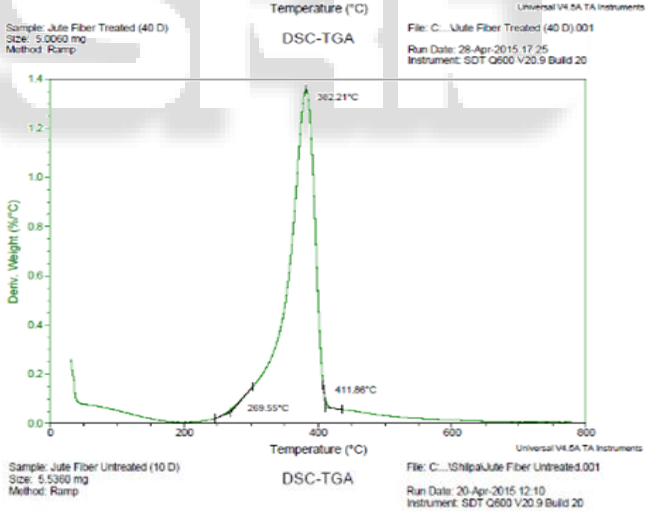
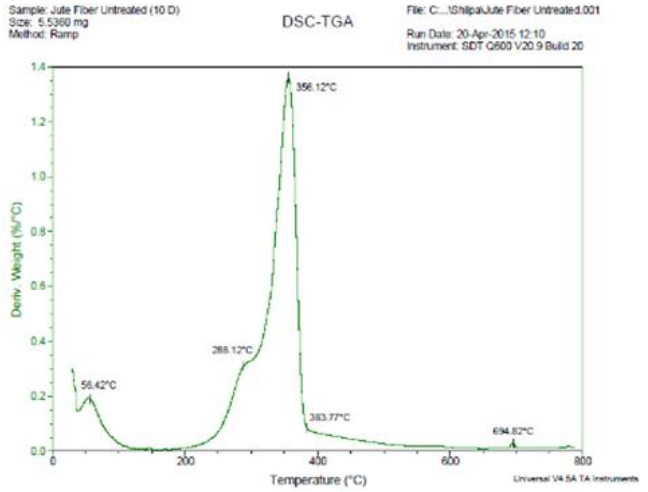


Fig. 6: DTG curves with plots of ln (β/T²) verses 10000/T for treated and untreated coir fibre in Kissinger method

The activation energy obtained are 257.84 and 108.03kJ/mol for treated and untreated coir fibre respectively shown in table







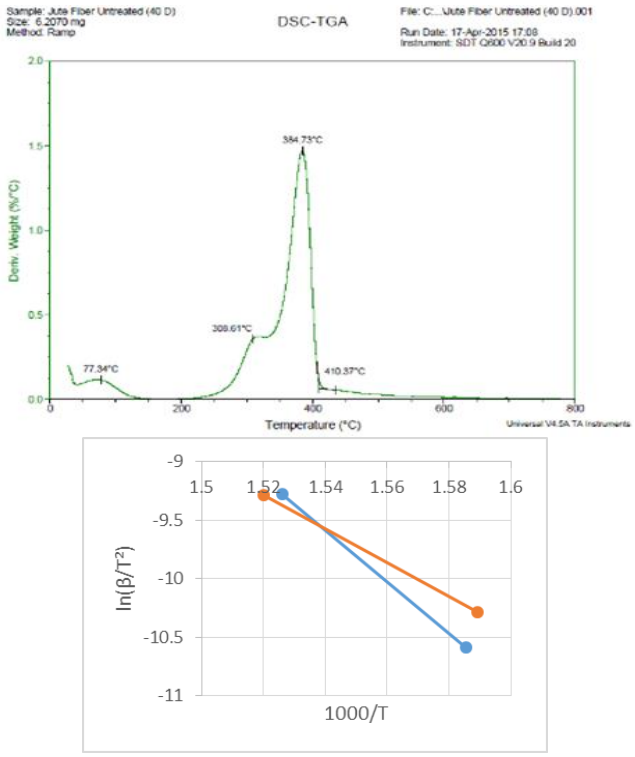
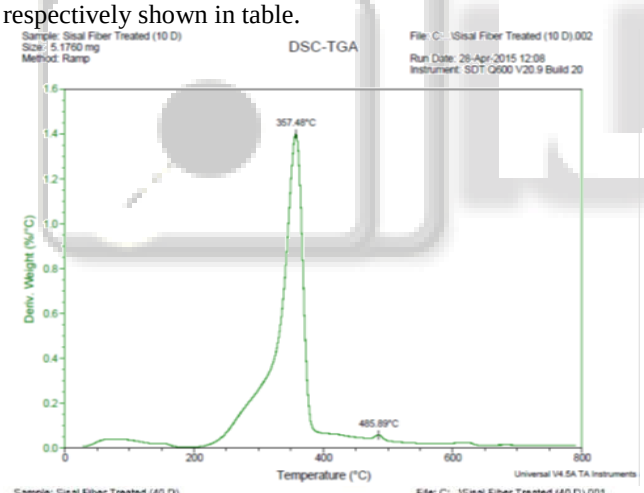
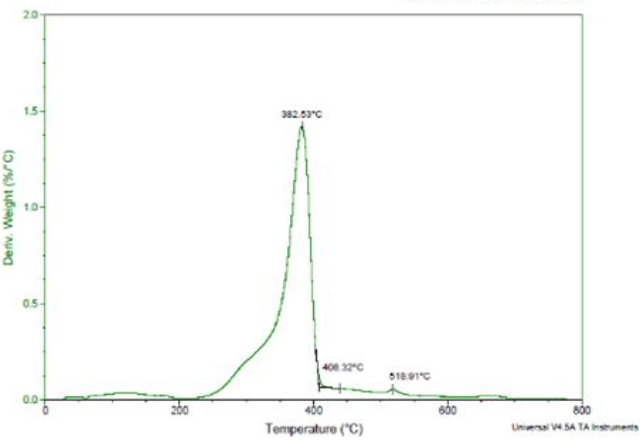
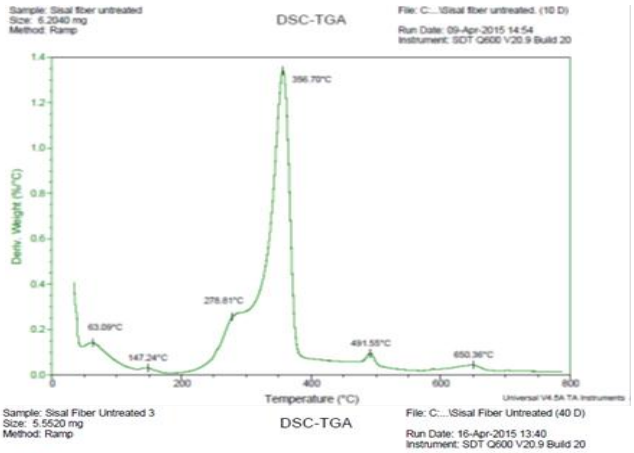


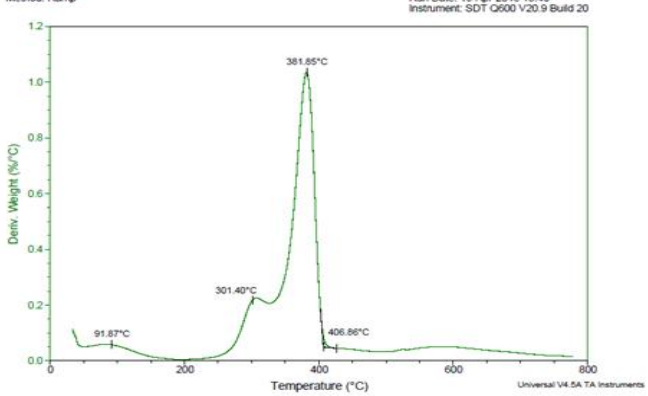
Fig. 7: DTG curves with plots of ln (β/T²) verses 10000/T for treated and untreated jute fibre in Kissinger method

The activation energy obtained are 183.55 and 156.00 kJ/mol for treated and untreated jute fibre respectively shown in table.









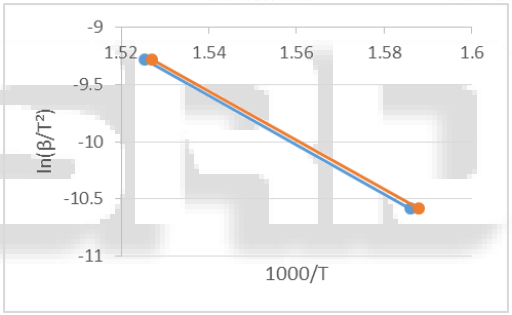


Fig. 8: DTG curves with plots of ln (β/T²) verses 10000/T for treated and untreated sisal fibre in Kissinger method

The activation energy obtained are 179.47 and 178.77kJ/mol for treated and untreated areca fibre respectively shown in table

Fibre sample		Activation energy(kJ/mol)
Areca	Treated	210.88
	Untreated	113.47
Coir	Treated	257.84
	Untreated	108.03
Jute	Treated	183.55
	Untreated	156.00
Sisal	Treated	179.47
	Untreated	178.77

Table 4: Activation Energy of selected fibre calculated by Kissinger method

V. CONCLUSION

1) The study gives the thermal decomposition of treated and untreated areca, coir, jute and sisal fibres preceded either two or three steps due to the chemical composition of the fibres. It was observed that studied fibres both treated and untreated fibres gives thermal stability above 200ºC.

2) The activation energy of both treated and untreated fibres were calculated from model free iso conversional method (Kissinger method), the values obtained are ranged from 170-260kJ/mol for treated fibres and are of untreated fibres values ranged from 105-160kJ/mol. Higher value of activation energy of treated coir fibre indicating the fibre is thermally stable i.e. 257.84kJ/mol and more energy is needed for the degradation process of this fibre compare to other.
3) May be these variation of the fibre properties is because of the fibre is an anisotropic material, the amount of its principal component, as well as inorganic components varies with geographical location, types of species, and complexity of growth, these variable directly affects the degradation process and also on activation energy.

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