Thermal Kinetics and Its Behavior of Waste Amaltash Seeds and Peels Biomass Using Thermo Gravimetric Analysis

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***Abstract*- The present study reports thermochemical characterization of two waste biomass materials namely, amaltash seed powder (ASP) and amaltash peels powder (APP). Thermogravimetric analysis (TGA) was used to determine pyrolysis kinetic parameters at five different heating rates (10-30 ^{o}C/min). Three model-free methods such as Flynn-Wall-Ozawa (FWO), Kissinger-Akahira-Sunose (KAS) and Kissinger were used to determine the kinetic parameters. Proximate and ultimate analysis confirms of these biomass have the potential for fuel and energy production. Kinetic parameters are in good promise with other reported biomass and the activation energy was found to be 118.70 kJ/mole and 136.34 kJ/mole from F-W-O model; 107. KJ/mole and 158.78 kJ/mole from KAS model; 103.258 kJ/mole, and 119.45 kJ/mole from Kissinger model for ASP, APP biomass respectively.**

Keywords: Amaltash seeds, Amaltash peels, biomass, pyrolysis, thermal kinetics.

I. INTRODUCTION

At present, the primary sources of energy include coal (28%), natural gas (21.40%), petroleum (32%), green fuel (10.30%), hydrothermal energy (2.40%), nuclear (4.70%), and other sources of renewable energy such as solar energy, tidal energy, wind energy, and geothermal energy [1]**.** In the recent years, scientific community has been used a numeral of resources as adsorbent including shells, and a variety of fruit seeds, sewage slags and biomass. The presence of this waste can cause undesirable effects on the health of the living organisms primarily through communications with enzymes in their cells [2].These wastes are applied to produce activated carbon [3]**.** According to a survey, about 500 million metric tons raw biomass is used annually [4]**.** Furthermore, 18,000 MW energy productionshave been achieved by using 120-150 million metric tons/annum of forestry and agricultural bio-waste [4]**.** About 700MW energy has been produced from sugar-cane waste [5]**.** Also, bio-waste supplies about 10-14% of worldwide energy. The cultivated bio-waste and waste biomass can be used for production of energy and fuel [6]. Productions of energy, fuel, and the value added chemicals are the best possible routes for the consumption of waste biomass. After harvesting and processing of agricultural products, a lot of residues are left which requires proper disposal. Unless disposed properly, it will decompose and will generate eventually methane gas [7]**.** Consumption of bio-waste for power and energy production could provide more work safety as well. Due to the high cost of commercial carbons, researchers are searching for the material which is cheap, affordable and easily accessible to produce activated carbon. In this respect, agricultural and industrial wastes can be those appropriate raw materials to produce appropriate activated carbon for the removal of heavy metals from the waste water **[**9-11].

Amaltash (*Cassia fistula*), commonly known as golden shower, purging cassia, Indian laburnum, or pudding-pipe tree, is a flowering plant in the subfamily, Caesalpiniaceae of the legume family, Fabaceae. The species is native to the Indian subcontinent (Jharkhand and Kerala) and adjacent regions of Southeast Asia. It is a popular ornamental plant and is also used in herbal medicine, supplement the diets of cattle, sheep, and goats fed with low-quality forages and waste to fuel or energy. Kinetic analysis of bio-waste is essential before the conversion of bio-waste into energy. Kinetic data of bio-waste provides information, which can be used for the process parameter optimization, designing of new gasification and pyrolysis reactor [8]. Moreover, it provides information about mathematical modelling simplification. The parameters forkinetic analysis include activation energy (Ea), frequency factor (A), and order of reaction (n). Thermo-gravimetric (TGA) analysis is thesimplest analytical tool to determine kinetic parameters of organicmaterials or different types of other thermochemical processes.

The present study is focused on the thermal kinetic of biomass to used material like amaltash seed powder (ASP) and amaltash peels powder (APP).

II. MATERIALS AND METHOD:

a. Sample collection and preparation ofamaltash seed & peels (ASP):

Amaltash seed and peels powder (ASPP) were collected from campus of Birla Institute of Technology, Mesra Ranchi, Jharkhand, India. ASPP has been taken and washed to remove impurities. After washing, seeds were oven dried at 60^0C for 48 hours and pulverized to less than 1.0 mm for better heat transfer efficiency. Steps for the preparation of bio char has been shown in Fig. 1. The powder has been kept in sheave shaker and all equal size particles have been distinguished. After getting all equal size particles the powder sample has been send for different characterisations and pyrolysis it at 400^0C[12].

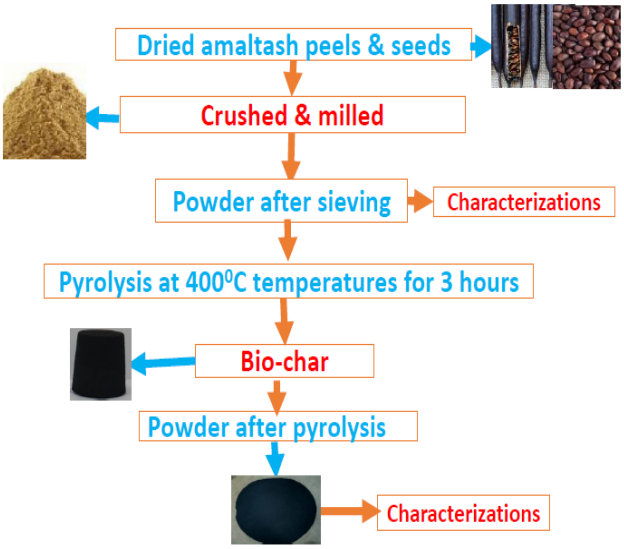

Fig. 1. Flow chart of amaltash seed powder (ASP) and amaltash peels powder (APP) preparation

b. Ultimate and Proximate analysis:

Ultimate analyses of elements (C, H, N and O) of the ASP and APP samples were carried out in an Elemental Analyser (M/s Elementar, Germany; Vario EL III). The analyser was connected with a column including two reactive beds, CuO, and electrolyte copper. A TCD was used for the detection of gases. The column was heated to 900 °C while helium gas was used as the carrier and reactive gases with the flow rate of 140 and 250 mL per minutes, respectively. ASPP samples (5.0 mg) were taken in small cup, putting into the column and the weight % of carbon, hydrogen, and nitrogen were calculated and also determine the bio-compositions present in the biomass ASPP such as hemicellulose, cellulose, and lignin.

Proximate analysis of Amaltash seed & peels powder (ASPP) was done using American Society for Testing and Materials (ASTM) standards. 1.0 gram of sun-dried ASPP was taken in a ceramic crucible and put in hot air oven operated at 105 °C for 1 hour. After 1 hour, the ASPP was removed from hot air oven and put in a desiccator for cooling. The weight difference between before and after heating was the responsible for the moisture content (MC) present in the ASPP. The volatile matter (VM) is an important constituent of ASPP which is directly related to the ignition rate of biomass. In a crucible (ceramics) 1.0 g of oven-dried biomass sample was taken and placed in the muffle furnace for 10 minutes at 925 ± 10 °C. After 10 minutes, the ASPP was removed and put in the desiccator. The initial and final weight difference provided the VM. Ash content was determined by putting 1gram of oven-dried ASPP in the same furnace at 580 ± 5 °C for 4 hours. The ASPP was removed from the furnace after 4 hours and put in the desiccator. The same ASPP was again put in the furnace until no further weight loss was observed. The weight difference of initial and final ASPP provided the amount of ash. The fixed carbon was determined by using the following equation:

Fixed Carbon (%) = 100− {MC (%) + VM (%) + Ash Content (%)} (1)

c. Characterisation:

Scanning electron micrographs and FESEM-EDX were recorded on Sigma-300, An accelerating voltage of 15kV and a magnification of 1000X were used. Thermo gravimetric analysis and differential thermal analysis were performed on a Shimadzu (Japan; DTG-60) in Nitrogen environment, at a different heating rate of 10-50ºC per minutes. Ultimate analyses of elements (C, H, N and O) of the Amaltash seed & peels powder (ASPP) samples were carried out in an Elemental Analyser (M/s Elementar, Germany; Vario EL III). Fourier transform infrared (FTIR) spectrum of the prepared catalyst was recorded in the range of 400-4000 cm^{-1} using Shimadzu (Corporation, Japan; IR-Prestige 21). For phase identification, X-ray diffraction (XRD) pattern was recorded using a Rigaku, Smart Lab 9kW diffractometer (Japan), using Cu-Kα radiation at 40 kV and 40 mA. The mean crystallite size (d) was calculated using the Debye-Scherer formula: $d=0.89\lambda/\beta\cos\theta$, where, d is the mean crystallite diameter, λ is the X-ray wavelength (1.54056 Å), and β is the effective line width of the observed X-ray reflection. β is the line broadening at full width at half maximum (FWHM), after subtracting instrumental broadening, in radian.

d. Thermal Kinetic:

The common rate equation governs in all kinetic studies can be generally written as follows:

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \quad (2)$$

Where $\frac{d\alpha}{dt}$ is the rate of conversion at a constant temperature, $f(\alpha)$ is the reaction model which describes the changes in the physical or chemical properties, k is the rate

constant, dependent on temperature T.
The conversion rate α (using TGA records) is defined as:

$$\alpha = \frac{w_o - w_t}{w_o - w_f} \quad (3)$$

Where w_o, w_t and w_f are the initial mass of the sample at t=0, mass of the sample at time t and mass of the sample at final degradation respectively.
According to the Arrhenius relationship, the rate constant is the function of temperature and can be written as follows:

$$k(T) = \mathrm{k}_0 \exp(\tfrac{-E}{RT}) \quad (4)$$

Where k_o is the pre-exponential factor, *R* is the gas constant (8.314 J/K mol), *and E*is the activation energy (kJ/mol).
Using equation (2) and (4) following equation can be derived:

$$\frac{\mathrm{d}\alpha}{\mathrm{dt}} = \mathrm{k}_0 \exp(\tfrac{-E}{RT})\ f(\alpha) \quad (5)$$

Equation (5) describes the relationship between the conversion rate, rate constant and temperature which is used for recording the experimental data. To conduct kinetic study in TGA one of the ways is to use a heating rate, $\beta = {}^{dT}/_{dt}$
Equation 4 can be written as follows:

$$\frac{\mathrm{d}\alpha}{\mathrm{dT}} = \frac{\mathrm{k}_0}{\beta}\exp(\tfrac{-E}{RT})\ f(\alpha) \quad (6)$$

Equation (6) is most basic equations used for kinetic study of thermal degradation.
E, activation energy can be estimated using various models. Generally used methods are Flynn-Wall-Ozawa (FWO), Kissinger-Akahira-Sunose (KAS) and Kissinger**[13-15].** In this study, we used F-W-O method which gives slope (-E/RT) from the line obtained by plotting $log\ \beta$ against 1/T at fixed degree of conversion.
F-W-O fitting equation is given below [2]:

$$\log f(\propto) = log\left\{\frac{k_0 E}{R}\right\} - \log\beta - 2.315 - 0.4567\ \frac{E}{RT} \quad (7)$$

III. RESULT AND DISCUSSION:

a. Physicochemical analysis:

Physicochemical characterization of two waste biomass materials such as amaltash seed powder (ASP) &amaltash peels powder (APP)along with cotton stalk and sugarcane baggage [16] is presented in Table 3.1. From Table 1 confirms that all biomass samples contain less than 10% of moisture. The biomass which contains less than 10% moisture is considered best feedstock for pyrolysis and combustion [17]**.** Moreover, biomass has benefit because unlike other fuel it does not contain a higher amount of N and S. Both amaltash seed powder (ASP) and amaltash peels powder (APP)(Table 3.1) observed with important calorific value (16.44-17.20 MJ per kg). Also, both biomasses observed with low nitrogen content with negligible sulphur content. These observed results indicate that this biomass can be used as feedstock for fuel, energy and bio-adsorbent production.

Table 1: Physicochemical characterization of Amaltash peels and Amaltash seeds

Analysis	Amaltash peels	Amaltash seeds	Cotton stalk Raj et al. (2015)	Sugar cane baggage (Raj et al. (2015)
Proximate analysis (wt.%)				
Moisture content	7.09 ± 0.3	6.88 ± 0.2	8.9	10.0
Volatile matter	77.03 ± 0.2	78.03 ± 0.1	71.0	76.0
Ash content	3.07 ± 0.03	2.14 ± 0.01	3.5	4.4
Fixed carbon	11.16 ± 0.1	13.09 ± 0.2	16.6	9.6
VM/FC	6.9	5.96	4.27	7.91
Ultimate analysis (wt. %)				
C	51.30	48.83	46.8	43.2
H	6.03	8.08	6.4	6.2
O	41.99	42.56	46.8	43.2
N	0.63	0.51	0.3	0.4
S	-	-	0.2	0.8
C/H	0.69	0.69	7.4	6.9
Heating value (MJ/kg)	16.44 ± 09	17.20 ± 09	19.2	17.2
Hemicellulose (HC)	15.35	14.59	19.2	18.7
Cellulose (C)	55.92	52.36	39.4	36.6
Lignin (Lg)	10.55	11.18	23.2	19.8

b. Thermo-gravimetric Analysis (TGA) and Differential Thermal Analysis (DTA):

The curve of TGA and DTA were used to study the thermal degradation behaviour of ASPP, as shown in **Figure 2**. The DTA plot of ASPP shows three major endothermic peaks which indicated decomposition occurs in three main processes . The initial weight loss of10% in the temperature range of 30-150^{o}C, mainlycorresponds to the evaporation of physically absorbed water. DTA curve also shows first sharp endothermic peak at 59^{o}C with change in enthalpy of -1.4 kJ/g. TG curve revealed that above 150^{o}C, thermal stability is gradually decreasing and decomposition of the ASPP occurs with the complete decomposition at 626^{o}C. The second stage decomposition process occurs in the temperature range of 150-332^{o}C (weight loss~ 64%), showing second endothermic peak at 152^{o}C with change in enthalpy of -1.67kJ/g. This result is attributed to the thermal depolymerisation of hemicelluloses, pectin's, the cleavage of glycosidic linkage of cellulose and some parts of lignin [18-19]. At a temperature range of 350-625^{o}C, third and last stage decomposition process occur at peak 415^{o}C (change in enthalpy of -3.02 kJ/g) showing weight loss of~ 99%. This indicates the thermal degradation reactions taking place for the major constituent of the biomass that is cellulose and remaining lignin [19-21].

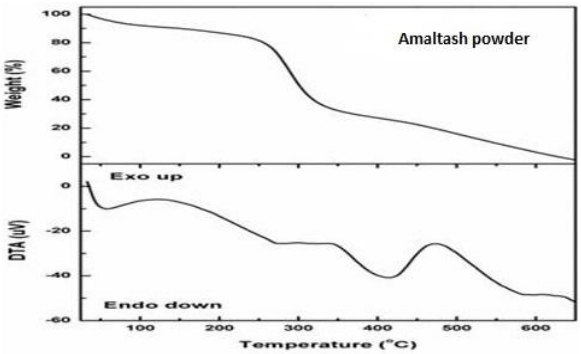

Fig.2. TG-DTA thermo grams of amaltash seed & peels powder (ASPP)

Table.2: Thermo-analytical data TG/DTG-DTA of amaltash seed& peels powder (ASPP)

Temperature range (^{o}C)	DTG Peak Temperature (^{o}C)	Weight loss (%)	DTA peak temperature (^{o}C)
30-150	47	10	58endo (-1.41 kJ/g)
150-332	293	64	151endo (-1.67 kJ/g)
350-625	297	99	414endo (-3.02 kJ/g)

c. Fourier Transform Infrared Analysis (FTIR):

The FTIR spectral analysis revealed several functional groups on the surface of biomass shown in figure 3. The absorption peak observed at wave-number 3279 cm^{-1} is associated with O-H stretching vibration. The wave-numbers around 2927 cm^{-1} and 2364 cm^{-1} are corresponding to the C-H aliphatic stretching vibration. The peak displayed at 1643 cm^{-1} is attributing to the stretching band of the carboxyl double bond from carboxyl functional group. The peak around 1150 cm^{-1} is indicative of P=O stretching present in phosphate group. It has been observed by the [22] Kim et al., 2015 the carboxyl group present in biomass plays a significant role in the cation metal removal. The peak displayed at wavenumber 1007 cm^{-1} is assigned to the O-H stretching of primary alcohol group. The peak at 929 cm^{-1} shows the C-C links in the bio-carbon. The presence of polar groups on the bio-carbon surface is likely to provide the considerable cation exchange capacity to the absorbent [23].

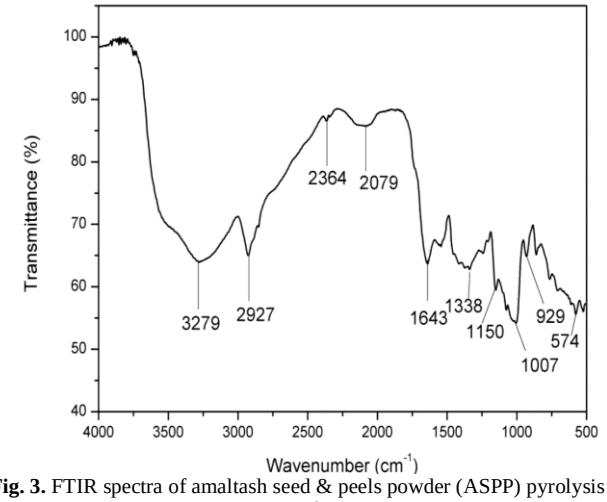

Fig. 3. FTIR spectra of amaltash seed & peels powder (ASPP) pyrolysis at 400^{o}C

d. Thermal kinetic study of amaltash:

(1). Activation energy of thermal kinetics of amaltash seed powder (ASP) &amaltash peels powder (APP):

Activation energy was estimated using TGA data at different heating rates (10, 15, 20, 25, and 30^{o}C/min). The average activation energy was determined using isothermal Flynn-Wall-Ozawa (FWO), Kissinger-Akahira-Sunose (KAS) and Kissinger methods from the thermal degradation conversion range of 0.1-0.9. Figure (3.5-3.10) shows the linear plot amaltash seed & peels powder (ASPP) at various conversion rates. At various thermal degradation conversion rates, Activation energy was estimated from the slope of the curves. Summary of the activation energy values with R^2 values are given in Table (3-8). From the result, it can be observed that the activation energy varies with the varying rate of conversion, indicating high degree of probability to present more than one step reaction. Higher activation values is observed in the middle con

version rate (α = 0.3-0.6) whereas lower activation energy values were observed for lower and higher conversion rate. Activation energy is the minimum amount of energy required to initiate a reaction. Activation energy is dependent on the pyrolysis reaction mechanism; higher value of activation energy indicates slower reaction [14]. This variation in activation energy is probably observed due to the mechanism involving the thermal decomposition of the biomass matter is different. This could be explained by the TGA curve (Figure 4-9). The thermal degradation temperature forα = 0.1-0.2 is around 270°C and for α = 0.5 is around 312°C. This is the part of the TGA curve where maximum thermal degradation takes place. The activation energy observed is 130.69 kJ/mol, which correspond to the degradation of hemicellulose, cellulose and lignin [25]. According to [26] Mohamed (2013), value of the activation energy indicates about the type of adsorption taking place, which is physical or chemical adsorption. For the physical adsorption processes activation values usually found in the range of 0-40 kJ/mol, while higher activation energies values i.e. in the range of 40-800 kJ/mol indicates chemical adsorption processes.

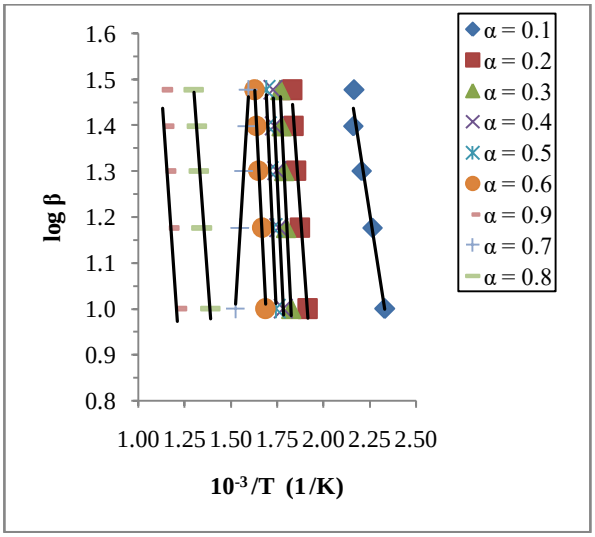

Fig. 4: Curves of fitting to kinetic model by F-W-O to various % conversion for ASP

Table 3: Kinetic parameters from F-W-O method with fitted equation for ASP

Conversion rate (α)	R^2	E, (kJ/mole)
0.1	0.97	46.54
0.2	0.98	99.88
0.3	0.99	145.77
0.4	0.99	151.36
0.5	0.99	154.92
0.6	0.99	143.63
0.7	0.99	120.02
0.8	0.97	99.23
0.9	0.97	107.08
	Average	**118.712**

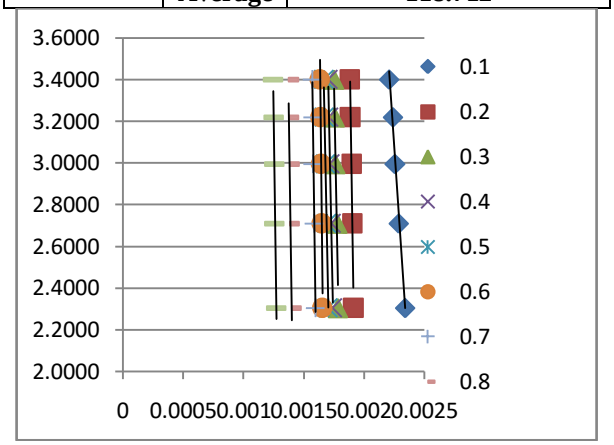

Fig. 5: Curves of fitting to kinetic model by F-W-O to various % conversion for APP

Table 4: Kinetic parameters from F-W-O method with fitted equation for APP

Conversion rate (α)	R^2	E, (kJ/mole)
0.1	0.9926	67.6658
0.2	0.9598	117.5495
0.3	0.9195	131.6486
0.4	0.9898	132.9790
0.5	0.9951	138.8483
0.6	0.9559	140.9671
0.7	0.9718	150.2153
0.8	0.9534	173.2369
0.9	0.9094	174.1285
	Average	136.36

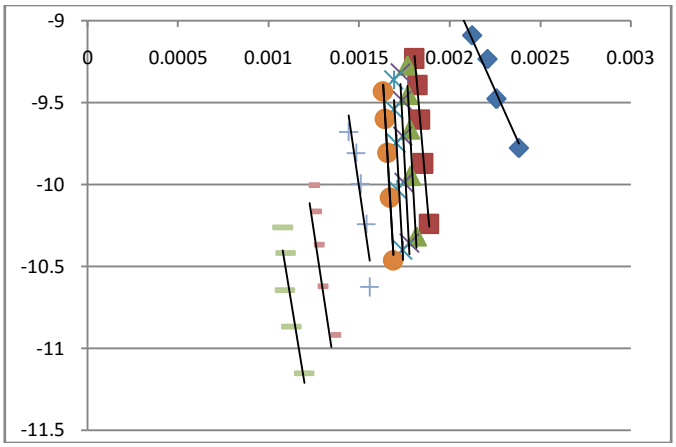

Fig. 6: Curves of fitting to kinetic model by KAS to various % conversion for ASP

Table 5: Kinetic parameters from KAS method with fitted equation for ASP

Conversion rate (α)	R^2	E, (kJ/mole)
0.1	0.97	20.5123
0.2	0.992	106.203
0.3	0.9128	166.3049
0.4	0.9014	174.4028
0.5	0.9306	164.1766
0.6	0.9912	153.0192
0.7	0.8928	64.79765
0.8	0.908	62.39241
0.9	0.8548	57.46055
	Average:	**107.6966**

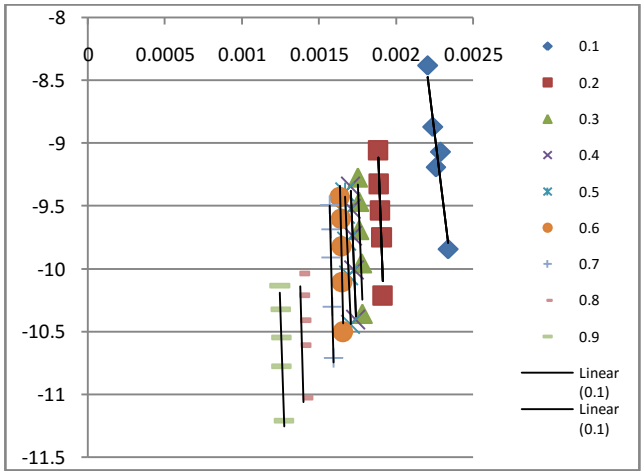

Fig. 7: Curves of fitting to kinetic model by KAS to various % conversion for APP

Table 6: Kinetic parameters from KAS method with fitted equation for APP

Conversion rate (α)	R^2	E, (kJ/mole)
0.1	0.9029	82.83072
0.2	0.933	150.7305
0.3	0.9136	154.2412
0.4	0.989	155.9531
0.5	0.9947	180.8964
0.6	0.9538	208.0279
0.7	0.9741	216.5896
0.8	0.9669	217.6416
0.9	0.933	218.1037
	average	158.785

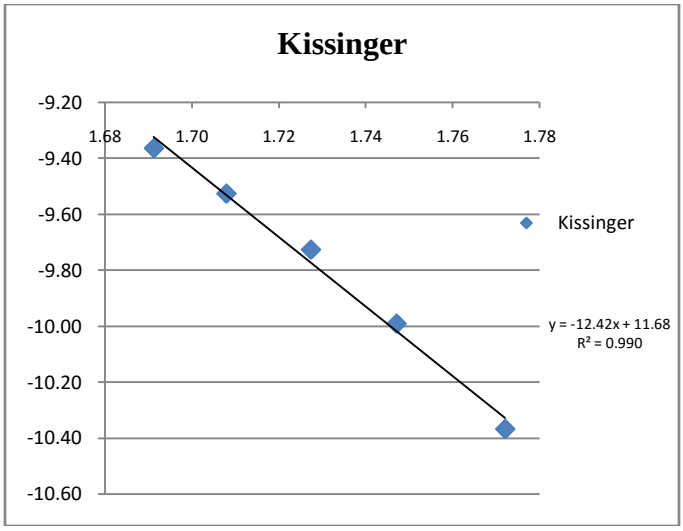

Fig. 8: Curves of fitting to kinetic model by Kissinger to various % conversion for ASP

Table 7: Kinetic parameters from Kissinger method with fitted equation for ASP

Kissinger				
Beta (deg C/min)	Tp(deg. C)	1000/Tp	1/Tp	ln(beta/Tp^2)
10.00	291.32	1.77	0.00	-10.37
20.00	305.92	1.73	0.00	-9.73
25.00	312.51	1.71	0.00	-9.53
30.00	318.28	1.69	0.00	-9.36
Activation energy: 103.25988 kj/mol				

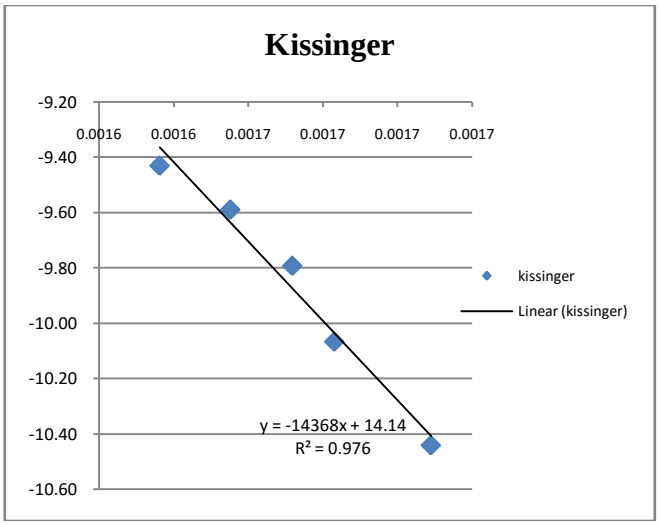

Fig. 9: Curves of fitting to kinetic model by Kissinger to various % conversion for APP

Table 8: Kinetic parameters from Kissinger method with fitted equation for APP

Kissinger				
Beta(deg C/min)	**Tp(k)**	**1000/Tp**	**1/Tp**	**ln(beta/Tp^2)**
10.00	585.15	1.7090	0.0017	-10.44
15.00	594.15	1.6831	0.0017	-10.07
20.00	598.15	1.6718	0.0017	-9.79
30.00	611.15	1.6363	0.0016	-9.43
Average activation energy: 119.45 kj/mol				

IV. CONCLUSION:

Pyrolysis behaviour and thermal stability of amaltash seed powder (ASP) & amaltash peels powder (APP)biomass were investigated by using thermo-gravimetric analysis. Thermo-gravimetric analysis confirmed that with increase in heating rate, degradation peak shifted towards higher region without negative breakdown behaviour. FTIR analysis confirmed the presence of useful functional groups in raw biomass. Thermo-gravimetric study of ASP and APP shows maximum thermal decomposition in the temperature range of 150-380^{o}C. Kinetic parameters are in good promise with other reported biomass and the activation energy was found to be 118.70 kJ/mole and 136.34 kJ/mole from F-W-O model; 107. KJ/mole and 158.78 kJ/mole from KAS model; 103.258 kJ/mole, and 119.45 kJ/mole from Kissinger model for ASP, APP biomass respectively.Based on these results, it is confirmed that these kinds of biomass can be used as potential feed-stocks for fuel or energy generation and bio adsorbent. We conclude that amaltash seed powder (ASP) & amaltash peels powder (APP)biomass based fuel or energy, bio-adsorbent, being a naturally, abundant and low-cost fuel and bio-adsorbent, waste material, might be a suitable local alternative for the removal of heavy metals from wastewater. This study shows a new trend for using waste materials as fuel or energy, adsorbent for the benefit of environmental pollution control.

V. ACKNOWLEDGEMENT:

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