Thermogravimetric and Kinetic Study of Pyrolysis of Corn Cob Biomass

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ABSTRACT

Agricultural residues are potential renewable biomass sources for bio-energy production. The objective of the work is to determine the pyrolysis kinetic parameters of corn cob biomass. Three different heating rates of 10, 20, and 30 °C/min were taken into account in the thermogravimetric analysis. The Kissinger, Flynn Wall Ozawa (FWO), and Kissinger Akahira Sunose (KAS) model-free methods were employed to calculate the kinetic parameters by the use of the data obtained from TGA. The thermal decomposition process shows three basic phases of pyrolysis: removal of moisture content, primary and secondary pyrolysis. The experimental values were compared with the obtained values from FWO and KAS models; implying that the model values were in good agreement with experimental results. The values of kinetic parameters obtained from Kissinger, FWO, and KAS methods are very similar to their average values of 115, 136, and 131 kJmol^{-1}, respectively. Gas Chromatograph-Mass Spectroscopy (GC-MS) analysis of pyrolysis products is obtained, showing that bio-char and bio-oil contain 10 and 15 different compounds, respectively.

1. INTRODUCTION

Biomass is a renewable energy source that is abundant in nature and has zero net carbon emission. Hence, it is widely used as feedstocks for biofuel production through thermochemical or biochemical conversion techniques. The thermochemical conversion includes combustion, liquefaction, gasification, pyrolysis, etc. Pyrolysis is the process of converting biomass into fuel at higher temperatures in an inert atmosphere. Pyrolysis has received remarkable attention for producing pyrolytic oils that can be used as fuel and serves the purpose to overcome the demand of petroleum oil reserves. The pyrolytic oil can be easily stored, upgraded, and transported; it is added to petroleum refinery feedstock later. On the other hand, it contains valuable chemicals that can be recovered and used [1,2].

The biomass characteristic is imperative for the selection of the proper energy conversion technique. Thermogravimetric analysis (TGA) is a common and widely used technique employed to study the thermal degradation of biomass [3]. Many authors have reportedly applied TGA to study the thermal degradation rate of different biomasses [4], coal [5], rice straw [6], bagasse [7], Miscanthus [8], forestry residue [9], agriculture waste fiber [10], and Folnak drug [11].

Various methods are available to analyze the biomass kinetic data and are classified into two types: model-free and model-fitting methods. In model-free or the iso-conversional method, the calculation is performed based on kinetic curves at different heating rates for the same value of conversion from which the activation energy is evaluated for the fitted conversion point, whereas the kinetic parameters are calculated using the function in a set of parameters in model-fitting methods and a predicted dataset returns. The error is the difference observed between the obtained data and the

model's prediction data for any given set of model parameters. The best parameters that minimize this difference are chosen for kinetic analysis [12,13]. The model-fitting method is mostly used to determine directly the kinetic constants from a TGA data obtained from a single solid-state reaction. The method enjoys a number of disadvantages, especially their inability to determine the appropriate reaction model for the non-isothermal condition. The method produces higher values of kinetic constant; hence, this method is abandoned and the iso-conversional methods are used instead. The advantage of the model-free method is its simplicity and ability to avoid errors relating to the selection of a kinetic model. These models estimate the activation energy, E, for a specific conversion. The disadvantage involved in this method is that a series of measurements are to be made for the same sample mass at different heating rates and inert gas flow whose differences can cause errors [14]. Based on Arrhenius law, the kinetic parameters can be calculated through different methods for different types of biomass [15]. An increase in heating rate results in a slight change in the conversion curve and a maximum decomposition rate towards higher temperatures. Kinetic parameters are extremely important for optimizing the process conditions and modeling the reactor. Many authors have studied thermogravimetric analysis of biomass material and determined the kinetic parameters of the sample, which are useful for pyrolysis design [16]. Prakash et al. [17] studied kinetic parameters of rice husk, saw dust, and wheat husk using thermogravimetric analysis. The analysis was carried out in an inert nitrogen atmosphere from the ambient temperature to 800 °C at a heating rate of 10 °C/min. The author reported kinetic parameters and the order of the reaction for all the samples. Kinetic parameters of 28 biomass samples were experimentally determined using thermogravimetric analysis for four different heating rates by Alvarez et al. [18]. Kumar et al. [19] stated that thermogravimetric analysis of corn stover was performed at

three different heating rates in nitrogen and oxidizing atmospheres. The authors determined the kinetics parameter, and found that mass losses of corn stover in both inert and oxidizing atmospheres occurred in three stages. Prakash and Sheeba Narayanan [20] studied the thermogravimetric analysis of coir–pith, bagasse, casuarina leaves, and groundnut shell. The samples were studied in an inert atmosphere from ambient temperature to 800 °C at a heating rate of 20 °C/min and reported the kinetic parameters. El-Sayed et al. [21] studied the thermogravimetric analysis of Egyptian biomasses such as sugarcane bagasse and cotton stalk powders at different heating rates. Observation showed two distinct reactions to the two biomasses, and the kinetic parameters were evaluated in the nitrogen atmospheric condition. Mansaray et al. [22] carried out the thermogravimetric analysis of four varieties of rice husk at a heating rate of 20 °C/min in an oxygen atmosphere and reported the kinetic parameters.

The objective of this study is to investigate the thermal behavior of corn cob and determine the effect of the heating rate. The pyrolysis products including bio oil and bio char are analyzed using Gas Chromatography-Mass Spectroscopy (GC-MS). The kinetic parameters of biomass can be used to design a gasification and pyrolysis reactor.

2. MATERIALS AND METHOD

2.1. Materials

Corn cob biomass was collected from a village in south Tamilnadu, and the initial moisture content of the sample was found to be 6.3 %. The sample was kept in a drier at 40 °C to remove the moisture and, then, the sample was ground. The powder form (Figure 1) of the biomass particle was analyzed by a particle size analyzer and was found to be 234 μm in size. The ultimate and proximate analysis of the sample is shown in Table 1.
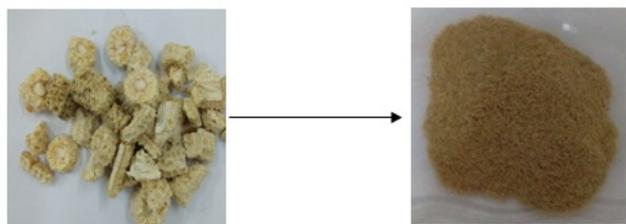

Figure 1. Corn cob biomass after grinding.

Table 1. Corn cob characterization.

Proximate analysis		Ultimate analysis	
Elements	Composition (wt %)	Elements	Composition (wt %)
Volatiles	63.7	Carbon	35.70
Fixed carbon	12	Hydrogen	8.06
Ash	18	Nitrogen	1.12
Moisture	6.3	Sulphur	0
HHV (MJ/kg)	18.12	oxygen	37.10

2.2. Thermogravimetric analysis

Thermal decomposition of biomass was analyzed using Perkin Elmer-Pyris 7 (Model Q500) thermogravimetric analyzer (TGA). The TGA balance sensitivity for the 1000 mg range is

1 μg -1000 mg; the operating temperature ranges from 15-1000 °C and the heating rate of furnace is from 0.1 to 100 °C/min. Nitrogen is used as an inert gas with a flow rate of 3.0 L/min, and the standard experimental procedure is followed in this study to analyze the Corn cob biomass sample. Three heating rates of 10, 20, and 30 °C/min are performed for the present experiment, and the TGA results are plotted.

2.3. Pyrolysis reactor setup

The pyrolysis experiment was carried out in the setup, as depicted in Figure 2. 50 g of biomass sample was taken in the pyrolysis reactor. The reactor was heated at a rate of 10 °C/min. The temperature of the reactor increased from ambient temperature, and the first oil drop was noticed after 38 min at 237 °C. The temperature of the reactor was maintained at 350-390 °C, and the condensed pyrolysis vapors were collected as bio oil for further analysis.
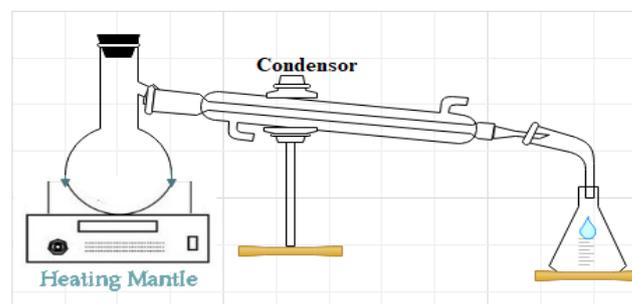

Figure 2. Illustration of experimental setup of pyrolysis reactor.

2.4. Model-free methods

The model-free approach is denoted by an iso-conversional method to analyze the activation energy on the points of conversion for isothermal or non-isothermal experiments. The application of the model-free method is consistent, and standard kinetic data can be obtained from non-isothermal data. The model-free equation for three different methods is given below [23].

Kissinger method:

$$l\left(\frac{\beta}{T_m^2}\right) = nln\left(\frac{AR}{E}\right) - \frac{E}{RT_m} \tag{1}$$

Flynn–Wall–Ozawa method (FWO):

$$ln\ (\beta) = ln\left(\frac{AE}{Rg(\alpha)}\right) - 5.331 - 1.052\frac{E}{RT} \tag{2}$$

Kissinger–Akahira–Sunose (KAS):

$$ln\left(\frac{\beta}{T^2}\right) = ln\left(\frac{AR}{E\ g(\alpha)}\right) - \frac{E}{RT} \tag{3}$$

where E is the activation energy in kJ/mol, T is the absolute temperature (K), T_m is the peak temperature (K) of the DTG curve, A is the frequency factor, (s^{-1}), (β) represents the different heating rates (°C/min), g (α) is a constant at a known value of fractional conversion, and R is the gas constant, $kJmol^{-1} K^{-1}$.

3. RESULTS AND DISCUSSION

TGA was performed to determine the thermal characteristics of corn cob at three heating rates. The variation of mass loss with respect to temperature was monitored to illustrate the

thermal degradation of the biomass sample. The TGA and DTG curves for corn cob at different heating rates (10, 20, and 30 °C/min) are shown in Figures 3 and 4. A common trend of decrease in mass loss with respect to temperature was observed.
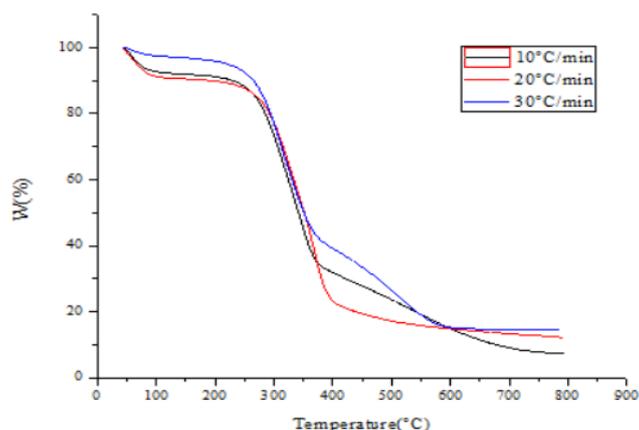

Figure 3. Thermal behaviour of biomass at different heating rates of corn cob.
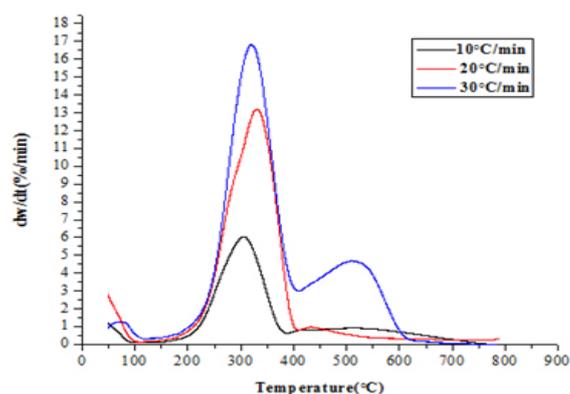

Figure 4. DTG curves of biomass at different heating rates of corn cob.

Biomass is made up of three major components: lignin, hemi-cellulose, and cellulose. Degradation rates may differ for each component on the basis of composition. Thus, to determine the thermal degradation behavior, the same kinetic parameter cannot be incorporated throughout its thermal transition of biomass. The thermal degradation profile of the corn cob at three different heating rates (10, 20, and 30 °C min^{-1}) under the inert nitrogen atmosphere is shown in Figure 3. According to Figure 3, the thermal decomposition is divided into three phases: moisture content, primary pyrolysis, and secondary pyrolysis. The first reaction zone concerns the release of moisture or dehydration at 29-98 °C for corn cob. The second stage is primary pyrolysis that corresponds to the decomposition of hemicellulose and cellulose between 98-390 °C for corn cob. It may correspond to the loss of volatile compounds in the sample and is referred to as the active pyrolysis stage due to the faster rate of degradation. It is followed by the third stage, i.e., secondary pyrolysis wherein the degradation of lignin is observed at 390-900 °C for corn cob. During this stage, the mass-loss rate is reduced due to non-volatile stable phenolic lignin residues. The degradation rates depend on the heating rates, and it was concluded that

the higher the heating rate, the greater the liquid yield during pyrolysis. The differential thermogravimetric analysis (DTG) plot for the sample is shown in Figure 4. It is shown that an increase in the heating rates results in shifting the temperature peaks to higher values without a change in the thermal decomposition outline. At different heating rates, the temperature peaks observed are 305.7 °C, 329 °C, and 326 °C at 10, 20, and 30 °C/min, respectively.

3.1. Kinetic analysis

The results obtained from TG/DTG analysis under inert atmospheric conditions for the biomass pyrolysis were used to determine the kinetic parameters. Three models such as Kissinger, Flynn Wall Ozawaand, and Kissinger-Akahira-Sunose were used to calculate the parameters such as activation energy and frequency factor. In the Kissinger method, the peak temperature (T_m) is observed from DTG curve (Figure 4) and the value is constant under different heating rates. A linear line is obtained using Kissinger method, as shown in Figure 5, from which kinetic constants are calculated. The activation energy and frequency factor are obtained from the linear regression line slope and intercept, as shown in Table 2. The activation energy and frequency factor are 115 kJmol^{-1} and 2.9×10^{10} min^{-1}, respectively, for the corn cob. The activation energy and frequency factor were calculated using KAS and FWO methods as a function of conversion. The model plots are shown in Figures 6 and 7, respectively. Different ranges of conversion from 0.2 to 0.65 are chosen for calculating the kinetic constants based on the model fitted to the linear line using the iso-conversional method. The activation energy and frequency factor obtained from two different iso-conversional methods are shown in Table 3. According to Table 3, activation energy values are not analogous at various extents of conversion, because most solid-state reaction mechanisms tend to have a complex multi-step reaction. Based on the tables, the activation energy rises from about 113 kJ mol^{-1} at initial conversions to nearly 170 kJmol^{-1} for 50 % conversion; afterwards, it has dropped to 100 kJ mol^{-1} at the end of the reaction. The activation energy value was low at the beginning due to the breaking of weaker bonds and the removal of volatile matters from the biomass structure. In the primary pyrolysis process of the given biomass, all the strong bonds present in the biomass are engaged; hence, larger activation energy is required to degrade these molecules. The activation energy value increased up to 50 % conversion, when primary pyrolysis proceeds further. The increase occurs due to the breaking of strong covalent bonds present in the biomass material.
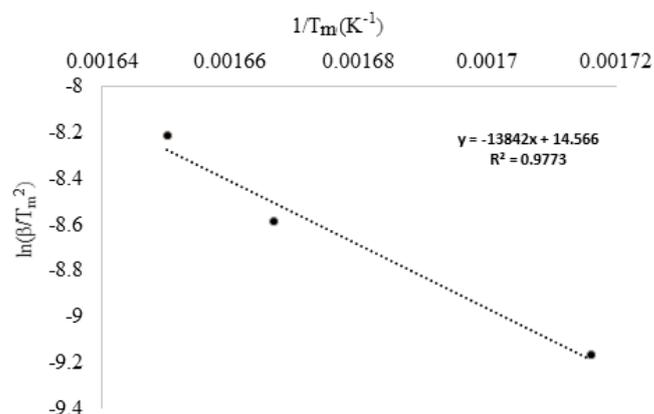

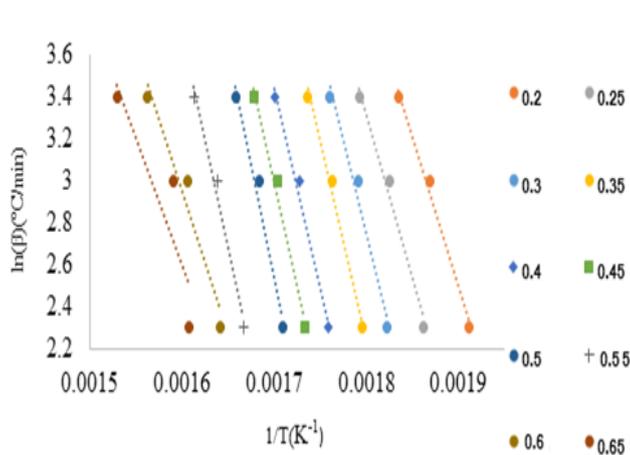**Figure 5.** Kissinger plot of corn cob at different heating rates.

Figure 6. Flynn Wall Ozawa plot of corn cob at different heating rates.
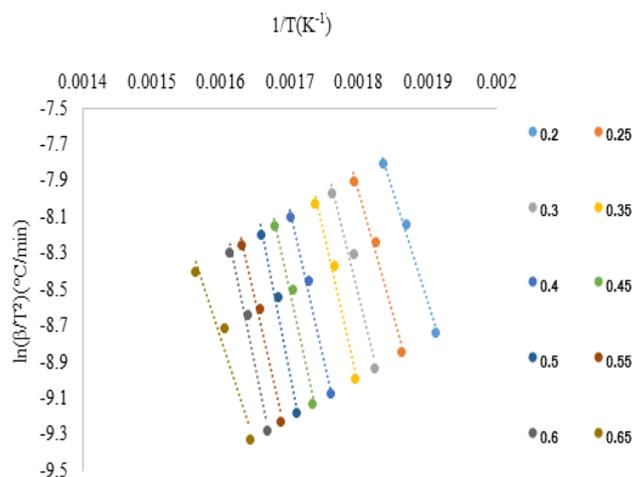

Figure 7. KissingerAkahiraSunose plot at different heating rates of corn cob.

Table 2. Kinetic parameters of corn cob determined using Kissinger method.

Sample	Heating rate (°C/min)	T_{max}	E (kJ/mol)	A (min^{-1})	R^2
Corn cob	10	305.7	115	2.9×10^{10}	0.97
	20	329			
	30	320			

Table 3. Kinetic parameters of con cob determined using Flynn-Wall-Ozawa method for three different heating rate.

Conversion (α)	E (kJ/mol)	A (min^{-1})	R^2	E (kJ/mol)	A (min^{-1})	R^2
	Flynn-Wall–Ozawa method			Kissinger Akahira Sunose method		
0.20	113.00	1.29×10^{11}	0.99	100.80	5.1×10^{6}	0.98
0.25	125.50	1.39×10^{12}	0.98	113.89	7×10^{8}	0.98
0.30	140.35	2.36×10^{13}	0.99	129.49	1.6×10^{9}	0.93
0.35	148.80	1.19×10^{14}	0.98	138.37	6.9×10^{9}	0.98
0.40	150.90	1.25×10^{14}	0.98	140.55	1.03×10^{10}	0.98
0.45	157.50	3.40×10^{14}	0.98	147.60	2.75×10^{10}	0.98
0.50	169.90	3.25×10^{15}	0.98	160.46	3.08×10^{11}	0.97
0.55	151.00	5.49×10^{13}	0.97	151.76	2.18×10^{10}	0.98
0.60	109.00	5.95×10^{9}	0.95	140.79	3.7×10^{9}	0.97
0.65	95.70	3.70×10^{8}	0.79	96.00	2.26×10^{5}	0.94

The conversion values go above 50 %, the activation energy slowly decreases because most of the stable bonds are broken during the decomposition process. In the next stage, the activation energy is low at higher conversion since the thermal decomposition decreases with an increase in temperature. At higher temperatures, the reaction taking place depends on the accessibility of molecules. Increasing temperatures reduces the probability of accessing the molecules; hence, the activation energy is low. The arithmetic means of the activation energy calculated by KAS and FWO were found to be 136 and 131 kJmol^{-1}, respectively, which are slightly closer to the average activation energy obtained from the Kissinger method (115 kJmol^{-1}). The results obtained by KAS and FWO methods are precise and consistent.

## 3.2. GC-MS analysis of bio char and bio oil

Figure 8 shows the obtained bio char and bio oil product yield. Yield of biochar, bio oil, and gas residues are 36 %, 37.64 %, and 26.36 %, respectively. The pyrolysis products were analyzed using GC-MS to determine the compounds produced during pyrolysis. The GC-MS analysis was done by the Agilent Technologies 7890B, the temperature and pressure were set at 185 °C and 8.0 Pa, and the septum purge flow was set at 3 ml/min. The volatile organic compounds peak area of bio char and bio oil are shown in Tables 4 and 5, respectively. According to the GC analysis, hydrocarbons of 18 % and 15.75 % are present in the bio char and bio oil, respectively. The aromatic esters of 31 % and 66.6 % are also present in the bio oil and bio char, respectively, and some other compounds of the mass spectra database match 90 % of the compounds. According to the table, plenty of compounds are formed due to the decomposition of lignin and cellulose present in the biomass.

Table 4. Aliphatic and aromatic hydrocarbon compounds detected in bio char.

Retention time (min)	Name of the compound	Molecular formula	Molecular weight (g/mol)	Peak area (%)
4.72	2-methylcyclopentanol	$C_6H_{12}O$	100.161	12
7.25	Propenamide N-hydroxymethyl	$C_4H_9NO_2$	103.121	7.012
10.97	4-Piperidinopyridine	$C_{10}H_{14}N_2$	162.236	11.0
14.17	Calcium bis (2,4 pentanedianato-0,0′)	$C_{10}H_{14}CaO_4$	238.296	9.0
16.17	Magnesium bis (2,4 pentanedianato-0,0′)	$C_{10}H_{14}MgO_4$	222.52	9.0
17.12	4H-1 Benzopyran 4-one,7-hydroxy 2 (4-hydroxyphenyl)	$C_{15}H_{12}O_4$	256.25	10.0
17.8	Phenol,2-Phenylmethyliminomethyl4-nitro	$C_{13}H_{10}N_2O_3$	242.234	10.0
18.83	10-octadecenoic acid, methyl ester	$C_{18}H_{34}O_2$	282.468	10.0
19.68	10,13 Eicosadienoic acid, methyl ester	$C_{21}H_{38}O_2$	322.533	10.0
20.68	Isopropyl stearate	$C_{21}H_{42}O_2$	326.565	11.0

Table 5. Aliphatic and aromatic hydrocarbon compounds detected in bio oil.

Retention time (min)	Name of the compound	Molecular formula	Molecular weight (g/mol)	Peak area (%)
4.35	4-cycloocten-1-one	$C_8H_{12}O$	124.183	3.2
5.65	Spiro[2,4]heptan-4-one	$C_7H_{10}O$	110.156	4.3
7.5	Octahydro-1-oxa cyclopropaindene	$C_9H_{14}O$	138.21	5.55
9.08	Phenol,2-ethyl	$C_8H_{10}O$	122.167	5.17
10.5	5-Nonynoic acid methyl ester	$C_{10}H_{16}O_2$	168.236	5.99
11.93	Eugenol	$C_{10}H_{12}O_2$	164.204	6.7
13.6	Cyclopenta[1,3]cyclopropa[1,2]cyclohepten 3[3aH]-one1,2,3,6,6,7,8-hexa-hydro-6-6-dimethyl	$C_{13}H_{18}O$	190.286	7.37
18.55	1-oxacyclopentadecan-2-one-15,15-dimethyl	$C_{14}H_{26}O_2$	226.36	8.25
19.58	Pentadecanoic acid,13-methyl-methyl ester	$C_{16}H_{32}O_2$	256.43	8.82
20.63	n-hexadecanoic acid	$C_{16}H_{32}O_2$	256.43	13.6
21.27	Oleic acid	$C_{18}H_{34}O_2$	282.468	10.1
22.67	Hexadecanoic acid-14-methyl-methyl ester	$C_{22}H_{42}O_4$	370.574	10.1
23.68	6,11-Eicosadienoic acid, methyl ester	$C_{20}H_{36}O_2$	308.506	7.86
26.12	Tetradecanoic acid 2-Iodo	$C_{14}H_{28}O_2$	228.376	6.3
30.28	Octadecanoic acid,2,3,dihydroxy propyl ester	$C_{21}H_{42}O_2$	282.468	3.89
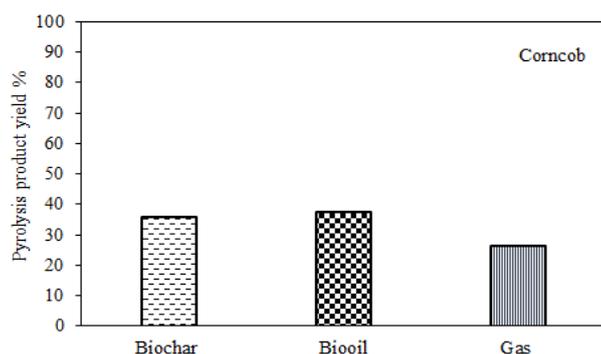
Figure 8. Pyrolysis products.

4. CONCLUSIONS

In this study, the kinetic analysis of pyrolysis of corn cob biomass was conducted through thermogravimetric analysis in the temperature range of 30-900 °C at three different heatingrates of 10°, 20°, and 30° C/min under the inert atmospheric condition. It was concluded that the primary pyrolysis of corn cob biomass process occurred in the temperature range of 240-360 °C. The kinetic parameters were calculated in accordance with the thermal behavior of corn cob by three different model-free methods such as Kissinger, Ozawa, and KAS. The results were useful to optimize the biomass pyrolysis process conditions. In Kissinger method, the kinetic parameters were the same for the entire pyrolysis

process. However, in FWO and KAS methods, frequency factor and activation energy varied with conversion during the process. The activation energy value obtained from the Kissinger method was115 kJ mol^{-1} and found within the range of values obtained by the FWO and KAS methods; it is very similar to their mean values that are 136 and 131 kJmol^{-1}, respectively.The value of the frequency factor also falls in the range of average values. The experimental results indicated that the values of kinetic constants were in good agreement with those of model-free methods, especially FWO and KAS. The intricacy of the pyrolysis process was satisfactorily described. The temperature study is useful in producing bio oil in a cost-effective way. The GC-MS results of bio oil showed that ester compounds were highly dominant; however, if separated, purified, and upgraded, bio oil can be used as biofuel on a large scale.

5. ACKNOWLEDGEMENT

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