



Isothermal, Dynamic and Kinetic Characteristics of Torrefied Corn Stalks

Anthonia, E. Eseyin^{1*}, Onyanobi, Abel-Anyebe², Juliet, D. Dodo¹, Kieran, I. Ekpenyong¹

¹Department of Chemistry, University of Jos, Plateau State, Nigeria

²Department of Environmental and Interdisciplinary Sciences, Texas Southern University, Houston Texas, USA.

*Corresponding author's Email: eseyinae@gmail.com

Abstract Corn stalks decomposition was about 45% at 300 °C. Torrefaction increased the HHV of torrefied corn stalks from 18.5 to 21.6 MJ/kg. Five weight loss phases were identified on this TG curve, relating to the peaks observed on the DTG curve. The fourth phase (325-420 °C) showed a weight loss of ~72% while the fifth phase (420-675 °C) recorded a negligible weight loss without any characteristic peak. The gaseous components identified by TGA–FTIR analysis are CO, CO₂ and H₂O. The reliability of the two-step, first-order reaction in series model showed that predictions were in agreement with the experimental data, which means that the torrefaction of corn stalks can be adequately described by a two-step model. This model exhibited high overall fits and the solid yields were predicted with high precision.

Keywords Corn stalks, Dynamic, Isothermal, Thermogravimetric analysis (TGA), Torrefaction and Two-step reaction model

1. Introduction

The global challenge to reduce dependence on fossil fuels and achieve a sustainable, renewable energy supply is real. Energy from biomass is carbon-neutral because the carbon dioxide released during its conversion is already part of the carbon cycle [1].

Direct feeding of biomass feedstock into a coal fired boiler for the production of heat and electricity has a number of limitations such as high moisture contents, huge investment on transportation and the problems associated with the storage of biomass, such as biological degradation as well as poor grindability, low energy/bulk density, and lower heating value. To minimize these limitations, a pretreatment method by a thermochemical conversion, called torrefaction is desirable.

Torrefaction is a thermal pretreatment technology. It is the isothermal pyrolysis of biomass at a temperature ranges of 200 - 300°C. Torrefaction is performed at atmospheric pressure in the absence of oxygen [2, 3]. Pretreatment alters biomass's physical properties and chemical composition and makes it more suitable for conversion. The pretreatment process can be a chemical, thermal, or mechanical process which helps in altering the amorphous and crystalline regions of the biomass and bring significant changes in the structural and chemical compositions, making the biomass easier to convert as shown in Fig. 1.



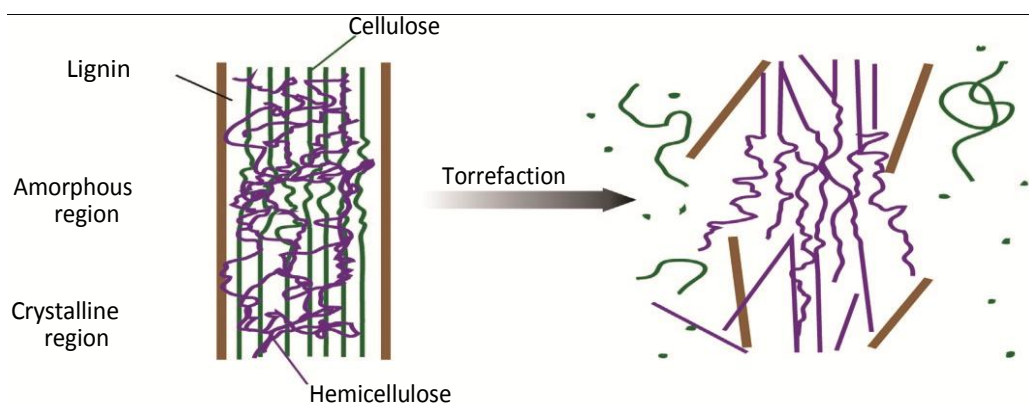


Figure 1: The Effect of torrefaction on biomass [4].

Corn stover is composed of 38-40% cellulose, 28% hemicellulose, 7-21% lignin, and 3-7% ash, on average [5, 6]. It is an important feedstock for the production of bioenergy and bio renewables due to its availability and proximity to existing biorefineries [7]. Kadam and McMillan,[8] reported that about 70% of corn stover is produced on no-till farms while 35% is produced on the farms with conventional tilling means and can be collected. This implies that on average, 40% of all available corn stover produced can be harvested in a sustainable manner.

Not much investigation has been carried out on corn stover biomass torrefaction. Nonetheless, corn stover has the potential of being an important near term feedstock for the production of bio-renewables. The benefits gained from the torrefaction of lignocellulosic biomass could be captured only if the process is positioned early in the supply chain, to utilize the feedstock without excessive pretreatment.

In spite of the extensive research on wood pyrolysis, few researchers have addressed the detailed differences encountered over the temperature range of torrefaction. More work is therefore required for a better understanding of the reaction mechanism and reaction kinetics of torrefaction. To better control torrefaction and develop more efficient reactors, the kinetics of species evolution and changes in the residual biomass during torrefaction need to be better understood [9].

The complex nature of thermal degradation has resulted in the existence of many competing ideas for biomass thermal degradation pathway. Due to a poor knowledge of a formal mechanism, many semi-empirical models have been developed to describe laboratory observations over a range of feedstock and conditions.

2. Materials and Methods

2.1. Preparation of sample

Dry corn stalks, were randomly sampled and collected from some farms in Jos, Plateau State, Nigeria. They were dried at a temperature of 105°C for 2 hours, cut into smaller pieces, crushed and sieved to a mesh size 125-250 μm .

2.2. Thermogravimetric (TGA) analysis

Thermogravimetric analysis (TGA) is usually performed to determine weight change as a function of temperature. TGA measurements are designed to minimize secondary reactions, using a small sample weight and particle sizes as well as fast carrier-gas flow rates to immediately remove volatile pyrolysis products, which are swept into the gas cell immediately they are formed.

Kinetic data studies were carried out using a TG (Q50, TA Instruments, USA). Sample loading was maintained at 10 ± 1 mg with particle size of 125-250 μm mesh to minimize the effect of heat and mass transfer. Thermogravimetric data were obtained following the temperature program with two stages of dynamic and isothermal heating. The sample was heated from ambient condition to 105 °C at 20 °C min^{-1} followed by an isothermal hold for 10 min. Then the sample was further heated to the target isothermal temperature ranging from 230 to 280 °C at a dynamic heating rate of 10 °C min^{-1} and held isothermally for 5 h. Inert atmosphere inside the furnace was maintained by a continuous flow of nitrogen gas at 100 mL min^{-1} (40 mL min^{-1} for balance purge and



60 mL min⁻¹ for sample purge). The instantaneous change in mass with respect to time and temperature as well as its derivative with respect to time (DTG) was continuously compiled by the software from TA Instruments.

Proximate (TG 701 LECO Thermogravimetric analyzer), ultimate (CHN 2000 and SC 144 DR LECO analyzer) analyses were performed in order to obtain the basic fuel properties of corn stalks.

3. Results and Discussions

3.1. Fuel Properties of Corn Stalks

Table 1 shows the results of proximate and ultimate analyses of raw biomass as well as HHV and LHV of torrefied biomass.

Table 1: Fuel properties of corn stalks

| Ultimate analysis of raw biomass (%) | | | | | Proximate analysis | | | | |
|--------------------------------------|-----|------|-----|-----|--------------------|--------|---------|------------------|------------------|
| C | H | O | N | S | FC (%) | VM (%) | Ash (%) | HHV (RB) (MJ/kg) | LHV (RB) (MJ/kg) |
| 49.5 | 6.2 | 40.7 | 0.9 | 0.1 | 16.2 | 68.2 | 6.9 | 18.5 | 18.1 |
| | | | | | | | | HHV (TB) (MJ/kg) | LHV (TB) (MJ/kg) |
| | | | | | | | | 21.6 | 20.3 |

FC-Fixed Carbon, VM-Volatile Mater, HHV-Higher Heating Value (on dry basis), LHV-Lower Heating Value (on dry basis), RW- Raw Biomass, TB - Torrefied Biomass.

3.2. Thermal decomposition of corn stalks

The thermal decomposition of hemicellulose and cellulose of biomass takes place in the temperature range of 160-360 and 240-390 °C respectively, while lignin decomposes over a wider range of 180-900 °C[10]. At low temperatures, the conversion of the samples is relatively low as reflected by the small peak area of 10 % at 230 °C and 15 % at 240°C as shown in Fig. 2. As the temperature increased from 250 to 300 °C, a faster torrefaction rate was observed, and the decomposition of the hemicellulose and subsequently, cellulose become more obvious. Corn stalks decomposition was about 45% at 280 °C.

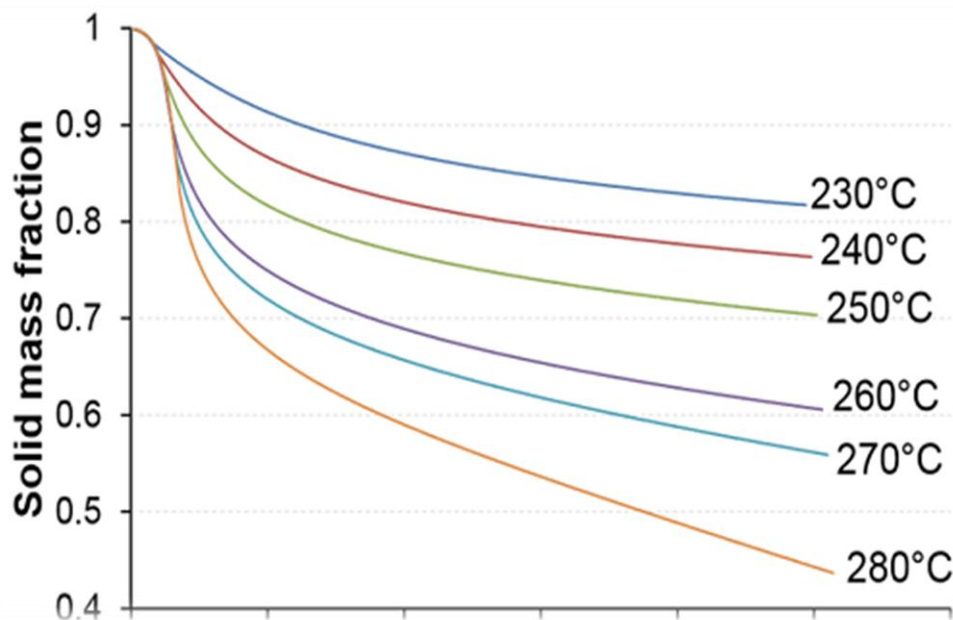


Figure 2: Experimental weight loss curve for the decomposition of torrefied corn stalks at various final temperatures



4. Kinetic characteristics of torrefied corn stalks

The two step reaction model, which was originally developed to describe the degradation of xylans by Di Blasi & Lanzetta,[11] was used in this study. This model has been adapted as a mechanism to describe other components and whole biomass. Researchers proposed that the degradation of (A) simultaneously produced volatile species (V_1) through rate constant k_{v1} and a solid pseudo-intermediate (B) through k_1 , which represents some partially degraded solid structure. B then undergoes a consecutive degradation to form additional volatile species (V_2) through k_{v2} and the final solid char C through k_2 as shown in Fig. 3.

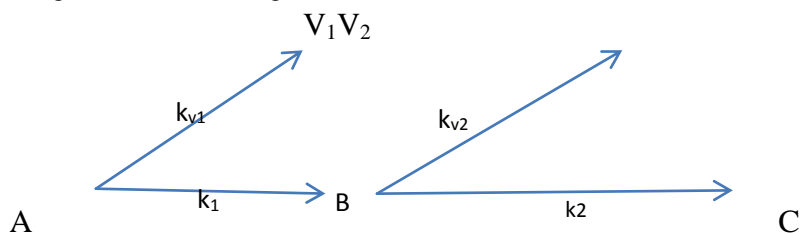


Figure 3: The two step torrefaction kinetic model [11]

Researchers observed that the first stage released more volatile components and occurred at much faster rates. The second stage was observed at temperatures above 523K, and occurred slower than the first stage. This was the first model that attempted to predict the volatiles released, independently of char formation.

The percentage Mass Yield (MY), Percentage Energy Yield (EY) and Energy Density Ratio (EDR) were determined, using the following formulae:

$$MY = \frac{M_{tb}}{M_{rb}} \quad (1)$$

$$EY = \frac{M_{tb} * HHV_{tb}}{M_{rb} * HHV_{rb}} \quad (2)$$

$$EDR = \frac{HHV_{tb}}{HHV_{rb}} \quad (3)$$

Where: M_{tb} = Mass (daf) of torrefied biomass; M_{rb} = Mass (daf) of raw biomass; HHV_{tb} = Higher Heating Value of torrefied biomass; HHV_{rb} = Higher Heating Value of raw biomass.

The two step torrefaction kinetic parameters are expressed in the differential equations 4–9 by Chew & Doshi [12].

$$\frac{dA}{dt} = -(k_1 + k_{v1})A \quad (4)$$

$$\frac{dB}{dt} = k_1A - (k_2 + k_{v2})B \quad (5)$$

$$\frac{dC}{dt} = k_2B \quad (6)$$

$$\frac{dV_1}{dt} = k_{v1}A \quad (7)$$

$$\frac{dV_2}{dt} = k_{v2}B \quad (8)$$

$$k_i = k_{oi} e^{\frac{E_{Ai}}{RT}} \quad (9)$$

Where, k_i is the reaction rate in the form of Arrhenius equations.

Therefore, the torrefied net solid yield $M(t)$ is the addition of A, B and C as expressed by Prins, et al [13] in equations 10 and 11.

$$M(t) = A + B + C \quad (10)$$

$$\frac{M(t)}{M_0} = \left(1 + \left[\frac{k_1 K_1 - k_1 K_2}{K_1(K_2 - K_1)} e^{-K_1 t} + \left[\frac{-k_1 K_1 + k_1 K_2}{K_2(K_2 - K_1)} e^{-K_2 t} + \frac{k_1 K_2}{K_1 K_2}\right]\right)\right) \quad (11)$$

The kinetic parameters for modeling the continuous process were obtained from TGA experiments as shown in Fig. 4.

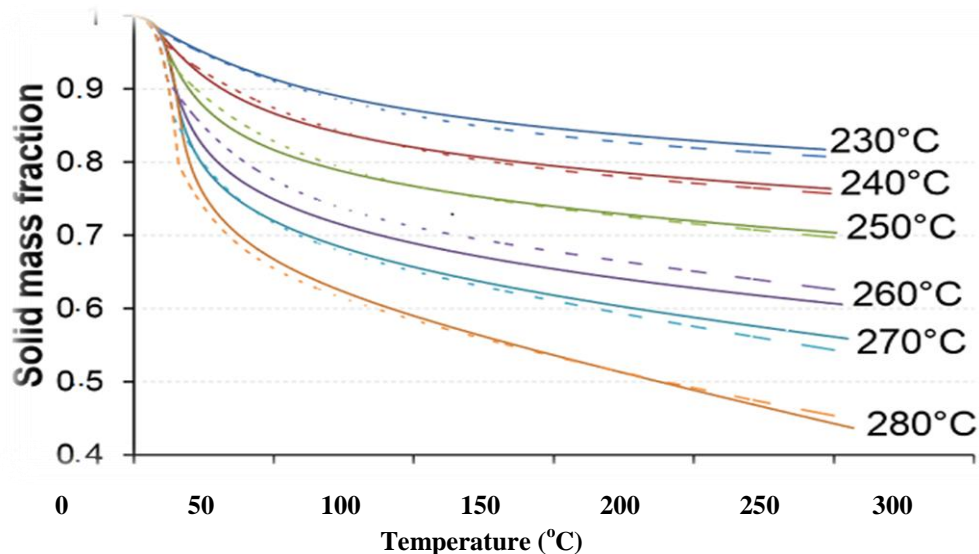


Figure 4: Experimental data (solid lines) and simulated data (dashed lines) for torrefied corn stalks

5. Isothermal and dynamic studies of torrefied corn stalks

Result of the isothermal and dynamic (variable temperature) studies of the torrefaction kinetics of corn stalks are presented in Fig. 5. Mass loss (TG) and derivative mass loss (DTG) curves for the thermal decomposition of corn stalks are also shown. Five weight loss phases were identified on this TG curve, which relate to the peaks observed on the DTG curve. The first phase corresponds to ~2.5% mass loss occurring between 25 and 150°C. This is attributed to the removal of water and light volatiles from the torrefied corn stalks.

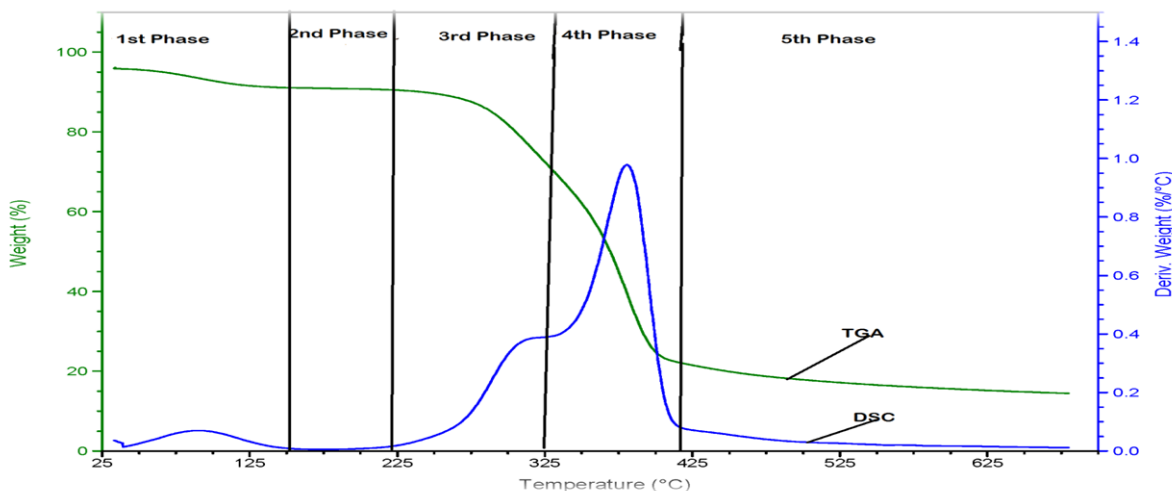


Figure 5: TGA and DTG curves of corn stalks, heated at $10^{\circ}\text{C min}^{-1}$

The second phase (150 - 225 °C) corresponds to a reduction of ~ 0% of the total mass. The third phase (225 - 325 °C) exhibits ~ 28% loss of the total mass which is mainly due to the decomposition of the hemicellulose fraction and



small cellulose dehydration. The fourth phase (325 - 420 °C) shows a weight loss of ~72%. This significant weight loss occurs mainly from cellulose degradation, which typically takes place at the temperature range of 240 - 350°C. This phase also includes the completion of hemicellulose decomposition. The fifth phase (420 -675°C) recorded a negligible weight loss without any characteristic peak. This phase represents the weight loss from lignin which is thermally stable and degrades over a wider temperature range.

6. FTIR spectra

FTIR and TGA together, give valuable information on the constituents of gaseous products released by the thermal treatment of biomass samples. TGA is cascaded with FTIR in this study to identify the torrefaction behavior of corn stalks and also measure the main gaseous constituents of the products released during the thermal treatment. The exhaust gas produced during the torrefaction process was monitored by FTIR by direct combination with TGA.

The result of the torrefaction process captured by the FTIR is presented in Fig. 6. The gaseous components identified by TGA–FTIR analysis are CO at 2079 cm⁻¹, CO₂ at 2918 cm⁻¹, and H₂O at 3335 cm⁻¹. The TGA–FTIR analysis shows that the emission of gaseous products increased, with increase in the torrefaction temperature. The relatively strong absorption peaks were an indication that some carbonyl compounds, aromatic hydrocarbons and phenols were formed gradually and also some lignin decomposition occurred.

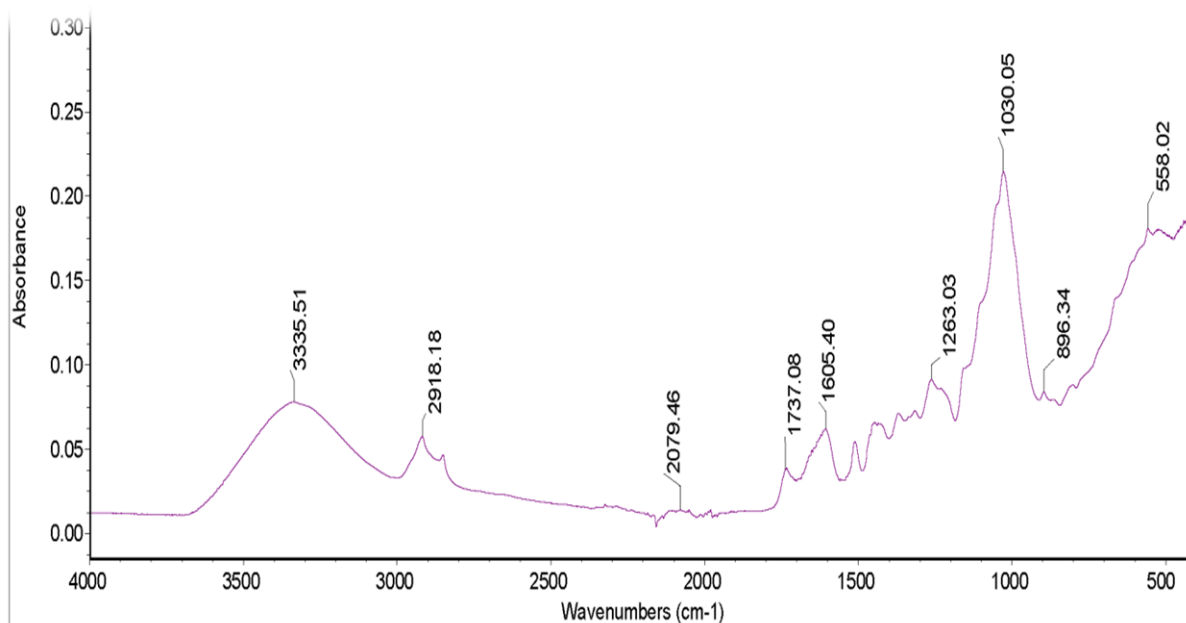


Figure 6: FTIR spectra of gases evolved in the torrefaction of corn stalks

7. Conclusion

As torrefaction temperature increased from 250 to 300 °C, a faster torrefaction rate was observed, and the decomposition of the hemicellulose and subsequently cellulose became more obvious. Corn stalks decomposition was about 45% at 280 °C. Generally, torrefaction at 230 °C released only some moisture and light volatiles from the corn stalks, indicating that torrefaction at this temperature had a relatively small impact in improving biomass property. Torrefaction at 260 °C caused a small amount of hemicellulose to be pyrolyzed, leaving cellulose and lignin relatively intact. At 280 °C torrefaction, large amounts of hemicellulose and cellulose were destroyed. Torrefaction increased the HHV of torrefied corn stalks from 18.5 to 21.6 (MJ/kg) and LHV from 18.1 to 20.3(MJ/kg).

Five weight loss phases were identified on the TG curve, relating to the peaks observed on the DTG curve. The first phase corresponds to ~2.5% mass loss occurring between 25 and 150°C. The second phase (150 - 225 °C) corresponds to a reduction of ~0% of the total mass. The third phase (225 - 325 °C) exhibits ~28% loss of the total



mass. The fourth phase (325 - 420 °C) shows a weight loss of ~72%. The fifth phase (420 - 675°C) recorded a negligible weight loss without any characteristic peak.

The gaseous components identified by TGA–FTIR analysis were CO, CO₂ and H₂O. The TGA–FTIR analysis shows that the emission of gaseous products increased with an increase in the torrefaction temperature.

A two-step, first-order reaction in series model took into account the mass loss during the heating period in calculating the kinetic parameters. The reliability of results was determined by simulating the isothermal experimental parameters. The predictions were in agreement with the experimental data. This means that the torrefaction of corn stalks can be adequately described by a two-step model. This model exhibited high overall fits and the solid yields were predicted with high precision.

References

- [1]. Arias, B.R., Peridac, C., Feroso, J.D., Plaza, M.G., Rubiera, F.G., & Pis-Martinez, J.J. (2008). Influence of torrefaction on the grindability and reactivity of woody biomass. *Fuel, Process Technology*, 89:169-175.
- [2]. Uslu, A., Faaij, A. B., & Bergman, P. C. A. (2008). Pre-treatment technologies, and their effect on international bioenergy supply chain logistics: Techno-economic evaluation of torrefaction, fast pyrolysis, and pelletisation. *Energy*, 33: 1206-1223.
- [3]. Zanzi, R., Ferro, D., Torres, A., Soler, P. B., & Bjornbom, E. (2002). Biomass torrefaction. The 6th Asia-Pacific International Symposium on Combustion and Energy Utilization. Kuala Lumpur, Malaysia.
- [4]. Sierra, R., Smith, A., Granda, C., & Holtzapfle, M.T. (2008). Producing fuels and chemicals from lignocellulosic biomass. Chemical Engineering Process, Society of Biological Engineering Special Section. *Biofuels*, 104, S10–S18.
- [5]. Ganjyal, G. M., Reddy, N., Yang, Y. Q., & Hanna, M. A. (2004). Biodegradable Packaging Foams of Starch Acetate Blended with Corn Stalk Fibers. *J. Appl. Ploy. Sci*, 93:2627-2633.
- [6]. Reddy, N. (2006). Structure and properties of natural cellulose fibres obtained from cornhusks, cornstalks, rice, wheat, soybean straw and sorghum stalks and leaves. Ph.D. Dissertation, University of Nebraska. Lincoln, NE.
- [7]. Pordesimo, L. O., Harnes, B. R., Sokhansanj, S., & Edens, W., C. (2005). Variation of corn stover composition and energy content with crop maturity. *Biomass Bioenerg*, 28:366374.
- [8]. Kadam, K. L., & McMillan, J. D. (2003). Availability of corn stover as a sustainable feedstock for bioethanol production. *Bioresource Technology*, 88:17-25.
- [9]. Eseyin, A. E., Steele, P. H., Pittman, Jr. C. U., Ekpenyong, K. I., & Soni, B. (2016). TGA torrefaction kinetics of cedar wood. *Journal of Biofuels*, 7:20-27.
- [10]. Medic, D., (2012). Investigation of torrefaction process parameters and characterization of torrefied biomass. Iowa State University: Ames, Iowa.
- [11]. Di Blasi, C., & Lanzetta, M. (1997). Intrinsic kinetics of isothermal xylan degradation in inert atmosphere. *Journal of Analytical and Applied Pyrolysis*, 40-41:287-303.
- [12]. Chew, J. J., & Doshi, V. (2011). Recent advances in biomass pretreatment-torrefaction fundamentals and technology. *Renewable and Sustainable Energy Reviews*, 15:4212-4222.
- [13]. Prins, M. J., Ptasinski, K., & Janssen, F. J. (2006). More efficient biomass gasification via torrefaction. *Energy*, 31:3458-3470.

