Product Distribution in the Low Temperature Conventional Pyrolysis of Nigerian Corn Stalks.

1. Anthonia, E. Eseyin
Department of Remedial Sciences,
University of Jos, Nigeria
Department of Sustainable Bioproducts,
Mississippi State University.
United States of America

2. **Kieran, I.Ekpenyong**
Department of Chemistry,
University of Jos, Nigeria.

3. S. M. Dangoggo
Department of Pure and Applied Chemistry,
Usmanu Danfodiyo University, Sokoto, Nigeria

4. **Onyanobi, Abel-Anyebe**
Science Laboratory Technology
Department, Benue State Polytechnic,
Ugbokolo, Nigeria.

5. Emad M. El-Giar
School of Sciences,
Universersity of Louisiana at Monroe,
USA

Corresponding Author: Anthonia, E. Eseyin. Department of Sustainable Bioproducts, Mississippi State University. United States of America.
Tel: +1 662 312 4884. E-mail: eseyinae@gmail.com.

Abstract

In view of the global energy crises and the ongoing renewable energy studies, clear understanding of the product distribution in the pyrolysis of lignocellulose from different corn plant components is required. Unextracted lignocellulose from the dry corn stalks was pyrolysed at 200°C and 250°C for 30 minutes, 60 minutes, 90 minutes and 120 minutes, respectively in an in house reactor. Liquid (bio-oil), gaseous and solid (bio-char) products were obtained. Their volumes and masses were determined. The volumes of the liquid and gaseous products produced increased with retention time and temperature while the masses of the solid products decreased with retention time and temperature. The pyrolysed corn stalks produced 17.93% bio-oil, 43.33% bio-char and 38.74% gases. The reaction order and rate constants were determined. The reaction was found to be first order. The bio-oil compounds that were detected by GCMS were identified from the MS library and characterized into: acids, ester, alcohol, phenol, alkane, multicomponent compounds and miscellaneous oxygenates. The bio-oils samples obtained were shown to be comparable with those produced by other processes.

Key words: Conventional Pyrolysis, corn stalks, unextracted lignocellulose, order, thermal decomposition, bio-oil, bio-char, retention time, rate constant.

1. Introduction

Currently, the global energy supply is to a large extent based on fossil fuels (oil, natural gas, coal). However, the reserves of these energy resources are finite. Because of the growing world population, the increasing energy consumption *per capita* and the evidence of global warming, it is necessary to find long-term alternative energy sources. The energy obtained from agricultural wastes or agricultural residues is a form of renewable energy and, in principle, utilizing this energy does not add carbon dioxide, which is a greenhouse gas, to the atmospheric environment, in contrast to fossil fuels [1].

Raw biomass, as a renewable energy resource, has been commonly used in thermo-chemical conversions for the production of solid, liquid and gaseous fuels. However, the utilization of raw biomass is limited because of poor grinding ability, low energy density, dispersed production location and storage difficulties [2-5].

Biomass has been recognized as a renewable resource for energy production and is abundantly available around the world [6]. Biomass utilization in mainstream energy uses is receiving great attention due to environmental considerations and the increasing demands of energy, worldwide [7]. Biomass is complex in nature, and contains a small amount of sulphur, nitrogen and ash, which make the combustion of bio-fuel to produce less harmful gas emissions such as nitrogen oxides (NO_x), sulphur dioxide (SO_2) and soot compared to conventional fossil fuels. In addition, zero carbon dioxide (CO_2) emission is possible from biomass fuel combustion because The CO_2 release from the combustion of bio-oil can be recycled into the plant by photosynthesis [8].

In the context of current energy problems, biomass has been found to be an eco-friendly alternative source of renewable energy. This has led many to look towards biomass as the only sustainable alternative to fossil fuels that is capable of yielding petroleum like products [9-13]. Pyrolysis has been found to be one of the most promising thermochemical technologies that has the potential of converting cheap, local, and abundant lignocellulosic biomass such as grasses, agricultural wastes , and trees into a useful form[14-17].

Having realized that biomass can function as an alternative source of fuel and chemical feedstock, the technologies available in the conversion of biomass to bio-energy and chemical feedstock are: pyrolysis, anaerobic digestion, hydro-carbonization, incineration and combustion under controlled atmosphere.

Several researchers have studied the pyrolysis of cellulose [18-28]. However, in view of the global energy crises and the ongoing renewable energy studies, clear understanding of the product distribution in the pyrolysis of lignocellulose from different corn plant components is also required. In order to maximize the production of bio-oil, several studies are required to define the different transformations that take place in the thermal decomposition of lignocellulose from corn stalks at 200^{o}C and 250^{o}C.

From the literature review of work done on biomass pyrolysis, there is no reported work on low temperature conventional pyrolysis of corn stalks as well as the products formed during low temperature conventional Pyrolysis. The aim of this research therefore, is to determine the products that are formed during low temperature pyrolysis of corn stalks and how these products can be effectively utilized.

2. Method.

The conditions and procedures involved in the preparation and decomposition (pyrolysis) of lignocellulosic material from corn stalks are described. A mass balance of all the reactants and products (solid, liquid and gas) formed after the decomposition was carried out.

2.1 **Preparation of crushed corn stalks.**

Dry corn stalks, were randomly sampled and collected from some farms in Jos, Plateau State, Nigeria. These were fractionated, washed in water to remove sand and dirt, and then dried in a Gallenkamp oven at a temperature of 105^{o}C for 2 hours to remove moisture. The corn stalks were cut into smaller pieces and crushed, using a Bico pulverizing machine. The crushed samples were sieved to obtain the mesh size of 250-300 um. This was used for the conventional low temperature pyrolysis.

2.2 **The reactor**

The reactor consisted of Pyrex tubes of 16cm length and 1.5cm internal diameter. The heating medium was a cylindrical brass block of 9cm height and 7cm diameter into which three thermal wells were drilled at approximately equal distance apart. Each well had a depth of 7cm and 1.7cm diameter. The block was heated electrically on a hot plate which had a temperature regulating device. A thermometer was placed in one of the wells to monitor the temperature of the system. This thermometer was held in position slightly above the bottom of the well by a clamp. Pyrolysis samples contained in two different test tubes were dipped into the remaining two thermal wells. These were connected via rubber bungs, rubber and glass tubes to water-filled, inverted burettes placed in a water trough for the collection of gas evolved in the reaction[29]. This reactor was assembled in house.

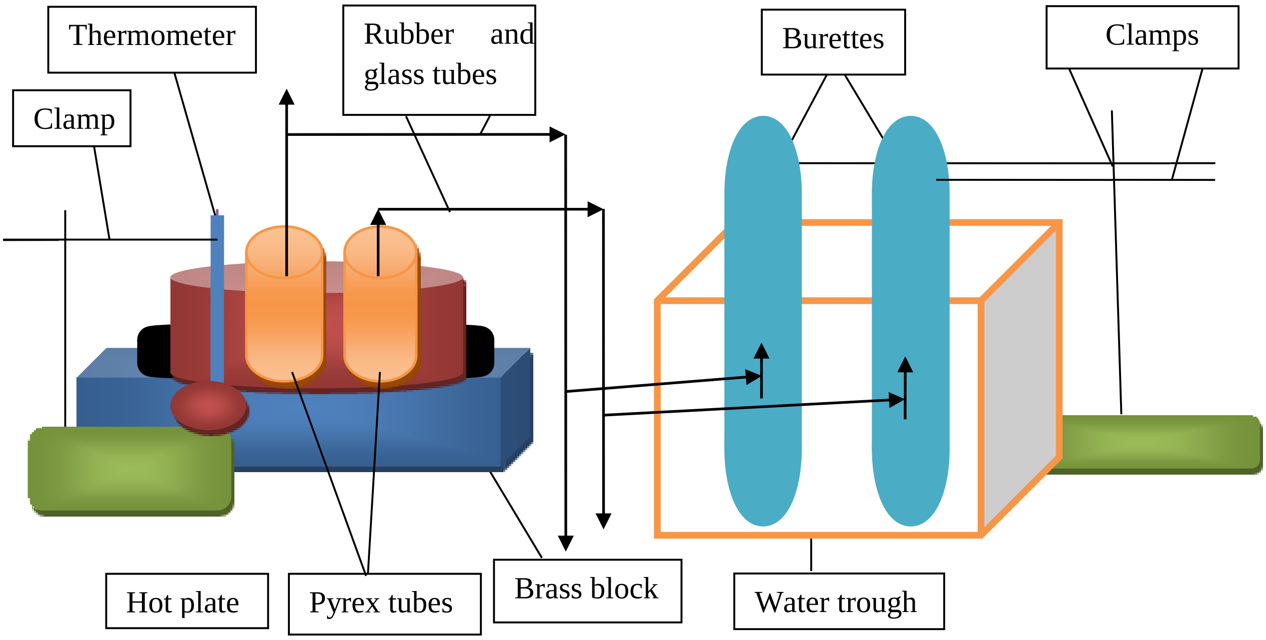


Figure 1. Schematic Diagram of the Reactor

2.3 **Pyrolysis in the reactor**

Sieved 3.00g samples of the corn stalks, was placed in 2 pyrex tubes by means of a plastic funnel. These tubes were placed in the wells of the already heated metallic heating block. Pyrolysis was carried out at 200°C and 250°C. The gases produced were collected over water. Gas volume measurements were made after 30 minutes, 60 minutes, 90 minutes and 120 minutes respectively. Two samples of the same material were used in each pyrolysis, and the average of the gas, bio-char and bio-oil volumes produced were recorded.

2.4 **The extraction process**

After pyrolysis, each sample was allowed to cool in the pyrex tube and then weighed (bio-char1).The weighed sample was introduced into a 500 ml soxhlet extractor. Extraction was carried out in n-hexane for 2 hours in each case. After the extraction, each sample (bio-char 2) was dried at room temperature and weighed again. The n-hexane in each case was evaporated leaving the bio-oil. The bio-oil volumes were then determined using a syringe and recorded.

2.5 **Detection of bio-oil compounds, using GC/MS**

Bio-oil compounds were detected in each bio-oil sample by GC/MS as follows:
0.2g of each bio-oil sample obtained was dissolved separately in 10 ml volume of methylene chloride. 2.4 micro liters of each solution was injected separately into the GC/MS and allowed to run for 67 min. The components of the bio-oil sample then passed into the mass spectrometer which plotted the spectrum as a graph on a computer screen. The acquisition parameters were - Oven: Initial temp 40°C for 4 min, ramp = 5°C/min to 280 °C, hold15 min, Inj = 270 °C, Vol = 0μL, Split = 5: 1, Carrier Gas = He, Solvent Delay = 2.0min, Transfer Temp = 225 °C, Source Temp = 210 °C, Scan: 35 to 550Da, Column 30.0m x 320μL. The compounds that were detected by the GCMS were identified from the MS library and characterized.

2.6 **Determination of percentage conversion of biomass to bio-oil**

The percentage of bio-oil formed was determined as described below: Density = Mass/Volume [30-32]. Density of corn stalk bio-oil is 1.075g/cm [33]. Using the most reactive sample (pyrolysed corn stalks @ 250°C for 2 hours), the volume of bio-oil produced was 0.5cm^3.

Mass of bio-oil produced = Density × Volume = 1.075 × 0.5 = 0.538g. The percentage of bio-oil formed, starting with the mass of biomass used is 0.538/3.00 × 100 = **17.93%** at 250°C.

2.7 **Determination of percentage conversion of biomass to bio-char**

Using the most reactive sample (pyrolysed corn stalks at 250°C for 2 hours), the mass of bio-char formed was 1.13g. Starting with the mass of pyrolysed sample (3g), the percentage of bio-char formed is 1.13/3.00 × 100 = **43.33%.**

2.8 **Determination of percentage of biomass to gases**

The percentage of gases produced was determined by difference. (100 – 17.93 - 43.33) = **38.74%**

2.9 **Determination of order of reaction**

Lignocellulose pyrolysis has been studied by measuring the weight loss as a function of temperature in a thermo gravimetric analyzer (TGA) [33]. The reaction being considered is endothermic, and the weight loss can fit with a first-order rate law and an activation energy of 240KJ/mol. [34, 35] The first order kinetic equation is kt =

$$\ln\left(\frac{a}{x}\right) \quad \text{or} \quad k = \frac{1}{t}\ln\left(\frac{a}{a-x}\right)$$

When t =0, i.e. at the beginning of the reaction, the amount that was changed x = 0, the constant is equal to – ln a. After time t, it is x. Using logarithm to base$_{10}$, k becomes:

$$k = \frac{2.303}{t} \log_{10} \left(\frac{a}{a-x}\right)$$

Inserting the values for a, and for (a – x) corresponding to different time, t during the course of the reaction should give a constant value of k.[34-36]. The graphical method may also be employed to cover the whole reaction period instead of calculating k for various time intervals. A first order plot of $\log_{10}$ (a- x) against t will be linear with a negative slope being equal to –k/2.303, thus enabling the specific reaction rate constant to be determined [34-36].

3.0 **Plot of $\log_{10}$ (a-x) vs t**

a = initial mass of corn stalks = 3.00g, x = decrease in weight of a, in time t. Therefore (a – x) is equivalent to weights of bio- char 2 in all cases. Figure 10 shows the plots of $\log_{10}$ (a-x) vs t for the pyrolysis of corn stalks at 250°C. Slope = $-2.29 \times 10^{-4} \text{min}^{-1}$. Since slope = -k/2.303, $k = (2.29 \times 10^{-4}) \times 2.303 = \underline{5.29 \times 10^{-4}\ \text{min.}}$

3. Results

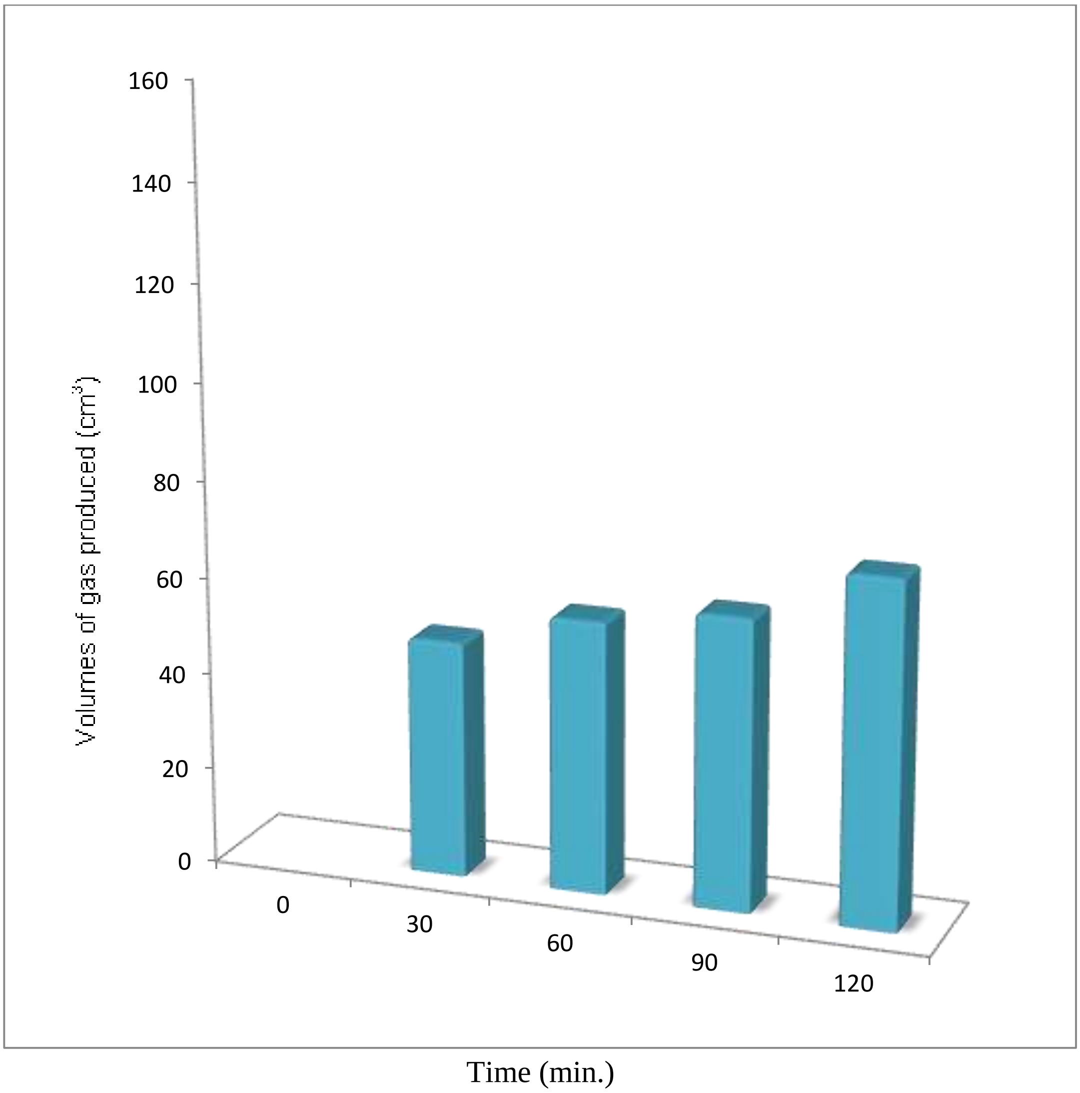


Figure 2. Plot of Volumes of Gas Produced in the Pyrolysis of Corn Stalks at 200°C. vs Time

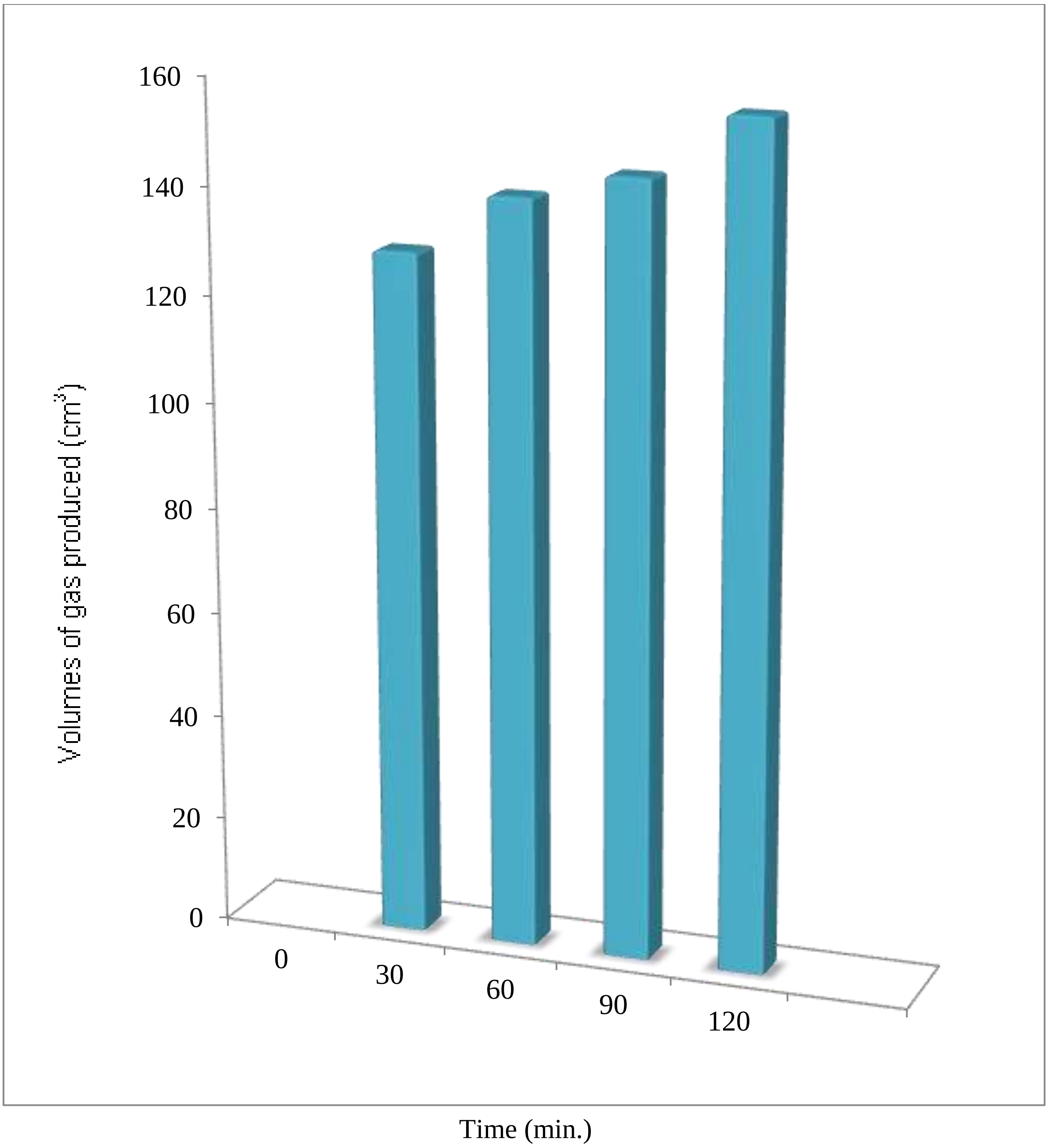


Figure 3. Plot of Volumes of Gas Produced in the Pyrolysis Corn Stalks at 250^{o}C vs Time

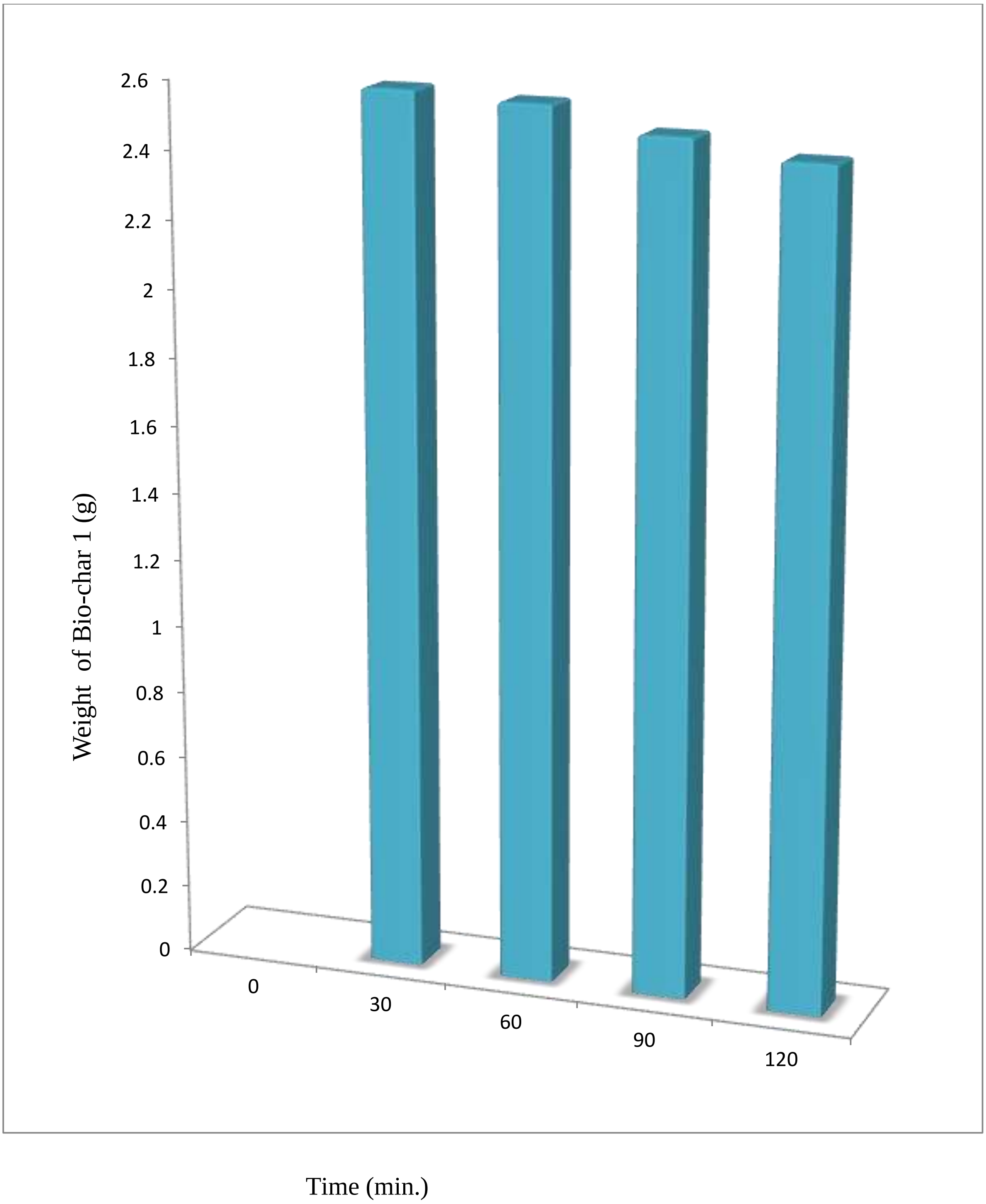
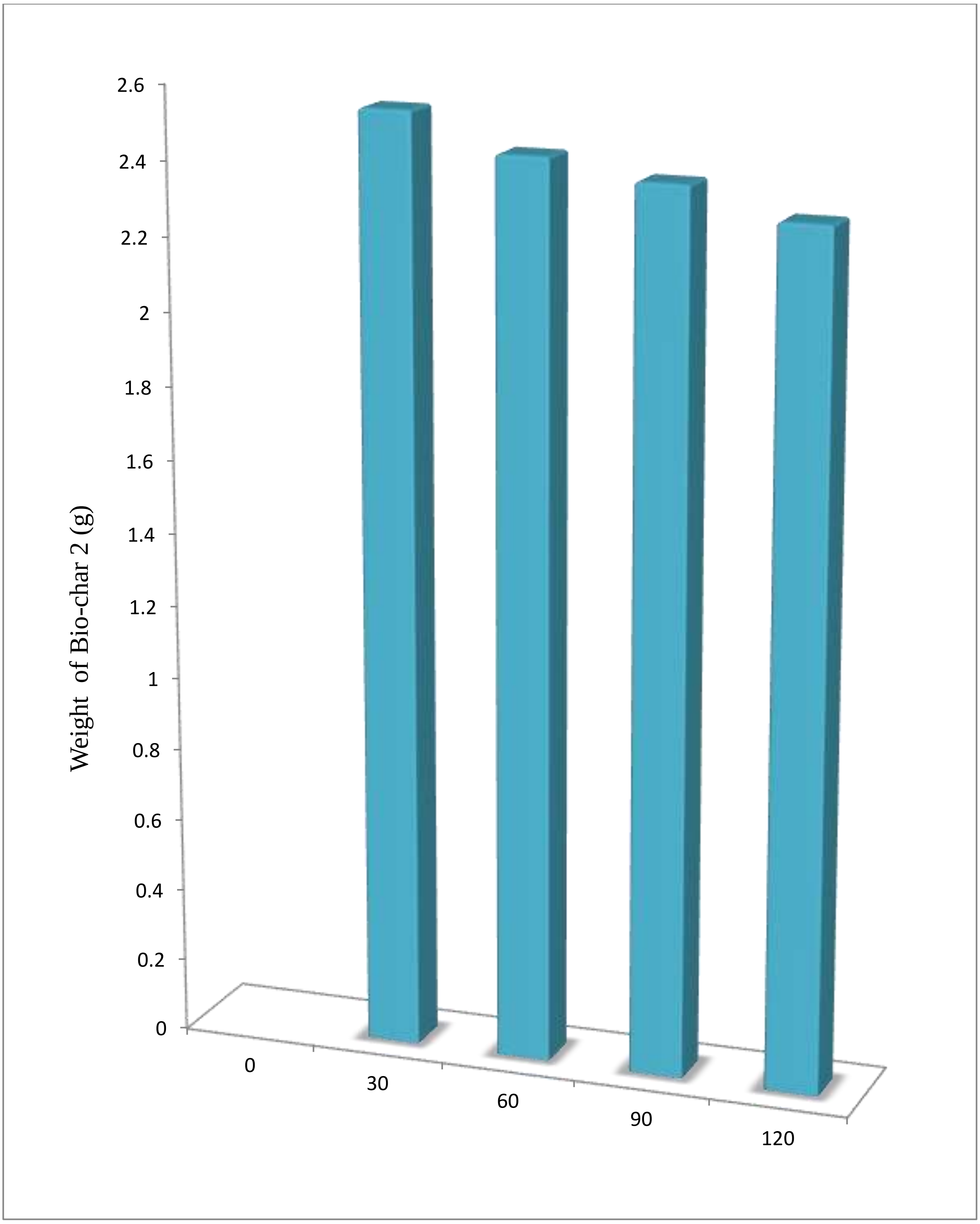
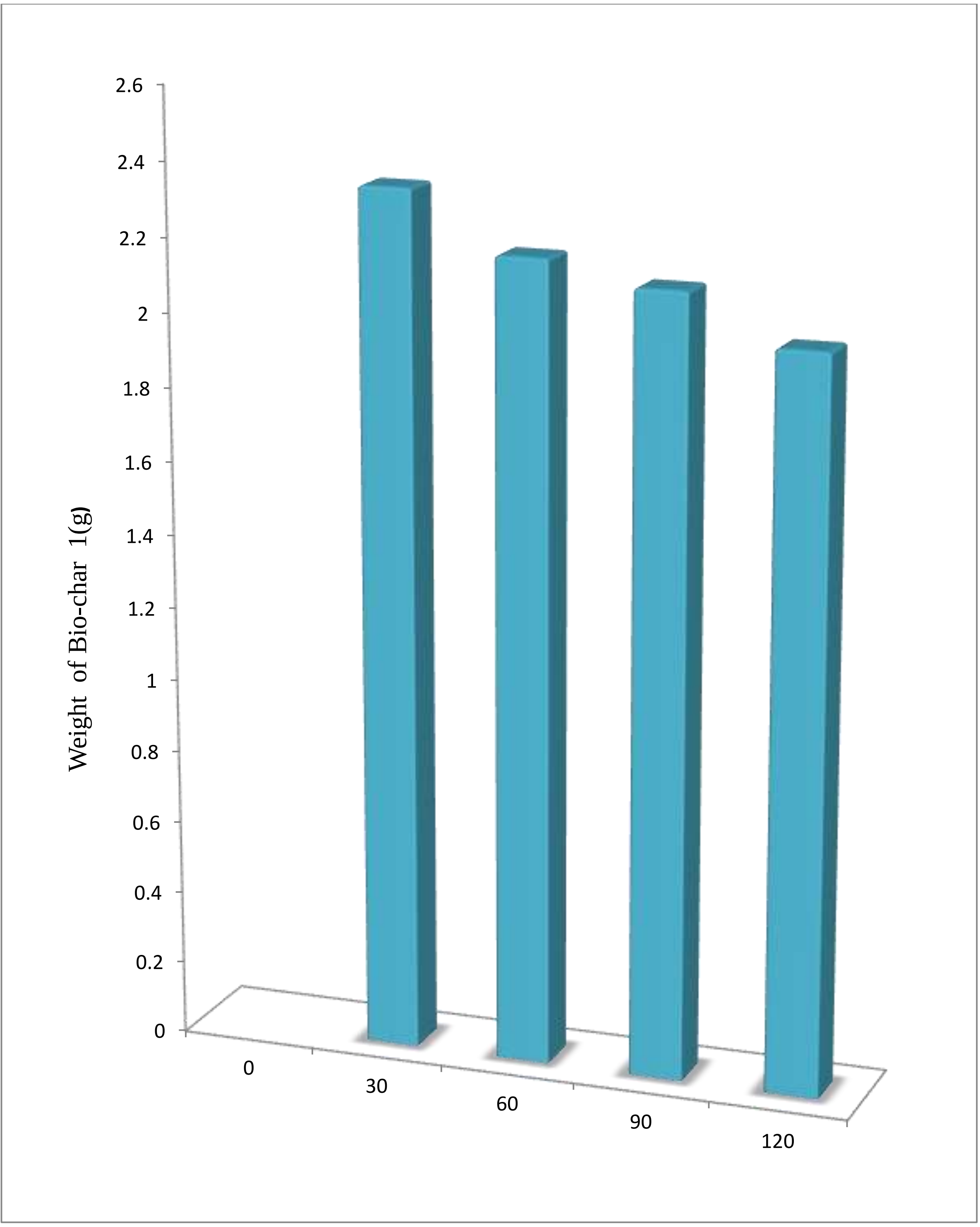


Figure 4. Plot of Weights of Bio-char 1 Produced in the Pyrolysis of Corn Stalks at 200^{o}C vs Time



Time (min.)

Figure 5. Plot of Weights of Bio-Char 2 Produced in the Pyrolysis of Corn Stalks at 200°C vs Time



Time (min.)
Figure 6. Plot of Weights of Bio-Char 1 Produced in the Pyrolysis of Corn Stalks at 250^{o}C vs Time.

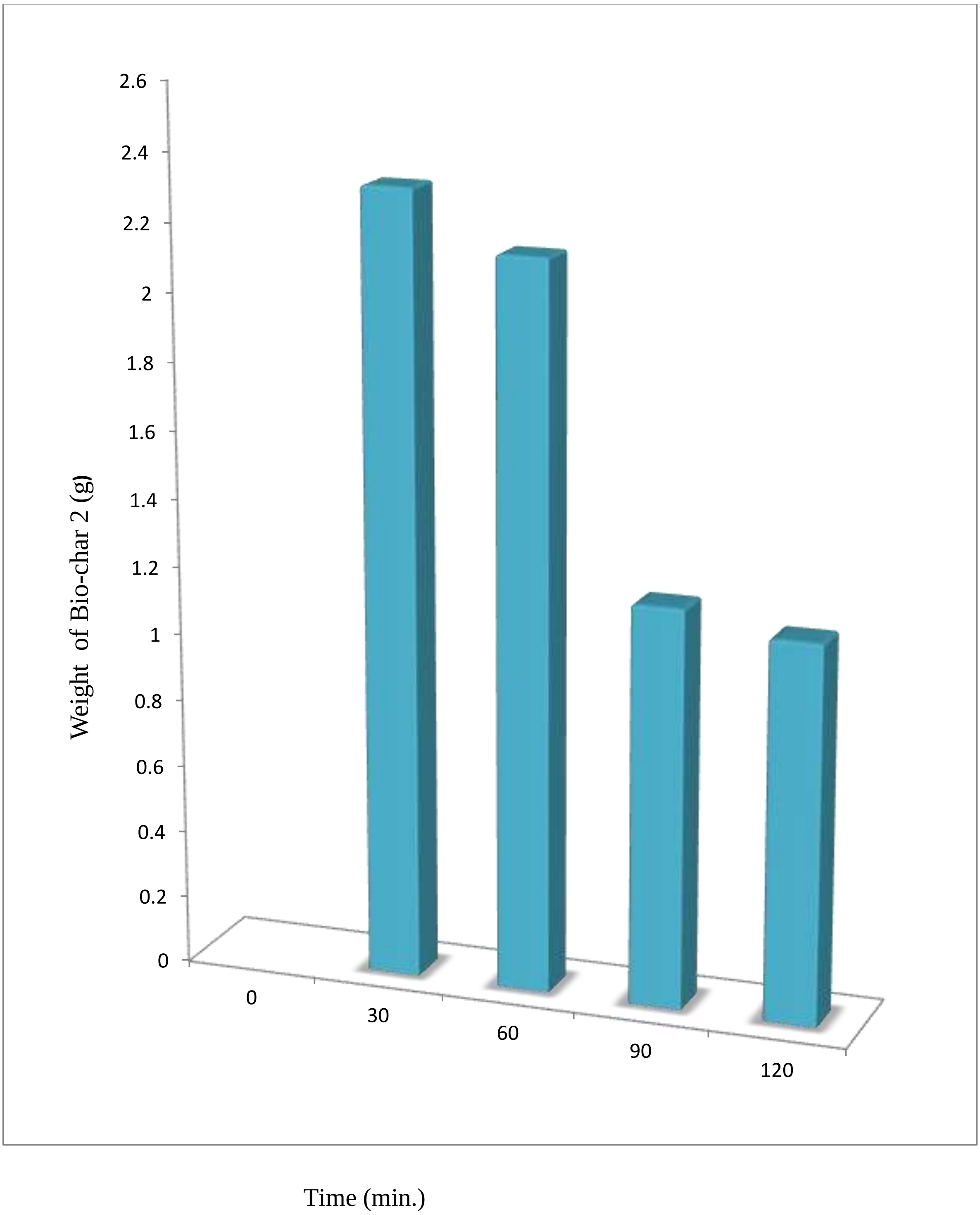
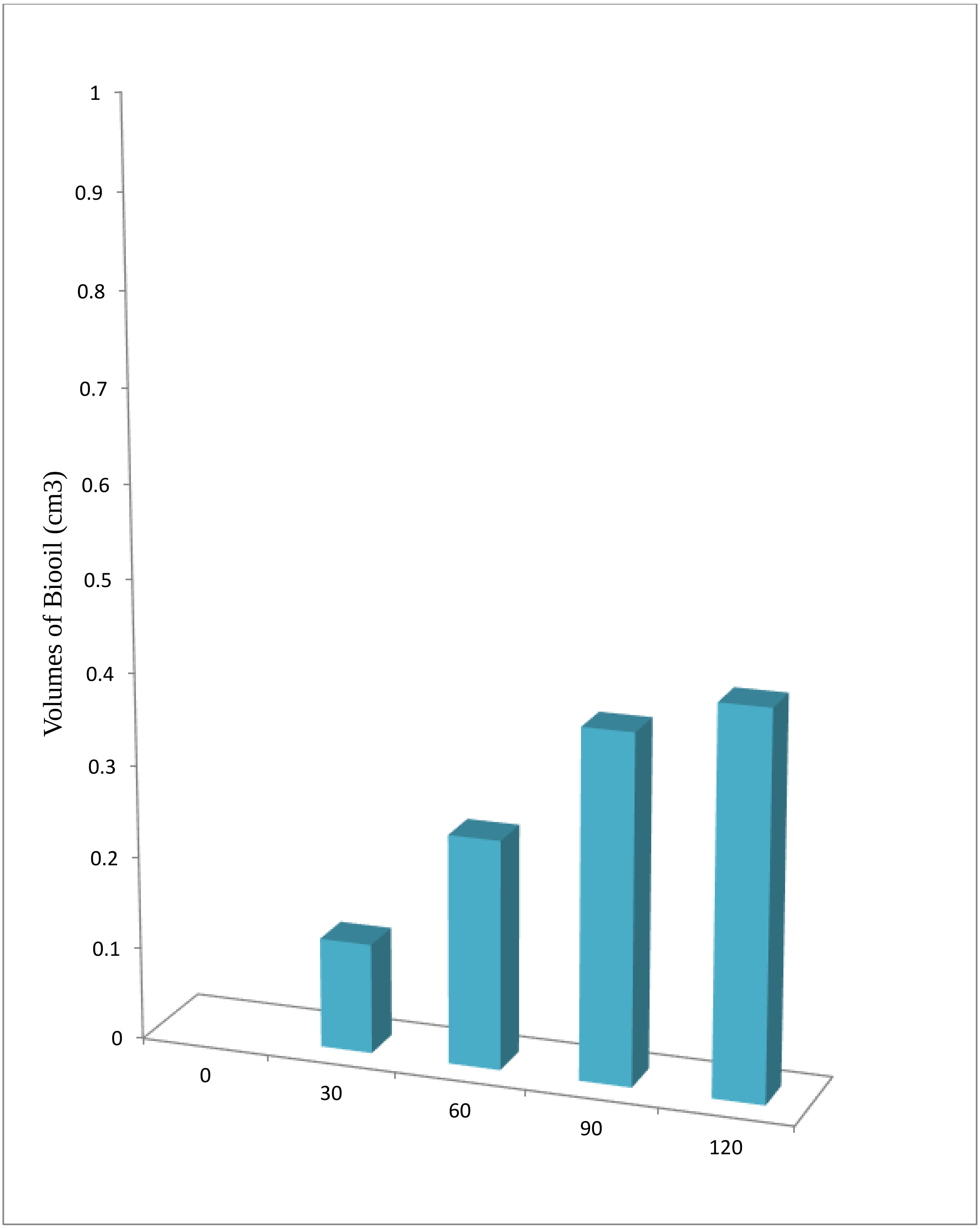
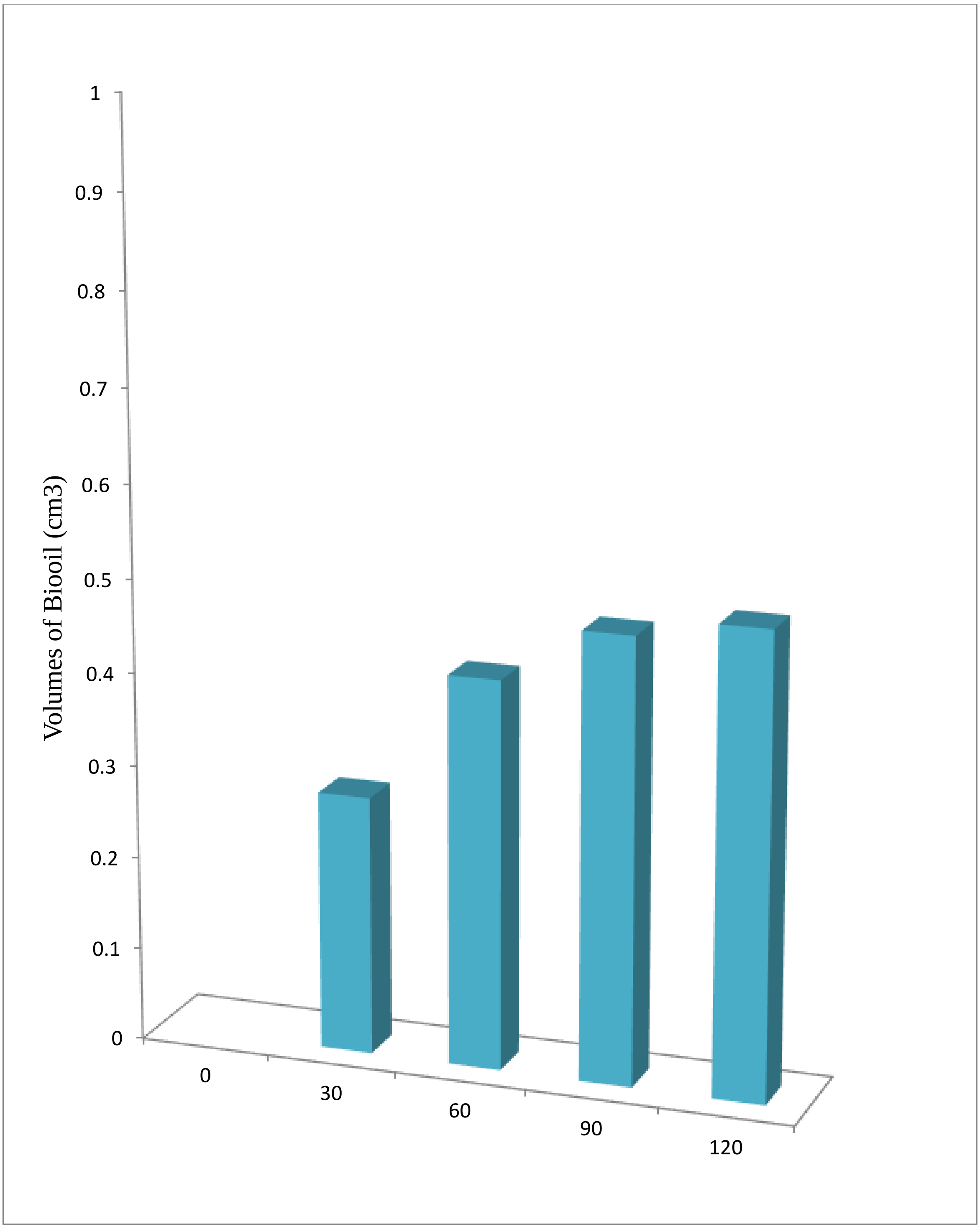


Figure 7. Plot of Weights of Bio-char 2 Produced in the Pyrolysis of Corn Stalks at 250°C vs Time.



Time (min.)

Figure 8. Plot of Volumes of Bio-oil Produced in the Pyrolysis of Corn Stalks at 200°C vs Time.



Time (min.)

Figure 9. Plot of Volumes of Bio-oil Produced in the Pyrolysis of Corn Stalks at 250°C vs Time

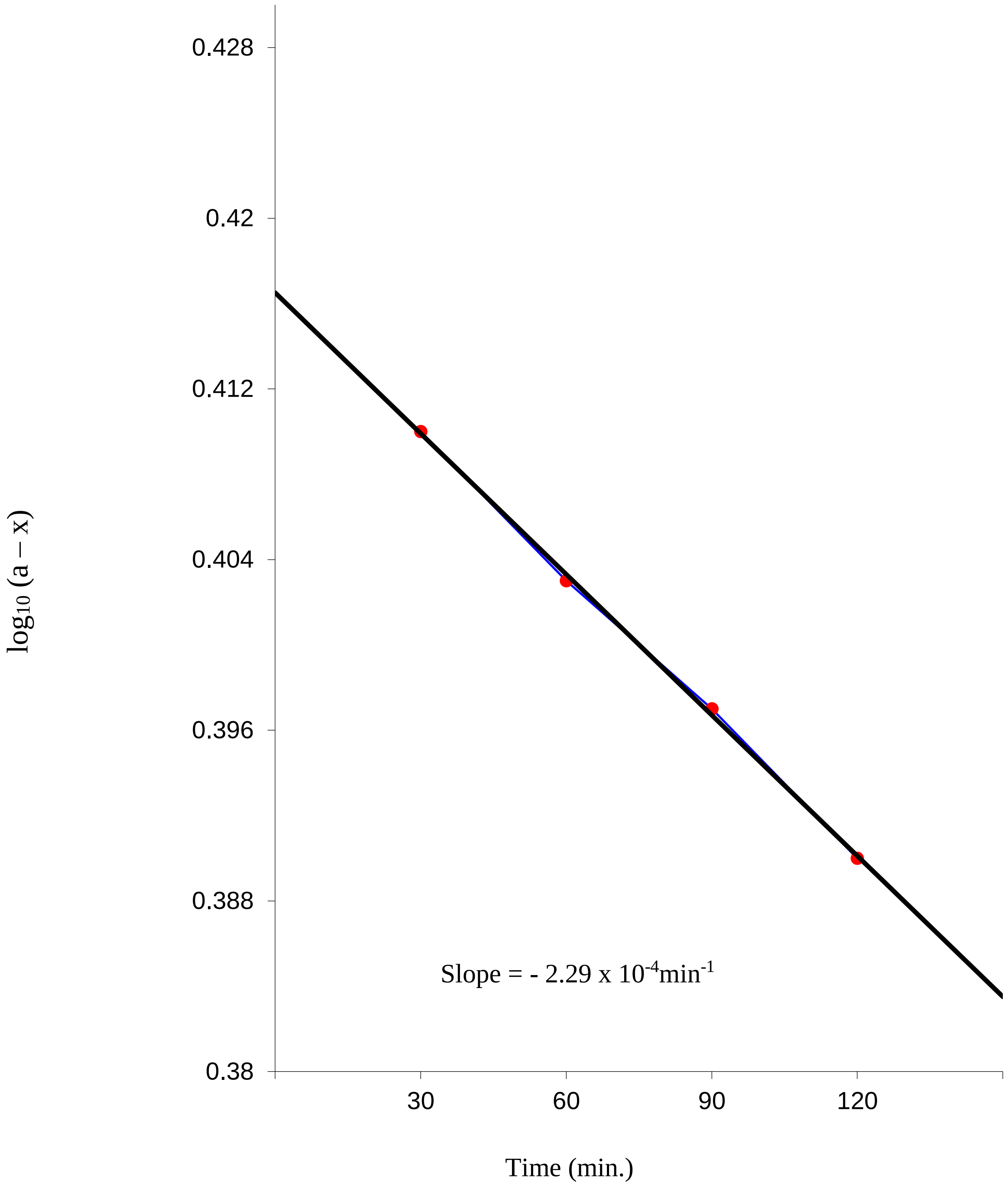


Figure 10. Plot of $\log_{10}$ (a – x) vs Time in the Pyrolysis of Corn Stalks at 250°C

Table 1. List of Bio-oil Compounds Detected in Bio-oils Produced in Pyrolysed Corn Stalks at 200°C and 250°C,

Retention Time, Library Match, CAS No. and Peak Area Percentages

Retention Time	Library Match	CAS No.	GC/MS Peak Area Percentage (mins)	
			Corn stalks Bio-oil @200°C Pyrolysis	Corn stalks Bio-oil @250°C Pyrolysis
3.68	Amylene hydrate	75-85-4	0.38	0.49
6.17	Cyclohexane,methyl-	1008-87-2	0.45	0.95
15.47	Cyclotetrasiloxane,octamethyl-	556-67-2	0.55	0.63
20.49	Cyclopentasiloxane,decamethyl-	541-02-6	0.91	1.36
21.57	Phenol,4-ethyl-	123-07-9	_	0.52
24.18	Butane,1,1-dibutoxy	5921-80-2	0.16	0.18
32.34	Dodecanoic acid	143-07-7	0.13	0.52
36.98	Tetradecanoic acid	544-63-8	0.60	1.63
39.60	Pentadecanoic acid	1002-84-2	1.32	1.89
41.37	n-Hexadecanoic acid	57-10-3	2.69	16.10
41.75	n-Butyl myristate	110-36-1	0.69	1.23
45.17	Octadecanoic acid	57-11-4	10.34	13.69
45.56	Hexadecanoic acid, butyl ester	111-06-8	2.50	14.80
51.44	1,2-Benzenedicarboxylic acid, diisooctyl ester	27554-26-3	_	1.62

Table 2. Classes of Compounds Detected in Bio-oils Produced in Pyrolysed Corn Stalks at 200°C and 250°C

Class	Compound
Acids	n-Hexadecanoic acid
	Octadecanoic acid
	Tetradecanoic acid
	Dodecanoic acid
	Pentadecanoic acid
Ester	n-Butyl myristate
Alcohol	Amylene hydrate
Phenol	Phenol, 4-ethyl-
Alkane	Cyclohexane, methyl-
Miscellaneous Oxygenates	1, 2-Benzenedicarboxylic acid, diisooctyl ester,
	Butane, 1, 1-dibutoxy
	Hexadecanoic acid, butyl ester
Multicomponent mixtures	Cyclotetrasiloxane, octamethyl-
	Cyclopentasiloxane, decamethyl-

4. Discussion.

4.1 Volumes of gas produced

The volumes of gas produced in the pyrolysis of lignocellulose from corn stalks, at 200^{o}C and 250^{o}C are shown in Figures 2 and 3 respectively. Fig 2 shows that the maximum gas yield was recorded at 120 minutes retention time. Gas production stopped at about 2 hours retention time and as such, the reaction was assumed to have terminated after 2 hours. Fig 3 shows the same trend but much more gas volumes were recorded at 250 ^{o}C compared to 200^{o}C because at a higher temperature, there was more decomposition and hence, production of more gas. The higher the retention time, the higher the volumes of gases that were produced.

4.2 Weights of bio-char produced

At 200^{o}C (Figs. 4 & 5) and 250^{o}C, (Figs 6 & 7), the weights of bio-char produced before and after extraction were found to be the least at 250^{o}C pyrolysis for 2 hours. In all cases, the weight of bio-char reduced with increase in reaction time. Generally, the weights of bio-char reduced with increase in temperature and retention time, as expected, because more decomposition took place at higher temperatures. At 250^{o}C, lower bio-char weights were recorded because; more decomposition took place at this temperature. Bio-chars from corn stalks have nearly twice as much as the energy potentials of their corresponding biomass feedstock and can be used as solid fuels in the form of briquettes for local cooking and heating in bakeries, especially in rural areas.

4.3 Volumes of bio-oil produced

Figs. 8 and 9 show the volumes of bio-oil produced in the pyrolysis of corn stalks at 200^{o}C and 250^{o}C. Pyrolysis at 250^{o}C generated a higher bio-oil volume. This indicates that more pyrolysis took place at a higher temperature and hence, more bio-oil production. It was observed that increase in reaction time produced more bio-oil. The bio-oils obtained were oily liquids with color ranging from light brown to darker brown as pyrolysis temperature increased.

4.5 Determination of order of reaction

The graphical method was used to determine the order of the reaction. The entire reaction period was covered. Using pyrolysis at the higher temperature, (250^{o}C), a plot of $\log_{10}$ (a- x) against t, is linear with a negative slope which is equal to –k/2.303 (fig. 10). This shows that the pyrolysis reaction is first order

4.6 Classification of the Bio-oil Compounds Detected in the Pyrolysed Corn stalks at 200 ^{o}C And 250^{o}C

The compounds that were detected in the Pyrolysed Corn stalks at 200 ^{o}C and 250^{o}C and their classes are shown in tables 1 and 2. The compounds that were detected had more area percentages at 250^{o}C than at 200^{o}C. However, Phenol,4-ethyl- and 1, 2-Benzenedicarboxylic acid, diisooctyl ester, that were detected in bio-oil that was produced at 250^{o}C pyrolysis were absent at bio-oil that was produced 200^{o}C pyrolysis. The acids that were detected (n-Hexadecanoic acid, Octadecanoic acid, Tetradecanoic acid, Dodecanoic acid and Pentadecanoic acid), had particularly high peak area percentages. Conventional low temperature pyrolysis of corn stalks can serve as a potential source of these acids. However, some peaks were not identified.

The bio-oil compounds detected in this research are similar to those detected in corn stover pyrolysis works done previously. Bio-oil from corn stover contains a lot of carboxylic acids, multi-ring aromatic compounds (Miscellaneous oxygenates), a few aromatic hydrocarbons, polar compounds (phenols and its derivatives), as well as multiple component compounds [33, 37-39]. During Bio-oil production, a large number of reactions occur. These include hydrolysis, dehydration, isomerization, dehydrogenation, aromatization, retro-condensation and coking [39] More than 400 organic compounds have been found previously in biooil [24].

These compounds can vary by more than one order of magnitude. The multicomponent mixtures are derived primarily from depolymerization and fragmentation reactions of the three building blocks of lignocellulose: cellulose, lignin and hemicellulose. Guaiacols and syringols are formed from the lignin fraction, whereas the miscellaneous oxygenates, sugars and furans are formed from the cellulose and hemicellulose. The esters acids, alcohols, ketones and aldehydes are likely formed from the decomposition of the miscellaneous oxygenates, sugars and furans [24].

Conclusion

Fast pyrolysis at 450-500^{o}C has the potential of contributing to the world's need for liquid fuels and ultimately, chemical production. However, smaller volumes of bio-oil can also be produced by low temperature conventional pyrolysis using a simple reactor. At 200^{o}C and 250^{o}C, cornstalks produced a moderately high volume of bio-oil. A lot of bio-chars that can be used as solid fuels in the form of briquettes for local cooking and heating in bakeries, especially in rural areas are also formed from low temperature conventional pyrolysis. Corn stalks were found to have a percentage conversion of biomass to bio-oil, bio-char and gases of 17.93% , 43.33% and 38.74% respectively at 250^{o}C. The pyrolysis reaction was found to be first order. The bio-oil samples obtained were characterized and found to contain acids, ester, alcohol, phenol, alkane, multicomponent compounds and miscellaneous oxygenates.

References

[1] McKendry, P., *Energy production from biomass (Part 1): Overview of biomass.* Bioresour Technol, 2002. **83** 2014 U.S. National Library of Medicine.: p. 37-46.

[2] Bates, R.B. and A.F. Ghoniem, *Biomass torrefaction: Modeling of reaction thermochemistry.* Bioresour. Technol., 2013. **134** 2014 p. 331-340.

[3] van der Stelt, M.J.C., et al., *Biomass upgrading by torrefaction for the production of biofuels: A review.* Biomass Bioenergy, 2011. **35** 2014 p. 3748-3762.

[4] Chen, D., Y. Zheng, and X. Zhu, *Determination of effective* moisture *diffusivity and drying kinetics for poplar sawdust by thermogravimetric analysis under isothermal condition.* Bioresour. Technol., 2012. **107** 2014 p. 451-455.

[5] Chen, D., J. Zhou, and Q. Zhang, *Effects of heating rate on slow pyrolysis behavior, kinetic parameters and products properties of moso bamboo.* Bioresour. Technol., 2014. **169** 2014 p. 313-319.

[6] Pearsall, N., *Renewable energy: power for a sustainable future by Godfrey Boyle.* Chem. Ind. 1996 2014 p. 758.

[7] Zhang, Q., et al., *Review of biomass pyrolysis oil properties and upgrading research.* Energy Convers. Manage., 2006. **48** p. 87-92.

[8] Tsai, W.T., M.K. Lee, and Y.M. Chang, *Fast pyrolysis of rice husk: Product yields and compositions.* Bioresour. Technol., 2006. **98** p. 22-28.

[9] Balat, M., et al., *Main routes for the thermo-conversion of biomass into fuels and chemicals. Part 1: Pyrolysis systems.* Energy Convers. Manage., 2009. **50** p. 3147-3157.

[10] Serrano-Ruiz, J.C. and J.A. Dumesic, *Catalytic routes for the conversion of biomass into liquid hydrocarbon transportation fuels.* Energy Environ. Sci., 2011. **4** p. 83-99.

[11] Bridgwater, A.V. and G.V.C. Peacocke, *Fast pyrolysis processes for biomass.* Renewable Sustainable Energy Rev., 1999. **4** p. 1-73.

[12] Stephanidis, S., et al., *Catalytic upgrading of lignocellulosic biomass pyrolysis vapours: Effect of hydrothermal pre-treatment of biomass.* Catal. Today, 2011. **167** p. 37-45.

[13] Huber, G.W., S. Iborra, and A. Corma, *Synthesis of Transportation Fuels from Biomass: Chemistry, Catalysts, and Engineering.* Chem. Rev. 2006. **106** p. 4044-4098.

[14] Vispute, T.P., et al., *Renewable chemical commodity feedstocks from integrated catalytic processing of pyrolysis oils.* Science, 2010. **330** p. 1222-1227.

[15] Mohan, D., C.U. Pittman, Jr., and P.H. Steele, *Pyrolysis of Wood/Biomass for Bio-oil: A Critical Review.* Energy Fuels, 2006. **20** p. 848-889.

[16] Lu, Q., et al., *Catalytic upgrading of biomass fast pyrolysis vapors with nano metal oxides: an analytical Py-GC/MS study.* Energies ,2010. **3** p. 1805-1820.

[17] Pandey, M.P. and C.S. Kim, *Lignin depolymerization and conversion: a review of thermochemical methods.* Chem. Eng. Technol., 2011. **34** p. 29-41.

[18] Zhang, Y., et al., *A review on the formation mechanism of levoglucosan during fast pyrolysis of cellulose.* Shengwuzhi Huaxue Gongcheng, 2014. **48** p. 53-59.

[19] Banyasz, J.L., et al., *Cellulose pyrolysis: the kinetics of hydroxyacetaldehyde evolution.* J. Anal. Appl. Pyrolysis, 2001. **57** p. 223-248.

[20] Yang, H., et al., *Characteristics of hemicellulose, cellulose and lignin pyrolysis.* Fuel, 2007. **86** p. 1781-1788.

[21] Li, S., et al., *Real-time evolved gas analysis by FTIR method: an experimental study of cellulose pyrolysis.* Fuel, 2001. **80** p. 1809-1817.

[22] Luo, Z., et al., *Mechanism Study of Cellulose Rapid Pyrolysis.* Ind. Eng. Chem. Res., 2004. **43** p. 5605-5610.

[23] Liu, Y., et al., *Method for preparing bio-oil via biomass pyrolysis*, 2014, Xiamen University, Peop. Rep. China . p. 8pp.

[24] Shafizadeh, F., *Introduction to pyrolysis of biomass.* J. Anal. Appl. Pyrolysis, 1982. **3** p. 283-305.

[25] Branca, C., C. Di Blasi, and R. Elefante, *Devolatilization of Conventional Pyrolysis Oils Generated from Biomass and Cellulose.* Energy Fuels, 2006. **20** p. 2253-2261.

[26] Essig, M.R., G.N., *Mechanisms of formation of the major volatile products from the pyrolysis of cellulose.* . p. 841-862.

[27] Joardder, M.U.H., et al., *Solar assisted fast pyrolysis: a novel approach of renewable energy production.* J. Eng. p. 252848/1-252848/10.

[28] Hu, H.-t., et al., *A review of biomass pretreatment technologies and their influences on pyrolysis products.* Shengwuzhi Huaxue Gongcheng, 2014. **48** p. 44-50.

[29] Ekpenyong, K.I., *Energy in chemical reaction design An Inaugural Lecture delivered at the University of Jos, 27 January, 2005* .

[30] Kotz, J.C.P., K. F .*Chemistry and chemical reactivity. 2nd edition.* 1991.

[31] Hill, J.W., *Chemistry for changing times. 4th edition.* 1984.

[32] Robinson, R.R., Odom, J. D. & Holtzclaw, Jr. , *Chemistry concepts and models.* 1992.

[33] Zhu, M.-z., et al., *Analysis of bio-oil produced from corn stalk by thermal decomposition.* Zhongguo Kexue Jishu Daxue Xuebao, 2006. **36** p. 374-377.

[34] Avery, H.E., *Basic reaction kinetics and mechanisms.* 1974.

[35] Adamson, A.W., *A Textbook of Physical Chemistry 3rd Ed*1986: Academic. 991 pp.

[36] Paula, P.A.a.J.d., *Atkins' Physical chemistry.* 2009.

[37] Yao, J.-z., et al., *Fast pyrolysis of corn straw.* Huagong Yejin, 2000. **21** p. 434-437.

[38] Li, S., et al., *Column chromatographic separation of bio-oil from fast pyrolysis of biomass.* Taiyangneng Xuebao, 2005. **26** p. 549-555.

[39] Diebold, J.P., *A Review of the chemical and physical mechanisms of the storage stability of fast pyrolysis bio-oils.* 2000.