



## Catalytic Fast Pyrolysis of Nigerian Corn Cobs for Bio-Oil Production

Anthonia, E. Eseyin<sup>1</sup> and Kieran, I. Ekpenyong<sup>2</sup>

<sup>1</sup>Department of Sustainable BioProducts, Mississippi State University, Mississippi State, MS 39762, USA.

<sup>2</sup>Department of Chemistry, University of Jos, Nigeria.

### ABSTRACT

Pyrolysis gas chromatography mass spectrometry (Py-GC/MS) studies were carried out on catalyzed and uncatalyzed Nigerian corn cobs at 500°C. The catalyst used was Pd-doped  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. The compounds produced in the catalyzed and uncatalyzed samples were similar but in different quantities. The Pd-doped  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, significantly reduced the quantities of acids and alcohols from 12.84% to 4.16% and that of miscellaneous oxygenates from 2.78% to 1.45%. The quantity of phenolic compounds, aldehydes and ketones, as well as furfural increased significantly. Pd-doped  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> has been shown to improve the quality of bio-oil by reducing the quantities of acids and miscellaneous oxygenates in order to make bio-oil less corrosive.

**Key words:** *Fast Pyrolysis, Py-GC/MS, Corn Cobs, Pd-Doped  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, Catalyst and Bio-Oil.*

### 1. INTRODUCTION

A lot of attention has been drawn to renewable energy because of the shortage of fossil fuels and carbon emission problems. In order to attain a sustainable environment, there is an urgent need to make a transition to renewable resources of energy. With increasing global energy demand and deteriorating atmospheric greenhouse effects, biomass has become a promising energy source due to its abundance, carbon-fixing, and carbon-neutral properties. If well-managed and regulated, biomass is a sustainable source of energy that offers significant life-cycle GHG savings compared to fossil fuels. The carbon dioxide produced from burning biomass is captured during plant growth and is perceived as carbon-neutral and able to reduce the net CO<sub>2</sub> emissions when displacing fossil fuel use (W.-H. Chen & Lu, 2003; W.-H. Chen & Wu, 2009; Fiaschi & Carta, 2006; McKay, 2006; McKendry, 2002).

Biomass is widely considered to be a major potential future energy source. Biomass was the main energy resource for human beings in the past until the industrial revolution, when petroleum begun to be widely used. Biomass is the largest of all renewable resources that are utilized worldwide in underdeveloped, developing and developed countries. It is more available than most renewables like wind and hydropower ("Drax, Biomass: The Fourth Energy Source," ; W.-H. Chen, 2011). 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 (Balat, Balat, Kirtay, & Balat, 2009; Bridgwater & Peacocke, 1999; Huber, Iborra, & Corma, 2006; Serrano-Ruiz & Dumesic, 2011; Stephanidis et al., 2011).

Parallel with the growing interest in biomass as an alternative source of fuel and chemical feedstock, there is an increased demand for innovative technologies for the conversion of biomass to bio-oils (W.-H. Chen, & Kuo, P.-C., 2011; Deng, Wang, Kuang, Zhang, & Luo, 2009). Among the currently used conversion processes are: pyrolysis, anaerobic digestion, hydro-carbonization, incineration, and combustion under

controlled atmosphere. Fast pyrolysis is a thermal decomposition process that takes place in the absence of oxygen to convert biomass into liquid products, non-condensable gases and solid chars (Bridgwater & Peacocke, 1999; Mohan, Pittman, & Steele, 2006). Pyrolysis is one of the most promising processes that converts lignocellulosic materials into transportation fuels and chemicals because it is one of the few techniques that offers the opportunity to use nearly all of the biomass (Mettler, Vlachos, & Dauenhauer, 2012).

Biomass has been known to compose mainly of cellulose, hemicellulose and lignin. Cellulose is a high molecular weight (10<sup>6</sup> or more g/mol) linear polymer of  $\beta$ -(1 $\rightarrow$ 4) linked D-glucose units in the <sup>4</sup>C<sub>1</sub> conformation. Biomass comprises about 40-50% cellulose. Unlike cellulose, which is homo polymer (homogeneous) carbohydrate, hemicellulose is a hetero polymer (mixture) of various polymerized monosaccharides such as hexoses (e.g., glucose, galactose, mannose), pentoses (e.g., xylose, arabinose) and sugar acids (e.g., glucuronic acid, 4-O-methyl glucuronic acid, galacturonic acid) (Saha, 2003; Sun, Lawther, & Banks, 1998). Hemicellulose constitutes 20-30% of biomass and can be easily hydrolyzed by an acid to produce its monomer components. Lignin is a highly complex three-dimensional cross-linked macromolecular substance that consists of substituted phenyl propane units (e.g., guaiacyl, syringal, and p-hydroxyphenyl), linked together by C-O and C-C bonds (Nadji et al., 2009).

Corn cobs, stalks and leaves are abundant biomass resources and it is advantageous for the lignocellulosic parts of corn plants to be converted to fuels in order to enhance the total crop value per acre, while relieving some of the pressure on food price inflation. Unfortunately, very little corn stover, is converted to higher value added products because most of it is discarded as waste or as low-grade fuels (Cao, Xie, Bao, & Shen, 2004; Lin, Keener, & Essenhight, 1995).

Generally, bio-oils are viscous, acidic, thermally unstable, and contain a high proportion of oxygenated compounds. The

quality of bio-oils can be improved by the addition of catalysts into the pyrolysis process. The catalyst is expected to enhance the cracking reactions of the heavy molecules in pyrolysis products, leading to the production of less viscous bio-oils, reduce the formation of carboxylic acids in order to make bio-oil less corrosive and enhancing the formation of more valuable products like hydrocarbons that can increase the heating value of bio-oil.

There are a number of publications on corn stover pyrolysis (Capunitan & Capareda, 2012, 2013; Dang, Yu, & Luo, 2014; Huang, Kuan, Chang, & Tzou, 2013; Ren et al., 2014; Shah et al., 2012; C. Yang et al., 2010; X. Yang, Dey Laskar, Ma, Zhang, & Chen, 2013; Yu, Ruan, & Steele, 2009; Zhong, Song, Zhang, Liu, & Xue, 2014) but to the best of our knowledge, none of these reports has focused on the effect of Pd-doped  $\gamma$ - $\text{Al}_2\text{O}_3$  catalyst on the fast pyrolysis of corn cobs. The current study aims at utilizing the waste of the corn plant- corn cobs, to generate bio-oils by catalytic fast pyrolysis. The catalyst is expected to reduce the formation of carboxylic acids in the bio-oil and in essence make the bio-oil less corrosive.

## 2. MATERIALS AND METHODS

### 2.1 Preparation of corn cobs

Dry corn cobs were collected from some farms in the city of Jos, Nigeria, the cobs were oven-dried at 120 °C for 2 hours, crushed in a Bauer Mill (Bauer Brothers Co., MN, USA) and screened to a particle diameter of 0.5-2 mm, using a universal vibrating screen. The catalyst was heated in an oven at 110°C for two hours to eliminate moisture. The ratio of corn cobs to Pd-doped  $\gamma$ - $\text{Al}_2\text{O}_3$  catalyst was 10:1. The corn cobs and Pd-doped  $\gamma$ - $\text{Al}_2\text{O}_3$  were homogenized, by mixing thoroughly in a mortar.

### 2.2 Pyrolysis-GC/MS procedure

4.0 mg of the ground sample was placed in a quartz capillary tube and then held in a CDS pyroprobe (500 series, model 5150). The pyroprobe was interfaced with a 300°C transfer line, into a platinum coil attachment. Each sample was pyrolyzed at 500 °C at 20°C/ms heating rate. The hold time at the pyrolysis temperature was approximately 10s. The pyrolysis vapors were directly transferred to the GC/MS (Model: Clarus 500 GC/MS, Perkin Elmer, Inc., MA, USA) which carried out the analysis. The transfer line and injector temperatures were kept at 300 °C. An Elite-35MS capillary column (30 m  $\times$  0.25 mm  $\times$  0.25  $\mu\text{m}$ ) was used for chromatographic separation. Helium (99.9%) was the carrier gas with a constant flow rate of 1 mL/min and a split ratio of 1:8. During the analysis of the pyrolytic products from the stalks, the GC oven was heated from 40 °C to 280 °C (2 min) with the heating rate of 10°C/min. The GC/MS interface was held at 280 °C and the mass spectrometer was operated in EI mode at 70 eV.

### 2.3 Product analysis

The peak area and peak area percentage of each pyrolytic product were identified and determined. The chromatographic peaks were discriminated and analyzed by means of the NIST MS library and other literature data (Artigues, Puy, Bartroli, & Fabregas, 2014; Samanya, Hornung, Apfelbacher, & Vale, 2012; J.-P. Sun, Sui, Zhang, Tan, & Wang, 2013; Zhang et al., 2013; Zhang et al., 2009). For each chemical composition, a calibrated peak area % was identified to represent its relative content. Besides, it was known that the products could not be collected during the Py-GC/MS experiments, and therefore, the yields of total organic pyrolysis products could not be determined. The total calibrated chromatographic peak areas were used to reveal the changes of product yields, because the mass of feedstock was kept exactly the same during each experiment. Pyrolysis of each sample was carried out three times, to determine the consistency of the experimental results. The peak areas were added and the average determined and presented. However, some peaks were not identified.

## 3. RESULTS AND DISCUSSIONS

### 3.1 GC/MS of pyrolyzed Nigerian corn cobs at 500°C

Figures 1 and 2 are the GC/MS chromatograms of the pyrolyzed Nigerian corn cobs. The two figures look similar with only slight differences.

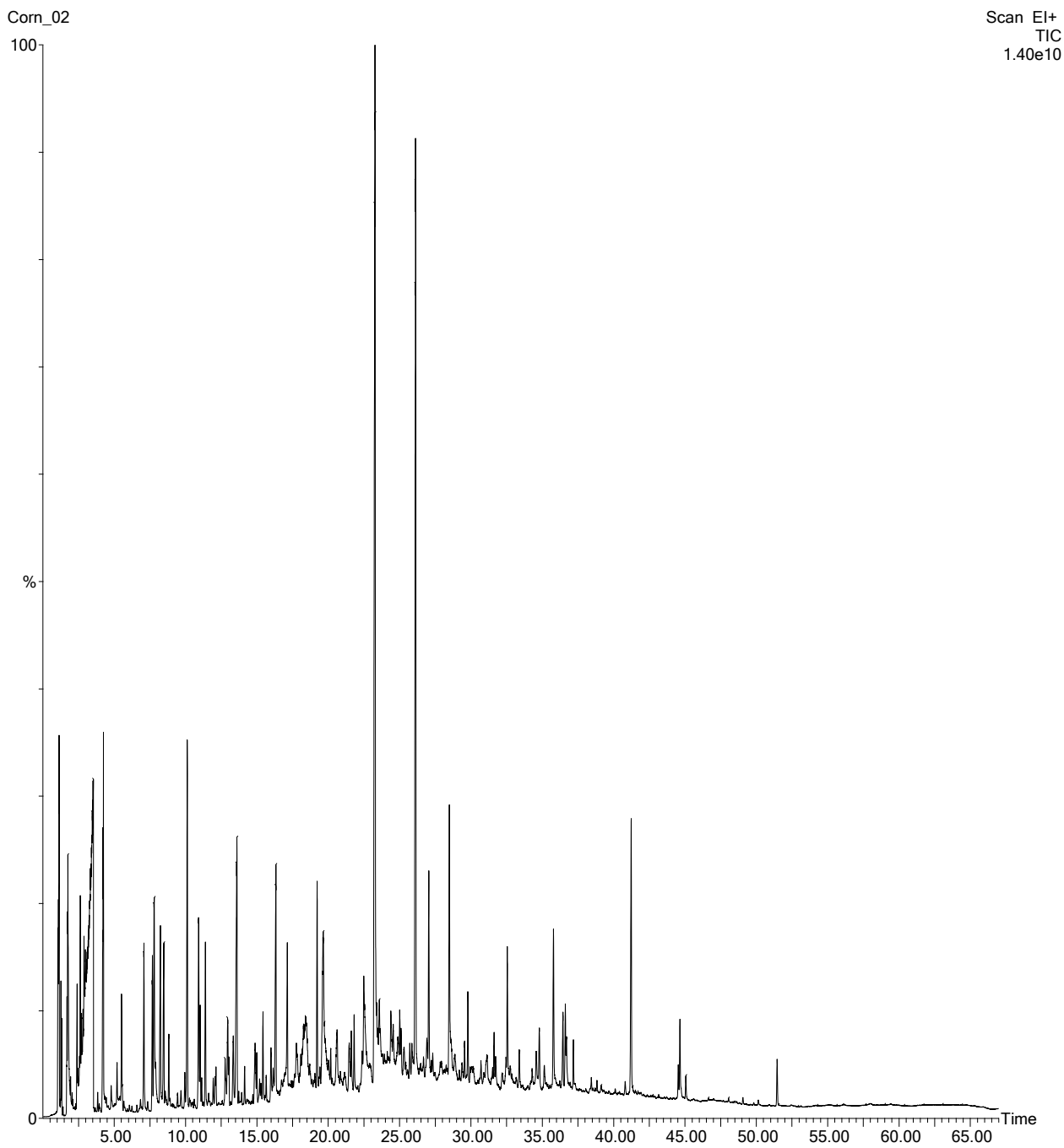


Figure 1. GC/MS of Uncatalyzed Corn Cobs

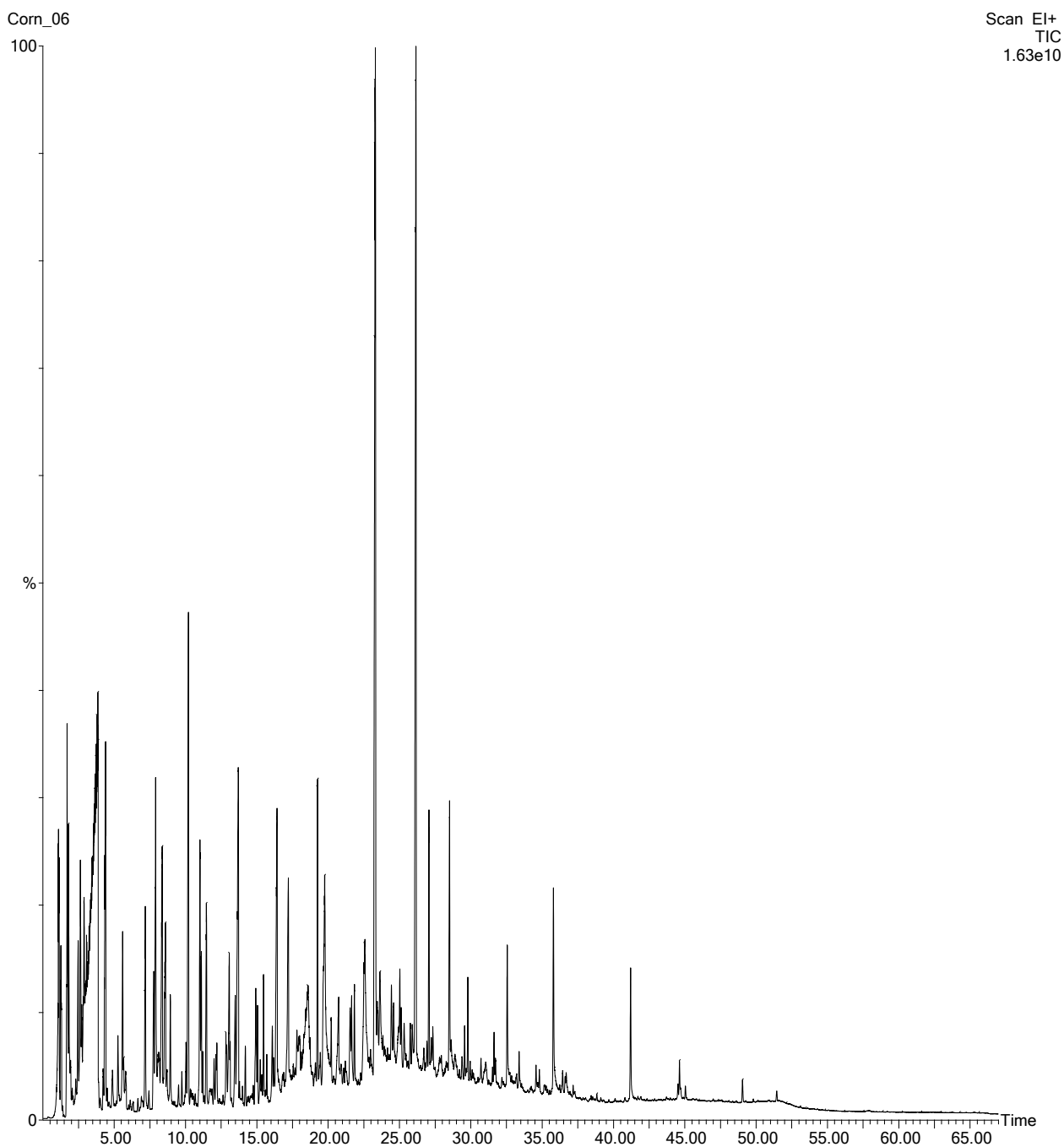


Figure 2. GC/MS of Catalyzed Corn Cobs

Table 1. Compounds Detected in the Py-GC/MS of Catalyzed and Uncatalyzed Corn Cobs

Retention Time (min)	Compound Name	Peak Area Percentage	
		Uncatalyzed Corn Cobs	Catalyzed Corn Cobs
1.67	1-Propane-2-ol,acetate	-	1.39
2.47	Acetaldehyde, hydroxy-	-	0.54
2.61	2,3-Butanedione	0.50	0.91
2.97	Acetic acid	10.97	1.10
4.23	2-Propanone, 1-hydroxy	2.22	2.34
5.58	Ethyl-1-propenyl ether	-	0.84
7.67	1-Hydroxy-2-butanone	0.68	1.53
8.23	Butanedial	1.07	1.41
8.47	Propanoic acid,2-oxo-, methyl ester	0.93	-
10.10	Furfural	2.06	2.56
10.90	2-Furanmethanol	0.99	1.18
11.38	2-Propanone, 1-(acetyloxy)-	0.94	1.03
12.94	2(5H)-Furanone	0.55	0.81
13.59	1,2-Cyclopentanedione	2.05	-
15.42	Phenol	0.44	1.47
17.12	1,2-Cyclopentanedione, 3-methyl	0.99	2.15
19.21	Phenol,2-methoxy	1.05	1.99
21.80	2,3-Dihydroxybenzaldehyde	0.44	0.42
22.57	1,2-Benzenediol	-	2.32
25.02	Phenol,4-ethyl-2-methoxy	-	1.73
26.11	2-Methoxy-4-vinylphenol	6.66	6.04
27.04	Phenol,2,6-dimethoxy	1.23	1.04
28.47	Vanillin	2.32	2.40

29.77	Phenol,2-methoxy-4-(1-propenyl)-	0.47	-
34.78	Benzaldehyde,4-hydroxy-3,5-dimethoxy-	0.43	-
35.77	Phenol,2,6-dimethoxy-4-(2-propenyl)-	1.17	2.35
36.44	Ethanone,1-(4-hydroxy-3,5-dimethoxyphenyl)-	0.46	-
36.60	4-Hydroxy-2-methoxycinnamaldehyde	0.47	-
41.22	n-Hexadecanoic acid	1.87	0.74

### 3.2 Comparative Py-GC/MS of the catalyzed and uncatalyzed pyrolyzed corn cobs, based on the compounds identified

Table 1 is a list of compounds detected in the catalyzed and uncatalyzed pyrolyzed corn cobs. Most of the compounds that

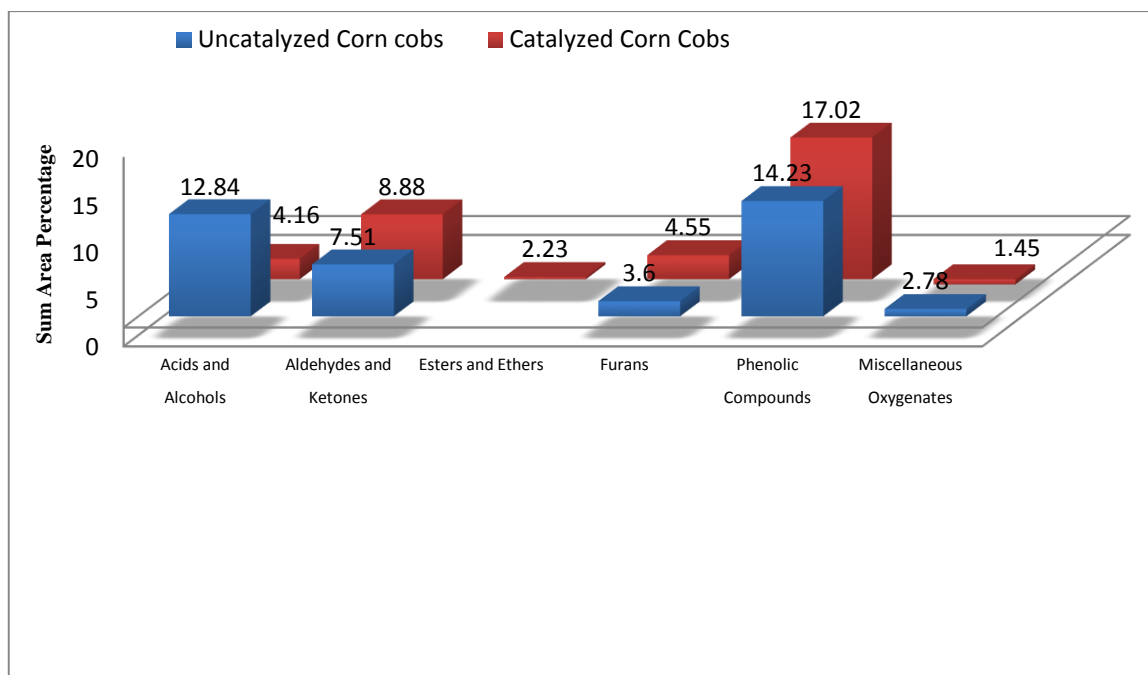
were produced by the uncatalyzed sample were also produced by the catalyzed corn cobs. However, compounds such as: 1-Propanol, acetate; Acetaldehyde, hydroxy-; Ethyl-1-propenyl ether; 1,2-Benzenediol and Phenol,4-ethyl-2-methoxy were produced by the pyrolyzed catalyzed corn cobs but were absent in the uncatalyzed sample. Propanoic acid,2-oxo-,methyl ester; 1,2-Cyclopentanedione; Phenol,2-methoxy-4-(1-propenyl)-; Benzaldehyde,4-hydroxy-3,5-dimethoxy-; Ethanone,1-(4-hydroxy-3,5-dimethoxyphenyl)- and 4-Hydroxy-2-methoxycinnamaldehyde were produced by pyrolyzed uncatalyzed corn cobs but absent in the pyrolyzed catalyzed sample.

### 3.3 Comparative Py-GC/MS of the catalyzed and uncatalyzed pyrolyzed corn cobs, based on the relative peak area% of the classified compounds

The compounds detected in the pyrolyzed catalyzed and uncatalyzed corn cobs were classified into: acids and alcohols: Acetic acid; n-Hexadecanoic acid and 1,2-Benzenediol. Aldehydes and ketones include: 2-Propanone;

1-hydroxy, 1-Hydroxy-2-butanone; Butanedial and 1,2-Cyclopentanedione. Among the phenolic compounds are: Phenol,2-methoxy; 2-Methoxy-4-vinylphenol and Phenol,2,6-dimethoxy. The miscellaneous oxygenates include: 2-Propanone,1-(acetyloxy)-; Propanoic acid,2-oxo-methyl ester and Dihydroxybenzaldehyde 4-Hydroxy-2-, methoxycinnamaldehyde. The furans are: Furfural; 2-Furanmethanol and 2(5H)-Furanone. Other classes of compounds are: esters and ethers.

The pyrolyzed uncatalyzed sample produced a relatively high percentage of acids and alcohols (12.84%) while the pyrolyzed catalyzed sample produced only 4.16% (Figure 3). The pyrolyzed catalyzed sample produced more aldehydes and ketones as well as furans. However, the pyrolyzed uncatalyzed sample did not produce any esters and ethers, while the pyrolyzed catalyzed samples produced 2.23%. The pyrolyzed catalyzed corn cob produced more phenolic compounds (17.02%) than the uncatalyzed sample (14.23%). The pyrolyzed uncatalyzed sample produced more miscellaneous oxygenates than the catalyzed sample. The Pd-doped  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst employed in this study increased the quality of bio-oil produced by decreasing the quantity of acids and miscellaneous oxygenates in the bio-oil and increasing the quantity of aldehydes and ketones, furans as well as phenolic compounds.



**Figure 3. Classes of Compounds Detected in the Py-GC/MS of Catalyzed and Uncatalyzed Pyrolyzed Corn Cobs**

Acids and ketones are majorly formed from hemicellulose because of its characteristic structure while furans and small-molecule aldehydes are produced by cellulose. Furfural is considered to have originated from hemicellulose by the concerted cleavage of the bond between oxygen and C-5 position on the xylose unit, followed by ring reforming between C-2 and C-5 position, by dehydration (Lv et al., 2013; Peng & Wu, 2010). Small molecular weight aldehydes originate mainly from the secondary decomposition of anhydrous sugars because under high temperatures, the anhydrous sugars (especially levoglucosan) that are generated from the direct conversion of the cellulose molecules can be further decomposed through possible dehydration, fission, decarbonylation, and decarboxylation reactions (Lv et al., 2013; Peng & Wu, 2010).

The production of aldehydes through the decomposition of anhydrous sugars was confirmed by the fact that very few anhydrous sugars are produced from the fast pyrolysis of cellulose at 500 °C. However, in this study, levoglucosan was not identified in both pyrolyzed samples. Ketones with slightly large molecular weights are formed mainly from the decomposition of sugar units and then recombination of the opened bonds (Shen, 2009). Monomeric phenols and cyclic compounds are formed from the fracture of ether linkages and the C-C bonds contained in the side chains of the lignin monomer. 2-Methoxy-4-vinylphenol and phenol,2,6-dimethoxy are formed from guaiacyl and syringyl lignin units respectively (Hosoya, Kawamoto, & Saka, 2009).

#### 4. CONCLUSION

Corn cobs, stalks and leaves are abundant biomass resources but unfortunately, very little corn stover is converted to

higher value added products such as bio-oil because most of it is discarded as waste or as low-grade fuels. Bio-oils are viscous, acidic, thermally unstable, and contain a high proportion of oxygenated compounds. The addition of catalysts into the biomass pyrolysis process is expected to enhance the cracking reactions of the heavy molecules in pyrolysis products, leading to the production of less viscous bio-oils and reduction in the formation of carboxylic acids in order to make bio-oil less corrosive.

The Pd-doped  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst that was employed in this study significantly reduced the quantity of acids and alcohols from 12.84% to 4.16% and miscellaneous oxygenates from 2.78% to 1.45%. The quantity of phenolic compounds, aldehydes and ketones as well as furfural increased significantly because of the presence of Pd-doped  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. This study has shown that the quality of bio-oils can be improved by the addition Pd-doped  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> to the pyrolysis process.

#### REFERENCES

- Balat, M., Balat, M., Kirtay, E., & Balat, H. (2009). Main routes for the thermo-conversion of biomass into fuels and chemicals. Part 1: Pyrolysis systems. [10.1016/j.enconman.2009.08.014]. *Energy Convers. Manage.*, 50, 3147-3157. doi: 10.1016/j.enconman.2009.08.014
- Bridgwater, A. V., & Peacocke, G. V. C. (1999). Fast pyrolysis processes for biomass. [10.1016/S1364-0321(99)00007-6]. *Renewable Sustainable Energy Rev.*, 4, 1-73. doi: 10.1016/s1364-0321(99)00007-6

- Cao, Q., Xie, K.-C., Bao, W.-R., & Shen, S.-G. (2004). Pyrolytic behavior of waste corn cob. [10.1016/j.biortech.2003.10.031]. *Bioresour. Technol.*, *94*, 83-89. doi: 10.1016/j.biortech.2003.10.031
- Capunitan, J. A., & Capareda, S. C. (2012). Assessing the potential for biofuel production of corn stover pyrolysis using a pressurized batch reactor. [10.1016/j.fuel.2011.12.029]. *Fuel*, *95*, 563-572. doi: 10.1016/j.fuel.2011.12.029
- Capunitan, J. A., & Capareda, S. C. (2013). Characterization and separation of corn stover bio-oil by fractional distillation. [10.1016/j.fuel.2013.04.079]. *Fuel*, *112*, 60-73. doi: 10.1016/j.fuel.2013.04.079
- Chen, W.-H., & Kuo, P.-C. (2011). Torrefaction and co-torrefaction characterization of hemicellulose, cellulose and lignin as well as torrefaction of some basic constituents in biomass. *Energy (Oxford, U. K.)*, *36*, 803-811.
- Chen, W.-H., & Lu, J.-J. (2003). Microphysics of atmospheric carbon dioxide uptake by a cloud droplet containing a solid nucleus. [10.1029/2002JD003318]. *J. Geophys. Res., [Atmos.]*, *108*, AAC11/11-AAC11/10. doi: 10.1029/2002jd003318
- Chen, W.-H., & Wu, J.-S. (2009). An evaluation on rice husks and pulverized coal blends using a drop tube furnace and a thermogravimetric analyzer for application to a blast furnace. [10.1016/j.energy.2009.06.033]. *Energy (Oxford, U. K.)*, *34*, 1458-1466. doi: 10.1016/j.energy.2009.06.033
- Dang, Q., Yu, C., & Luo, Z. (2014). Environmental life cycle assessment of bio-fuel production via fast pyrolysis of corn stover and hydroprocessing. [10.1016/j.fuel.2014.04.029]. *Fuel*, *131*, 36-42. doi: 10.1016/j.fuel.2014.04.029
- Deng, J., Wang, G.-J., Kuang, J.-H., Zhang, Y.-L., & Luo, Y.-H. (2009). Pretreatment of agricultural residues for co-gasification via torrefaction. [10.1016/j.jaap.2009.08.006]. *J. Anal. Appl. Pyrolysis*, *86*, 331-337. doi: 10.1016/j.jaap.2009.08.006
- Drax, Biomass: The Fourth Energy Source. Available from <<http://www.draxpower.com/biomass/>>, 2011 (accessed 11.3.15).].
- Fiaschi, D., & Carta, R. (2006). CO<sub>2</sub> abatement by co-firing of natural gas and biomass-derived gas in a gas turbine. [10.1016/j.energy.2006.07.026]. *Energy (Oxford, U. K.)*, *32*, 549-567. doi: 10.1016/j.energy.2006.07.026
- Hosoya, T., Kawamoto, H., & Saka, S. (2009). Role of methoxyl group in char formation from lignin-related compounds. [10.1016/j.jaap.2008.10.024]. *J. Anal. Appl. Pyrolysis*, *84*, 79-83. doi: 10.1016/j.jaap.2008.10.024
- Huang, Y.-F., Kuan, W.-H., Chang, C.-C., & Tzou, Y.-M. (2013). Catalytic and atmospheric effects on microwave pyrolysis of corn stover. [10.1016/j.biortech.2012.12.177]. *Bioresour. Technol.*, *131*, 274-280. doi: 10.1016/j.biortech.2012.12.177
- Huber, G. W., Iborra, S., & Corma, A. (2006). Synthesis of Transportation Fuels from Biomass: Chemistry, Catalysts, and Engineering. [10.1021/cr068360d]. *Chem. Rev. (Washington, DC, U. S.)*, *106*, 4044-4098. doi: 10.1021/cr068360d
- Lin, J.-L., Keener, H. M., & Essenhigh, R. H. (1995). Pyrolysis and combustion of corncobs in a fluidized bed: measurement and analysis of behavior. [10.1016/0010-2180(94)00143-G]. *Combust. Flame*, *100*, 271-282. doi: 10.1016/0010-2180(94)00143-g
- Lv, G., Wu, S., Yang, G., Chen, J., Liu, Y., & Kong, F. (2013). Comparative study of pyrolysis behaviors of corn stalk and its three components. [10.1016/j.jaap.2013.08.005]. *J. Anal. Appl. Pyrolysis*, *104*, 185-193. doi: 10.1016/j.jaap.2013.08.005
- McKay, H. (2006). Environmental, economic, social and political drivers for increasing use of woodfuel as a renewable resource in Britain. *Biomass and Bioenergy*, *20*(4), 308-315.
- McKendry, P. (2002). Energy production from biomass (part 1): overview of biomass. [10.1016/S0960-8524(01)00118-3]. *Bioresour. Technol.*, *83*, 37-46. doi: 10.1016/s0960-8524(01)00118-3
- Mettler, M. S., Vlachos, D. G., & Dauenhauer, P. J. (2012). Top ten fundamental challenges of biomass pyrolysis for biofuels. [10.1039/c2ee21679e]. *Energy Environ. Sci.*, *5*, 7797-7809. doi: 10.1039/c2ee21679e
- Mohan, D., Pittman, C. U., Jr., & Steele, P. H. (2006). Pyrolysis of Wood/Biomass for Bio-oil: A Critical Review. [10.1021/ef0502397]. *Energy Fuels*, *20*, 848-889. doi: 10.1021/ef0502397
- Nadji, H., Diouf, P. N., Benaboura, A., Bedard, Y., Riedl, B., & Stevanovic, T. (2009). Comparative study of lignins isolated from Alfa grass (*Stipa tenacissima* L.). [10.1016/j.biortech.2009.01.074]. *Bioresour. Technol.*, *100*, 3585-3592. doi: 10.1016/j.biortech.2009.01.074
- Peng, Y., & Wu, S. (2010). The structural and thermal characteristics of wheat straw hemicellulose. [10.1016/j.jaap.2010.03.006]. *J. Anal. Appl. Pyrolysis*, *88*, 134-139. doi: 10.1016/j.jaap.2010.03.006
- Ren, S., Lei, H., Wang, L., Yadavalli, G., Liu, Y., & Julson, J. (2014). The integrated process of microwave torrefaction and pyrolysis of corn stover for biofuel production. [10.1016/j.jaap.2014.04.008]. *J. Anal. Appl. Pyrolysis*, *108*, 248-253. doi: 10.1016/j.jaap.2014.04.008
- Saha, B. C. (2003). Hemicellulose bioconversion. [10.1007/s10295-003-0049-x]. *J. Ind. Microbiol. Biotechnol.*, *30*, 279-291. doi: 10.1007/s10295-003-0049-x



Serrano-Ruiz, J. C., & Dumesic, J. A. (2011). Catalytic routes for the conversion of biomass into liquid hydrocarbon transportation fuels. [10.1039/C0EE00436G]. *Energy Environ. Sci.*, 4, 83-99. doi: 10.1039/c0ee00436g

Shah, A., Darr, M. J., Dalluge, D., Medic, D., Webster, K., & Brown, R. C. (2012). Physicochemical properties of bio-oil and biochar produced by fast pyrolysis of stored single-pass corn stover and cobs. [10.1016/j.biortech.2012.09.061]. *Bioresour. Technol.*, 125, 348-352. doi: 10.1016/j.biortech.2012.09.061

Shen, D. K., & Gu, S. (2009). The mechanism for thermal decomposition of cellulose and its main products. *Bioresour. Technol.*, 100, 6496-6504.

Stephanidis, S., Nitsos, C., Kalogiannis, K., Iliopoulou, E. F., Lappas, A. A., & Triantafyllidis, K. S. (2011). Catalytic upgrading of lignocellulosic biomass pyrolysis vapours: Effect of hydrothermal pre-treatment of biomass. [10.1016/j.cattod.2010.12.049]. *Catal. Today*, 167, 37-45. doi: 10.1016/j.cattod.2010.12.049

Sun, R., Lawther, J. M., & Banks, W. B. (1998). Isolation and characterization of hemicellulose B and cellulose from pressure refined wheat straw. [10.1016/S0926-

6690(97)00040-X]. *Ind. Crops Prod.*, 7, 121-128. doi: 10.1016/s0926-6690(97)00040-x

W.-H. Chen, H.-C. H., K.-M. Lu, W.-J. Lee, T.-C. Lin. (2011). Thermal pretreatment of wood (Lauan) block by torrefaction and its influence on the properties of the biomass *Energy (Oxford, U. K.)*, 36(5), 3012–3021.

Yang, C., Zhang, B., Moen, J., Hennessy, K., Liu, Y., Lin, X., . . . Ruan, R. (2010). Fractionation and characterization of bio-oil from microwave-assisted pyrolysis of corn stover. [10.3965/j.issn.1934-6344.2010.03.054-061]. *Int. J. Agric. Biol. Eng.*, 3, 54-61. doi: 10.3965/j.issn.1934-6344.2010.03.054-061

Yang, X., Dey Laskar, D., Ma, F., Zhang, X., & Chen, S. (2013). Medium-temperature pyrolysis of corn stover improved by biopretreatment with white-rot fungi. [10.15376/biores.8.4.6383-6394]. *BioResources*, 8, 6383-6394, 6312 pp. doi: 10.15376/biores.8.4.6383-6394

Yu, F., Ruan, R., & Steele, P. (2009). Microwave pyrolysis of corn stover. *Trans. ASABE*, 52, 1595-1601.

Zhong, Z.-p., Song, Z.-w., Zhang, B., Liu, Z.-c., & Xue, Z.-y. (2014). Two-step catalytic pyrolysis of corn stover in a dual bed reactor. [10.4028/[www.scientific.net/AMR.1051.143](http://www.scientific.net/AMR.1051.143)]. *Adv. Mater. Res. (Durnten-Zurich, Switz.)*, 1051 143-147. doi: 10.4028/[www.scientific.net/AMR.1051.143](http://www.scientific.net/AMR.1051.143)