Low-Temperature Catalytic Pyrolysis of Corn Stalks – A Novel Route to the Production Of Bio-Oil And Valuable Chemical Feedstock

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ABSTRACT

Dry corn stalks were catalytically and uncatalytically thermally decomposed at 300 ºC for different retention times (2-6 h). The catalyst employed in the pyrolysis process was Pd-doped λ-Al$_2$O$_3$. The bio-oils produced were detected and identified using a gas chromatography/mass spectrometry (GC/MS). The results showed that the presence of the catalyst increased the bio-oil yield by approximately 50% relative to the uncatalyzed process. The bio-oils produced were found to contain carboxylic acids, esters, alcohols, phenols, alkanes, guaiacols, multi-component compounds, and miscellaneous oxygenates. Some of the compounds identified were produced in large volumes. The results of this study indicate that low-temperature catalytic pyrolysis of corn stalks is a promising technology for the commercial production of bio-oil and valuable chemical feedstock.

Key words: *Conventional Pyrolysis, Pd-Doped λ-Al$_2$O$_3$, Corn Stalks, Unextracted Lignocellulose, Thermal Decomposition, Bio-Oil, Retention Time, Catalyst, Valuable Chemical Feedstock.*

1. INTRODUCTION

In view of the oil crisis, the global Greenhouse effect, and the ever-increasing worldwide reliance on the Earth's finite supply of fossil fuel reserves (oil, gas, and coal), the world's attention has shifted towards finding other energy resources that are clean, convenient, cost-effective, and renewable. Among the alternative energy resources are nuclear and solar energy, wind power, and biomass.

Biomass is a renewable and sustainable source of energy that is available in every country and is expected to supply 10-20% of the world's energy supplies by 2050 [1]. The abundant sources of biomass include forest debris, animal wastes, energy crops, and agricultural residue [2]. Nearly every part of the world has biomass resources that can be tapped as biofuels to generate electric power. From coconut and rice husks, corn stalks to fast growing trees, from perennial grasses to scrap wood, there is probably an under-utilized form of biomass almost everywhere on Earth [2]. Accordingly, biomass currently offers a great potential source of energy especially for developing countries that have either limited or no fossil fuels [3].

Biofuels are energy-rich compounds that are categorized into four "generations". The first generation biofuels are produced directly from biomass suitable for food (e.g., sugars, starches, oil, animal fat, etc). These fuels include biodiesel, bio-ethanol, bio-alcohols, and bio-gases. The most common concern related to the first generation biofuels is the possibility of food shortage and increased food prices. The second generation biofuels are produced from non-food lignocellulosic biomass feedstock that does not compete with food production such as agricultural residues (e.g., corn stover, wheat straw, bagasse, switch grass, organic waste, etc)

[4-6]. Currently, both the first and second generation biofuels account for over 90% of the global biofuel production. The third generation biofuels are mainly made from microalgae, seaweeds, and quickly growing biomass sources. The main advantage of the algae-based biofuels is that the algae can be grown on land and water unsuitable for food crops. In addition, the biofuel can be converted to several fuels including jet fuel and diesel. The fourth generation biofuels are made from plants and biomass that are modified using organisms or advanced biochemical methods. In addition to being a source of renewable energy, the fourth generation biofuels is a way to capture and stored CO$_2$.

Biofuels are prepared from biomass through physical, biological, chemical or thermo-chemical (pyrolysis) processes. Out of all of these technologies, pyrolysis offers the most viable and efficient route for the production of fuel and chemical feedstock [7]. In addition, the products of the pyrolysis can be stored and transported. Moreover, pyrolysis has been the source of many basic organic chemicals such as methanol, acetic acid, and acetone for about a century now [7, 8]. Pyrolysis is a process that converts biomass directly into solid, liquid, and gaseous products by thermal decomposition in the absence of oxygen.

Because biomass contains different components with different thermal properties, biomass pyrolysis is a very complex process during which several reactions take place. These reactions can be influenced by several factors including the chemical or physical pretreatments of the raw materials, type of reactor, heating rate, pyrolysis temperature, residence time, pyrolysis atmosphere, and particle size [9].

Bio-oil consists of more than 300 organic compounds with different molecular sizes and functional groups. It also has

higher energy content and is cleaner than biomass [10]. All the products of biomass pyrolysis are valuable and can be used. Slow pyrolysis gives considerably higher water concentrations. At lower temperatures and longer residence times, the yield of pyrolysis oil decreases while char is formed in higher amounts [11, 12].

The use of heterogeneous catalysts in the pyrolysis of biomass to improve the bio-mass quality has gained an increased interest in the last decade. Most of the catalytic studies on biomass pyrolysis have been focused mainly on porous materials such as zeolites (e.g., ZSM-5), and mesoporous aluminosilicates. However, the major limitations of using relatively small pore zeolites are (i) a significant decrease in the organic yield, due to the increase of the production of water and gases, and (ii) a rapid catalyst deactivation by coke deposition [13]. These limitations motivated the search for other catalyst materials such as pure and doped mesoporous alumina (e.g., Pd-doped λ-Al_2O_3) which showed a higher thermal stability, low rate of deactivation, and a high selectivity.

Nigeria is located in the tropics and savannah region of the world, and as such, is well endowed with cellulosic materials. Corn is the most extensively grown plant in Nigeria. Unfortunately, most of the cellulosic materials from the corn plant are wasted annually through obnoxious bush burning for agricultural purposes [14].

Several studies have been reported on the production of bio-oil through catalytic pyrolysis [15-30]. However, to the best of our knowledge, there is no reported work on low-temperature conventional pyrolysis of corn stalks for the production bio-oil. Accordingly, the current study aims at the production of bio-oil from the pyrolysis of Nigerian corn stalks using a low-temperature conventional pyrolysis process with and without the use of Pd-doped λ-Al_2O_3 as a catalyst.

2. METHODS

2.1 Elemental analysis

To determine the % of C, H, and O in the corn stalks, elemental analysis was carried out using a CE440 Elemental Analyzer (EAI Exeter Analytical, Inc., UK). In the analysis, ethylene diamine tetra acetic acid (EDTA) was used as the control standard solution and He as the carrier gas. Approximately 0.60 g of the oven-dry corn stalks was wrapped in aluminum foil cups and burned. The combustion process occurred at 950 ºC in the combustion chamber with pure oxygen (99.993%). All measurements were conducted in duplicate, and the average results are reported.

2.1 Material composition analysis

Material composition analysis of corn stalks biomass was conducted for cellulose, hemicellulose, lignin, and extractives. Extractives included water, alcohol, and benzene. The hemicellulose and lignin contents were determined, based on acid hydrolysis in 2% (w/w), and 72% (w/w) sulfuric acid, respectively. The cellulose content was calculated by the water-loss method.

2.2 Preparation of pyrolysis samples

Dry corn stalks were randomly collected from some farms in the city of Jos, Nigeria. The stalks were washed in deionized water and dried in a Gallenkamp oven at a temperature of 105 ºC for 2 hours to remove the moisture. The stalks were then cut into smaller pieces and crushed using a Bico pulverizing machine. The crushed samples were sieved to obtain a mesh size of 250-300 ꞵm. In the catalyzed pyrolysis, the pelletized Pd-doped λ-Al_2O_3 was ground and sieved to 250-300 um mesh size. The catalyst was then homogenized with the crushed corn stalks using a mortar. In each pyrolysis, 3.0 mg of Pd-doped λ-Al_2O_3 was used per 3.0 g. of sample. The blend was then stored in a Pyrex tube in readiness for pyrolysis.

2.3 The reactor

The reactor used in this work (Fig. 1) was assembled in house. It consisted of Pyrex tubes (1.5 cm inner diameter and 16 cm length). The heating medium was a cylindrical brass block (7.0 cm diameter and 9.0 cm height) into which three thermal wells (1.7 cm diameter and 7.0 cm depth) were drilled at approximately equal distance apart. The brass block was heated electrically on a hot plate equipped with a temperature regulator.

To monitor the temperature of the system, a thermometer was placed slightly above the bottom of one of the wells. Pyrolysis samples, placed in two different test tubes, were dipped into the remaining two wells. As shown in Figure 1, the tubes were connected to water-filled, inverted burettes, placed in a trough for the collection of gas evolved in the reaction [31].
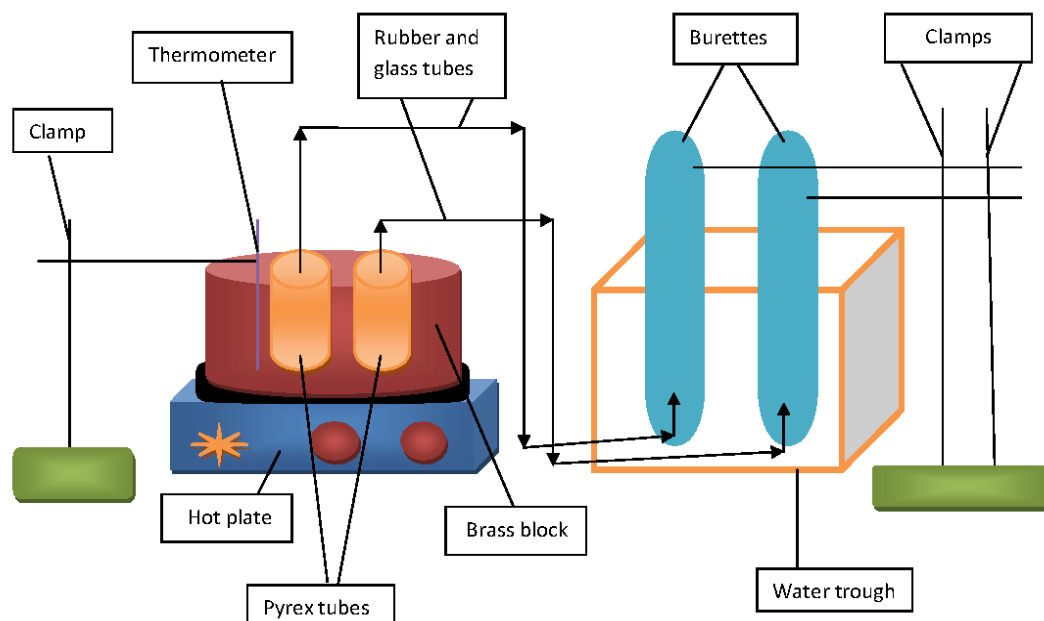
Fig.1 Schematic diagram of the reactor

2.4 The pyrolysis process

Sieved 3.00 g of each sample was placed in two Pyrex tubes and the tubes were placed in the wells of the already heated metallic heating block. Pyrolysis was carried out at 300 ºC for 2, 4, and 6 hours. Three samples of the same material were used in each pyrolysis, and the average of the bio-oil volumes produced were obtained and recorded.

2.5 The extraction process

After pyrolysis, each sample was allowed to cool in the Pyrex tubes. The cold sample was then introduced into a 500 mL Soxhlet extractor. Extraction was carried out in n-hexane for 2 hours in each case. After the extraction, the n-hexane was evaporated, leaving the bio-oil. The volume of the bio-oil was determined using a syringe.

2.6 pH measurements

The pH of the bio-oil produced was measured in deionized water. 1.00 g of the bio-oil was stirred with 50 mL of water to obtain a uniform solution. The pH of the solution was measured using a Thermo Orion pH meter (Thermo Scientific, Inc.).

2.7 Detection of the bio-oil compounds using GC/MS

Samples of the bio-oil obtained were analyzed using a Perkin-Elmer Clarus 500 GC/MS instrument. The calibration standards were obtained from Sigma-Aldrich and used without further purification. Concentrated stock solutions were prepared by weighing 0.100 g of each individual bio-oil to the nearest 0.1 mg, dissolving these standards in 2.0 mL of methanol. A sample of 2.4 μL 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 where the spectra were collected and saved.

3. RESULTS AND DISCUSSION

3.1 Proximate, ultimate, and material analyses

The results of proximate, ultimate, and material analyses of the corn stalks used in the pyrolysis for bio-oil production are reported in Table 1. The corn stalks were previously oven dried and as such, the water content was 0.00%.

Table.1. Proximate, ultimate, and material analyses of dry corn stalks used, in the low-temperature conventional pyrolysis.

Proximate Analysis	(%)
Moisture	0.00
Ash	6.89
Volatile	76.14
Fixed carbon	16.97
HHV (BTU/lb)	8153
MMF (BTU/lb)	8469
Ultimate Analysis	(%)
Carbon	60.30
Hydrogen	5.51
Nitrogen	0.85
Sulfur	0.10
Oxygen	33.24
Material Composition Analysis	(%)
Extractives	11.65
Cellulose	48.32
Hemicellulose	22.46
Lignin	16.20

3.2 pH Measurements

The pH value of bio-oils produced was found to be 2.86. This value is consistent with the values reported in literature [32]. In general, most bio-oils have a pH in the range of 2.0–3.8 because of the presence of carboxylic acids, mostly formic and acetic acids. The acids in the bio-oils are corrosive to common construction materials such as aluminum and carbon steel, especially at elevated temperature and high water content.

3.3 Volumes of bio-oils produced

Figures 2 and 3 show the volumes of bio-oil obtained in the uncatalyzed and catalyzed low-temperature pyrolysis of corn stalks at 300 °C, respectively, for retention times up to 6 h. As shown in both figures, the highest volume of bio-oil was produced at the maximum retention time (6 h). At retention times longer than 6 h, the volume of the bio-oil was smaller. In the uncatalyzed pyrolysis (Fig. 2), the bio-oil yield increased with increase in retention time with the largest volume formed at 6 h retention time. Figure 3 shows the effect of the Pd-doped λ-Al_2O_3 catalyst on the amount of bio-oil produced in the pyrolysis. It is particularly interesting to see that the presence of the catalyst increased the bio-oil yield at all studied retention times at such a low pyrolysis temperature.

Moreover, a comparison between Figures 2 and 3 clearly indicates the bio-oil produced in the catalyzed pyrolysis is about 50% larger than that produced in the uncatalyzed process
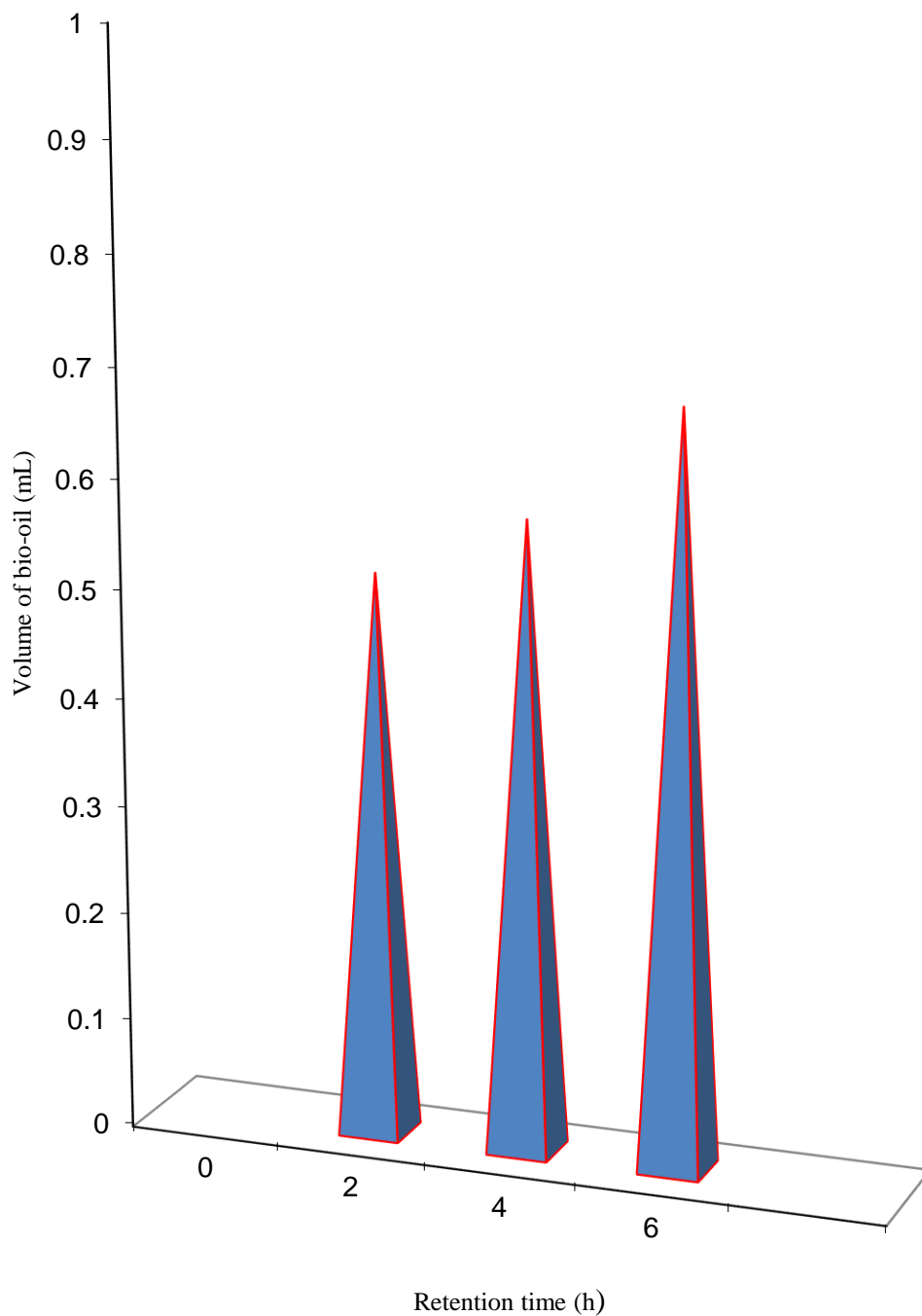
Fig. 2. Variation of the volume of bio-oil produced in the uncatalyzed pyrolysis of corn stalks with retention time, at 300 ºC.
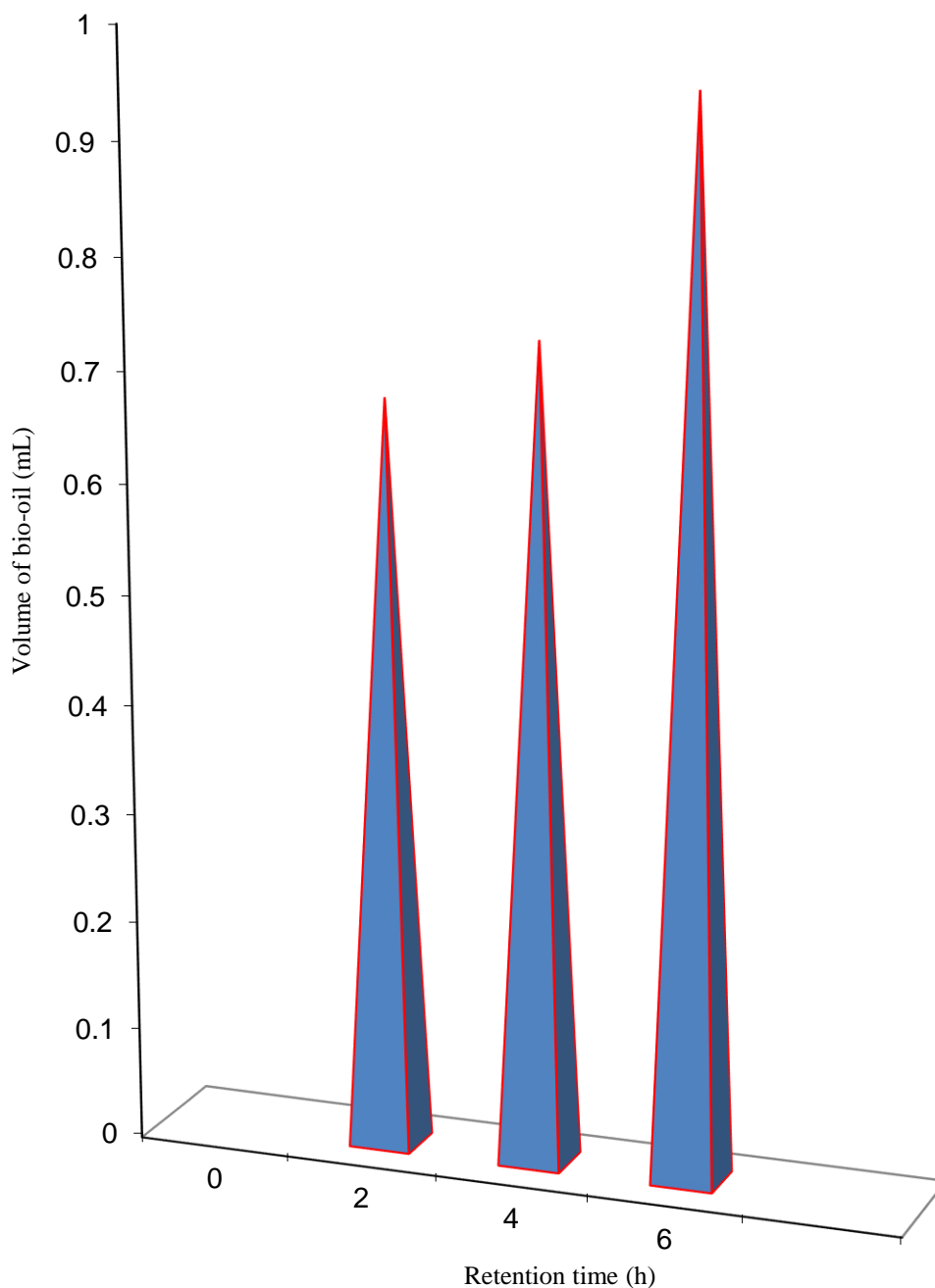
Fig. 3. Variation of the volume of bio-oil produced in the catalyzed pyrolysis of corn stalks with retention time, at 300 ºC.

3.4 GC/MS chromatogram

Figs. 4 and 5 show the GC/MS chromatograms of the bio-oils produced in the uncatalyzed and catalyzed pyrolysed corn stalks at 300 ºC, respectively. The two chromatograms are obviously different from each other. It can also be seen that the bio-oil compounds detected in the catalyzed sample had particularly larger peak area percentages. The GC/MS procedure was carried out three times and the compounds that were identified consistently were considered to be the actual compounds that were detected, using the GC/MS. The average of the peak area percentages were determined and used in the discussion. Many peaks were however, not identified.
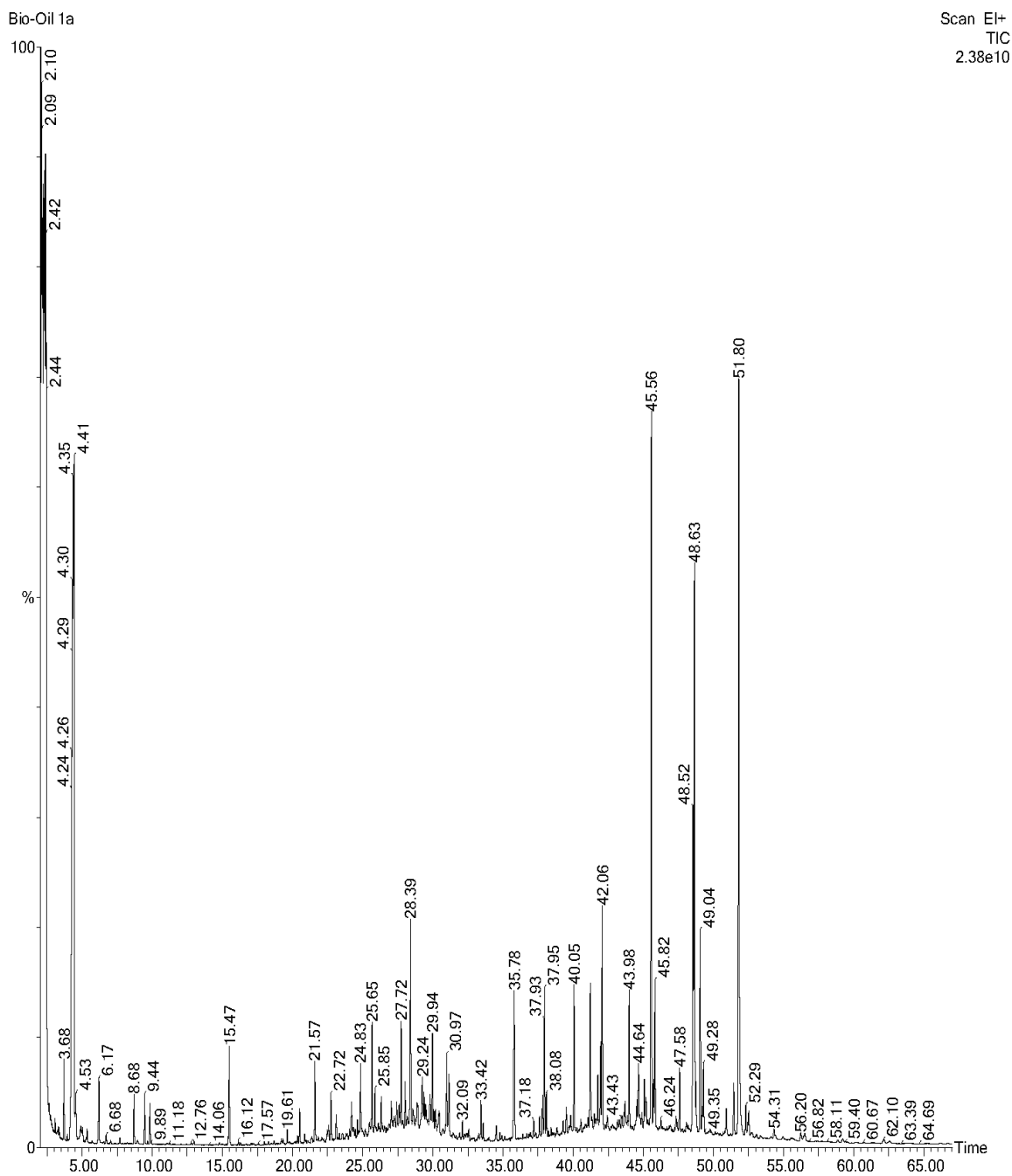
Fig. 4. GC/MS chromatogram for bio-oil produced from the uncatalyzed pyrolysis of corn stalks at 300 ºC.
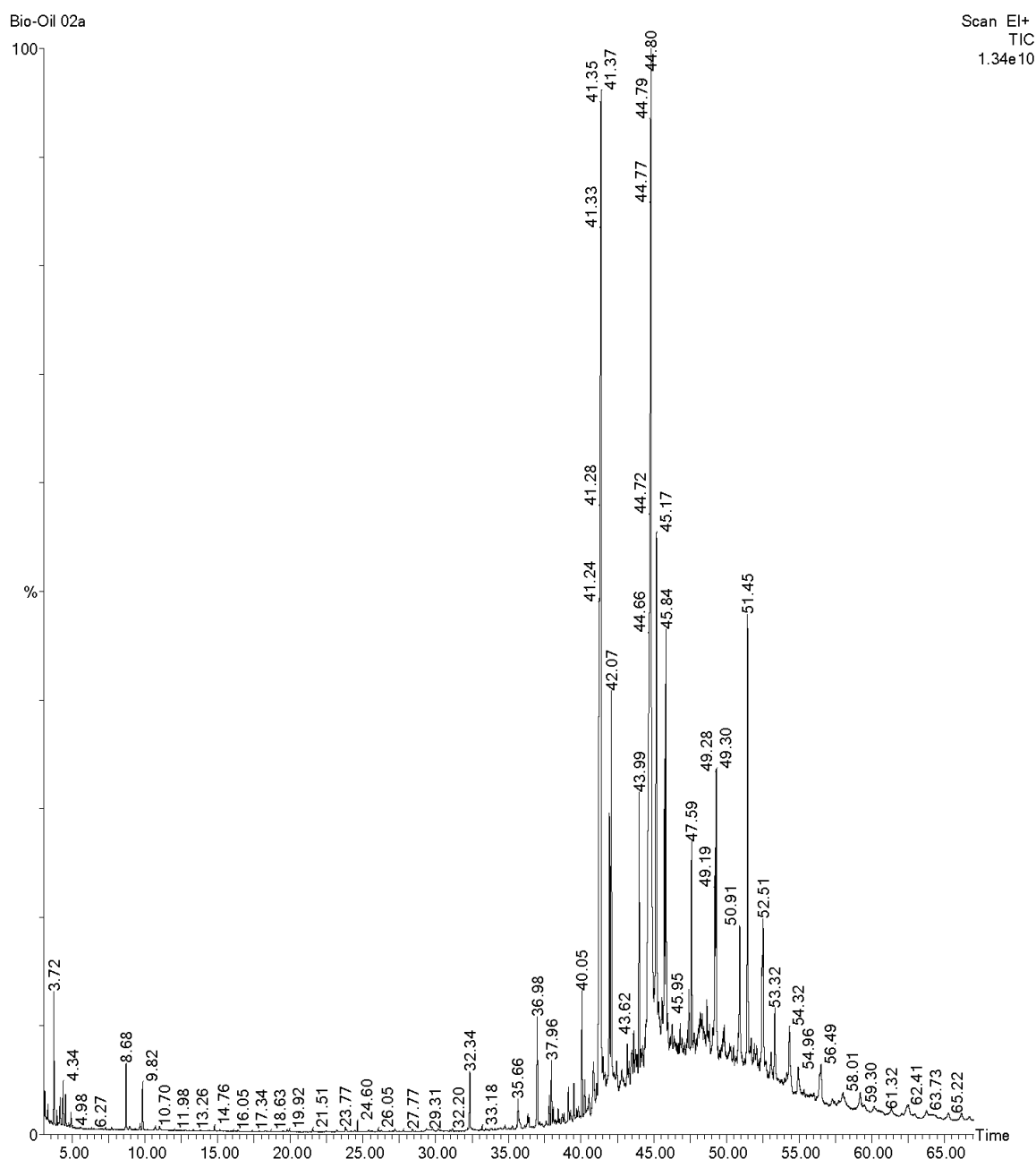
Fig. 5. GC/MS chromatogram for bio-oil produced from the catalyzed pyrolysis of corn stalks at 300 º

3.5 Classification of the bio-oil compounds detected in the catalyzed and uncatalysed, pyrolysed corn stalks

The bio-oil compounds detected, retention time, and peak area percentages are shown in Table 2 while the classes of the compounds identified are reported in Table 3. Most of the compounds identified were found in both bio-oil samples. However, octamethyl cyclotetrasiloxane, 1,1-dibutoxybutane, and 1,4-dimethoxybenzene were identified in the bio-oil produced in the uncatalyzed process while they were not identified in the bio-oil obtained from the catalyzed sample. On the other hand, 1-cyano-4, dimethyl-1-phenylphenyl ethaneperoxoic acid ester, 2-chloro-2-methylbutane, 1-(4-hydroxy- 3-methoxy phenyl) ethanone, 4-hydroxy-3,5-dimethoxybenzaldehyde, and 1-(4-hydroxy-3,5-dimethoxyphenyl) ethanone were identified only in the bio-oil produced in the catalyzed process.

A particularly large peak area percentage of acetic acid was identified in the uncatalyzed sample while n-hexadecanoic acid and n-butyl myristate were identified to have large peak area percentages in the catalyzed sample. Octadecanoic acid, butyl hexadecanoic acid ester and diisooctyl-1,2 benzenedicarboxylic acid ester were identified in the bio-oil produced in the catalyzed and uncatalyzed samples. Generally, it was observed that the peak area percentages of the compounds identified in the bio-oil produced from the catalyzed process were larger than those identified in the bio-oil produced from the uncatalyzed process. The compounds detected in both processes (Table 3) were classified into carboxylic acids, esters, alcohols, phenols, alkanes, guaiacols, multicomponent compounds, and miscellaneous oxygenates.

Bio-oil consists of more than 300 organic compounds. Compared to biomass, bio-oil is cleaner and has a higher

energy content [10]. The reactions that occur during bio-oil production include hydrolysis, dehydration, isomerization, dehydrogenation, aromatization, retro-condensation, and coking. The multicomponent mixtures are derived primarily from depolymerization and fragmentation reactions of the three building blocks of lignocellulose: cellulose, lignin and hemicellulose. The 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 [33]. The bio-oil compounds detected in this work are similar to those detected in maize stover pyrolysis works done previously [34-36].

Table 2. List of the bio-oil compounds detected in the catalyzed and uncatalysed, pyrolysed corn stalks at 300 ºC

Retention Time, t_R (min)	Library Match	Peak Area (%)	
		Bio-oil from Uncatalyzed Corn Stalks	Bio-oil from Catalyzed Corn Stalks
2.13	Ethaneperoxoicacid,1-cyano-4,4-dimethyl-1-phenylphenyl ester	–	0.23
2.10	Acetic acid	26.93	1.14
3.68	Amylene hydrate	0.87	0.98
4.34	2-Chloro-2-methylbutane	_	0.98
6.17	Methylcyclohexane	0.65	0.32
15.47	Cyclotetrasiloxane,octamethyl-	0.62	_
21.57	Phenol,4-ethyl-	0.41	0.12
24.83	Butane,1,1-dibutoxy-	0.36	_
25.65	Benzene, 1,4-dimethoxy-	0.48	_
28.39	Phenol, 4-ethyl-2-methoxy-	1.82	0.94
30.97	Ethanone,1-(4-hydroxy-3-methoxy phenyl)-	–	0.32
30.97	1,2,3-Benzenetriol	0.83	0.68
33.42	Dodecanoic acid	0.63	0.86
35.66	Benzaldehyde,4- hydroxy-3,5-dimethoxy-	–	1.35
37.93	Tetradecanoic acid	1.23	0.98
37.95	Ethanone,1-(4-hydroxy-3,5-dimethoxy phenyl)-	–	0.92
40.05	Pentadecanoic acid	1.15	1.87
41.37	n-Hexadecanoic acid	2.40	27.96
44.80	n-Butyl myristate	1.02	28.23
45.17	Octadecanoic acid	15.35	15.61
49.30	Hexadecanoic acid, butyl ester	10.50	6.54
51.45	1,2-Benzenedicarboxylic acid, diisooctyl ester	16.22	12.98

Table 3. Classification of bio-oil compounds detected in the catalyzed and uncatalyzed pyrolyzed corn stalks at 300ºC

Class	Compound
Carboxylic acids	Dodecanoic acid
	Tetradecanoic acid
	n-Hexadecanoic acid
	Octadecanoic acid
	Pentadecanoic acid
	Acetic acid
Esters	n-Butyl myristate
Alcohols	Amylene hydrate
	1,2,3-Benzene triol
Phenol	Phenol, 4-ethyl-
Hydrocarbon	Cyclohexane, methyl-
Guaiacols	Ethanone, 1-(4-hydroxy-3-methoxy phenyl)-
	Ethanone, 1-(4-hydroxy-3, 5-dimethoxy phenyl)-
	Benzaldehyde,4-hydroxy-3,5- dimethoxy-
	Benzene, 1,4-dimethoxy-
	Phenol, 4-ethyl-2-methoxy-
	Butane, 1, 1-dibutoxy-
Miscellaneous oxygenates	1, 2-Benzenedicarboxylic acid, diisooctyl ester
	Hexadecanoic acid, butyl ester
Multicomponent mixtures	Butane, 2-chloro-2-methyl-
	Cyclotetrasiloxane, octamethyl-
	Ethaneperoxoicacid,1-cyano-4,4-dimethyl-1-phenylphenyl ester

4. CONCLUSION

The second generation technologies produce biofuels from lignocellulose biomass feedstock such as agricultural wastes and forest harvesting residue. Agricultural wastes (e.g., the non-edible components of corn) are very abundant in Nigeria. In the current investigation, the uncatalyzed and catalyzed pyrolysed corn stalks collected from farms in the city of Jos, Nigeria was studied at 300 ºC at different retention times (up to 6 hours) in a simple, locally assembled reactor. The results showed that higher volumes of bio-oil were produced when the pyrolysis process was catalyzed with Pd-doped λ-Al$_2$O$_3$. The bio-oil yield in the catalyzed pyrolysis was about 50% larger than that produced in the uncatalyzed process. The GC/MS analysis indicated the presence of the following compounds in the obtained bio-oils: carboxylic acids, esters, alcohols, phenols, alkanes, multi-component compounds and miscellaneous oxygenates. Particularly, large volumes of acids and esters were identified in the bio-oils produced in both catalyzed and uncatalyzed pyrolysed corn stalks. The results of the present study indicate that low-temperature catalytic pyrolysis of agricultural wastes is a promising technology for commercial production of bio-oil and valuable chemical feedstock.

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