



Exceptionally High Yields of Hydrocarbons from the Catalytic Co-pyrolysis of Torrefied Corn Stalks with High Density Polyethylene

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Abstract

Torrefied corn stalks (TCS), torrefied corn stalks/high density polyethylene (TCS/HDPE), with and without zeolite catalyst (HZSM-5) were analyzed by Py-GC at 400, 500, and 600°C for the production of high yields of hydrocarbons. The highest yield of hydrocarbons (43.38%) was produced by TCS/HDPE/Cat. at 600°C. 21.83% yield was produced in the absence of HZSM-5 at 600°C. Lower yields were recorded at lower temperatures, with or without catalyst. The pyrolysis of TCS alone did not produce any hydrocarbon at any of the pyrolysis temperatures. Elemental analysis results showed that HDPE contained higher percentages of carbon and hydrogen than torrefied corn stalks. The thermogravimetric analysis results indicated that HDPE was more thermally stable than TCS. TCS decomposed at about 300°C while HDPE decomposed at about 475°C. Maximum weight loss was achieved at about 350°C and 500°C for TCS and HDPE, respectively.

Key words: Pyrolysis; Torrefied corn stalks; HZSM-5, High density polyethylene; hydrocarbons; PY-GC/MS

Introduction

The predicted increasing future global energy demand and deteriorating atmospheric greenhouse effects from combustion of fossil fuels have resulted in efforts to substitute biomass for fossil fuel energy sources. Biomass is abundant and has carbon-fixing and carbon-neutral properties (Chen & Lu, 2003; Chen & Wu, 2009; Fiaschi & Carta, 2006).

A simple thermal pretreatment process called torrefaction, has recently been applied, to improve the properties of biomass. Torrefaction is a thermochemical process that occurs at around 200-300°C in the absence of oxygen (Sadaka & Negi, 2009). Torrefaction pretreatment at 200-300°C improves biomass quality (Chen, Lu, & Tsai, 2012) and contributes to the flowability of biomass materials during feeding of combustion units.

Furthermore, torrefaction can effectively reduce biomass oxygen content, increase energy density, reduce transportation and storage costs and improve C/O ratio (Deng, Wang, Kuang, Zhang, & Luo, 2009; Patuzzi, Mimmo, Cesco, Gasparella, & Baratieri, 2013; Wannapeera & Worasuwannarak, 2012).

Thermochemical conversion of biomass is a renewable technology, since new biomass can be grown to replace that used for energy. This growth removes CO₂ from the atmosphere, counteracting the CO₂ emission generated when converting biomass to energy. When biomass is used as feedstock for power generation, it often exhibits undesirable properties.

If a current coal combustion unit is utilized to co-fire biomass with coal, there is a limit of approximately 10% on the amount of biomass co-fired. Some types of biomass have high ash content, which leads to the agglomeration of the bed material inside a reactor as well as fouling problems at the surface of boiler heat transfer tubing in combustion chambers (Oehman, Pommer, & Nordin, 2005; Pronobis, 2006; Romeo & Garetta, 2009). Raw biomass has low energy density and calorific value and high moisture and oxygen content (Chen & Kuo, 2011; Pimchuai, Dutta, & Basu, 2010).

Due to high rigidity, mechanical strength, low flowability and fluidization properties, biomass requires high grinding energy and is difficult to feed into boilers (J. Li, Brzdekiewicz, Yang, & Blasiak, 2012; Ohliger, Foerster, & Kneer, 2013; van der Stelt, Gerhauser, Kiel, & Ptasinski, 2011).

Some specific challenges to biomass use are: the land surface required to grow it (C. Higman) and high costs for collection and transportation (Biagini, Cioni, & Tognotti, 2005). After drying biomass, it can regain moisture and may rot during storage (Bergman, 2012). Biomass is hygroscopic and forms more soot during combustion than coal fired boilers. For co-firing of current coal combustion boilers, utilization of torrefied wood eliminates the limit on percentage of biomass combusted with coal. Therefore, in the form of torrefied wood a coal boiler can burn 100% torrefied wood without the need to invest high amount of capital for a dedicated biomass boiler. In order to enhance biomass utilization efficiency and limit the challenges mentioned above, a torrefaction pretreatment is beneficial (Acharjee, Coronella, & Vasquez, 2011; Mosier *et al.*, 2005; van der Stelt *et al.*, 2011; Zwart, Boerrigter, & van der Drift, 2006).

Torrefaction technology and its applications have advanced significantly (Agar & Wihersaari, 2012; Becer, Brosch, Wirtz, & Scherer, 2013; Bojner, 2011; Chen, Cheng, Lu, & Huang, 2011; Dhungana, Basu, & Dutta, 2012; Doassans-Carrere, Muller, & Mitzkat, 2014; Huang, Chen, Chiueh, Kuan, & Lo, 2012; Johnston, 2013; Kamdem, Pizzi, & Jermannaud, 2002; Makarov, Grachev, Zabelkin, & Pushkin, 2013; Pawlak-Kruczek, Czerep, Zgora, & Kruczek, 2014; Phanphanich & Mani, 2011; Srinivasan, Adhikari, Chattanathan, & Park, 2012; Stamm, 1956; Stanzl-Tschegg, Beikircher, & Loidl, 2009; Syu & Chiueh, 2012; Tjeerdsmas & Militz, 2005; Wilen *et al.*, 2013).

In the process of torrefaction, biomass undergoes partial decomposition, with the release of volatiles, which result in overall mass loss. Torrefaction leads to a loss of the fibrous structure of the biomass, primarily because of the decomposition of hemicellulose and depolymerization of cellulose. Furthermore, torrefaction also leads to a significant elimination of oxygen and moisture from the biomass increasing its calorific value, while decreasing the energy required for grinding and the cost of hauling a significantly heavier feedstock. The grinding energy for untreated pine chips and forest residues could be as high as 237 kWh/t compared to 23 kWh/t for similar biomass when torrefied (Deng *et al.*, 2009).

Substituting torrefied wood for biomass is also an effective method of reducing the water, acid and oxygen contents of bio-oil. These reductions, all increase bio-oil heating value (Chouchene, Jeguirim, Khiari, Trouve, & Zagrouba, 2010; Zheng *et al.*, 2012). Dehydration and decarboxylation reactions occur during torrefaction. Cellulose and lignin in woody biomass are decomposed at temperatures above 300°C (Wang, Xiao, Zhang, & He, 2010). In spite of the fact that 30 wt. % of biomass is lost to torrefaction, the torrefied product may retain up to 90% of the energy of the initial biomass content (van der Stelt *et al.*, 2011).

There has been a renewed emphasis on the production of chemicals and liquid fuels from biomass. Many types of catalysts, such as macroporous, (Lin, Zhang, Zhang, & Zhang, 2010; Thangalazhy-Gopakumar, Adhikari, Gupta, Tu, & Taylor, 2011) microporous, (Adam *et al.*, 2005; Iliopoulou *et al.*, 2012; Zhang, Zheng, & Xiao, 2013) and mesoporous (Bertero & Sedran, 2013; Jae *et al.*, 2011; Nilsen *et al.*, 2007) catalysts, have been synthesized and tested in catalytic fast pyrolysis experiments. However, HZSM-5 as a catalyst is plagued by short catalyst lifetime and low carbon efficiencies. Dehydrogenation and dehydration reactions that are catalyzed by HZSM-5 have been found to cause further reduction in the hydrogen content, leading to coke formation. Possibly, the incorporation of carbon and hydrogen rich co-reactants, such as waste plastics into the pyrolysis process along with biomass, could reduce these problems.

Farmers, over the years, have used plastics to increase crop yields, reduce the use of herbicides and pesticides as well as conserve water (Kyrikou & Briassoulis, 2007). The utilization of waste plastics in this form could have the advantage of alleviating a major waste disposal problem of plastics in a meaningful way. In this research, experiments in co-pyrolysis of torrefied corn stalks and HZSM-5 catalyst will be performed to produce high yields of hydrocarbons. The effects of temperature and catalyst on hydrocarbon yield will be discussed.

Materials and Methods

The corn stalks used in this study were sampled from some farms in Jos, Plateau State, Nigeria.

These were cut into small pieces, placed in a crucible and properly covered to prevent the inflow of air. This was then placed in an electric furnace and the sample torrefied at a temperature of 280°C for 30 min. The sample was air cooled (Abdullah H, 2009; Yuan JH, 2011) and labelled as torrefied corn stalks (TCS). The commercial high density polyethylene was obtained from TDL Plastics Inc. The Zeolite type catalyst (HZSM-5) was purchased from Acros Organics (Zeolite without alumina acid sites). Ratio $\text{SiO}_2/\text{Al}_2\text{O}_3 = 1000$). Prior to use, the catalyst was heated in an oven at over 110°C for two hours to eliminate moisture.

Preparation of TCS and HDPE

TCS and HDPE were ground individually in a Hamilton Beach blender, and sieved to a particle size of about 1-2 mm. Elemental analysis (C, H and N) was determined for both TCS and HDPE by Exeter Analytical Incorporation (EAI CE-440) elemental analyzer. The oxygen content was determined by difference.

Thermal gravimetric analysis (TGA) was conducted on TCS and HDPE samples to determine their optimum pyrolysis temperatures. TGA experiments were performed, using a SDT Q600 thermo gravimetric analyzer. In each experiment, 2 mg of each powdered sample was placed in the crucible of the thermo gravimetric analyzer. Each sample was heated from room temperature to 900 °C at a heating rate of 100 °C/min and then held at 900 °C for 20 min in an inert atmosphere. The inert atmosphere was produced by using pure nitrogen as the carrier gas with a flow rate of 40 mL/min.

Py-GC/MS experiments

TCS, TCS/HDPE and TCS/HDPE/Catalyst (Cat.) were individually homogenized, by mixing thoroughly in a mortar. The samples were then individually held in a CDS quartz tube with quartz wool packing. The TCS/HDPE ratio was 4:1 while the ratio of TCS/HDPE to catalyst was 10:1. About 3-5 mg of each of the following prepared samples: TCS, TCS/HDPE and TCS/ HDPE/Cat. was pyrolyzed and the pyrolysis products identified.

Pyrolysis experiments were conducted, using 5200 model pyrolyzer (CDS Analytical, Inc.). Based on the TGA results for TCS and HDPE, pyrolysis experiments were performed at 400, 500 and 600°C.

Pyrolysis of each sample was replicated three times, to provide consistency of experimental results. The biomass heating rate was 1000°C/s at 10 s pyrolysis time. These were kept constant for all experiments. The Py-GC/MS analyses were performed with the interface temperature set at 300°C with the ramp at 100°C/min. The pyrolysis vapors were carried directly by ultrahigh purity helium carrier gas stream (99.999%) through the transfer line to a Perkin Elmer Clarus 500 Gas Chromatograph /Mass Spectrometer (GC/MS) system. The transfer line temperature was set at 300°C and the carrier gas rate was 2mL/min. The GC was equipped with DB-5MS capillary column of 30m x 0.32mm ID x 1 µm film thickness.

The samples were injected in the split less mode and the injector temperature was 270 °C. The initial oven temperature of the GC was 40°C for 4 min. and then programmed at a rate of 4°C/min to 280°C, with a total run of 72 min. The MS detector was an electron impact ionization device operating at 70 eV with a source temperature of 210 °C and interface temperature of 225°C. The chemical component data obtained from the GC/MS were analyzed with a chemical integration program together with NIST mass spectral search library. The peak area percentages for the three runs were summed and the mean was calculated for each identified compound. However, compounds that were associated with some peaks were not identified by the NIST library.

Results and Discussions

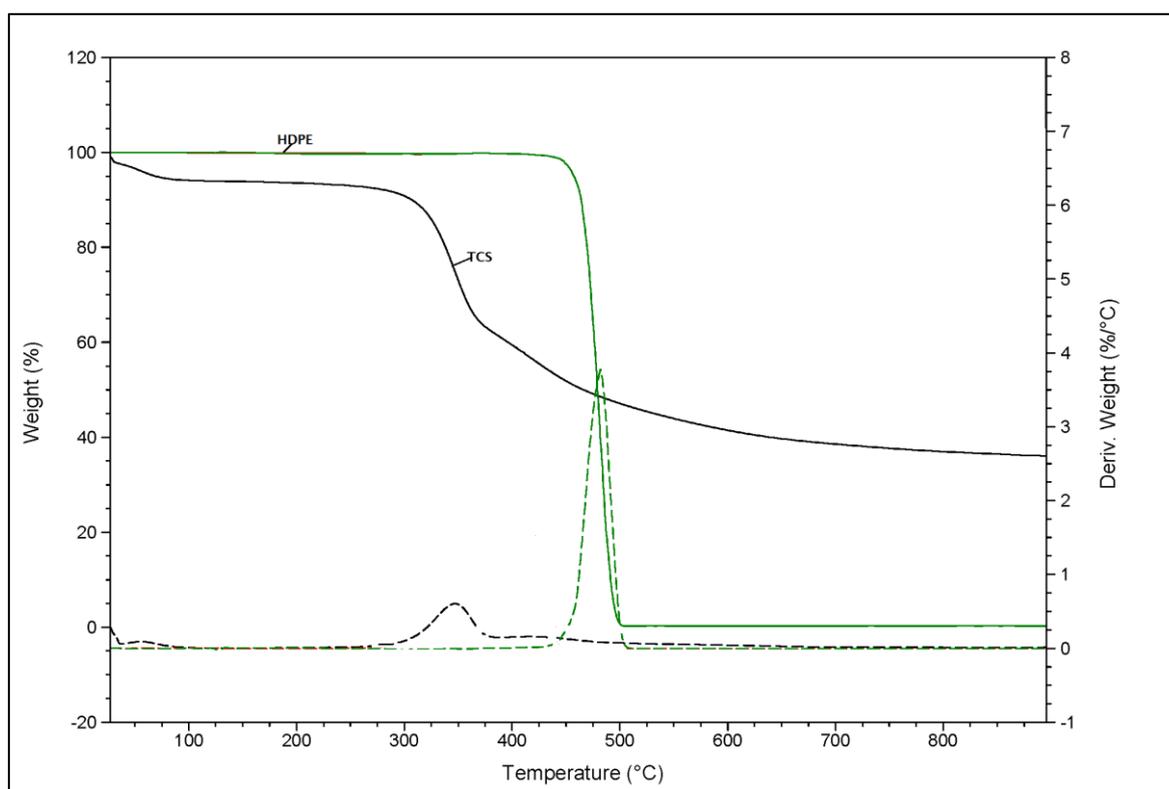
The elemental composition of TCS and HDPE is given in Table 1. HDPE has higher carbon and hydrogen compositions than TCS.

Table 1: Elemental composition of TCS and HDPE

Sample	% Carbon	% Hydrogen	% Nitrogen	% Oxygen
TCS	56.54	6.58	0.42	36.11
HDPE	84.97	14.30	0.73	0.00

Fig. 1 shows the weight-loss pattern for TCS and HDPE at a heating rate of 100°C/min which is the intermediate heating rate applied to the samples. This figure indicates that TCS is more thermally

unstable than HDPE. TCS decomposed at about 300°C while HDPE decomposed at about 475°C. Maximum weight loss was achieved at about 350°C and 500°C for TCS and HDPE, respectively.

**Figure 1:** TGA of TCS and HDPE

Classification of compounds detected

Tables 2, 3 and 4 indicate the retention time, compounds detected, formulae and peak area percentages in the pyrolysis of samples at 400°C, 500°C and 600°C. The compounds detected by the GC/MS were identified from the MS library and characterized into acids, ketones, guaiacols, syringols, miscellaneous oxygenates, alcohols, furans, sugars, hydrocarbons, esters, and aromatics. At all the pyrolysis temperatures, no hydrocarbon was detected when only TCS was pyrolysed. However when HDPE was co-pyrolysed with the

TCS, hydrocarbons were detected with their yields increasing with increase in temperature.

TCS/HDPE/Cat. produced exceptionally high yields of hydrocarbons. The hydrocarbons identified had relatively large peak area percentages compared to the other compounds identified. It is interesting to note that the hydrocarbons identified had long chains of carbon atoms. In the elemental composition analysis investigation, HDPE had high % of carbon and hydrogen which was responsible for the high yields of hydrocarbons detected. The hydrocarbon identified are: Propane, 1,3-diphenyl-; 1-Propene,

3-(2-cyclopentenyl)-2-methyl-; 1,3- Dotriacontane; Heptacosane and Tetratriacontane.
 Diphenylpropane; 1-Butene, 1,3-diphenyl-;

Table 2: Major pyrolytic compounds detected at 400 ° C pyrolysis with their retention time (RT), formulae and peak area percentages

RT	Compound name	Formula	TCS	Peak area percentage	
				TCS/HDPE	TCS/HDP E/Cat.
6.50	Acetic acid	C ₃ H ₆ O ₂	14.03	-	-
16.33	2-Furancarboxaldehyde, 5-methyl-	C ₆ H ₆ O ₂	2.15	-	-
21.54	Phenol, 4-methoxy-	C ₉ H ₁₀ O ₃	3.44	-	-
21.72	Phenol, 4-methoxy-, acetate	C ₉ H ₁₀ O ₃	-	-	2.94
22.49	4H-Pyran-4-one, 3-hydroxy-2-methyl-	C ₆ H ₆ O ₃	0.96	-	-
25.51	Benzene, 1,4-dimethoxy-	C ₈ H ₁₀ O ₂	6.07	-	-
25.58	2 - methoxy - 3 - methyl – phenol	C ₈ H ₁₀ O ₂	6.07	-	-
25.64	Phenol, 2-methoxy-4-methyl-	C ₈ H ₁₀ O ₂	-	5.83	-
26.76	2-Furancarboxaldehyde, 5-(hydroxymethyl)-	C ₆ H ₆ O ₃	1.57	1.18	3.54
27.95	1,4-Benzenediol, 2-methoxy-	C ₇ H ₈ O ₃	0.76	-	-
28.65	Phenol, 4-ethyl-2-methoxy-	C ₉ H ₁₂ O ₂	0.48	-	-
29.95	2-Methoxy-4-vinylphenol	C ₉ H ₁₀ O ₂	1.38	-	-
31.14	Phenol, 2,6-dimethoxy-	C ₈ H ₁₀ O ₃	0.43	-	-
31.43	Phenol, 2-methoxy-4-(2-propenyl)-	C ₁₀ H ₁₂ O ₂	-	-	-
31.75	1,2,3-Benzenetriol	C ₆ H ₆ O ₃	1.43	-	0.61
32.86	Vanillin	C ₈ H ₈ O ₃	0.63	1.65	1.39
34.55	Phenol, 2-methoxy-4-(1-propenyl)-	C ₁₀ H ₁₂ O ₂	1.56	0.55	0.33
35.64	Ethanone, 1-(4-hydroxy-3-methoxyphenyl)-	C ₉ H ₁₀ O ₃	0.98	0.49	-
36.75	Levogluconan	C ₆ H ₁₀ O ₅	16.72	0.49	3.30
37.01	2-Propanone, 1-(4-hydroxy-3-methoxyphenyl)-	C ₁₀ H ₁₂ O ₃	-	0.51	-
37.84	3-Hydroxy-4-methoxybenzoic acid	C ₈ H ₈ O ₄	0.60	-	-
43.60	Tetradecanoic acid	C ₁₄ H ₂₈ O ₂	-	0.30	0.31
48.06	Hexadecanoic acid, methyl ester	C ₁₇ H ₃₄ O ₂	-	-	0.23
48.99	Hexadecanoic acid	C ₁₆ H ₃₂ O ₂	-	2.79	5.80
53.71	Octadecanoic acid	C ₁₈ H ₃₆ O ₂	-	2.78	8.66

Table 3: Major pyrolytic compounds detected at 500 ° C pyrolysis with their retention time (RT), formulae and peak area percentages

RT	Compound name	Formula	TCS	Peak area percentage	
				TCS/HDPE	TCS/HDPE/ Cat.
15.22	2(3H)-Furanone, 5-methyl-	C ₅ H ₆ O ₂	-	3.67	-
19.22	1,2-Cyclopentanedione, 3-methyl-	C ₆ H ₈ O ₂	-	-	1.89
21.66	Phenol, 2-methoxy-	C ₈ H ₈ O ₂	-	-	3.03
21.72	Phenol, P-methoxy-, acetate	C ₉ H ₁₀ O ₃	0.57	1.55	0.56
27.13	2-Furancarboxaldehyde, 5-(hydroxymethyl)-	C ₆ H ₆ O ₃	3.82	4.27	3.34
31.18	Phenol, 2,6-dimethoxy-	C ₉ H ₁₂ O ₃	0.55	-	-
32.18	1,2,3-Benzenetriol	C ₆ H ₆ O ₃	-	0.81	0.84
32.95	Vanillin	C ₈ H ₈ O ₃	1.06	1.03	0.92
34.56	Phenol, 2-methoxy-4-(1-propenyl)-	C ₁₀ H ₁₂ O ₂	0.40	0.65	0.59
34.76	Phenol, 2-methoxy-4-propyl-	C ₁₀ H ₁₄ O ₂	-	0.36	-
35.74	Ethanone, 1-(4-hydroxy-3-methoxyphenyl)-	C ₉ H ₁₀ O ₃	0.53	-	-
36.57	1,6 - anhydro - beta - D – manno	C ₆ H ₁₀ O ₅	-	0.73	1.44
37.69	Levoglucosan	C ₆ H ₁₀ O ₅	-	0.88	2.29
38.37	beta.-D-Glucopyranose, 1,6-anhydro-	C ₆ H ₁₀ O ₅	2.57	-	-
49.10	Hexadecanoic acid	C ₁₆ H ₃₂ O ₂	0.15	4.92	7.78
53.74	Octadecanoic acid	C ₁₈ H ₃₆ O ₂	3.21	4.71	10.85
61.74	1-Propene, 3-(2-cyclopentenyl)-2-methyl-1,1-diphenyl-	C ₂₁ H ₂₂	-	3.56	15.72

Table 4: Major pyrolytic compounds detected at 600 ° C pyrolysis with their retention time (RT), formulae and peak area percentages

RT	Compound name	Formula	TCS	Peak area percentage	
				TCS/HDPE	TCS/HDPE/ Cat.
8.60	2-Furancarboxaldehyde, 5-methyl-	C ₆ H ₆ O ₂	0.48	-	-
11.96	Ethanone, 1-(2-furanyl)-	C ₆ H ₆ O ₂	0.58	-	-
21.81	Phenol, 4-methoxy-, acetate	C ₉ H ₁₀ O ₃	1.13	-	-
24.89	2-Methoxy-4-methylphenol	C ₈ H ₁₀ O ₂	0.79	-	-
25.40	Phenol, 2-methoxy-4-methyl-	C ₈ H ₁₀ O ₂	1.75	0.90	-
26.28	Phenol, 2-ethoxy-	C ₈ H ₁₀ O ₂	5.58	-	-
27.07	2-Furancarboxaldehyde, 5-(hydroxymethyl)-	C ₆ H ₆ O ₃	1.48	2.76	4.16
27.13	2-Furaldehyde, 5-(hydroxymethyl)-	C ₆ H ₆ O ₃	-	-	2.76
28.66	Phenol, 4-ethyl-2-methoxy-	C ₉ H ₁₂ O ₂	0.57	2.96	-
29.05	1,2-Benzenediol, 4-methyl-	C ₇ H ₈ O ₂	-	2.36	-
29.95	2-Methoxy-4-vinylphenol	C ₉ H ₁₀ O ₂	-	2.96	-
31.77	Phenol, 2-methoxy-4-propyl-	C ₁₀ H ₁₄ O ₂	0.81	-	-
31.42	Phenol, 2-methoxy-4-(2-propenyl)-	C ₁₀ H ₁₂ O ₂	-	-	0.35
32.97	Vanillin	C ₈ H ₈ O ₃	-	0.48	1.37
34.47	4 - methyl - syringol	C ₉ H ₁₂ O ₃	0.95	-	-
34.59	Phenol, 2-methoxy-4-(1-propenyl)-	C ₁₀ H ₁₂ O ₂	-	0.48	0.73
35.00	2-methoxy-4-propyl-phenol	C ₁₀ H ₁₄ O ₂	0.81	-	-
35.77	Ethanone, 1-(4-hydroxy-3-methoxyphenyl)-	C ₉ H ₁₀ O ₃	0.64	-	-
38.79	Levoglucofan	C ₆ H ₁₀ O ₅	0.43	1.69	5.92
41.05	1,3-Diphenylpropane	C ₁₅ H ₁₆	-	2.07	3.65
44.43	1-Butene, 1,3-diphenyl-	C ₁₆ H ₁₆	-	2.67	3.26
49.05	Hexadecanoic acid	C ₁₆ H ₃₂ O ₂	0.67	0.38	5.54
49.94	Nonadecane	C ₁₉ H ₄₀	-	-	3.62
53.73	Octadecanoic acid	C ₁₈ H ₃₆ O ₂	0.56	2.46	3.62
62.86	Dotriacontane	C ₃₂ H ₆₆	-	6.92	11.83
62.88	Heptacosane	C ₂₇ H ₅₆	-	4.10	10.62
67.05	Tetratriacontane	C ₃₄ H ₇₀	-	6.07	13.65

Quantification of hydrocarbons produced

Fig. 2 is a graphical representation of the peak area percentages of the hydrocarbons produced in the individual pyrolysis of TCS, TCS/HDPE and TCS/HDPE/Cat. at 400, 500 and 600°C. The highest yield of hydrocarbons was recorded in the

pyrolysis of TCS/HDPE/Cat. at 600°C. However, when a catalyst was not employed, 21.83% hydrocarbons was produced at 600°C. Lower yields were recorded, with and without a catalyst at lower temperatures. The pyrolysis of TCS alone did not produce any hydrocarbon at any of the pyrolysis temperatures.

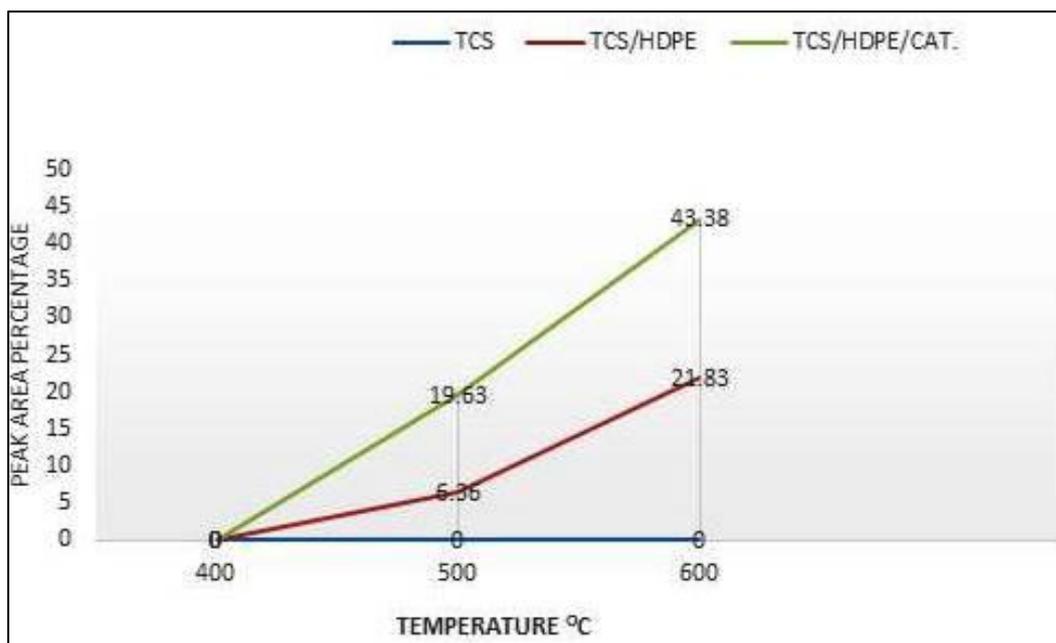


Figure 2: Peak area percentages of hydrocarbons produced in the pyrolysis of TCS, TCS/HDPE and TCS/HDPE/Cat. at 400, 500 and 600°C pyrolysis

Effect of catalyst on pyrolysis products

The catalytic fast pyrolysis of biomass carbon with HDPE over HZSM-5 led to the formation of hydrocarbons, with a yield enhancement or selectivity change over the sum of their individual pyrolysis products. This effect is likely due to the enhanced conversion of biomass carbon to hydrocarbons at the expense of coke formation because of the higher concentration of hydrogen and carbon reactants (Dorado, Mullen, & Boateng, 2014; H. Zhang, 2014; X. Li *et al.*, 2014).

Conclusion

The elemental analysis of TCS and HDPE indicated that HDPE has higher carbon and hydrogen compositions than TCS. The weight-loss pattern for TCS and HDPE at a heating rate of 100°C/min indicated that TCS is more thermally unstable than HDPE. TCS decomposed at about 300°C while HDPE decomposed at about 475°C. Maximum weight loss was observed at about 350°C and 500 °C for TCS and HDPE, respectively.

Torrefaction leads to a loss of the fibrous structure of TCS, primarily because of the decomposition of hemicellulose and depolymerization of cellulose. There has been a renewed emphasis on the production of chemicals and liquid fuels from biomass. HZSM-5, a catalyst with a three-dimensional pore structure, and a pore size of 5.5-

5.6Å has been shown to have good characteristics for the production of hydrocarbons from biomass. When waste plastics are catalytically co-pyrolyzed with TCS, to produce high yields of hydrocarbons, it could have the advantage of alleviating a major waste disposal problem of plastics in a meaningful way.

The co-pyrolysis of TCS and PDPE in the presence of HZSM-5 catalyst at a 400, 500 and 600°C produced many compounds. These compounds were characterized into acids, ketones, guaiacols, syringols, miscellaneous oxygenates, alcohols, furans, sugars, hydrocarbons, esters, and aromatics. When quantified, exceptionally high yields of hydrocarbons were found to have been produced at the highest pyrolysis temperature when HZSM-5 was employed.

When pyrolysis takes place, free radical chain reactions occur. When these free radicals react with hydrocarbons, new hydrocarbon and new free radicals are produced. Also, free radicals can decompose into hydrocarbons and new radicals. As expected, the highest yield of hydrocarbons was produced by TCS/HDPE/Cat. at 600°C (43.38%). However, 21.83% yield was produced when HZSM-5 was not employed at 600°C. Lower yields were recorded at lower temperatures. The pyrolysis of TCS alone did not produce any hydrocarbon at any of the pyrolysis temperatures.

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