

Catalytic Conversion of Waste Polyethene Bags (Groceries Bags) to Liquid Fuels Over 6wt%WO₃/γ-Al₂O₃ Catalyst, Mild Temperature and Atmospheric Pressure

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ABSTRACT

The catalytic pyrolysis of waste polythene bags was conducted at a temperature of 500°C and atmospheric pressure utilizing local fabricated pyrolysis reactor for the process. The 6wt%WO₃/γ-Al₂O₃ catalyst was synthesized via impregnation method and characterized with scanning electron microscope (SEM), Fourier transform infrared (FT-IR) and Brunauer–Emmett–Teller (BET) and applied for the catalytic pyrolysis of waste polythene bags. The results indicated that the catalyzed reaction took shorter time to obtain the liquid fuels as against the uncatalyzed reaction and both liquid fuels resembled the conventional diesel by physical appearance (orange color) and burning properties, the caloric values of catalyzed and uncatalyzed found to be 40.8 and 39.6Mj/Kg respectively as against 40Mj/Kg of the conventional diesel. The total of thirty seven (37) compounds were identified from the uncatalyzed pyrolyzed oil while total of fifty four (54) compounds were detected in the liquid products obtained from the catalyzed pyrolyzed oil. The results revealed that 1-undecene found in the uncatalyzed products was isomerized and alkylated to 4-undecene-5-methyl (E) in the catalyzed pyrolyzed oil. Again, the 1-Dodecene that was found in the uncatalyzed product was found to be isomerized to 4-dodecene (E) in the catalyzed product. More so, 1-tridecene and 2-tetradecene detected in the uncatalyzed product were equally isomerized to 2-tridecene (E) and 7-tetradecene respectively in the catalyzed oil.

Keywords: Pyrolysis, groceries bags, WO₃/γ-Al₂O₃ based catalyst, atmospheric pressure

1.0 INTRODUCTION

The polythene bags (groceries bags) are found to be a common household available in almost everyone house in Nigeria. The polythene bags are designed versatile such that they are flexible, convenient, durable and affordable and these properties made it to be part and parcel of day to day necessary of life. More so, people are making significant efforts to make sure that the polythene bags continue to be of great benefits to them [Gidigbi, 2020]. As such, polythene bags are used widely in many places such as markets, stores, restaurants, industries, vendors etc., and the usage of these polythene bags increased significantly in the past few decades. For many years, the urban and rural settlements of Nigeria found it difficult to avoid the ugly and unhygienic littering of landscape by the waste polythene bags. The non-biodegradable nature coupled with the improper disposal of the waste polythene bags caused environment pollution and issue of space [Arabiourrutia et al., 2020]. The waste polythene bags found its way into the water bodies, causing marine waste plastic pollution which has long been considered as the source of micro-plastic thereby affecting the marine organisms [Dumbili and Henderson, 2020] and are also found to clog drainages

resulting to flooding as witnessed in many Nigerian cities. Maintaining blocked drainages is a task that requires huge capital investment and professional involvement. As such, there is need to have an effective waste polythene management strategies in order to properly arrest the environmental pollution related to waste polythene bags. Due to the high accumulation of waste polythene bags in Nigeria, recycling will be a better option for managing this kind of waste and creating jobs to the Nigerian population. The conversion of waste polythene to important substances have been reported in many scientific literature [Kumar and Mohanty, 2020; Stanley et al., 2020; Harussani et al. 2022]. Therefore, this paper seeks to find a suitable way to mitigate the problems faced by the environmental consequences of accumulation of waste polythene bags in Nigeria and the way out.

2.0 EXPERIMENTAL

2.1. Materials

Analytical grades 99% ammonium metatungstate hydrate (Sigma-Aldrich), A 98% aluminum oxide (Sigma-Aldrich) and distilled water were used for the synthesis of the catalyst.

2.2. Synthesis of catalysts

The 6wt%W/ γ - Al_2O_3 catalyst was synthesized via impregnation method. Briefly, 0.16g $(\text{NH}_4)_6\text{H}_2\text{W}_{12}\text{O}_{40} \cdot \text{XH}_2\text{O}$ was weighed and dissolved in 2.5 mL distilled water to form an aqueous solution. Then 1.880 g of alumina was added slowly with constant stirring to the aqueous solution thereafter a slurry was obtained. The obtained slurry was dried at 110°C in an oven for 12 hours. All the dried catalyst sample was grinded and mixed thoroughly then calcined in a muffle furnace at 500 °C for 4 hours.

2.3 Characterization of the Catalyst

The structural morphology of the catalyst was determined using a scanning electron microscope (SEM). The catalyst was coated with a thin layer of gold by a sputter-coater and then examined at an accelerating voltage of 40 kV with Phenom world 800-07334 SEM (Thermo Fisher scientific). Fourier transform infrared (FT-IR) spectra was reported within the wavelength range of 400-4000 cm^{-1} using FTIR-8400S spectrophotometer (Shimadzu). The Brunauer–Emmett–Teller (BET) surface area, total pore volume, microporous volumes and average pore diameter determined by AutoSorb-6iSA Quantachrome instrument at -196 °C using N_2 adsorption-desorption measurements.

2.3.1 Sampling

Waste polythene bags were randomly collected (sampled) from Rijiyar Dorowa Area in Sokoto South local government area of Sokoto State. The samples were handpicked with the aid of protective gloves into a container and taken to the Chemistry Laboratory of Umaru Ali Shinkafi Polytechnic, Sokoto for further treatment.

2.3.2 Pre-treatment of Sample

Samples were cleaned with running water and then sun dried, after which they were cut into pieces with the aid of a scissors.

2.3.3 Catalytic Pyrolysis of Waste Polythene Bags

Catalytic pyrolysis of waste polythene bags was carried out using a locally constructed pyrolysis reactor and 6wt% $\text{WO}_3/\gamma\text{-Al}_2\text{O}_3$ material was used as catalyst. The pyrolysis chamber was filled to the capacity with the pre-treated waste polythene bags. The reactor was heated at a temperature of 500°C and under atmospheric pressure, 20 minutes into the pyrolysis process the pyrolyzed oil was observed to have condensed out from the reactor while for the uncatalyzed pyrolysis it took about forty minutes before the emergence of the liquid oil out of the reactor. And the pyrolysis process lasted for 2 hours. When the pyrolysis time elapsed, the pyrolytic oil was

collected into sample bottles. The collected pyrolyzed samples were investigated using GCMS-QP2010SE Gas Chromatography Mass Spectrophotometer (Shimadzu) equipped with a 30m×0.32mm, Rxi-624 Sil MS capillary column (Restek Corp.).

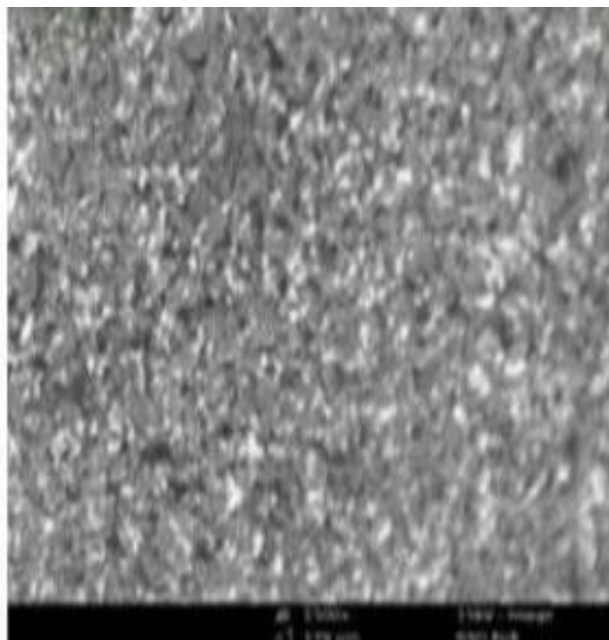


Figure 3.1: SEM micrograph of 6wt% $\text{WO}_3/\gamma\text{-Al}_2\text{O}_3$

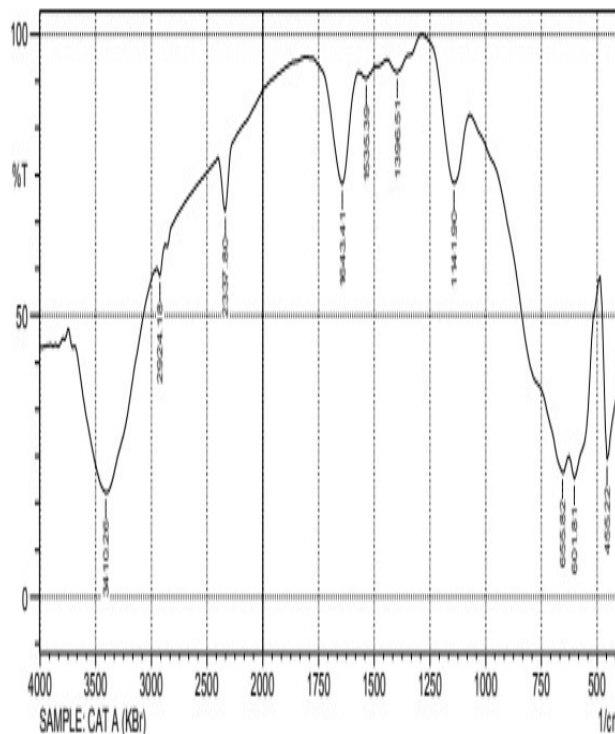


Figure 3.2: FTIR spectra of 6wt% $\text{WO}_3/\gamma\text{-Al}_2\text{O}_3$ catalyst

Table 3.1: Textural characteristics of the catalysts calcined at 500 °C

Catalyst	BET ^a (m ² /g)	V _{total} ^a ^b (m ³ /g)	V _{micro} ^{ac} (m ³ /g)	D ^{ad} (nm)
6wt%WO 3/γ-Al ₂ O ₃	422.99	0.260	0.177	2.800

D: Average pore diameter; V_{total}: Total pore volume; V_{micro}: Micro porous volume;^aDetermined by multipoint BET equation; ^bDetermined by the BJH cumulative adsorption pore volume;^cDetermined by the DR method micro volume;^dDetermined by the DA method pore diameter.

Figure 3.2 indicates the infrared absorption peaks of the catalyst. The absorption peaks of 1689 cm⁻¹ is attributed to the physically absorbed water molecules [Babich and Moulijn, 2003]. The observed peaks between 500 and 1000 cm⁻¹ in the Al₂O₃ spectrum are connected to Al–O vibrations in O–Al–O and Al–O–Al of pure alumina [Babich and Moulijn, 2003]. The broad band at 3450–3786 cm⁻¹ in the sample is attributed to the stretching vibrational property of OH⁻ [Babich and Moulijn, 2003].

The strong absorption peaks at 1631 cm⁻¹ and 3431 cm⁻¹ are connected to interatomic vibrations [Babich and Moulijn, 2003]. The Table 3.1 shows that the catalyst exhibited a significant BET surface area (422.99m²/g), total volume (0.26m³/g), micro volume (0.177m³/g) and pore diameter (2.8nm). This could significantly be attributed to its hierarchical smooth textural surface that covered that catalyst. There are many acyclic hydrocarbons that were detected in the pyrolyzed oils which include 1,4-octadene, 2-Undercene, 4-Undercene-5-methyl (E)-, 1,4-Octadiene, 2-Dodecene (z)-, 4-Dodecene (E)-, 2-Tridecene (E), 1-13-tetradecadiene, and 1-octadecene that were identified by the GC-MS. This result is in conformity with the results obtained by Farshi and Ravishankar, 2017; Manickavelan et al., 2020. The non-aromatic cyclic compounds that were found in pyrolyzed oils are Cyclodecane, Cyclohexane-1-methyl-4-(1-methylethenyl)-trans, 3-methoxy-2-methyle-cyclohex-z-enom, Cyclooctane-methyl, Cyclooctane-1,5-dimethyl, Cyclopentane hexyl, and 2-H2H-Azepin-2-one,1,5,6,7 Tetrahydro. Again, this result is in agreement with findings of Farshi and Ravishankar, 2017; Yao et al. 2020.

Table 3.2: Peak No., Retention time, and names of compounds found in the uncatalyzed pyrolyzed oil from waste nylon

Peak Number	Retention Time	Possible Compound
1	6.3	Cyclopropane-1-methyl-2-pentyl
2	7.7	Benzaldehyde
3	8.0	1-pentadecyne
4	8.1	1-decene
5	9.5	Acetophenone
6	9.9	Undecene
7	10.6	2-p-Nitrobenzoyl-1,3,5-Tribenzyl
8	11.1	Benzoic acid
9	11.3	1-Dodecene
10	6.27	Cyclopropane-1-methyl-2-pentyl
11	11.8	Benzoic acid, methyl ester
12	12.2	1-tridecene
13	13.87	4-ethyl benzoic acid
14	14.11	2-tetradecene
15	8.0	Pentadecyne
16	16.48	1,13-tetradecadiene
17	17.76	Heptadecane
18	19.77	Inonadecene
19	18.82	Octadecene
20	19.83	Ninadecane
21	25.0	Eicosadiene
22	26.2	Heptacos-1-ene
23	26.5	Hexacosane
24	22.6	Hexadecane
25	23.4	Tricosene
26	25.03	Pentacos-1-ene
27	28.61	Eooctacos heptafluorobutyrate
28	27.6	Tetracosene

29	6.30	2-Heptyne
30	8.28	Decyl heptyl ether
31	9.15	E-14-hexadecenal
32	9.50	Acetophenone
33	9.63	Cyclooctane, methyl
34	9.87	2-hexyne-6-chloro
35	10.59	Ethanedione, diphenyl
36	11.51	Piperidine-4-propyl
37	12.69	3-nanoe-1-ol

Table 3.3: Peak No., Retention time, and names of compounds found in the catalyzed pyrolyzed oil from waste nylon

Peak number	Retention Time	Compound
1	5.4	Cyclodecane
2	6.3	2-Heptyne
3	8.0	1,4-Heptane
4	8.1	3-methoxy-2-methyle-cyclohex-z-enom
5	8.3	Decyl heptylether
6	9.2	E-14-Hexadecanal
7	9.3	Cyclohexane-1-methyle-4-(1-methylethenyl)-trans
8	9.5	Acetophenone
9	9.6	Cyclooctane-methyl
10	9.7	1,4-octadene
11	9.9	2-Hexane 6-chloro
12	10.0	1-(3-Hydroxypropyl)-2-piperidinone
13	10.1	2-Undercene,
14	10.6	Ethanedione, Diphenyl
15	11.0	4-Undercene-5-methyl (E)-
16	11.5	Benzoic acid
17	11.5	Piperidine-4-propyl
18	11.6	2-Dodecene (z)-
19	11.7	4-Dodecene (E)-
20	12.7	3-Nonen-1-ol, (z)
21	12.8	Quinoline decahydro-trans-
22	12.9	E-2-Octa Decedecen-1-1-ol
23	12.9	Piperidine-4-propyl
24	13.0	2-Tridecene (E)
25	13.1	Decyl ester
26	13.2	Cyclopentane, hexyl
27	14.0	7-Tetradecyne
28	14.2	Quinoline decahydro-trans-
29	14.3	2-Azido-2,4,4,6,6-Pentamethylheptane

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30	15.3	E-11 (13-methyl) tetradecen-1-ol acetate
31	15.4	2-H2H-Azepin-2-one,1,5,6,7 Tetrahydro
32	15.5	Carbonic Acid, decyl nonyl ester
33	16.5	1-13-tetradecadiene
34	16.6	1-octadecene
35	16.7	1-tridecene
36	17.6	1-13-tetradecadiene
37	17.7	1-heptadecane
38	18.7	Ethane,2-(9-octadecenylexy)-1-
39	18.8	Cyclooctane-1,5-dimethyl
40	19.8	Chloroacetic acid, undecyl ester
41	20.7	Carbonic acid, octadecyl 2,2,2-Trichloroethyl ester
42	21.7	Henicos-1-ene
43	21.8	Octacosane, 2-methyl-
54	22.6	1-hexacosene

Furthermore, many aromatic compounds that were found in the pyrolyzed oil, these compounds include Benzaldehyde, Acetophenone, Benzoic acid, Benzoic acid, methyl ester, 4-ethyl benzoic acid, Piperidine-4-propyl, Ethanedione, Diphenyl, 1-(3-Hydroxypropyl)-2-piperidinone, Quinoline decahydro-trans-, 2-Azido-2,4,4,6,6-Pentamethylheptane and 2-H2H-Azepin-2-one,1,5,6,7 Tetrahydro. Interestingly, this result found to be similar to the research work carried out by Murthy and Shetty, 2020; Yao et al. 2020

The 1-undecene was found in the uncatalyzed product while it is isomer and alkylated (4-undecene-5-methyl (E)) product was detected in the catalyzed pyrolyzed oil. Moreover, 1-Dodecene was identified in the uncatalyzed pyrolyzed oil while 4-dodecene (E) isomer was found present in the catalyzed pyrolyzed oil. Again, 1-tridecene was detected in the uncatalyzed product and its isomer 2-tridecene (E) was found in the catalyzed pyrolyzed oil. Furthermore 2-tetradecene and 7-tetradecene isomer were found in the uncatalyzed and catalyzed products respectively. More so, the caloric values of catalyzed and uncatalyzed pyrolysis oil was found to be 40.8Mj/Kg and 39.5Mj/Kg respectively using Bomb Calorimeter (Model-IKA C2000) which are found to be close to that of conventional diesel 42Mj/Kg (Zaher and Gad, 2018). The smooth textural properties and high BET surface area of the catalyst supported the good performance of the catalyst.

4.0 CONCLUSION

The results of the pyrolysis experiment showed that both the uncatalyzed and catalyzed pyrolysis processes of waste nylon produced liquid fuels that resembles physical appearance of diesel. The GC-MS indicated that, the fuels contained many important compounds similar to the ones available in conventional diesel fuels. More so, the catalyst seems to be a better candidate for both isomerization reaction of 1-undecene, 1-dodecene, 1-tridecene and 2-tetradecene to their corresponding isomers. The liquid fuel was found to be flammable like diesel and test it on diesel engine when blend with conventional diesel.

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