PARAFFINS AND POLYAROMATIC HYDROCARBONS FROM WASTE PET UNDER SLOW HEATING RATE PYROLYSIS

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Abstract

Poly Ethylene Terephthalate (PET) a polyester is one of the thermoset plasticsor synthetic fibres produced by step growth polymerization. It is in high demand world overbecause of its intrinsic properties especially for liquid substances.

In Nigeria, particularly Lagos State tonnages of PET are disposed of indiscriminately as wastes unchecked thereby contributes to flooding and ecosystem to breed mosquitoes. Due to its non-biodegradablenature recyclingvia thermolytic is commonly used for its conversion to either liquid fuels or chemical feedstock.

In this study local materials were used to convert waste PET via pyrolysis to obtain liquid volatile organic compounds (VOC) and solid organic compound at temperatures 90^oC*-*124^oC*, which upon analysis using SRI 8610C GC-FID instrument showed that the products contained saturated paraffins (*C_{11}*-*C_{19}*) and poly aromatic hydrocarbons (PAHs) from simple naphthalene up to complex benzoperylene and indenopyrene. The use of local chalk or its mixture with inorganic base shows advantages over inorganic base lime for it reduces gases and little or no water formation in the course of pyrolysis.*

Keyword: Paraffins, Polyaromatic Hydrocarbons, Waste PET and Pyrolysis

1.0 Introduction / Literature Survey

Poly Ethylene Terephthalate (PETE or PET) is one of the synthetic polymers derived from petroleum-based materials called petrochemicals by condensation polymerization.

Generally, synthetic polymers are often called plastics, which in turn, are classified into two divisions or groups namely thermoplastics and thermo-set plastics. Thermoplastics can be repeatedly softened or melted and hardened by heating and cooling. This is possible because the atoms and molecules are joined end-to-end into a series of long, but purely of carbon chains. These long carbon chains are independent of the others. Thus, the structure in which the backbone is primarily built of carbon atoms make thermoplastics resistant to degradation or hydrolytic cleavage of chemical bonds. As a result of this, they are considered non-bio degradable articles. Examples are polyolefins and polyesters (Al-Sabagh, Yehia, Eshaq, Rabie and Elmetwally, 2016).

Thermo-set plastics are usually liquid or malleable prior to curing and designed to be molded into final form. They are solidified after being melted by heating so the process of changing from the liquid state to the solid state is irreversible.

In contrast to the linear structure of thermoplastics, thermo-set plastics have a highly cross-linked structure. Because the main chain of thermo-set plastics is made of heteroatoms, hence they are potentially susceptible to degradation by the cleavage of chemical bonds such as ester bonds or amide bonds. Examples are PET, phenol-formaldehyde resin (bakelite) and polyurethane (Al-Sabagh*et al*., 2016; kyaw and Hmwe, 2015).

Problems of study

Globally PETE has become the most widely used thermoset plastics in our daily life for the production of containers, bottles, fibers and so on.

Al-Sabagh*et al*., (2016); Anke, Jan, Carlo and Raf, (2011) report mentioned that the overall production of polyesters (especially PETE) world over in year 2000 was 25-30 million tonnes, and had increased by year 2012 to 55 million tonnes.

This is not surprising because of the high demand in PETE (or polyesters) consumption for the productions of fibers and molding resins for textile applications, as well as in food packaging and bottle markets for glass substitute has rapidly increased over the recent years.

Lagos-State (Nigeria) alone with population of over 5-10% total Nigeria population, generates annually quantum volumes of waste thermoplastics of which PETE takes 30-45% of total generated plastic solid waste (PSW). Lagos state is the only state that serves as seat of many industries, hence the generation of waste thermoplastics (PETE and Polyolefins) is due to the fact that almost all industries especially food and drink processing including fast food restaurants use them to package their products. Producers of drinks find it convenient to use PETE as packaging because of its intrinsic properties suitable for large capacity, light weight and pressure-resistant containers.

Like any other thermoplastics, PETE does not rot, neither biodegradable, so its load on environment has result in environmental pollution and threat to residents of Lagos owing to indiscriminating dumping by the users after service. This has caused excessive flooding in every community in Lagos in particular residents of riverine areas during heavy pour rain due to clogging of drainages. Besides, continuous demand of PETE or post-consumption caused waste accumulation in the landfill which consumed a lot of spaces that also contributed to the environmental problem that calls for concern.

Since PETE is synthetic polyester and petrochemical based products, the rising in it demand led to the depletion of crude oil as part of non-renewable fossil fuel.

The alternatives which have been developed so far as part of plastic waste management were recycling and energy recovery methods. Because of some drawbacks of this recycling method of PETE to its monomer due to its labour cost for the separation process and water contamination have reduced the process sustainability. For this reason and many others, this present study shall focus solely on chemical recycling of PETE using inorganic materials (both synthetic and local) as catalysts for energy recovery to compensate the high energy demand which presently prevalently militating factor for Nigeria economy growth.

Because plastics are light-weight, inert and non-biodegradable except under thermolysis, and for the fact that they are insulator, the following features with respect to thermal degradation are common: low-surface area, poor heat transfer, exceptional tensile strength during melting process, absorb heat and stick to anything cooler, which results in exigent "glue" that will seize or bind some of the largest high-torque feed technologies (Bordynuik, 2013).

For instance, acrylonitrile-butadiene-styrene (ABS), thermally degraded into fuel oils differently with respect to other polymers due to the pressure of nitrogen (N) in its structural units (Mohammed and Moinuddin, 2013). The presence of N in ABS degradation oil has resulted in corrosion of engine parts and the formation of very harmful compounds when the oils are used as fuel.

Table 1: Heat Requirements for Pyrolysis of PET and other Plastic Solid Waste (PSW)

PSW	C (J/g)	C_p (J/g. ^oC)
PET	214.35	1.44
PS	678.55	1.30
PE	257.65	2.30
PP	361.80	1.70
PC	148.00	1.20
ABS	473.85	1.42
PMMA	472.00	1.47
Nylon	364.15	1.70

Anke, Jan, Carlo and Raf, (2011)

Anke*et al.*, (2011) studied the cracking of waste PET to chemicals and energy, by thermal degradation of the mixed plastic wastes found that the process is more complex than degradation of single plastic because of the possible interactions during decomposition in the plastic bulk and interactions between the components of the mixture and the low molecular weight products and free radicals formed by the scission of the polymeric chains. They asserted that these can affect the quality of pyrolysis products and are hence of importance when the pyrolysis products need to meet high-quality standards for use as feedstock or fuels.

Meanwhile, it is reported that the heat required for PET pyrolysis is 214KJ/kg which is about 5% of the calorific value of PET. The spectrum of their study covered kinetic and thermodynamic parameters which are used to describe the pyrolysis of PET. They demonstrated that the kinetic constants are a function of the heating rate of PET and that reaction kinetic follows first-order. Also determined was activation energy, pre-exponential factor, heat of reaction. It was reported that a fairly high temperature ramp (450^0C) is required during dynamic experiments to obtain correct values of the kinetic parameters. The product yields and compositions have been examined and confirmed that the PET pyrolysis potential through its production with the use of bubbling fluidized bed (NFB) or circulating fluidized bed (CFB) of both a carbonaceous residue with adsorbing characteristics and a mixture of organic acids and esters can possibly be used as chemical feedstock or as fuel. It has been demonstrated that the carbonaceous residue (char) can be upgraded to a substitute for commercially available activated carbon.

The most likely thermal cleavage mechanisms that may occur in the thermally weak linkages, C – O bonds along the polymer chains especially those located at the adjacent position of C = O bonds are most likely subject to thermal cleavage with further degradation to phthalic and benzoic acid and possibly to benzene with CO_2 release.

Mohammed and Moinuddin, (2013) studied the conversion of PET and PS in batch reactor with different catalyst (ZnO and Al_2O_3) and activated carbon into fuel and observed that total conversion rate was 78.3%. The product fuel analysis using GC/MS, showed that the fuel had hydrocarbon group compounds such as benzene content, oxygen content, nitrogen content, halogenated and alcoholic group.

Bajus and Hajekova, (2010) experimentally demonstrated the thermal cracking of seven components mixed plastics – polyolefin and PET in batch reactor at temperatures between 350^0C to 500^0C at atmospheric pressure to obtain oils/waxes. They observed the presence of PS, PVC and PET in the feed stock has greatly positive effect on the formation and yields of gases and oil/waxes when compared with the thermal cracking of individual and mixed polymers. It was also detected the presence of PS, PVC and PET in model mixed plastics increased the formulation of carbon monoxide and carbon dioxide in the gas and benzene, toluene, xylenes, styrene in the liquid (oil/waxes) products.

Khaing and Chaw, (2015) have studied effect of various catalysts for the transformation of mixed plastic (PET inclusive) wastes to fuel oil in fixed bed reactor. The catalysts used are predominantly local clays, dolomite and synthetic catalysts, zinc oxide, found that between the temperatures 32 to 380^oC; liquid fuel yield was 63.76-67.06%, gas yield- 19.92-28.52%. The highest of liquid fuel was obtained from one of the natural clays (Mabisan clay) at range temperature 220^oC to 370^o C for 1.5 hours. The resulting fuel products are predominantly alkane and alkene groups with some waxes.

Also experimental work and studied by Moinuddin Mohammed, (2013) on the conversion of PET waste using calcium hydroxide ($Ca(OH)_2$) as catalyst found that at set heating temperature around 405^oC quick melting of PET occurs. At 20 minutes the heating mantle temperature dropped to 315^oC. The whole vapours were condensed within 35 minutes of the experiment. The collected product is viscous yellowish liquid with an obnoxious odour.

In 2011 Siddiqui and Redhwi studied the pyrolysis reaction of PET in reactor system consisting of stainless steel vessel of 100 cm^3 capacity equipped with precise temperature control and motorized stirrer with RPM (that is a batch pressurized autoclave reactor). Study showed that about 2-8 g of the sample was used when the reaction vessel was stirred using a magnetic drive. The result obtained was used to establish the fact that the solubility of the unreacted PET in polar essential steps towards the development of scaling relationship to larger scale processes. and non- polar solvents (HPLC grade hexane, toluene and tetrahydrofuran, THF) that PET polymer was highly insoluble in THF and n-hexane but slightly soluble in toluene solvents. They remark that pyrolysis reactions of PET into gases and liquid fuels under different set of operating conditions were 78% - 95% conversion with addition of AIBN initiator.

Vakili and Fard, (2010) had used hydrolysis base conversion of waste PET to its feedstock monomers. In this experiment, sodium hydroxide (NaOH) is chosen as suitable reagent for the process and for the attainability of purity of the products to be acceptable. It was also observed the optimum value temperature for reaction between the PET and NaOH was 180^oC and reaction conversion was 92% while reaction time was3 hrs. The amounts of products form were 200 ml (ethylene glycol) and 453 g (terephthalate salt) per kg of PET consumed. The optimum value of temperature for reaction between sodium terephthalate and hydrochloric acid, HCl at 90^oC was 88% conversion. The reaction time in this step was about 90 minutes and that for 166 g HCl per 453g sodium terephthalate used; 433 g terephthalic acid was recovered.

Al-Salem and Lettieri in their published article 2010, studied the dynamic pyrolysis of PET and Polystyrene (PS) in a micro-thermobalance reactor during which they determined the kinetic parameters of the depolymerization reactions within the thermal degradation process. It was observed that the overall kinetic rate constants (k_o) and activation energies (E_o), for PET, the value of E_o estimated from the modeled was 180.08 kJ/ mol as compared with the experimental results (180.02 kJ/ mol). PS activation energy was estimated to be 158.15 kJ/mol. This finding provides a fundamental understanding on the behavior of these plastics during pyrolysis and therefore serves as

2.0 Experimental

2.0.1 *Materials*

Waste (or post consumer) drinking water PET bottles
Scissors, Sieve, pestle and mortar
Weighing balance
Thermometer (0-360^0C or 0-600^0C)
Heating mantle with regulator (100 kW)
Two-neck, (250ml or 500ml), round-bottom reactor with a condenser
Measuring cylinder – 25ml
Alkaline Earth salts
* $Ca(OH)_2$ Calcium hydroxide
* Local chalk (Efun)
Raw corn-Pap (Ogi)

2.0.2: **PET bottles – collection & preparation**

The post- consumer PET water bottles were sourced around Yaba College of Technology and LASU (Epe Campus) environs. The caps and label were removed (with hand), cleaned and sun-dried to remove any trace of moisture. The quantity collected was shredded to pellets form (of non-uniform sizes) with scissors.

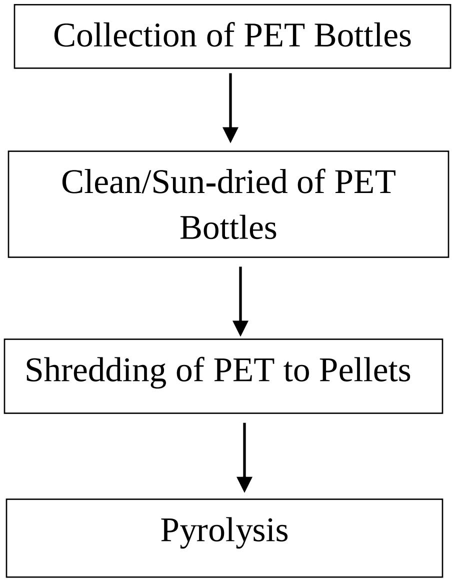
2.0.3 Reagents Procurement/Preparation

1. The commercial analar grade Ca $(OH)_2$ was purchased from chemicals dealer at Ojuelegba, Lagos State.

2. The ***local chalk***(known as Efun in native tongue) was purchased in substantial quantities from herbal Seller at Bariga market in Lagos State. The whole chalk was crushed and ground to powdery using pestle and mortar.
3. ***Raw-corn Pap***

This is a locally processed food made from fermented white corn. The raw starch was procured within LASU (Epe Campus) mini-market. The raw starch was spread on cleaned tray and sun-dried for one or two weeks.

Flow-diagram depicting PET-preparation



2.1 Process Descriptions

A. Sample A(2): **PET and Ca $(OH)_2$ – Pyrolysis**

The thermal Degradation of PET with Ca $(OH)_2$ was carried out in accordance with the method described in the work of Moinuddin *et al*., (2011).

Sample Preparation and Placement

Totalweight ($Ca(OH)_2$ + PET sample (pellets)) =120 grams

Procedure Description

The first half of the total weight of $Ca(OH)_2$ was introduced into the heating flask followed by total amount of waste PET (Pellets). Finally the second half of $Ca(OH)_2$ was put to cover the sample in order to ensure all the formed terephthalate and benzoic acid have intimate contact with $Ca(OH)_2$ upon decarboxylation.

The heat regulator set at 90-100 kW, the heating flask was heated at room temperature at normal atmospheric pressure (1 atm). At temperature of 90^0C, all the vapour had been condensed. Below this temperature, no vapours were formed and the experiment was concluded. Total time for the process to complete wasbetween 39-40 minutes.

Total volume of the product obtained was 14ml (a mixture of water and brownish – yellow color liquid oil) in which water takes large proportion.

The use of $Ca(OH)_2$ serves as catalyst but also assists in decarboxylation and absorption of carbon-dioxide according to the reactions:

$$Ca(OH)_2 \xrightarrow{\Delta} CaO + H_2O_{(g)}$$

$$CaO_{(s)} + CO_2 \xrightarrow{\Delta} CaCO_{3(g)}$$

Overall

$$Ca(OH)_2 + CO_2 \xrightarrow{\Delta} CaCO_{3(s)} + H_2O_{(g)}$$

B. Sample B (1): **Corn Pap and PET**

Sample Preparation and Placement

Total weight (Pap + PET (pellet)) = 150 grams

Procedure

The procedural steps were the same as described (in A). The whole content was heated for 15 minutes at a range of temperature 37^0C – 90^0C. Before the attainment of 90^0C, the initial vapor produced suspected to be gases could not be condensed instead were vented off into the surrounding air. Towards 60^0C all the non-condensed vapors (perhaps CO_2 and hydrocarbon gases) had ceased. Between 60-90^0C more of vapors were formed and condensed into a collector via condenser pipe.

The product obtained was reddish brown liquid (a miscible mixture of water and volatile hydrocarbons) up to 25ml in volume.

C Sample C(3): **Chalk and PET**

Totalweight (Chalk + PET (Pellet)) = 240 grams

The same procedure as in A was followed. The flask was heated at ambient temperature (36^0C). Around 80^0C the vapour had started forming and condensing. However, as the temperature rose to 100-120^0C more vapour was formed but the condensed vapour, was a mixture of solid and liquid which was absorbed and made the product a yellowish substance. The product was then washed off the condenser pipe with copious water. The whole process was completed at 1hr 19 minutes.

The product was left for some days at room temperature to dry; but turned off white color. This suggests that the liquid that formed alongside the solid consists of volatile hydrocarbons.

D Sample D(4): Chalk + $Ca(OH)_2$ and PET IN RATIO 1:1:1

The slaked lime and chalk were homogenized (mixed). Portion of it was put into the heating flask followed by the portion of PET. This was done intermittently but ensured the whole weight of PET was completely covered with left portion of lime and chalk mixture. The apparatus was set up for heating at 36^{o}C till 112^{o}C during which all vapours were condensed and collected. The experiment was completed at about 53 minutes. The condensate was a mixture of brown liquid oil and creamy yellowish wax and little amount of water.

E Sample E(5): Chalk + $Ca(OH)_2$ and PET IN RATIO 1:3:2

The experimental procedure and process was the same as discussed in D. The heating flask and its content were heated at 36^{o}C till the temperature reached 124^{o}C and remained steady. At this point whole vapours were condensed and collected for almost 66 minutes. The product was a colloidal solution of gel golden yellow oil and brown oil.

Figure1: Product from the experiment

Table 2.1: Showing summary of experimental data

Expt.	Description	Duration	Temp.(^{o} C)	Product Qty
A	**PET and Ca $(OH)_2$**	**40 min.**	**36-90**	**14ml (brownish yellow liquid+H_2O)**
B	**Corn Pap and PET**	**15 min.**	**36-90**	**25ml (reddish or orange liquid)**
C	**Chalk and PET**	**79 min.**	**36-120**	**6.4 g (off white crystal)**
D	**Chalk + $Ca(OH)_2$ and PET in ratio 1:1:1**	**53 min.**	**36-112**	**10 ml (brown liquid oil + creamy yellowish wax)**
E	**-Chalk+$Ca(OH)_2$and PET in ratio1:3:2**	**66 min.**	**36-124**	**8 ml (Colloidal solution of gel golden yellow oil + brown oil)**

2.2 Instrumentation Analysis

The product(s) obtained from each experiment was sent to laboratory for analysis using SRI 8610C FID (Flame-Ionization Detector)-Gas-Chromatography (GC) instrument.

3.0 RESULTS AND DISCUSSION

3.1 Sample Preparation / Purification

The samples were labeled A, B, C, D and E. The solvents Acetone and n-Hexane (Analar grade) were used to dissolve and extract the volatile organic compounds that may likely present in each product. The sample to solvent mix ratio was 1:2.

Table 3.1 gives the summary of the total hydrocarbons with their concentrations (mg/l) present in each analyzed sample as appeared in the chromatograms.

3.2 Analysis of Samples

The purified samples after being subjected to gas chromatography-FID the analytes obtained in each sample areinterpreted based on chromatograph result and are summarizedas shown in Table 3.2with respect to their concentrations (mg/l)/Retention Time, RT (sec). The chemical components present in the samples are categorized into Aliphatic Hydrocarbons and Poly Aromatic Hydrocarbons (PAHs). In sample A, there are eight aliphatic hydrocarbons and five PAHs detected from the pyrolysed waste PET and slaked lime [Ca $(OH)_2$].

In sample B (product from pyrolysis of waste PET and raw corn-Pap) nine aliphatic hydrocarbons and three PAHs were detected.

The sample C which was obtained from pyrolysis of waste PET with calabash chalk upon analysis contained eight aliphatic hydrocarbons and five PAHs.

In samples D and E in which the proportions of slaked lime and calabash chalk were varied it was observed that the number of aliphatics and PAHs also varied when compared to the number obtained in samples A and C. In D the analysed product contained five aliphatics and six PAHs when the ratio of slaked lime to chalk was 1:1 while at ratio 1:3 in sample E the numbers of aliphatics and PAHs in the product were seven respectively. However, dibenzoanthracene and indenopyrene were additional PAHs found in samples D and E with concentration 0.0001825 mg/l, 0.00005131 mg/l and 0.0001335 mg/lrespectively.

Table 3.2: Summary Showing Total Hydrocarbons as Detected and Recorded by GC-FID

	Total Hydrocarbons									
	Components Name, Composition (mg / L) and Retention Time (RT)									
	SAMPLE A (2)		**SAMPLE B (1)**		**SAMPLEC (3)**		**SAMPLE D (4)**		**SAMPLE E (5)**	
	Component/ composition(mg/l)	**RT sec**	**Component/ composition(mg/l)**	**RT sec**	**Component/ composition(mg/l)**	**RT sec**	**Component /composition(mg/l)**	**RT sec**	**Component/ composition(mg/l)**	**RT sec**
ALIPHATIC (Saturated)	**Undecane (0.01974 mg/l)**	**37.88**	**Nonane (0.6177 mg/l)**	**25.66**	**Undecane (0.0.01133mg/l)**	**47.09**	**Undecane (0.6149 mg/l)**	**9.300**	**Decane (0.003813 mg/l)**	**7.166**
	Tridecane (0.2401 mg/l)	**13.46**	**Undecane (0.04984 mg/l)**	**9.24**	**Tridecane (0.03159 mg/l)**	**13.47**	**Duodecane (2.7925 mg/l)**	**11.470**	**Duodecane (0.2691 mg/l)**	**11.660**
	Tetradecane (0.08930 mg/l)	**30.63**	**Duodecane (0.04710 mg/l)**	**23.42**	**Tetradecane (0.05247 mg/l)**	**30.65**	**Tridecane (0.6813 mg/l)**	**13.540**	**Undecane (0.7331 mg/l)**	**18.683**
	Pentadecane (0.1914 mg/l)	**34.79**	**Tridecane (0.02954 mg/l)**	**26.76**	**Pentadecane (0.4552 mg/l)**	**17.25**	**Tetradecane (0.3225 mg/l)**	**15.276**	**Tridecane (0.5978 mg/l)**	**40.535**
	Hexadecane (0.0346 mg/l)	**20.42**	**Tetradecane (0.03379 mg/l)**	**45.94**	**Hexadecane (0.04294 mg/l)**	**20.40**	**Octadecane (0.04440 mg/l)**	**66.993**	**Tetradecane (0.1910 mg/l)**	**30.549**
	Heptadecane (0.02768 mg/l)	**76.27**	**Pentadecane (0.4278 mg/l)**	**34.83**	**Heptadecane (0.01566 mg/l)**	**25.57**			**Heptadecane (0.01384 mg/l)**	**51.079**
	Pristane (0.002026 mg/l)	**120.13**	**Hexadecane (0.01762 mg/l)**	**225.91**	**Pristane (0.0008242 mg/l)**	**29.91**			**Pristane (0.003396 mg/l)**	**119.751**
	Octadecane (0.001658 mg/l)	**66.54**	**Heptadecane (0.01105 mg/l)**	**253.37**	**Octadecane (0.007026 mg/l)**	**99.73**				
			Pristane (0.0002305 mg/l)	**120.21**						
POLYCYCLIC AROMATIC (PAHs)	**Naphthalene (0.01415 mg/l)**	**7.38**	**Naphthalene (0.2533 mg/l)**	**7.280**	**Acenaphthylene (0.002586 mg/l)**	**11.48**	**Naphthalene (0.3109 mg/l)**	**7.430**	**Naphthalene (0.02670 mg/l)**	**36.845**
	Fluorene (0.002042 mg/l)	**13.70**	**Benzofluoranthene (0.0005971 mg/l)**	**28.230**	**Acenaphthene (0.002763 mg/l)**	**12.43**	**Acenaphthylene (0.1850 mg/l)**	**34.556**	**Acenaphthylene (0.04825 mg/l)**	**11.570**
	Anthracene	**16.83**	**Benzopyrene**	**28.973**	**Fluoranthene**	**20.65**	**Acenaphthene**	**12.346**	**Fluorene**	**27.006**

	(0.0002429 mg/l)		(0.0006094 mg/l)		(0.009691 mg/l)		(0.005333 mg/l)		(0.02317 mg/l)	
	Fluoranthene	20.66			Benzoanthracene	25.49	Fluorene	27.169	Benzofluoranthene	85.375
	(0.003413 mg/l)				(0.001304 mg/l)		(0.05831 mg/l)		(0.009882 mg/l)	
	Chrysene	49.90			Benzoperylene	33.56	Dibenzoanthracene	32.970	Benzopyrene	86.529
	(0.004418 mg/l)				(0.0004527 mg/l)		(0.0001825 mg/l)		(0.001185 mg/l)	
							Benzoperylene	66.836	Indenopyrene	32.620
							(0.001447 mg/l)		(0.0001335 mg/l)	
									Dibenzoanthradene	32.920
									(0.00005131 mg/l)	

Table 3.3 clearly shows the comparison of the total hydrocarbons in each sample with respect to their concentrations (mg/l). The component bar chart in figure 2 illustrates which hydrocarbon is present in each of the samples in large quantity and the one in least quantity.

Table 3.3: Showing the total Hydrocarbon against its concentration (mg/l) in each sample

		CONCENTRATION (mg/l) of Total Hydrocarbon				
	Total Hydrocarbon	**Sample A(2)**	**Sample B (1)**	**Sample C (3)**	**Sample D(4)**	**Sample E(5)**
1	Nonane	0	0.6177	0	0	0
2	Decane	0	0	0	0	0.003813
3	Undecane	0.01974	0.04984	0.001133	0.6149	0.7331
4	Duodecane	0	0.0471	0	2.7925	0.2691
5	Tridecane	0.2401	0.02954	0.03159	0.6813	0.5978
6	Tetradecane	0.0893	0.03379	0.05247	0.3225	0.191
7	Pentadecane	0.1914	0.4278	0.4552	0	0
8	Hexadecane	0.0346	0.01762	0.04294	0	0
9	Heptadecane	0.02768	0.01105	0.01566	0	0.01384
10	Pristine	0.002026	0.0002305	0.0008242	0	0.003396
11	Octadecane	0.001658	0	0.007026	0.0444	0
12	Naphthalene	0.01415	0.2533	0	0.3109	0.0267
13	Fluorene	0.002042	0	0	0.05831	0.02317
14	Anthracene	0.000243	0	0	0	0
15	Fluoranthene	0.003413	0	0.009691	0	0
16	Chrysene	0.004418	0	0	0	0
17	benzofluoranthene	0	0.0005971	0	0	0.009882
18	Benzoperylene	0	0	0.0004527	0.001447	0
19	Acenaphthylene	0	0	0.002586	0.1904	0.04825
20	Acenaphthene	0	0	0.002763	0.005333	0
21	Benzoanthracene	0	0	0.001304	0	0
22	dibenzoanthracene	0	0	0	0.0001825	5.131E-05
23	Benzopyrene	0	0.0006094	0	0	0.001185
24	Indenopyrene	0	0	0	0	0.0001335

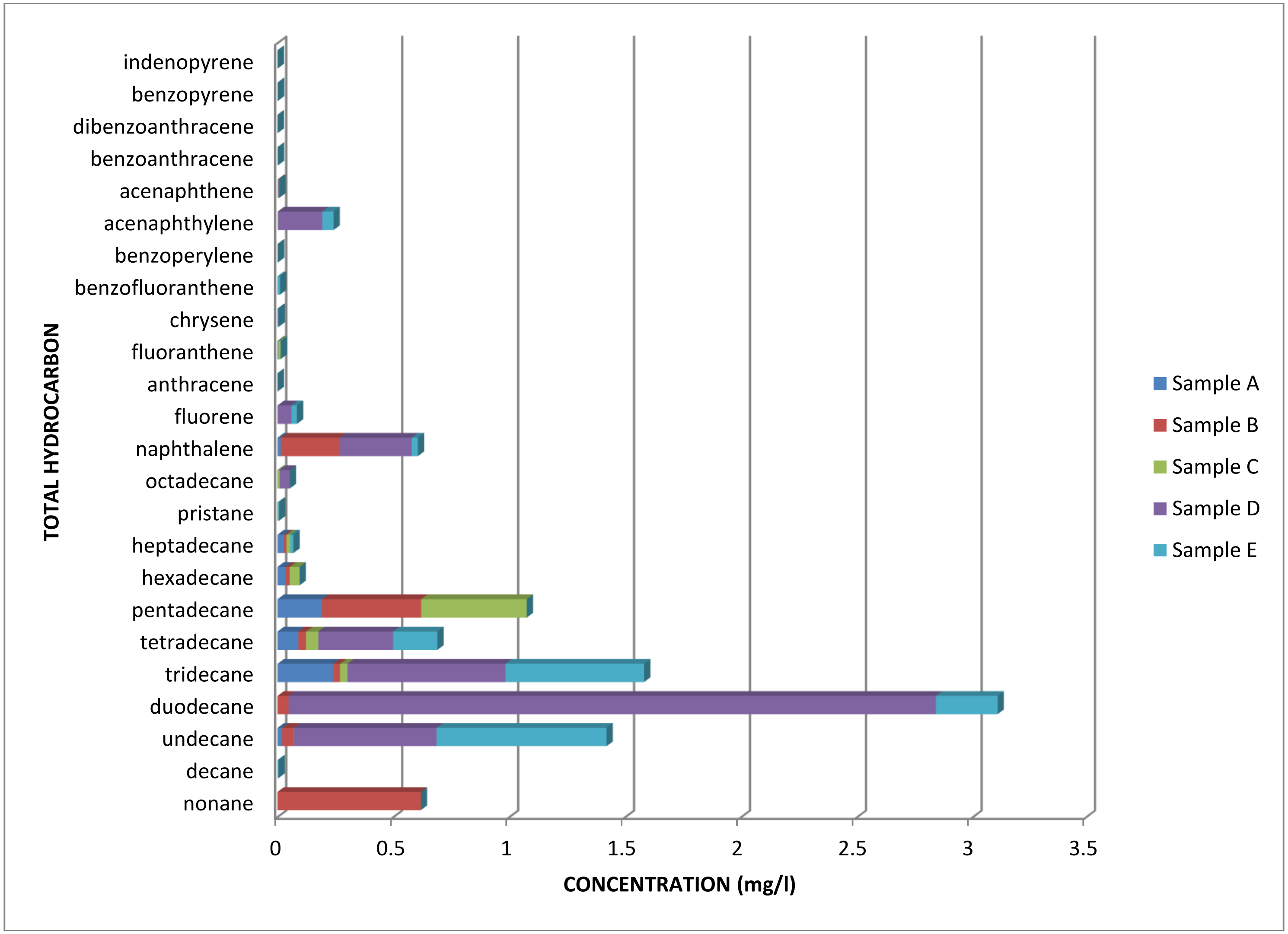


Figure 2: shows the bar component chart comparisons of the total hydrocarbons concentration (mg/l) from each sample

From the above figure only, sample B contained nonane in addition to other aliphatic found in other samples in concentration of 0.6177 mg/l. Decane was only present in sample E that was obtained when the proportion of lime and chalk was mixed in ratio 1:3. Common to all samples was undecane in varying concentrations however it has highest concentration in samples D and E.

Duodecane is virtually present in all the pyrolysed PET products except samples A and C. Its concentration (2.7925 mg/l) in sample D is very high than in sample E whose concentration (0.2691mg/l), in turn, high than sample B (0.04710 mg/l).

Each sample contained tridecane in varying concentration but its concentration in samples D, E and A are more significant.

Tetradecane concentration is observed to be greater in sample D than in A and E.

Also noticed was the fact that the concentrations of hexadecane up to octadecane were less significant virtually in all the samples as depicted in the chart.

The poly aromatic hydrocarbons detected were present in very minute amounts except naphthalene, fluorene and acenaphthylene in all the samples. Naphthalene concentrations in samples B and D were much higher than A or E.

Acenaphthylene concentration is more noticeable in both samples D and E.

4.0**Conclusion**

In this research, pyrolysis method has been used to reclaim fuel energy compounds of paraffinic origin and complex aromatics from waste PET with the aid of local materials and calcium hydroxide as catalysts at very low heating rate. The result obtained from analysis are similar to those obtained by other researchers (especially Khaing and Chaw, 2015) who have studied the conversion of the same material.

These hydrocarbons can serve as primary feed stocks for petrochemical industries. For example, many of the poly aromatic hydrocarbons contained in the sample products have been reported as precursors for the manufacturing of dye stuff, pharmaceuticals and pesticides. Although they are carcinogenic when not moderately used.

In this experiment also it was noted that in as much as heating rate and temperature and type of catalyst influence the pyrolysis product, it is therefore concluded that the use of calabash chalk (local inorganic material widely distributed in some part of Africa countries particularly Nigeria) mixed in equal proportion or mixed such that the amount of local material is more than the lime enhanced the catalytic conversion of waste PET to aliphatic and poly aromatic hydrocarbons within temperature range of 90-124^{0}C.

4.1 Recommendation

The use of local material (Calabash chalk) and Calcium Hydroxide in varying proportion effectively convert waste PET to hydrocarbons of significant petrochemicals. However further study should still be carried on the improvement for the use of this local material and other alkaline earth salts. Also, to understand fully the kinetic breakdown of the material (PET) the use of the following instruments is essential: Thermogravic analysis and Derivative thermogravic analysis must be used to monitor the thermodynamics parameters that can be used to develop kinetic model for the pyrolysis transformation of waste PET.

References

Al-Sabagh, A.M.;Yehia, F.Z.; Eshaq,Gh.; Rabie, A.M.; and Elmetwally, A.E. (2016): Greener Routes for Recycling of Poly Ethylene Terephthalate Elsevier Egyptian Journal of Petroleum 25:53-64

Al-Salam, S.M. and Lettieri, P. (2010): Kinetics of Poly Ethylene Terephthalate (PET) and Poly Styrene (PS) Dynamic Pyrolysis; World Academy of Science, Engineering and Technology 42; 1253-1261

Anke, B. Jan, B.; Carlo, V. and Raf, D. (2011): Polymeric Cracking of Waste Poly Ethylene Terephthalate to Chemicals and Energy; Journal of the Air and Waste Management Association, 61:7, 721-731.

Bajus, M. and Hajekova, E. (2010): Thermal Cracking of the Model Seven Components Mixed Plastics into Oils/Waxes; Petroleum and Coal 52 (3) 164-172.

Bordynuik, John W. (2013): Viable Production of Diesel from Non-Recyclable Waste Plastics, Proceedings of the 21st Annual North American Waste-to-Energy Conference, Fort Myers, Florida, USA, 1-10.

Khaing, T.K. and Chaw, S.H. (2015): Effect of Various Catalysts on Fuel Oil Pyrolysis Process of Mixed Plastic Wastes; International Journal of Advances in Engineering & Technology, Vol. 8, Issue 5, 794-802.

Kyaw,K.T. and Hmwe,C.S.S. (2015): Effect of Various Catalysts on Fuel Oil Pyrolysis Process of Mixed Plastic Wastes Int. J. of Advances in Eng& Technol 8 794

Miskolczi, N. (2013): From Crude Oil to Plastics and Routes for Waste Polymer Utilization

Mohammed, M.R. and **Moinuddin, S**. (2013): Waste Poly Ethylene Terephthalate (PETE) and Poly Styrene (PS) into Fuel; International Journal of Scientific & Technology Research volume 2, Issue 7, 176-189

Moinuddin, S.Aminul, K; Mohammed, M.R; Mohammed, M; and Din Mohammed, A.S.M,(2011): Waste Poly Ethylene Terephthalate (PETE-1) Conversion into Liquid Fuel; Journal of Fundamentals of Renewable Energy and Applications Vol. 1:1-5

Siddiqui, M.A. and Redhwi, H.H. (2011): Recycling of Waste Polyethylene Terephthalate (PET) into Feedstock Monomers; NSTI – Nanotech Vol. 3:781-782

Vakili, M.H. and Fard, M.H. (2010): Chemical Recycling of Polyethylene Terephthalate Wastes; World Applied Sciences Journal 8 (7): 839-846