PYROLYSIS PROCESS STUDIES FOR POST CONSUMER POLYETHENE WASTE CONVERSION AND UPGRADING OF THE PYROLYSIS OIL

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Abstract

Pyrolysis is a waste to energy conversion technology that operates in oxygen free environments. Pyrolysis can be applied in the sustainable management of plastic wastes through conversion to liquid and gas fuels which are chemically similar to fossil fuels. This study was carried out to implement a suitable and cost-effective recycling technology that will help solve severe pollution problems resulting from poor management of waste plastics in urban and rural set-ups in Kenya. The paper aims to conduct pyrolysis process studies for post-consumer polyethene waste conversion and characterization of the resultant liquid products. This was conducted in a locally assembled pyrolysis reactor at temperatures ranging between 200 to 350 °C for periods 1 to 2 hours. Low Density Polythene (LDPE), High Density polythene (HDPE) and Polypropylene (PP) were used in the experiments. Plastic waste materials were collected from the open dumpsites, washed, sun-dried, sorted out according to resin codes, sliced and pelletized into small pieces of dimensions of 2 mm. The samples were feed in the preheated reactor for conversion and the liquid collected in glass jars. Fractionation was conducted to partition the crude into petrol at 150 °C and diesel at 350 °C. HDPE, LDPE and PP produced 720±1.64, 696.07±1.67 and 602.08±2.01 ml of crude oil for 1 kg of wastes respectively. Diesel yield was 72%, 70% and 60% for HDPE, LDPE and PP respectively while petrol was 6%, 8% and 6% respectively. HDPE, LDPE and PP produced 1 %, 5 % and 1 % of solid residue respectively. The results showed that over 90% conversion of plastic waste into fuel products is achievable through pyrolysis process.

Key words: Pyrolysis, waste to energy, LDPE, HDPE, PP

1.0 Introduction

Plastics have found a lot of use in the modern world. This is due to their versatility and are mainly used as packaging materials because they are light, durable, affordable and can be used over and over again (Thompson et al., 2009a). The plastic material is man-made and comes in various types depending on its application. Polypropylene (PP) is the most widely used plastic type in the world today followed by Polyethylene (PE) (Qiao-fen, 2000). There are many other forms of other plastics whose applications depend on intended purpose.

Large production and use of plastics for various applications has resulted in huge volumes of plastic wastes. (Bahri, 2005). This has lead to proliferation in the environment as a result of accumulation and fragmentation of plastic waste since most of it is non-degradable and highly resistant to light, acids and other tough conditions (Thompson et al., 2009b). Plastic waste presents a huge problem by choking and starving marine and wildlife, littering the surrounding environment and blocking drainage systems and water bodies (Thompson et al., 2009a).

Burning of plastics in open fires, landfills or by use of municipal solid wastes (MSW) incinerators releases gas emissions such as the greenhouse gases (GHG's) that cause global warming (Lithner *et al.*, 2011). Other emissions include the persistent organic pollutants (POP's) such as dioxins and furans (Gilpin R. et al., 2003). These are persistent, very toxic and keep circulating in the environment once generated. They are carcinogenic (Lai et al., 2001, Ribas-Fito et al., 2001) and have endocrine disrupting effects in a range of biota (Nkwachukwu *et al.*, 2013).

Plastic is derived from oil refining waste products that constitute petrochemicals produced from fossil oil and gas (Bordynuik, 2013). The structural forms of plastic polymers differ from one type to the other depending on the nature of plastic type required for the specific application. PE plastic for example appears as LDPE and HDPE. The LDPE is the branched version of polythene that comes in 2 grades according to the average densities. There is the linear low density polythene (LLDPE) of density 0.925 g cm^{-3} and the LDPE of density range between 0.930 to 0.935 g/cm^3 (Andrady and Neal, 2009). HDPE is the linear versions of polythene. It has a closely parked crystal structure due to the low degree of branching. It has a higher density of about 0.941 g/cm^3 or more (Jawad, 2010). PP structure constitutes hydrocarbon chains made from the monomer propylene. The amorphous and crystal structures have a density of about 0.855 g/cm^3 and 0.946 g/cm^3 respectively. Other components are added to plastics during their manufacture to improve on their properties and performance. These include additives such as fillers, colorants, thermal stabilizers and plasticizers (Andrady and Neal, 2009).

Plastic waste has great economical value that is yet to be exploited in most of the developing countries where advanced MSW management technologies such as pyrolysis are yet to be fully implemented (Eisa and Visvanathan, 2002). Energy recovery from plastic waste could become an alternative means of obtaining cheap fuel (Bordynuik, 2013). In some of the developed nations such as the US, plastics are being recycled in an effort to create an alternative fuel sources (Hopewell *et al.,* 2009). In Kenya, transport and other manufacturing industries have continued to be over dependent on petroleum for fuel despite of its high cost in the current market price (British Plastics Federation., 2008). Recycling of post-consumer plastic waste for energy recovery through a cost effective and an environmentally friendly process is now our new challenge. This calls for the development of a home grown pyrolysis process system and carrying out optimization studies of the process so as to make it economical and implementable.

2.0 Methodology

2.1 Pyrolytic Reactor Design

The pyrolysis process was conducted in a pyrolysis reactor made of mild steel and stainless steel. The reactor has a height of 20 cm, an external diameter of 11 cm and an inner diameter of 8 cm. The reactor was capped with a ball valve to make it airtight and fitted with an outlet tube system at the top. The tubes had an outer diameter of 300 mm and an inner diameter of 200 mm. The tubing system was passed through a condenser made of a 20 L container that was filled with cold water at a temperature of 25 °C. A pressure gauge of 1- 250 bars was connected to the top of the reactor. A thermocouple with a digital temperature recorder was connected to the reactor to control and monitor the internal reaction temperature during the pyrolysis process. High purity Nitrogen gas was purged into the reactor at a flow rate of 2 liters/minute to maintain an oxygen free environment. The reactor was heated to a temperature range of 200 to 350 °C using a 2 Kw electric coil for a period of 1-2 hours. Plate 1 below shows the pyrolysis batch reactor used in this study for oil production.

Plate 1: Pyrolysis batch reactor used for oil production

2.2 Sample Collection and Preparation

Plastic waste materials of LDPE, HDPE and PP were collected from the open dumpsites. Samples were washed with water and detergent, then rinsed with distilled deionized water. The clean samples were sun-dried and sorted out according to resin codes developed by the Society of Plastic Industries (SPI). The samples were sliced and pelletized into small pieces of dimensions of 2 mm.

2.3 Pyrolytic Conversion of HDPE, LDPE and PP Waste Plastics

Batches of 500 g of pellets were introduced in the pre-warmed reactor at 200 °C. Nitrogen gas was purged into the reactor at a flow rate of 2 L/min. The sample was heated at rate of 5 ^{0}C/min until a temperature of 350 ^{o}C was attained. The incondensable gases produced from the reactor were evacuated using the outlet tube system. The gases were passed through a condensation chamber that was operated at room temperature and the condensed oil stored in appropriate glass bottles and gases flared. The solid residue was weighed for each batch and stored in precleaned containers. Optimization studies were carried out by varying reactor temperature within the range of 200 °C - 350 °C, reaction times were also varied and catalysts used. The effects of temperature, reaction times and use of catalysts were correlated with the distribution of gas, liquid and residues yields.

2.4 Mass Balance Analysis

The mass balance was determined after the reaction was completed. This was done by adding the amount of residue and that of mixed oil, then subtracting this from the initial amount of plastic material pyrolysed thus establish the amount of gas produced and determine the product distribution for the yield obtained with different pyrolysis conditions for each reaction process.

2.5 Energy Balance Determination

Energy balance was computed for the process. This was done by calculating the amount of input energy used by the reactor to convert 1 kg feedstock to oil and by the fractional distiller to obtain petrol and diesel from the mixed oil. The output energy for the conversion of 1 kg feedstock to various products was obtained by calculating the value of the products yielded. The difference between input and the output energy gave the energy balance of the entire process.

2.6 Fractional Distillation

Upgrading of the mixed oil collected from the pyrolysis reactor was done through fractional distillation. The mixed oil was transferred into a 1 L round bottomed flask connected to a fractionating column. The system was heated to temperature range of 150 to 350 °C. Petrol and diesel were recovered in separate volumetric flasks at temperatures of 150 °C and 350 °C respectively.

3.0 Results and Discussions

3.1 Pyrolytic Conversion Product Distribution and Mass Balance Results for HDPE, LDPE and PP Waste Plastics

The pyrolysis process was performed under atmospheric pressure. Products distribution and mass balance results were obtained for all the plastics assessed. Table 1 below shows the results obtained from pyrolysis of 500 g of PP, LDPE and HDPE in the temperature range of 200-350 °C and with heating rates of 5, 10 and 15 °C/min.

Table 1: Pyrolysis of 500 g of PP, LDPE and HDPE with heating rates of 5, 10 and 15 °C/min

		Product distribution for plastic pyrolysis in the temperature range of 200 - 350 °C.					
Parameters	Heating rate	PP		LDPE		HDPE	
		Mass (g)	Yield % (w/w)	Mass (g)	Yield % (w/w)	Mass (g)	Yield % (w/w)
Diesel	5 °C/min	301.22±1.5	60	348.21±0.97	70	359.64±1.67	72
	10 °C/min	291.18±0.67	58	326.32±0.85	65.6	329.67±1.26	66
	15 °C/min	266.07±0.65	53	309.91±0.38	62.3	312.69±1.15	62.6
Gasoline	5 °C/min	31.85±0.67	6	41.07±0.33	8.3	29.49±0.56	6
	10 °C/min	37.17±0.55	7	37.61±0.65	7.6	24.56±0.25	5
	15 °C/min	42.47±0.34	8	30.68±0.28	6.2	19.66±0.75	4
Gas	5 °C/min	157.29±1.33	32	83.88±1.23	17	103.82±2.14	21
	10 °C/min	167.12±1.75	34	118.43±0.87	24	140.74±2.45	28
	15 °C/min	174.49±2.34	35.5	171.70±0.65	34.8	165.38±3.67	33
Solid residue (char)	5 °C/min	9.64±0.63	2	26.84±1.18	5	7.5±0.83	1
	10 °C/min	4.81±0.9	1	16.13±1.97	3	3.18±0.67	1
	15 °C/min	4.57±0.86	1	5.38±2.05	1	3.36	1

As the heating rate increased, the product yield from HDPE, LDPE and from PP decreased in the order for 72 > 66 > 62.6 %, 70> 65.6> 62.3 and 60> 58> 53 respectively. Gas yield from HDPE, LDPE and PP increased in the order 21 <28 <33, 17 < 24 <34.8 and 32< 34< 35.5 respectively while char yield remained relatively constant at 1%. These results agree with the observation made by, (Siddiqui & Redhwi, 2009) as he found out that low heating rates and reaction temperatures used in a batch reactor did not promote the production of light hydrocarbons. This corresponds to the low yield of petrol oil and gas as observed.

Amounts of solid residue (char) recovered from all the plastics assessed were in the range of 1- 5 %. This shows that complete thermal decomposition of almost all the plastic material was achievable at the temperature range of 200 - 350 °C. Thus high temperatures with low reaction and residence times allowed complete chemical decomposition of the polymeric materials. This results agree with the observation made by, (Aboulkas et al., 2010). This minimized the probability of having carbonization reaction that promotes formation of large amounts of char. The differences in crystal structure of the 3 plastic types assessed had an influence on the amount of oil yield obtained. The density/crystallinity of the polymeric materials decrease in the order HDPE>LDPE>PP. This corresponds to the amounts of oil yield obtained as shown in Table 1. The results of the present study agree with those reported by, (Miskolczi et al., 2006, Aboulkas et al., 2010). The results showed that over 90 % conversion of plastic waste into fuel products is achievable through the set pyrolysis process conditions. This is because plastic is derived from oil refining waste products that constitute petrochemicals produced from fossil oil and gas (British Plastics Federation., 2008).

3.2 Effect of temperature on the reaction time and oil yield

The experiment was performed under atmospheric pressure and at temperature ranges of 200-350, 350-450 and 400 to 500 °C so as to assess the temperature effect on reaction time and oil yield. Results for products distribution obtained from the assessed plastics were as shown in table 2 below.

Table 2: Products distribution obtained at temperature ranges of 200-350, 350-450 and 400 to 500 °C

		Product distribution for plastic pyrolysis					
Parameters	Reaction temperature range_ (°C)	PP		LDPE		HDPE	
		Mass (g)	Yield % (w/w)	Mass (g)	Yield % (w/w)	Mass (g)	Yield % (w/w)
Diesel	250-350	301.22±1.5	60	348.21±0.97	70	359.64±1.67	72
	350-450_	276.07±0.45	55	343.24±0.67	69	339.64±1.16	68
	450-500 _	271.02±0.33	54	338.28±0.10	66	349.65±1.15	67
Gasoline	250-350	31.85±0.67	6	41.07±0.33	8	29.49±0.56	6
	350-450	36.94±0.33	8.2	415.94±0.45	8	34.32±0.25	7
	450-500	47.78±0.52	9	46.26±0.75	9	39.32±0.75	8
Gas	250-350	157.29±1.33	32	83.88±1.23	17	103.82±2.14	21
	350-450	167.97±1.75	34	98.81±2.04	20	108.53±2.45	22.8
	450-500	174.22±1.67	35.4	113.85±1.98	23.2	115.10±3.67	23.3
Solid residue (char)	250-350	4.86±0.33	1	26.84±1.18	5	7.5±0.83	1
	350-450	9.64±0.73.59	2	10.57±0.93	2	7.32±0.67	1
	450-500	4.97±0.53	1	5.79±1.32	1	7.84±0.45	1
wax	250-350	4.54±0.23	1	6.84±0.18	1.5	6.74±0.43	1.4
	350-450	3.86±0.76	0.8	4.37±0.74	1	5.31±0.27	1.2
	450-500	2.97±0.33	0.6	3.79±1.56	0.8	3.34±0.33	0.7

For increased temperatures of above 450 ˚C results showed a decrease in diesel yields and an increase in formation of light hydrocarbons of gaseous products and petrol yield. This results agree with the observations made by, .(Jixing Shuyuan L. et al., 2003). The heavy hydrocarbons get cracked into light Hydrocarbons as the pyrolysis temperatures rise. This has also been confirmed by other authors (Wunderlich, 2005, Walendziewski and Steininger, 2001, Aboulkas et al., 2010, Saha and Ghoshal, 2005). The optimization curves in figure 4.3-.7 below show the results obtained from the study.

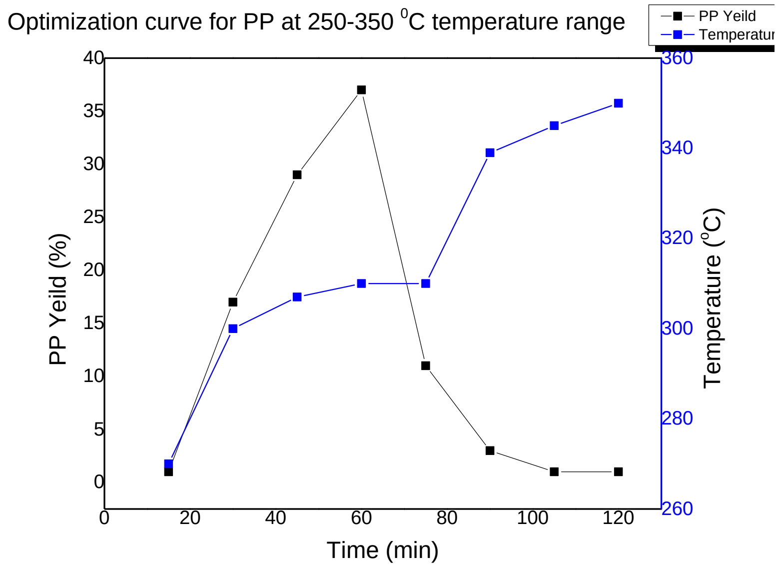


Figure 4.3: Optimization curve for PP

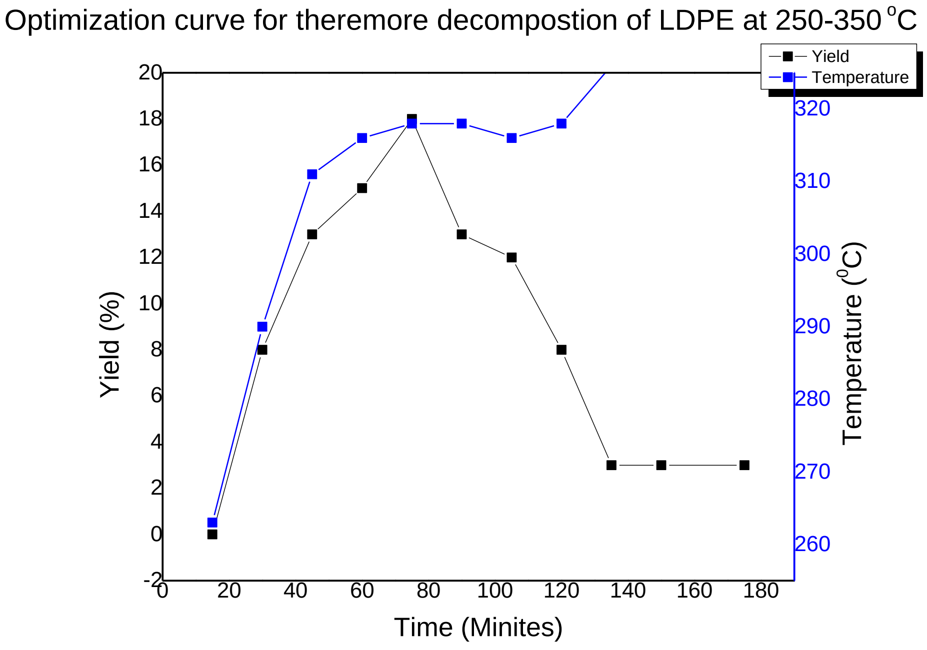


Figure 4.4: Optimization curve for LDPE

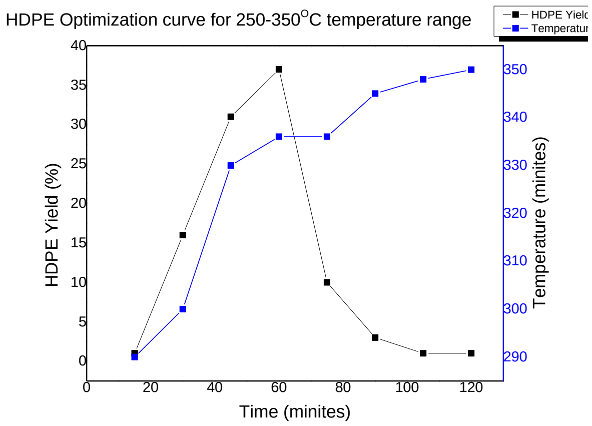


Figure 4.5: HDPE optimization at 250-350 °C

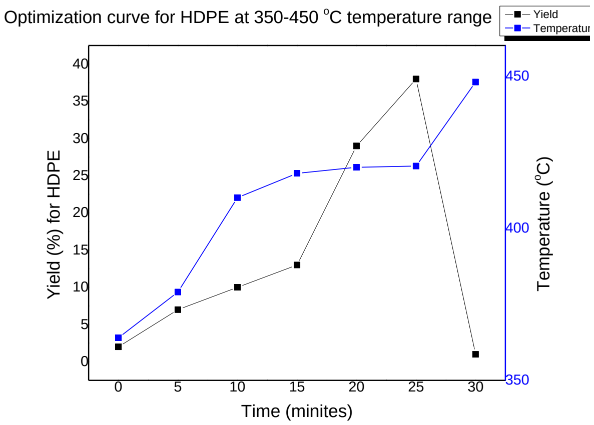


Figure 4.6: HDPE optimization at 350-450 °C

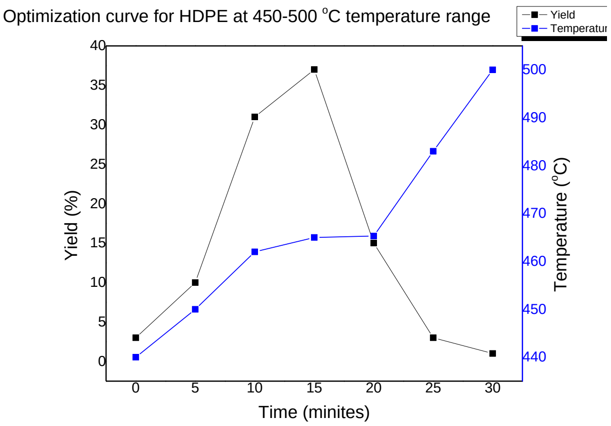
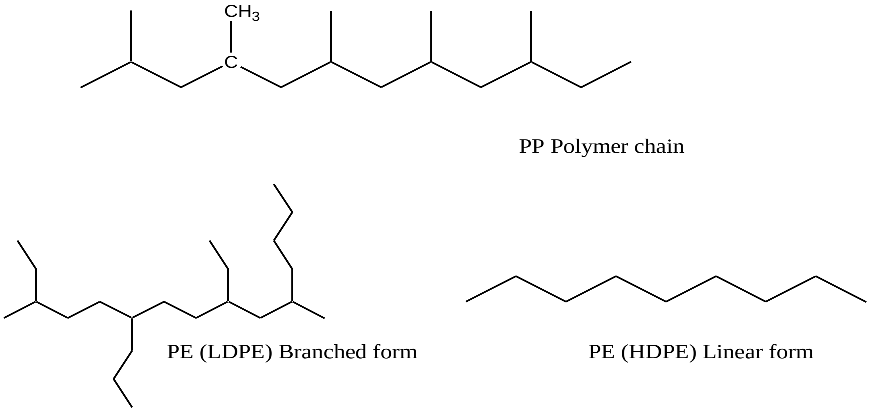


Figure 4.7: HDPE optimization at 450-500 °C.

The trends observed in the optimization curves for the three categories of plastics assessed showed that temperatures increased until the cracking temperature for plastic feedstock was attained. At this point, the reaction temperatures remained relatively constant until all feedstock had been pyrolyzed and thereafter increased towards the end of the reaction. It was observed that as the reaction temperatures increased, the reaction time decreased in the order 60 >25 > 15 minutes respectively. The cracking temperatures at which optimum yield of oil occurred from the 3 plastic types assessed decreased in the order HDPE (336 °C) >LDPE (318 °C) >PP (310 °C), HDPE(420 °C) > LDPE (398 °C) > PP (392 °C) and HDPE (465 °C) > LDPE (442 °C) > PP (434 °C) at temperature ranges of 250-350, 350-450 and 450-500 °C respectively. These results agree with the observation made by, (Laresgoiti et al., 2004).

When the temperatures rise above the decomposition temperature during pyrolysis, cracking's occur at the most unstable bonds in the molecular structure (Wade, 1995). Stability of carbon bond according to the dissociation energies for C-C bond of primary, secondary, and tertiary carbons decrease in the order: Methane > primary (355)> secondary(351) > tertiary (339) (McMurry, 2000). PP polymer chain is of lower thermal stability as compared to that of PE. This corresponds to the observed cracking temperatures at which optimum yield of oil occurred from the 3 plastic types assessed. This was attributed to the differences in the chemical structure and composition of the 3 plastics assessed (Siddiqui and Redhwi, 2009). PP constitutes C-C and C-H bonds arranged in the form of repeating groups of methylene just like that of PE. However in place of hydrogen molecules, there are methyl groups attached to the polymer chain with a C-H at tertiary carbon position (McMurry, 2000). PP polymer chain is of lower thermal stability as compared to that of PE whose C-H is at a secondary carbon atom and thus more stable (Wade, 1995). During pyrolysis, the methyl group accelerates the breaking of C-C chemical bonds through random-chain scission so as to produce low molecular weight products more rapidly and at much lower decomposition temperatures than that observed in PE (Wade, 1995). This is illustrated in Figure 4.8.



PP Polymer chain

PE (LDPE) Branched form

PE (HDPE) Linear form

Figure 4.8: Illustration of the chemical structures and composition of PP, LDPE (Branched form) and HDPE (Linear form) of PE

3.3 Energy Balance

Material mass balance for HDPE was calculated as followers; 1kg feed of the HDPE waste plastics gave approximately (800ml) yield of Crude oil. Fractional distillation of the crude oil yielded 60 ml/ 6 % petrol and 720 ml /72 % diesel and .205 (g) gas and 15 (g) of char were recovered from the process. Thus the total output energy for products was as followers;

Output: petrol + diesel = (0.06 x 100 sh) + (0.7 x 90 sh) + (gas)Z Nm^3 =69 sh + Z Nm^3/sh

The Input (energy) used by the reactor for pyrolysis of 1 kg HDPE was 2 kw and the input (energy) consumed during Fractional distillation of the mixed oil was 1 kw . Thus;

In put (energy) = 3 kw X 15 ksh/kw = 45 shillings

Difference: Output (69) - Input (45) = $^+$24 sh + Z Nm^3/sh

The plant was found to be economically viable and environmentally profitable since it is self-sustaining and helps to solve the problem of post-consumer plastic waste management.

4.0 Conclusions

Optimization studies showed that a rise in temperature helped to minimize the reaction time thus the cost of production. According to the findings of this project research, thermal pyrolysis conducted with low heating rates of 5 °C and at reaction temperature range of 350-450 °C provided best conditions for production of relatively high yields of diesel oils at minimal reaction time and cost. This has also been confirmed by in a study conducted by (Siddiqui & Redhwi, 2009). The plant is economically viable since it is self-sustaining and helps to solve the problem of post-consumer plastic waste management thus becoming environmentally profitable.

Management of post-consumer plastic waste through pyrolysis technology is thus more profitable if implemented in large scale for diesel oil production. However, the challenge of having a continuous supply of waste plastics for recycling should be assessed to ascertain the sustainability of the plant if the project was to be implemented on large scale. The major breakthrough for this project has been in the provision of a solution to the waste plastics management problem phased by most of the urban centers and rural set-ups in Kenya. The project will also present an alternative means of obtaining cheap and affordable fuel to the local community.

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