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Synthesis of Liquefied Petroleum Gas from Waste Plastics and Performance Analysis in a Home based Cooking Cylinder

Chinta Sandeep Kumar
Associate Member, Aeronautical Society of India, New Delhi, India

***Abstract*: In the recent years it is quite common to find in newspapers and publications that plastics are turning out to be a menace. Days are not so far when earth will be completely covered with plastics and humans will be living over it. All the reasoning and arguments for and against plastics finally land up on the fact that plastics are non-biodegradable in nature. The disposal and decomposition of plastics has been an issue which has caused a number of research works to be carried out in this regard. The present work involves the synthesis of a petroleum-based liquefied gas by the pyrolysis of waste plastics. Pyrolysis involves the degradation of the polymeric materials by heating them in the absence of oxygen. The pyrolysis of plastics yields on average 45–50% of gases, 35–40% of oil, and 10–20% of tar, depending on the pyrolysis technology. According to previous research, there are some cases where a high amount of liquid petroleum gas yield, more than 80 wt %, could be produced in the pyrolysis of individual plastic, which is higher than the pyrolysis of wood-based biomass in general.**

***Keywords*: waste plastics, pyrolysis, hydro treating, fuels, renewable gas, waste-to-lpg, sustainable energy, green energy.**

1. Introduction

Estimates show that less than 5% of the plastic manufactured each year is recycled, with production of the material set to increase by 3.8% every year until 2030, adding to the 6.3 billion tones churned out since production began 60 years ago. The majority ends up in our oceans, posing a disruption to marine ecosystems, which researchers predict would take a minimum of 450 years to biodegrade, if ever.

The solution of plastics-to-lpg holds promise in not only curbing such pervasive pollution but also providing a significant economic benefit to regions.

The technique of recycling waste plastic and polyethenes through pyrolysis started some 20 years back. Recycling of waste plastic and polythenes has become very important as they are non-biodegradable and pose a threat to our environment. The different types of plastics used are Polyethylene terephthalate (PET), High-density polyethylene (HDPE), Low-density polyethylene (LDPE), Polyvinyl chloride (PVC), Polypropylene (PP) and Polystyrene (PS). Among six main plastics, low density polythene (LDPE) is used in various field such as grocery bags, water hoses, garbage cans, film, containers etc. LDPE consists of more branches which make it weaker in intermolecular force, and as a result it has less hardness and tensile strength. LDPE is ductile as compared to HDPE as it has side branching and a less crystalline structure which allows it to be moulded easily. It is resistant to water, and thus can be used in manufacturing of plastic bags, foils etc. In contrast HDPE has less branching and thus has a higher strength. Due to its good strength, HDPE is used in making oil containers, bottles, toys and more. It is the third largest plastic type found in solid waste category.

Under pyrolysis conditions, plastic wastes can be decomposed into three fractions: gas, liquid and solid residue. The liquid products are usually composed of higher boiling point hydrocarbons. From investigations it is seen that various factors like calorific value, density, viscosity etc. obtained with this gas are comparable with other liquefied gases especially liquefied petroleum gas. Pyrolysis was performed at temperatures between 500 and 700°C. The yield of products obtained was totally different. 88.76% gas and for other it was 18.44 residue and 57.11% of oil. From the tests conducted it was established that as temperature increased the aromatic compounds in the gas also increased. The molecular weight also gets affected. The feedstock types strongly affect the product yields and the quality of liquid and solid products. HDPE waste produces the highest liquid fraction.

2. Literature Survey

Thermal Pyrolysis The effect of temperature and the type of reactor on the pyrolysis of waste HDPE has been studied and some of the results are reviewed.

Wallis et al. (Wallis MD et al. 2007) have done the thermal degradation of high density polyethylene in a reactive extruder at various screw speeds with reaction temperatures 4000C and 4250C. A continuous kinetic model was used to describe the degradation of the high density polyethylene in the reactive extruder. It was found that purely random breakage and a scission rate which had a power law dependence on molecular size of 0.474 best described the experimental data. The greatest discrepancy between the model prediction and the experimental data was the large molecular size region at short residence times; however, this only accounted for a very small percentage of the total distribution and was attributed to the presence of fast

initiation reaction mechanism that was only significant at low conversions.

Conesa et al. (Consea JA et al. 1994) studied the production of gases from polyethylene (HDPE) at five nominal temperatures (ranging from 5000C to 9000C) using a fluidized sand bed reactor. HDPE primary decomposition and wax cracking reactions take place inside the reactor. Yields of 13 pyrolysis products *(methane, ethane, ethylene, propane, propylene, acetylene, butane, butylenes, pentane, benzene, toluene, xylenes and styrene)* were analyzed as a function of the operating conditions. From the study of HDPE pyrolysis in a fluidized sand bed reactor, they have found that yield of total gas obtained increased in the range 5000C – 8000C from 5.7 to 94.5%, at higher temperatures, the yield of total gas decreased slightly, the formation of methane, benzene and toluene was favored by high residence times, but ethane, ethylene, propane, propylene, butane, butylenes and pentane undergo cracking to different extents at increasing residence times and/or temperature, the maximum yield of total gas obtained at 8000C from HDPE pyrolysis was 94.5% with the following composition: *20% methane, 3.8% ethane, 37% ethylene, 0.2% propane, 4.7% propylene, 0.3% butane, 0.4% butylenes, 2.2% pentane, 24% benzene, 2.1% toluene, 0.01% acetylene and 0.02% xylenes and styrene.*

Walendziewski et al. (Walendziewski J et al. 2001) reported the thermal degradation of polyethylene in the temperature range 370–4500C. In the case of thermal degradation of polyethylene, an increase in degradation temperature led to an increase of gas and liquid products, but a decrease of residue (boiling point >3600C). However, the increase of gas was not too large as compared to the sharp decrease of residue with increase of temperature. Similar results were obtained in the catalytic degradation and hydro cracking process. *The result of analysis of gas products obtained by the pyrolysis of polyethylene at 500º - 700ºC is summarized in the Table 1 Table 2 Composition of gas products obtained from pyrolysis of polyethylene at 700 ºC*

3. Methodology

In order to have a proper background study on technologies available for conversion of waste plastics to fuel, literature survey is carried out to know its various applied method throughout the globe, they are summarized below. From this crude oil various products petrol, diesel and kerosene etc. can be obtained by distillation. This process can convert all HDPE waste plastic to different grade fuels and specially jet grade fuel. After reviewing these various literatures, we can see that different forms of Pyrolysis processes have been employed for the conversion of plastic wastes to efficient fuels and also successfully tested as well.

Pyrolysis is generally defined as the controlled heating of a material in the absence of oxygen. In plastics Pyrolysis, the macromolecular structures of polymers are broken down into smaller molecules or oligomers and sometimes monomer units. Further degradation of these subsequent molecules depends on a number of different conditions including (and not limited to) temperature, residence time, presence of catalysts and other process conditions. The Pyrolysis reaction can be carried out with or without the presence of catalyst accordingly, the reaction will be thermal and catalytic Pyrolysis. Since majority of plastic used are polyolefin, so extensive research has been done on this polymer which is summarized as below. Thermal Pyrolysis of Polyolefin The non-catalytic or thermal Pyrolysis of polyolefin is a high energy, endothermic process requiring temperatures of at least 500– 700 °C.

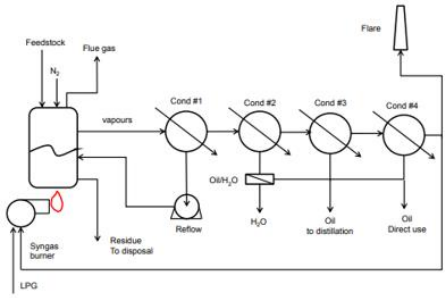

Fig. 1. Simplified process flow diagram of the pyrolysis plant. LPG: Liquid Petroleum Gas

Fig. 2. HDPE made medical waste

Fig. 3. Model used for extract LPG

A. Advantages of pyrolysis process

a) Volume of the waste is significantly reduced (90%)
b) Solid, liquid, and gaseous fuel can be produced from the waste,
c) Storable/transportable fuel or chemical feed stock is obtained,

d) Environmental problem is reduced,
e) Desirable process as energy is obtained from renewable sources like municipal solid waste or sewage sludge,
f) The capital cost is low.

There are different types of pyrolysis process. Conventional pyrolysis (slow pyrolysis) proceeds under a low heating rate with solid, liquid, and gaseous products in significant portions It is an ancient process used mainly for charcoal production. Vapors' can be continuously removed as they are formed. The fast pyrolysis is associated with tar, at low temperature (850–1250K) and/or gas at high temperature (1050–1300 K). At present, the preferred technology is fast or flash pyrolysis at high temperatures with very short residence time.

4. Calculations and Result

Table 1
Pyrolysis gas analysis

Property	Value
HDPE	Calorific Value: 40.5 Viscosity : 5.08 Density : 0.89 Pour Point : -5 Flash Point : 48
0 % recovered at 82.5º C	-
0 % recovered at 175.4º C	-
0 % recovered at 270.5º C	10%
0 % recovered at 375.2 º C	18%
0 % recovered at 429º C	27%
0 % recovered at 513.5º C	37%
0 % recovered at 570º C	48%
0 % recovered at 647.9º C	69.5%
0 % recovered at 680º C	76%
0 % recovered at 703.5º C	88.7%

More specifically, the main product is in the liquefied petroleum gas range, attributed to 88.76 wt % of the total pyrolysis gas produced. A significant (product diesel range) is also, accounting for 57.14. wt % of the pyrolysis oil, while there is a small yield of wax (18.44 wt %)

A. Effect of temperature on HDPE

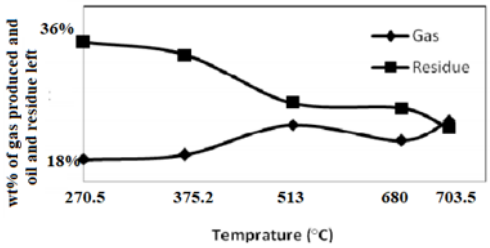

Fig. 4. Effect of temperature on distribution of oil and residue left and gas produced

Initiation: Initiation may occur on some defected sites of the polymer chains. For instance, an olefin linkage could be converted into an on-chain carbonium ion by proton addition:

$$–CH2CH2CH = CHCH2CH2− + HX \rightarrow CH2CH2+CHCH2–CH2CH2+X−$$

The polymer chain may be broken up through β- emission:

$$–CH2CH2+CHCH2–CH2CH2− \rightarrow CH2CH2CH = CH2++CH2\ CH2+$$

Initiation may also take place through random hydrideion abstraction by low-molecular-weight carbonium ions (R+):

$$–CH2CH2CH2CH2CH2– + R+ \rightarrow –CHCH2+CHCH2CH2−+RH \quad (6)$$

The newly formed on-chain carbonium ion then undergoes β-scission.

Depropagation: The molecular weight of the main polymer chains may be reduced through successive attacks by acidic sites or other carbonium ions and chain cleavage, yielding in gas oligomer fraction (approximately C30–C80). Further, cleavage of the oligomer fraction probably by direct β-emission of chain-end carbonium ions leads to gas formation on one hand and a liquid fraction (approximately C10–C25) on the other.

Fig. 5. Gas stored in a tube container and testing

Table 2
Comparison of gas from waste plastics with regular home based gas (LPG)

S. No.	Specifications	Home based cooking cylinder	Gas from waste plastic
1	Specific density at 15°C	2.2	2.1
2	Gross Calorific Value at 15°C (liquid)	11830	11790
3	Net Calorific Value at 15°C		
4	Molecular weight(gm/mole)	51-54	50.9
5	Air required for combustion	28	26
6	Explosive limit (vol% of vapor in air gas mixure)	2 to 9.5	3 to 12
7	Specific volume of Gas per kg at 15°C	0.42	0.45
8	Physical state at 15ºC	gas	gas
9	Boiling Point at 1atm (C)	(-)13	(-) 16
10	Freezing Point (C)	(-)153	(-) 172
11	Critical Temperature	243	276
12	Critical Pressure (psia)	570	590
13	Auto-ignition temperarure in air at 1 atm	490	510
14	Color	Colorless	Colorless
15	Odor	Odorless	Odorless
16	Toxity	Non Toxic	Non Toxic
17	Reid Vapor Pressure	5-7	4-9
18	Gross Calorific Value at 15°C (Vapor)	25226	23779
19	Net Calorific Value at 15°C (Vapor)	10896.36	98765.45
20	Liquid Density at 15ºC (kg/litr)	0.5550	0.4912

5. Conclusion

This review has provided brief information of plastic pyrolysis for each different type of plastic. We also come to know the affecting parameters on liquid oil yield. Based on the on literatures studied, pyrolysis process is most preferred method to minimize plastic waste due to its potential to efficiently energy from plastic waste to valuable liquid petroleum gas.

Pyrolysis has been effective compared to other disposal methods, because it can reuse the energy and the raw materials contained in those waste, reducing thereby the environmental impacts caused by the inadequate disposal of these waste plastics.

1) A liquefied petroleum gas has been produced from waste plastic (HDPE).
2) HDPE waste produced the highest liquid fraction. However, the heavy gas fraction was still high in the gas from HDPE waste.
3) Unlike in the existing recycling system, no plastic item is rejected in the new method.
4) The trials have been successful in disintegrating all kinds of plastics including polythene, bottles, bags, tyres, charring plastics such as toffee covers and thermocol.

6. Future Scope

Pyrolytic gas has paved way for alternate fuel but it is not commonly used as LPG. There are very few Pyrolysis plants available in India and world. There is still lot of scope left in Pyrolysis.

1) Research work can be conducted on unusual combination of raw material like for instance bio mass and polythenes or bio mass and plastics.
2) Role of catalyst cannot be ignored in Pyrolysis. Modifications in catalyst may prove more beneficial for overall yield of the pyrolytic gas.
3) Overall optimization of the process to achieve more economical and environment friendly method.
4) Pyrolysis plant can be integrated with other systems and equipment for easy removal of gas and it's by products.

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