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Enrichment of Pyrolysis Fuel Synthesized from Plastic

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ABSTRACT: This research paper is about the conversion of plastic waste into fuel with the use of catalytic Pyrolysis process. Generally, plastics used in this operation are Polyethylene, High-density Polyethylene, Polyvinyl chloride, Low density polyethylene, Polypropylene and polystyrene. Fuel from plastics like PE, PP and LDPE has less impurity in it and the production is also much simpler considerably, but while working with the PVC and PS there is significant amount of chlorine (Cl) and sulfur(S) content available in the fuel, availability of this two components is undesirable. Our main objective is to remove the Cl and S content from the oil with the use of catalyst column and cracking process of plastic in the reactor with the adequate mixture of ZnO, Bentonite clay and Kaolin clay. When the vapor pass through the catalytic column the impurities reduced by adsorption on the catalyst.

KEYWORDS: Catalytic Pyrolysis, Plastic Recycling, Alternative fuel, Pyrolysis.

I. INTRODUCTION

Nowadays, the use of plastic-based

Materials are on the rise all over the world, posing a dilemma in terms of trash management. There are a variety of methods for dealing with plastic trash, including: incineration, recycling, reuse, and land disposal, among other options. The current century has also been hampered by a lack of natural oil along with plastic waste management. As a result, the idea of transforming plastic waste into energy sources is highly appealing, pyrolysis is used for this. One of the best solutions with long-term management has been demonstrated by the process. Pyrolysis is the process of heating organic/polymeric materials in the absence of oxygen. Pyrolysis is derived from Greek words pyro and lysis, which means “fire” and “cutting” respectively. Pyrolysis normally processed at high temperature. There are different kinds of pyrolysis processes such as Flash pyrolysis, Ultra pyrolysis, Catalytic pyrolysis, Vacuum pyrolysis practiced, but for the plastic feed Catalytic pyrolysis is perfect.

Pyrolysis is a process that combines two processes: heating and cutting. Cutting involves the degradation of large chain hydrocarbon or complex structures. The product of pyrolysis of plastic is gas and liquid, whereas the residues are formed in solid phase. In comparison to plastic feed, liquid products include shorter chain hydrocarbons. Here, the result is quite comparable to commercial fuels and can be utilized as a substitute for traditional fuel.

The addition of a catalyst to the pyrolysis procedure enhanced both the liquid output and the hydrocarbon dispersion. Catalyst additionally improves the reaction rate. For the plastic feed natural zeolites, alumina-silica based catalyst, and others(Bentonite clay, kaolin clay, red mud) can be employed. One of the primary issues with the pyrolysis reaction is wax production in the liquid fuel. According to various investigations, a slightly acidic catalyst is employed to degrade wax for liquid fuel.

[1]. Pyrolysis methods currently in use:

Pyrolysis of waste plastic for the production of liquid gasoline is now a regular operation on a wide scale. Catalytic pyrolysis is more widely utilized, with catalyst such as ZnO, Silica, Alumina, Natural zeolites, Kaolin clay, and other natural clays. For the conversion of plastic waste to fuel in the pyrolysis process, several existing processes requires only one catalyst, some of them include the conversion of propylene using kaolin clay as a catalyst, which yields 80% liquid fuel, 9% gas, 5% char, and the remaining wax. However, at 450 °C, it is obtained with a particular plastic to catalyst ratio of 3:1. Another example is the conversion of propylene using a silica-alumina catalyst, which yields 91 percent liquid fuel, 8% gas, 1% char, and the rest is wax at 500 °C. However, pyrolysis of a mixture of plastic such as LDPE, PP, PC, and PVC using ZnO as a catalyst produces 47-60 percent liquid fuel and the remainder is gas. As a result, the yield of the pyrolysis process decreases dramatically with the addition of plastic and rendering the present technique unprofitable.

[2]. Pyrolysis Method Proposed:

As we know, when a mixture of different plastics is used as input, the existing techniques produce a low yield of liquid fluid. We may combine the properties of two or more catalysts in this novel system to achieve the most ideal result, which has high liquid yield and a little amount of gas, char, and wax produced. In this suggested project, we used a variety of HDPE, LDPE, PS, and PVC plastics, as well as ZnO, Bentonite clay, and Kaolin clay in various proportions as catalysts. ZnO is utilized for efficient hydrocarbon chain cracking, however it also lengthens the reaction time. It does not reduce the amount of Cl and S content. While Bentonite and kaolin clay which have high silica to alumina ratio, are employed to decrease the reaction time while minimizing the quantity of sand Cl in the vapor coming from the pyrolysis chamber. As a result of the combined effect of three catalyst, the cumulative reaction time has been reduced, and the yield of liquid fuel with low Cl and S content has increased.

Using a variety of catalyst for different types of plastic feed combination leads in a higher yield of product, a shorter reaction time, and a more cost-effective process.

[3]. Advantages of Pyrolysis:

Pyrolysis is a simple yet cost-effective solution to a variety of key issues, including plastic waste management, rubber waste management, and many more.

It is suitable for the processing of a wide range of feedstocks. The pyrolysis method has the advantages of being able to handle non-degradable waste plastic and rubbery materials. In terms of plastic waste, the pyrolysis reaction can reduce the amount of plastic that ends up in landfills, resulting in less pollution of the land and water.

Pyrolysis is a sustainable process that produces few or no harmful gases and leaves no solid waste. In comparison to other plastic recycling processes such as incineration, pyrolysis leaves no hazardous waste in both the gaseous and solid states.

[4] Define the issue:

Because of the rise in plastic waste, the demand for pyrolysis-based fuel production has surged. When pyrolysis uses a mixture of plastic waste containing HDPE, LDPE, PP, PS, and PVC plastic as a raw material the conversion time is excessively long, and the pyrolysis fuel contains considerable amounts of Cl and S, making it unsuitable for use as a commercial fuel. As a result, the concentration of Cl and S in the fuel was increased in order to decrease the reaction time and raise the calorific value. Zinc Oxide, Bentonite clay, and Kaolin clay are three catalyst that should be employed in varying proportion. Zinc Oxide is used to crack the hydrocarbon chain efficiently, while Bentonite clay and Kaolin clay are used to minimize the reaction time and Cl and S content in the fuel, increasing the calorific value of the fuel at the same time.

II. EQUIPMENT DEVELOPMENT

[1]. Reactor Design:

The reactor is usually a closed cylindrical vessel that can sustain a specified temperature and pressure in order to create the necessary conditions for the reaction to take place. This reactor does not require an impeller because it is primarily utilized for the pyrolysis process. The pyrolysis process necessitates a high temperature (up to 500 °C), which necessitates the use of a heating system. A 2.4 kW electric heater is used as a heating source in this reactor, and it is protected by a insulation cover. This reactor consist five parts such as Shell(core chamber), Head(blind flange), Bottom, Electric Heater, Insulation Cover.

[1.1] Inner Shell Design:

The shell design is the initial phase in the reactor design process. The core chamber is another name for the shell. Only at this point, there is a reaction. Design of this consist three steps such as Enlisting of parameters and calculations, Drawing.

[1.1.1] Require Parameter Enlistment:

This section is concerned with the required pressure, temperature condition, process mode, feed quantity, material phase, and so on, various parameters are fixed depending on these conditions. As a result, it can be used in subsequent phases. Here some fixed parameters,

-Process temperature should be around 450-500 °C
-Process occurs at ambient pressure.
-This shell is normally used for batch mode and the capacity of batch is 1 kg.
-Reaction occurs at high temperature and liquid and vapor is generated inside the chamber therefore corrosion less material should be used as MOC of the reactor.

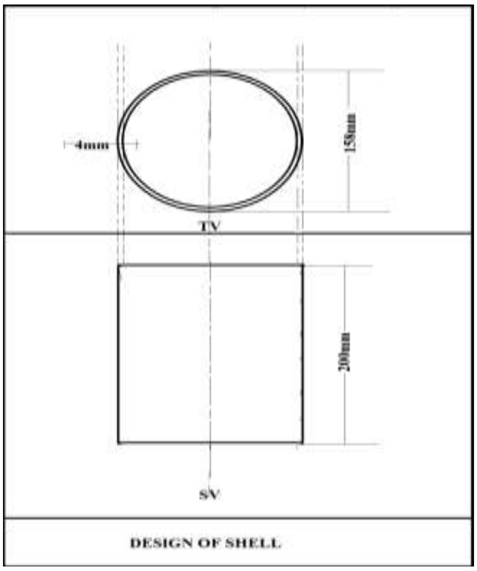
Parameter	Quantity/Material	Reason
Inside Core Temperature	450-500 °C	Required Temperature
Inside Core Pressure	1 atm	Does not required pressure
Feed Amount	1 kg	Batch Capacity
MOC	SS304	Corrosion resistant stainless steel

(Required Parameters)

Based on the theoretical calculations,
-The height of shell(l) should be **200mm**
-The diameter of the shell(D) should be **150mm**
-The thickness of the shell(t) with maximum internal pressure 30 atm and minimum internal pressure of 0.90atm should be **4mm.**

[1.1.2] Drawing of Shell:

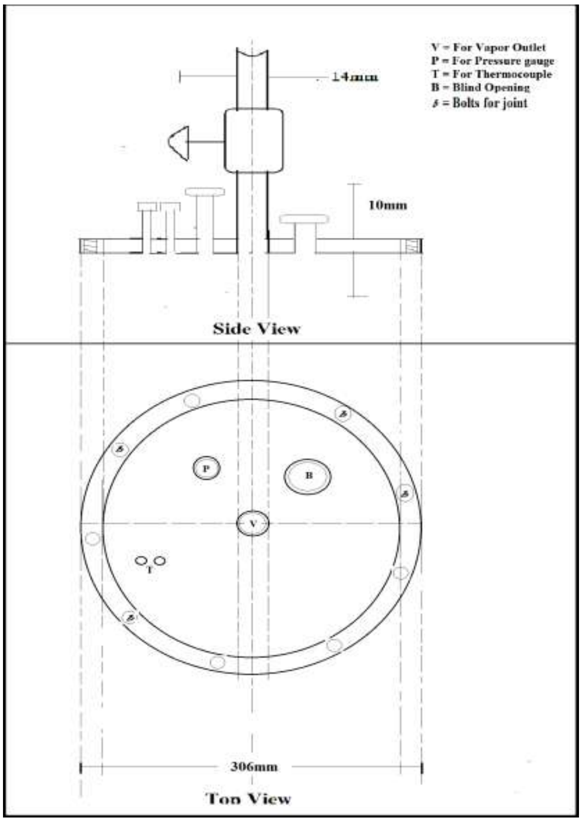
The drawing of shell consists with the all calculated data for the shell and is drawn with proper scale.



(Drawing of Shell)

[1.1.2] Drawing of Shell Head:

The drawing of head contains the side view and top view of the head and the information regarding the opening and its dimensions are also mentioned in the drawing.



(Drawing of Head)

-The bottom section has the similar thickness as the shell, which is **4mm,** and it is linked to the shell via welding operation.

-As per the calculations and the requirement of the process, heater load should be **1.7756 KW**. This is the minimal load required to reach inner shell temperature 500 °C. The heater also adhere to the requirements outlined in the preceding section.

-As per the theoretical calculations the value of heat transfer coefficient should be near **6.67 Wk/m^2**. Therefore estimated radius of the insulation is **16.49mm.**

[2]. Packed Column Design:

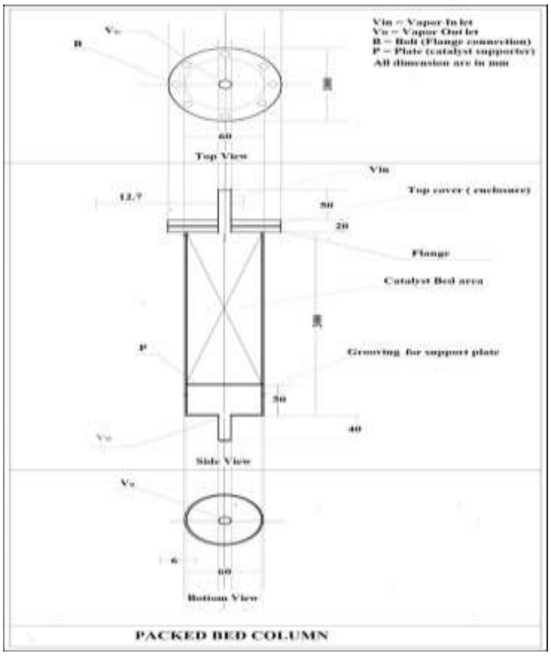
The packed column is used in chemical engineering for a variety of processes such as distillation, absorption, and adsorption. However, in this case, the packed column is mostly used for adsorption. Adsorption occurs at the surface of the packing materials in a packed column(BC & KC).The pyrolysis reactor vapor is sent to the packed column for adsorption. Here, a packed column is employed to enhance the vapor while also removing impurities.

[2.1]. Calculations for Column Design:

PC is primarily utilized to support the packing material, and the diameter and length of PC are estimated based on the catalyst required. The volume value can be calculated from the material quantity. Here, we choose 500 gm of packing material for one batch. With the help of this theoretical calculations, we can define that height of column required is 300mm and Diameter of column required is 6omm. For this application we choose a borosilicate glass as MOC for the column as it have less cost and fulfilled our requirement.

[2.2]. Drawing of Column:

The drawing of packed column contains the top view, side view, and bottom view. The drawing of the PC consist all the dimension of it.



III. MATERIALS AND METHODS

[3.1]. Materials:

Any long hydrocarbon chain organic substance can be utilized as a feed for the pyrolysis reaction, which transforms it into a smaller chain component. Plastic is used as a feed material in this case. As waste, there are normally two types of plastic available;

-Thermoplastic(HDPE, LDPE, PP, PE)

-Thermosetting plastic(Backelite, Epoxy, Polyester etc.)

With the use of a pyrolysis reactor, thermoplastic cracking is more easier than thermosetting plastic.

PVC, HDPE, PP, PS, LDPE are some of the most common plastic using as a feed. For the reaction, Bentonite clay, Kaolin clay(Hydrophilic), and Zinc Oxide are utilized as catalyst. Catalyst demands a high yield with a low operating temperature and a short processing time. Catalyst also lowers the toxicity levels of fuel.

[3.2] Pyrolysis with Catalyst:

Catalytic pyrolysis is more effective than any other type of pyrolysis for plastic cracking. Catalysts are put inside the reactor or in a separate packed column in this kind of pyrolysis. Catalytic pyrolysis is slightly more complex than single-step pyrolysis in terms of design. Reaction of pyrolysis when a catalyst is utilized in that, two mechanisms operate at the same time.

-Thermal Cracking: In this process, the only factor that influences the cracking of any organic material is the amount of heat applied. And for this type of reaction, the temperature differential is the only driving force. Random chain scission, chain end scission, and side group elimination are all possible

-Chemical Cracking: In this case, the catalyst plays a critical role in cracking. In this case, the catalysts accelerate the rate of cracking and produce new structures. Certain catalysts are more effective than others. The waste plastic produces vapor inside the pyrolysis reactor, because the molecular weight of these vapors is higher than that of air, an appropriate method for transporting them out of the reactor is required. There are two distinct techniques for transporting those vapors: the use of inert gas (N_2) and the creation of a vacuum, the inert gas process often yields a higher liquid yields. We wanted to employ an inert gas mechanism instead of a vacuum mechanism because it is more efficient. For vacuum, we need a reactor that survives the vacuum, which raises the capital cost and adds a lot of complexity with the purpose of controlling.

[3.3] Properties of Materials:

Name of Polymer	Density(g/cm^3)	Melting point(°C)
HDPE	0.93-0.97	130.8-140
LDPE	0.91-0.94	115-120
PS	1.04	230
PVC	0.96-1.05	240

We used discarded plastic as our feed source because that was the general goals. As a result, we used waste plastic, which was collected both from industries and from residents.

[3.4] Catalyst:

1. Bentonite Clay:

It's alumina-silicate clay that can be found in abundance in nature. The hydrophilic surface of Bentonite clay has a large number of active sites.

It has a number of unique qualities, including strong water absorption, swelling properties, and high porosity. Various studies have shown that by producing acidity, Bentonite can speed up the pyrolysis process and reduce wax production. It also absorbs pollutants like as sulfur and chlorine. Because of the low Si:Al ratio, it is acidic in nature.

Name	Composition
SiO_2	46%
Al_2O_3	17%
TiO_2	6%
CaO	2.5%

(Composition of Bentonite clay)

2. Kaolin Clay:

It's also alumina-silica based clay, which can be found in abundance in nature. The surface of kaolin clay is hydrophilic, with a large number of active sites. The porosity of kaolin clay is high. With a molecular weight of 258 g/mol, it is an odorless white powder.

Name	Composition
SiO_2	43.12%
Al_2O_3	46.07%
TiO_2	0.74%
CaO	0.03%

(Composition of Kaolin clay)

[3] Zinc Oxide:

ZnO is an odorless yellow solid that is water insoluble. Because of its high absorptive and sticky nature, it is an inorganic chemical with a wide range of application in skin care products. It is primarily manufactured synthetically. ZnO has a molecular weight of 81.4 g/mol. It has a bitter flavor, is odorless, and has an extremely high boiling point. In water, it is insoluble, although it is slightly soluble in dilute acid.

IV. EQUIPMENTS:

[1]. Pyrolysis Reactor:

Batch mode reactors are commonly employed in lab scale experiments or for analysis. It's also employed in low capacity plants since it allows for more flexibility and control. Heat is provided for batch mode reactors by several types of furnaces. Batch mode is typically used for scientific research.

(Fabricated Reactor)

Previous design procedures resulted in the fabricated of the reactor depicted in figure. The MOC of this reactor is SS304 with thickness of 4mm. The reactor is equipped with thermocouple, pressure gauge, valves, and insulation, the heating source is an electric heater. The usage of each of the four openings in this reactor is described above. This reactor makes regulating the heating rate very simple. A pressure gauge is also included in the manufactured reactor, with a range of 1-7 atm (a), because of this cerawool is utilized as an insulting material in the reactor.

(Top view of fabricated reactor)

(Bottom view of fabricated reactor)

[2] Packed Column:

In batch mode, pyrolysis reactors with capacities of 1-2 kg create fewer vapors than those with various contacting patterns. For lab scale technique, glass can be used as the MOC for a packed bed column. Here for this project Bentonite clay and kaolin clay is used in the packed column. And the amount of packed material is determined by the plastic-to-catalyst ratio of each batch. The packed column is connected to the pyrolysis reactor on the one side and the condenser on the other. The active sited of the catalyst eliminate certain vapor pollutants in a packed column.

(Packed bed column)

The packed column depicted in figure created using the design methods discussed above. This PC is made up of three parts: a glass cylinder and two flanged apertures. The PC is constructed of 6mm thick borosilicate glass. The inlet and outlet of PC has 14mm inside diameter.

[3] Condenser:

The vapor enters the condenser after passing through the packed column. According to market demand, the product must be in the liquid form, which necessities vapor condensation.

(Condenser)

We used cold water as the coolant and a double pipe type condenser for this lab scale operation. Cold water creates a liquid phase fuel that can be used for a variety of purposes. Because this condenser produces partial condensation rather than total condensation, a certain proportion of non-condensable gases are produced.

[4] K-Thermocouple and Controller:

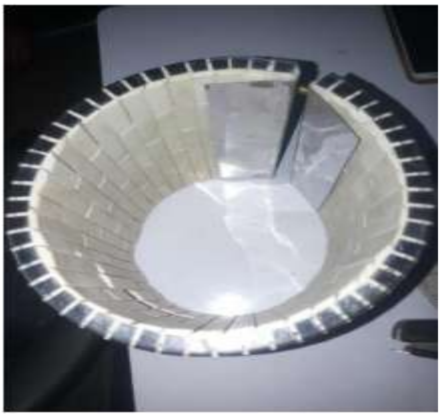
The reaction taking place at 450-500 °C, which necessitates the use of a thermocouple to monitor the process temperature. The length of thermocouple rod is defined here depending on the design data for the reactor.

(Controller, Heater & Thermocouple)

To manage the heating rate and indicate the process temperature for a specific k-type thermocouple, a k-type PID controller is required. Figure depicts the controller that was utilized.

[5] Ceramic Band Heater:

The electric heater is employed as a heating source for the newly manufactured reactor. The heater and required parameters are chosen based on the heater’s design, which was discussed above. The wire used for heater power supply should have qualities that allow it to tolerate high temperature. Fiber glass coated wire is utilized for this purpose.



(Heater)

[6] Experimental Setup:

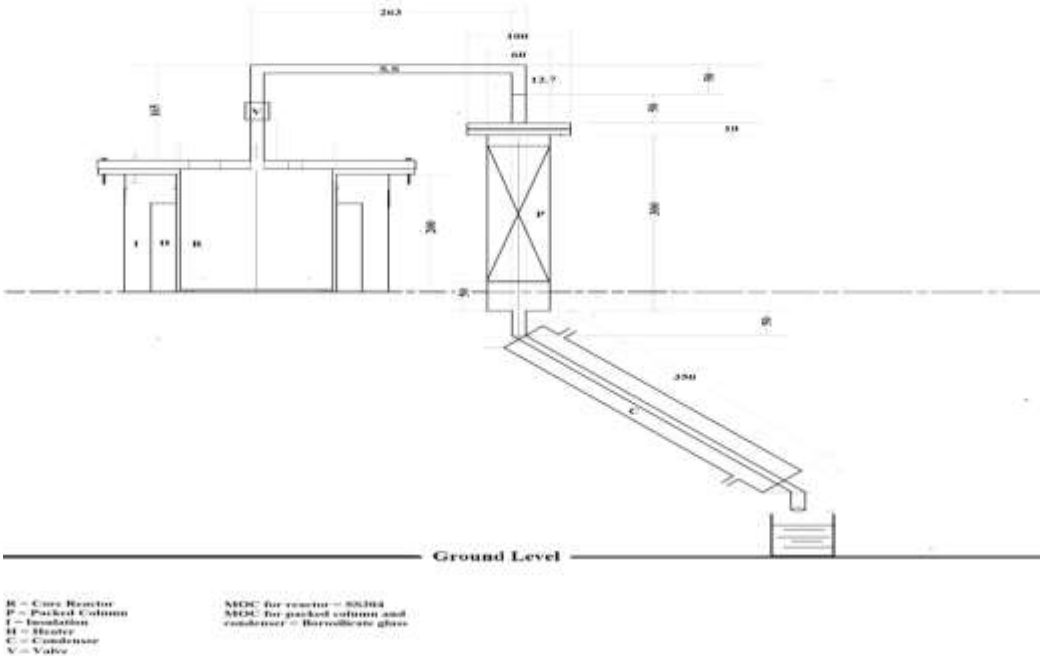
A schematic diagram of the experimental setup is constructed based on the newly fabricated reactor, PC, and heater, as well as the required process. Figure depicts he process's experimental setup.

A pyrolysis reactor, condenser, packed bed column, heater, insulation, pipe, and beaker are among the components of the experimental setup. Pipes connected the reactor, the PC, and the condenser. The dimension of actual components is also included in the schematic. The following are the hypothesized steps for oil synthesis:

Mixtures of polymer used as feed are, HDPE, LDPE, PVC, PS. Then the mixture was pyrolysed in the chamber at high temperature. The cracked vapor obtained from the pyrolysis chamber has potential impurity of the Cl and S. The vapor is then passed through the catalytic packed bed consisting of the pellets of Bentonite and Kaolin clay, which absorbs the impurity present in vapor

After passing trough packed bed column the vapor is then condensed in the condenser using water as a coolant.

The liquid product from the condenser was then collected and transferred to the separating funnel for the separation of short HC, long HC and moisture.



(Experimental Setup for the process)

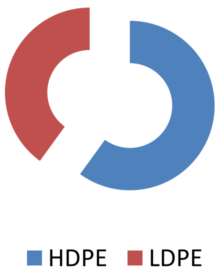
(Actual Experimental Setup)

V. RESULTS & ANALYSIS

[1] Bio-Diesel Synthesis without catalyst:

The feed material used in this preliminary experiment was generally the mixture of the High Density Polyethylene and Low Density Polyethylene granules.

Feed composition by weight basis;
HDPE- 240gm
LDPE- 160gm.



(Feed Composition)

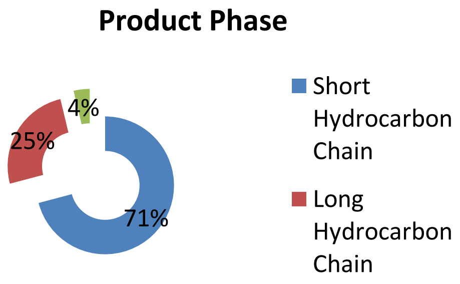
Process Temperature- 380 °C and the rate was around 5-6 °C/min.
Process Time- 1) First Vapor: 4 min 38 sec
2) Last Vapor: 63 min 35 sec

Product Analysis:

From 400gm of polymer mixture, 315 ml of liquid product was obtained through pyrolysis. The distribution of product phases on a volume and weight basis is shown below,

Product phase(Volume Basis)	
Short Hydrocarbon Chain	218 ml
Long Hydrocarbon Chain	78 ml
Moisture	11.56ml

(Product Composition)



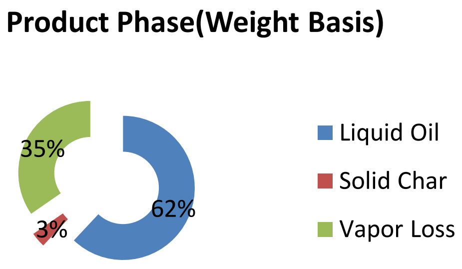
(Product Composition on Volume Basis)

Overall density of the sample was obtained experimentally by measuring mass and the volume of the sample, The density of the sample was obtained **0.80 g/ml.**
-Phase distribution on the weight basis are given below-

Product phase(Weight Basis)	
Liquid Oil	248 gm
Solid Char	13.5 gm
Vapor Loss	138.6 gm

(Product composition on weight)

Here, the amount of the total liquid product obtained was 307.56 ml and the residual char obtained from the reaction chamber was 13.5 gm. The total vapor loss in the process was 143 gm.



(Product composition on weight basis)

Density of the liquid product with short hydrocarbon chain was experimentally measured with the help of **pycnometer.**

-Flash Point Measurement:

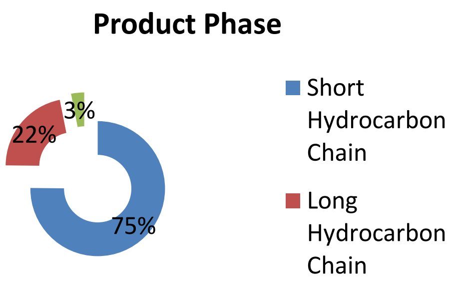
Observation Table	
Temperature(°C)	**Flash Observation**
30	No
32	No
34	No
36	Momentary Flash
38	Yes
40	Yes

The flash point of Bio-Diesel was obtained at **36 °C**
-The calorific value of the Bio-Diesel was measured by Bomb calorimeter, the calorific value gained was around 9200.22 kcal/kg.
-The sulphur content was obtained by the ASTM D 129-00 method, which was found to ne 0.456 (% of wt).

[2] Bio-Diesel synthesis with catalysts:
After adding the catalyst with process the process time reduces with the almost same temperature conditions, catalysts help to reduce the batch time of the process. Process temperature: 380-385 °C.
-Process Time: First Vapor- 3 min 48 sec
Last Vapor- 54 min 12 sec

Product Analysis after Adding Catalyst:
From 400 gm of feed mixture with catalysts, 327 ml of pyrolysis oil was obtained, the distribution of product phases on a volume and weight basis is shown below,

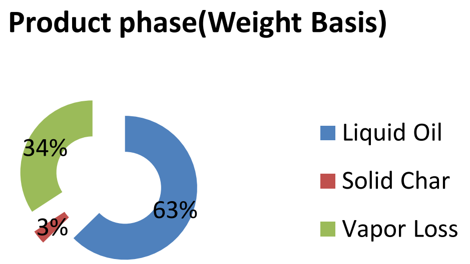
Product Phase(Volume Basis)	
Short Hydrocarbon Chain	232 ml
Long Hydrocarbon Chain	67 ml
Moisture	9.7 ml



(Product Composition)
(Product Composition on Volume Basis)

Overall density of the sample was obtained experimentally by measuring mass and the volume of the sample, The density of the sample was obtained **0.7477g/ml.**
-Phase distribution on the weight basis are given below-

Product phase(Weight Basis)	
Liquid Oil	252 gm
Solid Char	12.6 gm
Vapor Loss	137.6 gm



(Product Composition on Weight Basis)
Density of the liquid product with short hydrocarbon chain was experimentally measured with the help of **pycnometer.**

-Flash Point Measurement:

Observation Table	
Temperature(°C)	**Flash Observation**
30	No
32	No
34	No
35-36	Yes
38	Yes
40	Yes

The flash point of Bio-Diesel was obtained slightly before **36 °C**
-The calorific value of the Bio-Diesel was measured by Bomb calorimeter, the calorific value gained was around 9829.35 kcal/kg.
-The sulphur content was obtained by the ASTM D 129-00 method, which was found to ne 0.258 (% of wt).

VI. CONCLUSION:

Based on the preliminary literature assessment of pyrolysis of plastic, we find that producing fuel through the pyrolysis process is more sustainable than alternative plastic waste management processes such as incineration, land filling, and other recycling processes. Pyrolysis of a combination containing different plastics in varying proportions, such as HDPE and LDPE, employing numerous catalyst such as ZnO, Bentonite clay, and Kaolin clay, results in an increase in liquid fluid and a decrease in wax formation. The acidic nature of the catalyst causes a reduction in Cl and S content in liquid fuel.

Based on the results of the experiment, we can deduce that any pyrolysis reaction must take place in a closed, airtight reaction chamber with the right heating source, as the heating rate has a significant impact on the pyrolysis process. And the yield obtained without catalysts was around 62% and with the catalyst that was 63% with good reduction in moisture content. With the catalyst sulphur content is reduced and as a affect the density of fuel is also decreased, negligible drop in the flash point was observed and considerable increment in the calorific value of the fuel had seen.

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