

PYROLYSIS OF WASTE PLASTICS: A CASE STUDY OF POLYETHYLENE

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ABSTRACT

The global plastic production increased over years due to the vast application of plastics in many sectors. The continuous demand of plastics caused the plastic wastes accumulation in the landfill consume a lot of spaces that contributed to the environmental problem. The rise in plastics demand led to the depletion of petroleum as part of non-renewable fossil fuel, since plastics were the petroleum-based material. Some alternatives that have been developed to manage plastics wastes were recycling and energy recovery method. However, there were some drawbacks of the recycling method as it required high labour cost for the separation process and caused water contamination that reduced the process sustainability. Due to these drawbacks, the researchers have diverted their attentions to the energy recovery method to compensate the high energy demand. Through extensive research and technology development, the plastics waste conversion to energy was developed. As petroleum was the main source of plastic manufacturing, the recovery of plastic to liquid oil through pyrolysis process had a great potential since the oil produced had high calorific value comparable with the commercial fuel. This paper reviewed the pyrolysis process for each type of plastics and the main process parameter that influenced the final end product such as oil, gaseous and char. The key parameters that were reviewed in this paper include temperatures, types of reactors, residence time pressure, catalyst, type of fluidizing gas and its flow rate. In addition, several view point to optimise the liquid oil production for each plastic were also discussed in this paper. Pyrolysis of waste plastic material with emphasis on polyethylene (PE) was aimed at disposing the non-biodegradable materials as a means of pollution control and to recover possible useful chemical compound from it. A cylindrical pyrolysis capsule of 703.80cm³ was constructed with mild steel to pyrolyse 3.15g of PE. The pyrolysis cake obtained at the end of pyrolysis was found to have the following properties: Density – 0.862 kg/cubic metre, has hardness of 50mm, which is suitable for use as filler and polishing materials for civil engineering works.

Keywords: Plastics wastes, pyrolysis, liquid product, fuel energy recovery.

1.1 Introduction

Thermal degradation of waste plastics in an inert atmosphere has been regarded as one of productive methods, because this process can convert waste plastics into hydrocarbons that can be used as either fuels or chemical. From a consumer's point of view as to reusing recycled plastics, it would be favourable if the recycled materials were available easily, safe, sound and cheaply.

Therefore, one can recognize that the conversion process of waste plastics into oil is a better choice, if the conversion process provides the best yield for hydrocarbon oil having a good combustibility and a better calorific value.

However, the oil converted from waste plastics is regarded less attractive than even any petroleum with low quality, because of waxing, offensive odour and degradation processes have been studied by many researchers, in spite of being faced with a number of difficulties of employing catalysts in a large-scale plastic pyrolysis reactor.

Recently, catalytic degradation studies employing various zeolite and non-zeolite type catalysts have been reviewed by Buekens and Huang. It is certainly known that zeolite type catalyst in the degradation process of plastics have shown a positive effect on the quality of products. Among zeolite type catalysts, HZSM-5 reportedly yields more gas fraction and aromatic hydrocarbons in the catalytic degradation of polyethylene. Also, this catalyst increases the ratio of branched hydrocarbon to normal hydrocarbon and decreases the formation of straight chain paraffins and olefins.

Sharrette et al. reported that the gaseous material rich in C₃-C₅ olefins was obtained in high yield from the catalytic degradation of high-density polyethylene (HDPE) over HZSM-5 in a fluidized bed reactor.

Shakkata et al. and Van Grieken et al., using batch type reactors reported that ZSM-5 accelerated the degradation of plastics, especially polyethylene PE, giving a large production of gaseous materials and a low oil yield.

Amorphous silica-alumina also shows a great activity on cracking PE and polypropylene to lighter hydrocarbons. Since amorphous silica-alumina appears to have a higher fraction of total acidity in the strong acid range, it might tend to favour tight binding of carbenium ions to the surface and to carry out continuous cracking.

On the other hand studies employing mesoporous aluminosilicate such as MCH-41 suggest that it increases the product character and also reduce the reaction temperature.

Most literature on thermal and catalytic degradation of plastics is concerned with the product yields or partial semi-quantitative analyses, so that the catalytic efficiency of cracking, aromatization, or isomerisation is not much quantitative. Precise hydrocarbon composition of oil products will make it possible to understand the catalytic efficiency and predict the oil quality. Therefore, we envisioned that it is worthwhile to investigate the efficiency of zeolite

and non-zeolite type catalysts in catalytic degradation of waste HDPE by the hydrocarbon analysis of oil products.

1.2 Aims and Objectives

This work is aimed at the production of oils and gaseous hydrocarbons from the pyrolysis of waste plastics, and also to compare the amount of the gasoline range hydrocarbon gotten from pyrolysis to that of the one gotten from catalyzed process. This work will also provide us with the opportunity to know the amount of the solid product that can be gotten from the thermal degradation of the plastic waste.

1.3 Importance of the Work

The successful transformation of the plastic wastes into valuable fuel and other petrochemical precursors, will go a long way in reducing, if not complete elimination of the unsightly looks given to our streets and cities by pure water litters and the associated health hazards. Consequently, a huge amount of money which would have been used for waste management can be conserved by the government.

1.4 Purpose of the Work

The availability of the cheap feed stock materials (plastic wastes), and the depleting oil well calls for an alternative means for the production of oils and gaseous hydrocarbons of economic importance. Finally, the money that would have been used in the disposal of the wastes could be directed to other meaningful projects by the government.

2. LITERATURE REVIEW

This section puts into perspective works and related topics that were previously carried out in the past with regards to the production of oils and gaseous hydrocarbons from waste plastics. This we shall do considering the following sub-topics:

- 2.1 Plastics recycling
- 2.2 Effects of crystallinity on the melting temperature of polymers
- 2.3 Problems with recycling polymers
- 2.4 Limitation of past work
- 2.5 Environmental and social impact
- 2.6 Technology description of waste plastics recycle to produce liquid fuels.

2.1 Plastics Recycling

At the moment much of plastic materials used in short term packaging applications ends up taking up valuable landfill space. Both synthetic and naturally occurring polymers will generally last in these sites for long period of time because they don't get the necessary exposure to ultra-violet (UV) and microbes to degrade. Yet they are taking up space and none of the energy put into making them is being reclaimed.

Reclaiming the energy stored in the polymers or plastics can be done through incineration, but this can cause environmental damage by release of toxic gases into the atmosphere. Recycling is a viable alternative in getting back some of this energy in the case of some polymers.

Raw materials for plastics are obtained from petroleum, a limited non-renewable resource. Using recycled plastic to replace the petroleum in some cases will help make this resource last longer.

As petroleum prices increase, it is becoming more financially viable to recycle polymers rather than produce them from raw materials. The most commonly recycled materials are PET (used in fizzy drinks bottles) and high-density polyethylene (HDPE) used in milk bottles and washing up liquid bottles. This is because the original properties of the materials are sufficient to be used for this application without large quantities of additives, which are difficult to remove on recycling.

2.2 Effects of Crystallinity on the Melting Temperature of Polymers

Polymers like polyethylene can vary in their degree of crystallinity from between 20% and 80%. The more crystalline the molecules, the more energy are needed to cause the molecules to separate and melt. Amorphous polymers, on the other hand, will have lower melting points. The degree of crystallinity in the original component needs to be carefully controlled. Crystallinity is impeded by lack of order in the polymer chains. The presence of side chains to the polymer and tactic, tacticity are factors, which will impede crystallization. Crystallinity is also affected by the way the material is processed.

2.3 Problems with Recycling Polymers

- Cost of collection and separation of materials.
- Unavailability of stream of clean homogenous material
- Unavailability of suitable market for products
- Lack of public pressure
- Because current manufacturing plants are set up to produce plastics from scratch, they are inefficient when used to recycle plastics.
- Expensive to collect and sort
- Removal of additives like dyes and fillers, in cases where there are a lot of these present: the energy required to purify these plastics is greater than that required to produce the plastics from crude oil. In this case, it is preferable to recover the energy in these plastics by using them as fuel to provide power, however, this can lead to excess toxic gas emission. Additives are less widely used in beverage containers and plastic bags, which makes these more easily recyclable.
- Thermosets are difficult to recycle because of the chemical crosslinks formed in them (e.g. sulphur linkages formed by vulcanization in elastomers like polyisopoprene). Chemical reactions have occurred resulting in a new material different from that involved in the feed process. They can however be crushed and used as insulation.

- The clean plastic flakes are melted together, extruded through small holes, and chopped into pellets.
- The bags of recycled plastic pellets are taken to factories where they are melted and made into new products.
- In the case of soft drink bottles the recycled pellets are combined with virgin material fresh from petroleum. These are then melted and moulded into performs.
- The bottles are blown into another mould to form the full size bottle this is often done at the bottling plant where they are filled and sealed.
- Once consumed they are delivered back to the recycling plant after household recycling.

2.4 Limitations of Past Work

Polymer waste can be regarded as a potential source of chemicals and energy. Methods for recycling approaches are being investigated. Chemical recycling, i.e. conversion of waste polymers into feedstock or fuels, has been recognized as an ideal approach and could significantly reduce the net cost of disposal. Several reports described the conversion of polymer waste by non-catalytic thermal degradation. Other reports address the role of acid catalysts in the catalytic degradation of polymers. Although the result of these studies has been the improved of the catalyst, there is still a need to develop kinetic models to describe the experimental results and to facilitate the further development of a process to industrial scale. Papers concerning kinetic modelling of catalytic process for polymer degradation have great limitations, which are shared with the study of other complex reaction schemes such as catalytic cracking and reforming. The kinetic models proposed in the literature can be grouped into:

- i. Kinetic models based on thermal analysis of the weight loss curves,
- ii. Kinetic models based on reaction mechanism and elementary steps and
- iii. Models with lumping schemes.

In the case of thermal analysis, the shortcoming is in general excessive simplification either in the assumed kinetic scheme or in the handling of experimental data. Kinetic models with individual reaction steps lead to a great number of kinetic parameters, whose application for the simulation of industrial reactors is difficult. In the lumped kinetic models, the large numbers of individual constituents in a complex feedstock are grouped into the broad but measurable categories of compound classes, with simplified reaction networks between the lumps. These lumped models may be useful for the needs of reactor design, but there still exist some inherent limitations. Firstly, the approach often fails to extrapolate to different feedstocks because of composition differences within the same defined lumps. Secondly, coarsely lumped models cannot be utilized to interpret the effects of catalyst properties on the phenomenological aspects of catalytic properties because fundamental catalytic reaction mechanisms are not incorporated into the kinetic scheme. Thirdly, insufficient detail exists in the lumped models to predict subtle changes in product properties.

Mechanistic considerations of catalytic degradation of hydrocarbons have largely been focused on small molecules (less than C₁₆) rather than on macromolecules such as polymers. The literature available involving the mechanistic considerations for catalytic polymer degradation is rather scarce. For example, Ishihara and co-workers gave only a qualitative mechanistic description by using intramolecular rearrangement of chain end secondary carbenium ions for the catalytic decomposition of polymers, but these results were not used to provide a kinetic model. The objective of this work is use a kinetic/mechanistic model to study the production rates and product selectivity on the catalytic reactions of different polymers with various catalysts, and provide some basis to enhance the potential benefit of catalytic polymer recycling.

The oil converted from waste plastics is regarded less attractive than even any petroleum with low quality, because of waxing, offensive odour and deterioration of colour. To overcome such shortcomings, catalytic degradation processes have been studied by many researchers, in spite of being faced with a number of difficulties of employing catalysts in a large-scale plastic pyrolysis reactor.

2.5 Environmental and Social Impact

Demands for plastic goods have been increasing very fast worldwide along with the rapid growth of its economy. It is estimated that the annual plastic consumption will reach tens of millions ton. The government has to spend millions of dollars on disposal of the plastic wastes every year – collection, transportation and piling in suburban areas, costing about \$2.5 per ton. These solid wastes have caused serious pollution and increasingly occupied more and more land that is already short for the country's large population.

On the other hand, energy shortage is also more and more serious in Nigeria, especially in rural areas. The problem is challenging every decision maker at all levels. Energy shortage is threatening the substance living of whole rural population, and is increasingly worsening the ecological conditions there that have been seriously damaged due to the same reason, putting the country in a vicious cycle. There inhabited by almost one hundred and fifty million people, trees are cut and grasses are rooted out and collected as household or domestic fuel and for other basic needs.

Rural surplus labours are growing dramatically. Hardly being absorbed locally, several millions of people have migrated from rural areas into cities but still having to face the similar unemployment problem.

Development and promotion of technology of conversing plastic wastes into liquid fuels will contribute to resolving all these problems. At present Nigeria is the leading producer of plastics in West Africa. If 35% can be recycled, that means 1,260,000 tons. Then at least 900 factories, each with a capacity of 1000 tons, need to be set up that will produce 2.65 billion Yuan. These factories would add 265 million Yuan to government revenue in the form of tax while creating millions of dollars of profit for themselves.

Average of 40 workers including engineers and technical assistants would be needed in each of the factories to manage the production. Plus those who will be accordingly employed by plastic recycling station, about ten thousand jobs could be created. The ideal place to set up factories like this are suburban and rural areas where most of the recycling agents are located and plastic wastes are piled and where gasoline and diesel fuels are in short supplies and thus the products can be consumed locally without necessity of being transported out. This is where Likun Chemical Plant is located, and thus does not have to worry about transportation cost.

Therefore, promotion of this technology is not only profitable for the enterprise itself, but also has the following impacts: increasing local people's income, creating more jobs, alleviating the short supplies of energy and reducing the problem of pollution in addition to generating revenues for government.

2.6 Technological Description of Waste plastics Recycle to Produce Liquid Fuels

2.6.1 Raw Materials

The raw materials used to produce liquid fuels include polyethylene, polypropylene and polystyrene from plastic wastes such as plastic film for farm use, woven bag for cement, urea, foam PS lunch boxes and packing materials, and food package bag, etc.

2.6.2 Conversion Process

Plastic wastes are cleaned from impurities – they are washed and dried, and then fed into a cracking vessel under normal pressure. Here cracking and catalysis take place on special catalysts to generate hydrocarbon oil, which is then fractionated to separate gasoline and diesel respectively. Below is the process flow chart:

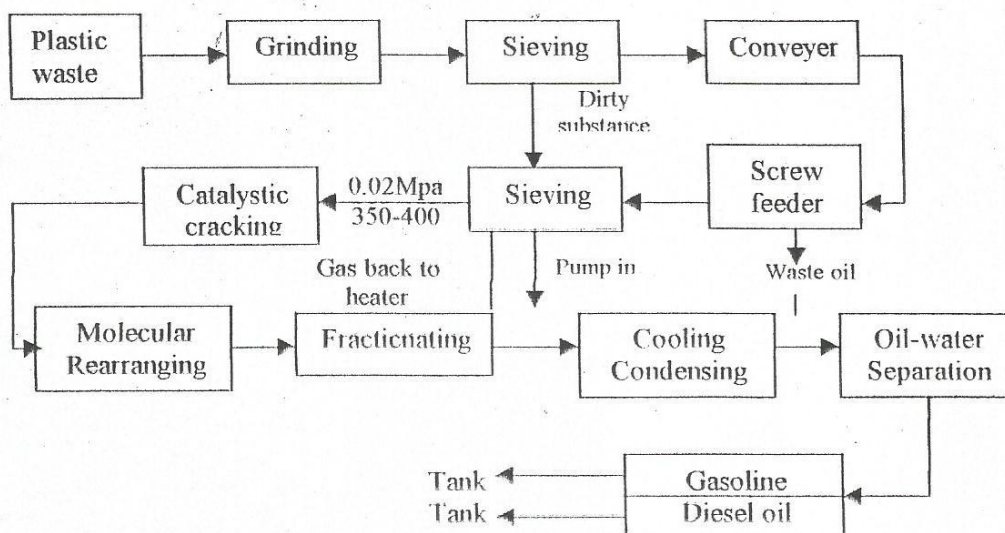


Figure 2.1: Catalytic cracking of waste plastics

2.6.3 Technical Features

Under atmospheric pressure and temperature about 400⁰C, the operation is continuous – from feeding of raw materials, producing gasoline and diesel to discharging of gas and solid residues. With an automated blending device at the bottom of the reaction container, coking is effectively prevented. The whole process it is stable, safe and reliable. DL catalysts are specially developed with high reactivity, responsive to specific products. Effluent vapour from reaction is directly fed to fractionators for obtaining liquid fuels (gasoline and diesel). Solid residue is recycled as production fuel. A little non-condensable hydrocarbon gas is burnt out, and therefore, no pollution is created.

The processing is adoptable to different types of raw materials such as plastic waste, waste solvent oil, waste diesel fuel, waste lubricating oil, vegetable oil bottom, etc.

2.6.4 Product Quality

The quality of the gasoline has been tested with the following testing results:

Table 2.1: Quality of various gasoline products

Item	GB 484-93 Specification	Test data
Octane number (research method) No. $\frac{3}{4}$	93	95.5
Distillation range:		
IBP, OC not $\frac{3}{4}$		46
10% distill off, OC not $\frac{3}{4}$	70	62
50% distill off, OC not $\frac{3}{4}$	120	102
90% distill off, OC not $\frac{3}{4}$	190	149
Dry point, OC not $\frac{3}{4}$	205	185
	98	97
Saturated vapour pressure, KPA not $\frac{3}{4}$	74	52
Actual gum, mg/100ml not $\frac{3}{4}$	5	3.6
Induction period, min not $\frac{3}{4}$	480	925
Sulfur content, not $\frac{3}{4}$	0.15	0.015
Copper corrosion (50 OC, 3h)	Pass	Pass
Water soluble acid or base	None	None
Acidity, mg KOH/100ml not $\frac{3}{4}$	3	0.112
Mechanical impurities and moisture	None	None
Density (20 OC) g/cc	Not specified	0.7278
Doctor's test	Pass	Pass

2.6.5 Economic Analysis

The capital investment for a conversion line with a capacity of producing 1000 tons of gasoline/diesel annually totals 1,300,000 Yuan or \$162,500 (exchange rate: \$100=800 Yuan) in China. The market price of liquid fuels in China is 1.85 Yuan per litre for gasoline, and 1.70 Yuan per litre for diesel fuel (price of 1994). Converted to weight basis, the average price is 2,400 Yuan a ton.

Cost wise, sales price of plastic wastes listed by recycling agent is 700 Yuan/ton, and utility cost for production include bituminous coal at 220 Yuan/ton, and electricity at 0.5 Yuan/kwh, plus average wage per labour of 600 Yuuan/month while monthly output of liquid fuels produced by Likun Plant is 100 ton/month. Below are costs and benefit estimations of producing one ton of liquid fuel from waste plastics.

Table 2.2: Economic analysis of gasoline production cracking waste plastics

Items	Unit Price (Yuan)	Amount	Subtotal (Yuan)
Raw material: Plastic waste	700/ton	1.43 tons	1001.00
Utilities: Electricity		240 Kwh	120.000
Coal	0.5/kwh	0.5 ton	110.00
Water	220/ton	Little	Negligible
Catalysts and chemicals			50.00
Depreciation	8% of capital		62.50
Overhead	3% of sales	2400 Yuan	72.00
Insurance	1.5% of sales	2400 Yuan	36.00
Marketing	5% of sales	2400 Yuan	120.00
Storage facilities	0.5% of sales	2400 Yuan	12.0
Salary	600 Yuan/person	100 Ton/month	180.00
Tax	6% of sales	2400 Yuan	144.00
Total cost (without considering salaries)			1907.50

3. PRINCIPLES OF PYROLYSIS

Pyrolysis is the thermal degradation of waste in the absence of air to produce carbon, pyrolysis oil (which also contains the gasoline range hydrocarbon, lumped into one) and synthetic gas.

Pyrolysis recycling chemically decomposes organic materials by heat in the absence of oxygen. Pyrolysis typically occurs under pressure and at operating temperatures above 430oC (800oF). In practice, it is not possible to achieve a completely oxygen-free atmosphere.

Because some oxygen is present in any pyrolysis system, a small amount of oxidation occurs. If volatile or semivolatile materials are present in the waste, thermal adsorption will also occur.

Organic materials are transformed into gases, small quantities of liquid, and a solid residue containing carbon and ash. The off-gases may also be treated in a secondary thermal oxidation unit. Particulate removal equipment is also required. Several types of pyrolysis units are available, including the rotary kiln, rotary hearten furnace, or fluidized bed furnace. These units are similar to incinerators except that they operate at lower temperatures and with less air supply.

Both pyrolysis recycling and the gasification recycling process turn wastes into energy rich fuels by heating the waste under controlled conditions. In contrast to incineration, which fully converts the input waste into energy and ash, these processes deliberately limit the conversion so that combustion does not take place directly. Instead, they convert the waste into valuable intermediates that can be further processed for materials recycling or energy recovery i.e. synthesis gas, oils and char.

3.1 Equipments Design

The equipment design involves the design of the reactor capsule and the bending of glass tubes to suit the requirements.

3.2 Date on the Reactor Capsule

Material of construction: mild steel

Shape: cylindrical

Height: 14.0cm

Diameter: 8.0cm

Thickness: 6.0mm

Volume: $\pi r^2 h = 703,80\text{cm}^3$

3.3 Materials of Construction and Safety

The reactor is a model design with basic configuration and features required. It is a cylindrical mild steel vessel with spherical ends. The external surface has a smooth finishing. The reactor was a low pressure system; however, the thickness was adequate enough to withstand my unexpected alteration of the reaction processes.

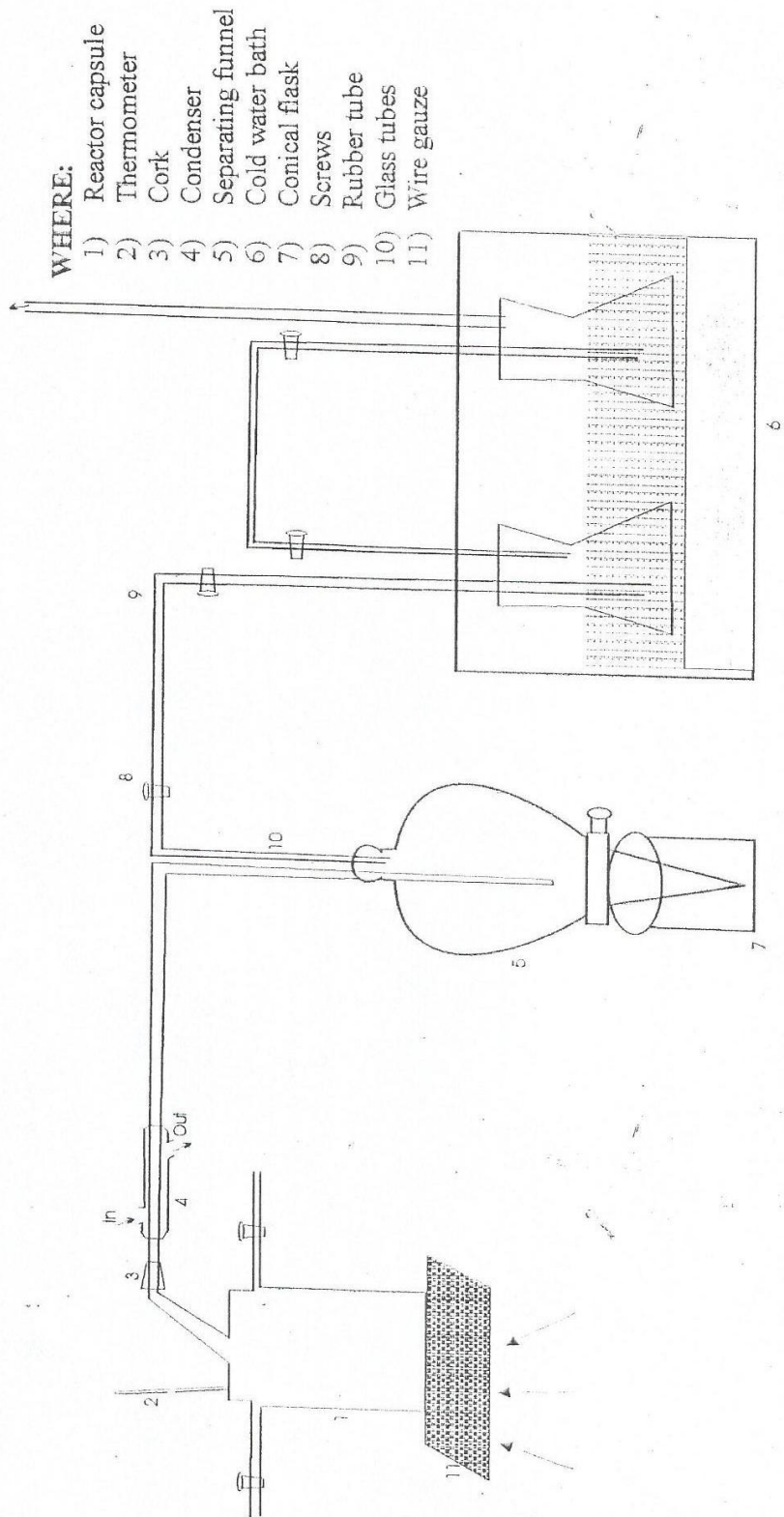
A pipe connection whereby, a 12mm diameter pipe is obliquely produced from the reactor for the removal of vapour and gaseous products. Provision for insertion of a thermometer is also made to record the process temperature. The cap and the main capsule are tightened during use with the aid of four (4) reverted butterfly bolts. There is allowance in the bolt threading design

for ease removal. A high temperature gasket is placed in-between the cap and the capsule to prevent gases leakage.

Despite the thickness, mild steel is a good conductor of thermal energy and will not take too much time to heat up to the required temperature and fuel wastage.

3.4 Apparatus

1. The reactor capsule with 4 butterfly bolts
2. Thermometer (0oC – 360⁰C)
3. Gas cooker as heat source
4. Condenser
5. Gas tubes (diameters = 12mm, 20mm)
6. Rubber tubes (diameter – 12mm, 20mm, 6mm)
7. Corks (wooden and rubber), of various sizes – 10
8. Separating funnel – 500ml
9. Conical flask – 250ml (3)
10. Rubber tubes screws (10)
11. Water bath
12. Retort stand
13. Measuring flask – 250ml
14. Wire gauze piece
15. Gasket piece
16. Beaker 250ml (2)
17. Hammer and a flat metal plate
18. Neutral Vaseline
19. Knife
20. A pair of scissors
21. Screw driver (flat)
22. Razor blade
23. Sulphuric acid to clean the condenser internal rusts



EQUIPMENT LAYOUT

3.5 Experiment and Detail

3.5.1 Size Reduction

Sizes of plastic wastes were reduced to an affordable size averaging 1cm by 1cm to increase the surface area. This was carried out with the aid of:

1. Flat metal plate
2. Hammer
3. Knife

The reduced plastics were washed with tap waters and left to dry and packaged ready for use.

3.5.2 Feed

The feed is the waste plastic cracked, washed and dried. We have feed 1 and feed 2. Feed 1 is polyethylene plastic of various type and feed 2 which is PVC.

3.5.3 Experimental Procedure

The cracked and washed plastic wastes (feed) were loaded to the reactor capsule to fill. Weighed and the apparatus were fitted as shown in the equipment layout.

4. EXPERIMENTAL RESULTS AND ANALYSIS

Solid cake was collected and weighed. It was approximately 164g for the PE runs respectively.

Result

Table 4.1: The Experimental Result is Given Below

Feed	Mass of Feed in Gram (g)	Mass of Cake Gram	Final Temperature °C
1	3.15	164	175

Initial temperature 31⁰C

Density of cake 0.862kg/m³

Hardness of cake 50mm

Diameter of cake 70mm

Volume of cake 192447.5mm³

Stress = 50 x 0.022 x 1000 = N

Stress at rupture = $\frac{1100N}{Area} = \frac{1000}{3848.9.5}$

= 0.285N/m²

Analysis

Due to the aforementioned problem of power and water supply, the practical runs were unduly prolonged. The analysis was based on qualitative aspects of analysis. The qualitative aspect of the analysis was to determine the types of functional groups and the specific compounds present.

Observation

After a while, the separating funnel was filled with dew and there was some kind of burning smell but some hydrocarbon gases escaped during the experiment, and liquid was not obtained due to the escape of the gases rise which was not condensable at room temperature

5.1 Results and Discussion

The process reduced the plastic waste to an appreciable percent with char remnant in the reactor capsule. It was obtained in the case that is more than 40% by volume of feed were reduced. However, if the reaction variable especially the temperature is increased could increase the volume reduction better than what was obtained. This invariably, provides a useful technique for the controlling of plastic wastes material which are non-biodegradable.

On the other hand, the solid cake needs to be heated and purified to its respective compound and then proper identification made. However, due to the aforementioned problem encountered in the course of the work, this aspect of the work could not be concluded. But it is hoped that, solid cake with aromatic smell contains useful compounds that can be economically similar.

5.2 Recommendations and Conclusion

Research project of this type are quite tasking, time-consuming and involve finance, and requires highly equipped laboratory for the analysis.

- Therefore, I recommend that research project of this type should be given to a team of project students.
- The authorities concerned (government and management of school) should properly equip the laboratories to enable such works to be carried out safely and effectively.
- Authorities concerned should assist research project students financially.

However, from the figures and literatures, pyrolysis, is a better technique for treating plastic wastes. More attention should be drawn especially now that plastic waste is becoming a major problem of land and air pollution.

Plastic waste treatment is a geared attention by all environmentalists including the chemical engineer. Research on this area ought to be a major concern. Pyrolytic treatment of plastic waste should be encouraged since useful chemical compounds could be derived from it, if proper design(s) of recovery is/are included. The formation of such compound is due to the secondary transformation of compounds formed in the initial heat treatment.

Pyrolysis is also preferred to some existing and commonly used techniques of waste disposal since it drastically minimizes the formation of hazardous oxides, for the fact that the oxygen required for such formation is limited.

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