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Conversion of plastic into Bio-oil by pyrolysis (catalyst method)

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ABSTRACT:

Catalytic pyrolysis of waste plastics using low cost binder-free pelletized bentonite clay has been investigated to yield pyrolysis oils as drop-in replacements for commercial liquid fuels such as diesel and gasohol 91. Pyrolysis of four waste plastics, polystyrene, polypropylene, low density polyethylene and high-density polyethylene, was achieved at a bench scale (1 kg per batch) to produce useful fuel products. Importantly, the addition of binder-free bentonite clay pellets successfully yielded liquid based fuels with increased calorific values and lower viscosity for all plastic wastes. This larger scale pyrolysis study demonstrated that use of a catalyst in powder form can lead to significant pressure drops in the catalyst column, thus slowing the process (more than 1 hour). Importantly, the use of catalyst pellets eliminated the pressure drop and reduced pyrolysis processing time to only 10 minutes for 1 kg of plastic waste.

The pyrolysis oil composition from polystyrene consists of 95% aromatic hydrocarbons, while in contrast, those from polypropylene, low density polyethylene and high density polyethylene, were dominated by aliphatic hydrocarbons, as confirmed by GC-MS. FTIR analysis demonstrated that low density polyethylene and high density polyethylene oils had functional groups that were consistent with those of commercial diesel (96% similarity match). In contrast, pyrolysis-oils from polystyrene demonstrated chemical and physical properties similar to those of gasohol 91. In both cases no wax formation was observed when using the bentonite clay pellets as a catalyst in the pyrolysis process, which was attributed to the high acidity of the bentonite catalyst (low SiO_2:Al_2O_3 ratio), thus making it more active in cracking waxes compared to the less acidic heterogeneous catalysts reported in the literature. Pyrolysis-oil from the catalytic treatment of polystyrene resulted in greater engine power, comparable engine temperature, and lower carbon monoxide (CO) and carbon dioxide (CO_2) emissions, as compared to those of uncatalyzed oils and commercial fuel in a gasoline engine. Pyrolysis-oils from all other polymers demonstrated comparable performance to diesel in engine power tests. The application of inexpensive and widely available bentonite clay in pyrolysis could significantly aid in repurposing plastic wastes.

Key words: catalytic conversion, catalyst, waste plastic, bentonite clay.

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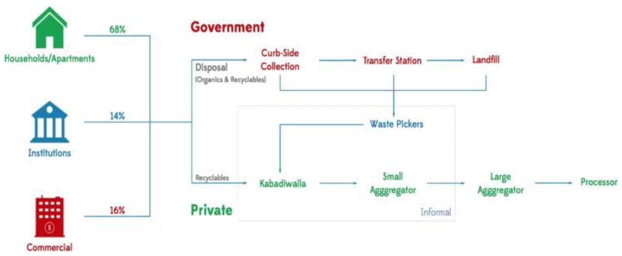
INTRODUCTION:

Our next idea is in the Waste Management space, Chennai, generates 1.8M tons of waste every year. That is 4,842 tons of waste per day! And the more shocking part is that 91% of the collected waste is dumped in open **landfills Waste** consists of Organics, Recyclables and Discards. Waste collected from households (68%), institution (14%) an commercial establishments (16%) goes from the curb side collection to the transfer stations and ultimately to the landfills. Our current waste management economics are not dependent on segregation but rather a truck tipping model because of which segregation is not enforced at the waste generator level.

90% of the recyclables are generated from households and shops. While this is a huge number in terms of total contribution, if we isolate each household or a shop, they generate very small amount of waste. So processors who work on these recyclables rely on medium or bulk aggregators to integrate it into their value chain and meet their demands.

If we look at this problem at an Urban India level, the results are even more,

Segregation of waste in INDIA



So that the waste is being segregated in this manner in that the types of waste are being collected as data in which in that the which we have to note is the amount of plastic being segregated.

In which we could able to see that plastic plays the second major role part of waste that is generated and also segregated too…. In that if we reduce that part the recycling process can be done easily and the landfill areas also get reduce about (25%-40%).

Apart from this, the major part of Tamil Nadu govt approved landfill areas of waste data shows that most of the part are recyclable waste in that also the major part is plastic.

Site	Biodegradable	Recyclabes	Inert	Domestic Hazardous
Kodungaiyur	52.4%	30.5%	16.95%	0.195%
Perungudi	52.7%	31.5%	15.6%	0.17%

Land fill area of Perungudi

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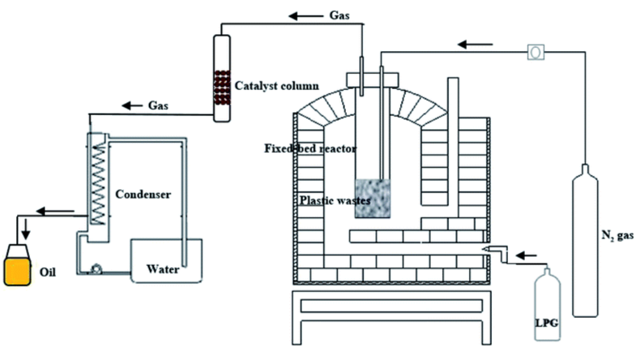
Land fill area of Kodungaiyur

OBJECTIVE:

1. To reduce landfill areas used for plastics.
2. To reduce the fuel used in conventional pyrolysis method.
3. To reduce the production and usage of plastic.
4. To create another way of source to generate fuel for future generation.
5. To make usage of fuel even more "Economical"

NECESSITY:

1. To reduce Land pollution and Air pollution done by using plastics.
2. To overcome these methods like Land filling, incineration and recycling, are the three available methods of utilizing plastic waste



Schematic diagram of plastic pyrolysis setup.

Methodology flow chart:

PLASTIC

↓

REACTOR

↓

BENTONITE (CATALYST)

↓

CONDENSER

↓

BIO-OIL

↓

COMBUSTIBLE GASES

TYPES PLASTICS:

Plastic Type	General Properties	Common Household Uses
1 PETE Polyethylene Terepthalate	Good gas & moisture barrier properties High heat resistance Clear Hard Tough Microwave transparency Solvent resistant	Mineral Water, fizzy drink and beer bottles Pre-prepared food trays and roasting bags Boil in the bag food pouches Soft drink and water bottles Fibre for clothing and carpets Strapping Some shampoo and mouthwash bottles
2 HDPE High Density Polyethylene	Excellent moisture barrier properties Excellent chemical resistance Hard to semi-flexible and strong Soft waxy surface Permeable to gas HDPE films crinkle to the touch Pigmented bottles stress resistant	Detergent, bleach and fabric conditioner bottles Snack food boxes and cereal box liners Milk and non-carbonated drinks bottles Toys, buckets, rigid pipes, crates, plant pots Plastic wood, garden furniture Wheeled refuse bins, compost containers
3 V Polyvinyl Chloride	Excellent transparency Hard, rigid (flexible when plasticised) Good chemical resistance Long term stability Good weathering ability Stable electrical properties Low gas permeability	Credit cards Carpet backing and other floor covering Window and door frames, guttering Pipes and fittings, wire and cable sheathing Synthetic leather products
4 LDPE Low Density Polyethylene	Tough and flexible Waxy surface Soft – scratches easily Good transparency Low melting point Stable electrical properties Good moisture barrier properties	Films, fertiliser bags, refuse sacks Packaging films, bubble wrap Flexible bottles Irrigation pipes Thick shopping bags (clothes and produce) Wire and cable applications Some bottle tops
5 PP Polypropylene	Excellent chemical resistance High melting point Hard, but flexible Waxy surface Translucent Strong	Most bottle tops Ketchup and syrup bottles Yoghurt and some margarine containers Potato crisp bags, biscuit wrappers Crates, plant pots, drinking straws Hinged lunch boxes, refrigerated containers Fabric/ carpet fibres, heavy duty bags/tarpaulins
6 PS Polystyrene	Clear to opaque Glassy surface Rigid or foamed Hard Brittle High clarity Affected by fats and solvents	Yoghurt containers, egg boxes Fast food trays Video cases Vending cups and disposable cutlery Seed trays Coat hangers Low cost brittle toys
7 OTHER	There are other polymers that have a wide range of uses, particularly in engineering sectors. They are identified with the number 7 and OTHER (or a triangle with numbers from 7 to 19).	Nylon (PA) Acrylonitrile butadiene styrene (ABS) Polycarbonate (PC) Layered or multi-material mixed polymers

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DATA COLLECTION AND ANALYSIS:

REACTOR:

Pyro = heat. Lysis = break down.

Plastic Pyrolysis is a chemical reaction. This reaction involves the molecular breakdown of larger molecules into smaller molecules in the presence of heat. Pyrolysis is also known as thermal cracking, cracking, thermolysis, depolymerization, etc. At any given temperature the molecule is in vibrating stage. This is called molecular vibration. The frequency at which molecules vibrates is directly proportional to the temperature of molecules. During pyrolysis, the object's molecules are subjected to very high temperatures leading to very high molecular vibrations. At these high molecular vibrations, every molecule in the object is stretched and shaken to such an extent that molecules start breaking down into smaller molecules. This is pyrolysis.

For Example:

The simplest example of pyrolysis is food cooking. When you cook food the temperature of food increases leading to higher molecular vibrations and breakdown of larger complex molecules into smaller and simple molecules. After cooking larger food molecules are pyrolyzed into smaller in simpler molecules which are easy to digest.

In which for this process we use the steel container as the reactor, so which is done as a "prototype" for the experiment.

BIO-OIL:

There was no output at low temperature range and the process was carried out between the temperature ranges of 330∘ C and 490∘ C in the reactor for about two hours and forty minutes. The vapor products of pyrolysis were carried out through two condensers. The condensers were cooled by water and the condensed "Bio-oil" was collected into to the collectors. The non-condensed gas was flared to the atmosphere and the char was collected from the reactor after completion of pyrolysis cycle.

TABLE 1: Testing methods for fuel properties measurement

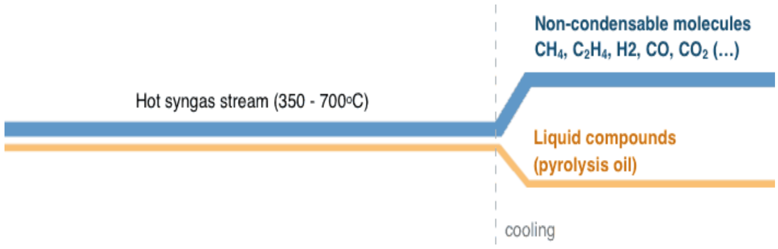
BENTONITE (CATALYST):

While in this catalyst method we use the chemical composition of bentonite clay from product specification from Vidhaya enterprises, SIDCO industrial Estate., Ambattur, was found to be SiO_2 46 wt%, Al_2O_3 17 wt%, Fe_2O_3 6 wt%, Na_2O 1.5 wt%, CaO [illegible] wt% and TiO_2 0.2 wt%. Bentonite clays have a similar composition to SiO_2 and Al_2O catalyst previously investigated as pyrolysis catalysts. Bentonite also had some compositional similarities to kaoline and red mud. The chemical compositions of kaoline were Al_2O_3 46.07 wt%, SiO_2 43.12 wt%, TiO_2 0.74 wt%, CaO 0.03 wt% and others while red mud had Fe_2O_3 36.5 wt%, Al_2O_3 23.8 wt%, TiO_2 13.5 wt%, SiO_2 8.5 wt%, CaO 5.3 wt%, Na_2O 1.8 wt% and others. Low ratio of SiO_2/Al_2O_3 indicated the acidity of the catalyst, thus highlighting the possible acidic nature of the bentonite catalyst. So, the bentonite catalyst (low SiO_2:Al_2O_3 ratio) in that the ratio of (1:4) is mixed or added with the reactor, the proportion is if we took 1kg of plastic waste the catalyst of 4kg should be added, this is the ratio we took in this analysis.

Calcium bentonite is proved to be the efficient catalyst for pyrolysis of different plastics by improving the quality and quantity of oil and reaction time. The optimum condition for the higher plastics oil yield for all the plastic types in the experiments was at 500 °C with 1:4 catalysts to plastic ratio.

Bentonite

COMBUSTABLE GASES:



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Properties	Test method
Density	IS-1448
Flash point	IP-36
Fire point	IP-36
Pour point	IP-16
Specific gravity	IS-1448
Kinematic viscosity	IS1448-P25
Gross calorific value	IS-1448

TABLE 2: Characteristics of waste plastic pyrolysis oil.

Properties	WPPO
Viscosity at40°C (cSt)	1.980
Density at 40°C (g/cc)	0.7477
Carbon residue (wt%)	0.5
Ash content (%)	0.036
Sulphur content (% of wt.)	0.246
Flash point (°C)	15
Pour point (°C)	<−15
Fire point (°C)	20
Calorific value (kcal/kg)	9829.35

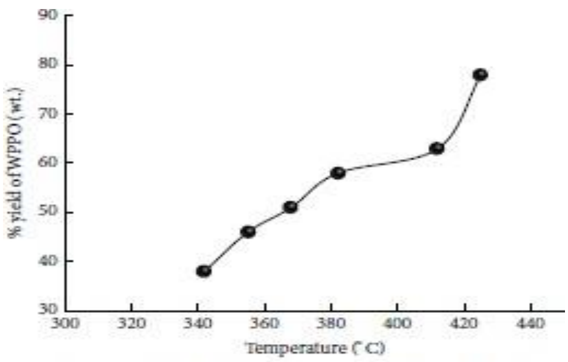

FIGURE 2: Effect of temperature on product yield.

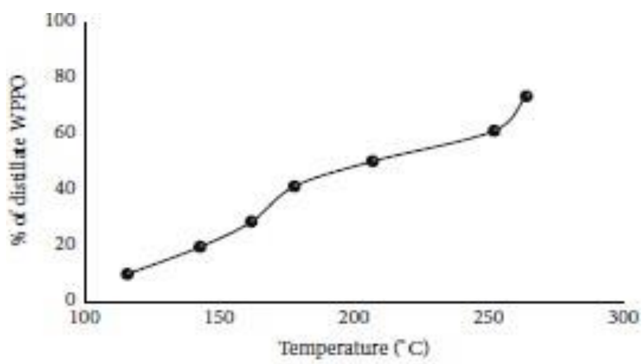

FIGURE 3: Effect of temperature on distillate product yield.

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Temperature of the flame obtained by burning the gas:

At periodic intervals after the commencement of the reaction the gas was burnt in a burner and the temperature of the flame was noted using a thermocouple. The observed flame temperatures at various time intervals are given in Table 6

Cat/Pol	Time(min)		
	15	30	45
0.1	410	574	340
0.15	484	630	415
0.2	535	725	472

Flame temperature (∘C) of the gas at various time intervals

Photographic view of hydrocarbon burring using catalyst:

CONCLUSION:

The application of bentonite clay as pelletized catalyst in pyrolysis of plastic wastes, PS, PP, LDPE and HDPE has been successfully achieved. After pyrolysis with bentonite, the calorific value of liquid oils higher than thermal experiments. The GC-MS and FTIR results showed that the oils from PS had mainly aromatic hydrocarbons in gasoline range (C_5–C_9), while PP, LDPE and HDPE had longer aliphatic hydrocarbons making them suitable for use in diesel engines. Importantly, the use of catalyst pellets eliminated the pressure drop and reducing pyrolysis processing time to only 10 minutes for 1 kg plastic wastes. No wax formation was observed when using the bentonite clay pellets as a catalyst in the pyrolysis process, this was attributed to the high acidity of the catalyst (low SiO_2:Al_2O_3 ratio) of bentonite, thus making it more active in cracking waxes compared to the less acidic heterogeneous catalysts previously reported in the literature. The emissions and performance features of diesel and gasoline engines with pyrolysis-oils were also investigated. In terms of emissions, the using of bentonite as catalyst for pyrolysis of PS resulted in lower carbon monoxide (CO) and carbon dioxide (CO_2) for gasoline engine. Catalytic oil produced from PS resulted in higher gasoline engine power, while catalytic oils from PP, LDPE and HDPE demonstrated similar values when compare with commercial fuels. For both systems the engine temperature did not significantly differ from commercial fuels when using the catalytic pyrolysis oils. Based on these results, it can be concluded that bentonite could be effective catalyst in a pelletized form for pyrolysis of plastic and may open doors to the production of liquid fuels from wastes. The thermal pyrolysis of mixed plastic leads to the production of fuel oil which is a valuable resource recovery. It also reduces the problem of disposal of waste plastic. In this work, thermal pyrolysis of waste plastic is carried out because use of catalyst is costly and regeneration of catalyst is a difficult task. Mixed plastic pyrolysis yields a mixture of oil and gas and produces very small amount of char. Higher pyrolysis temperature and longer reaction times increase the gas yield and decrease char production. Highly volatile products are obtained at low temperature. Liquid yield increases as the holding time increases from 1 hr to 2 hr, but as the holding time increases from2 hr to 3 hr, the liquid yield decreases. The maximum oil yield was 77.03% at 2 hr. The liquid obtained in this process is relatively greater volume and low boiling range. Distillation of fuel-like liquids shows more light fractions at higher temperature and longer time. Physicochemical properties of obtained fuel oil can be exploited to make highly efficient fuel or furnace oil after blending with other petroleum products. However, further studies are necessary to utilize this oil as fuel or feeds tock. This study shows that LDPE can be completely converted into hydrocarbons using fly ash as a catalyst. When cat/pol ratio is 0.1 97% conversion is observed with 75% oil formation. Though increase in cat/pol ratio results in 100% conversion the yield the oil is decreased by increase in cat/pol ratio. The fractions of the plastic oil can be used as substitute for diesel. The flame temperature of the flame obtained by burning the gas is higher when cat/pol ratio is 0.2. This is because of more gaseous hydrocarbons are released when cat/pol ratio is 0.2.Pyrolysis of plastic wastes (LDPE polymer) produced pyrolytic oil that could be considered as an alternative fuel. The physical properties of the oil were similar to that of kerosene. However, a more detailed analysis should be conducted to assure further utilization of the oil. Pyrolysis using a zeolite catalyst produced more oil than that without a catalyst. The optimum temperature for the process was 350°C, which gave a maximum oil yield as high as 52.6% vol/w (with zeolite) and 51.7% vol/w (without catalyst).

REFERENCE:

IS code:

- Testing methods for fuel properties measurement &Physical parameters study.
- IS-1448-P16 for Density.
- IS-1448 P-32 for Specific gravity.
- IS-1448-P25 for Kinematic viscosity.
- IP-36 for flash point and fire point.
- IP-16 for pour point.
- Gross calorific value was determined as per IS-1448.

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