PERFORMANCE ANALYSIS OF CATALYTIC DEGRADATION OF WASTE PLASTIC INTO FUEL OIL

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Abstract— *This Paper involves catalytic degradation of waste plastic into fuel range hydrocarbons like petrol, diesel and kerosene etc. A breaking of catalytic is a process in which waste plastic were melted and cracked without oxygen at very high temperature, the resulting gases were cooled by condensation and resulting crude oil was recovered. From this crude oil various products like petrol, diesel and kerosene etc. can be obtained by distillation.*

This process mainly consists of four units (1) reacting vessel or reaction chamber (2) condensation unit (3) receiving unit (4) distillation unit. More specifically the degradation of waste plastic except polyvinyl chloride (PVC) and polyethylene terephthalate (PET) over two commercial grade cracking catalysts, containing 20% and 40% ultra-stable Y zeolite, respectively, was studied in a semi-batch reactor. Also the effect of polymer catalyst ratio was studied on the formation of liquid hydrocarbons. The best results were obtained when polymer catalyst ratio was 4:1 and after this ratio the liquid yield decreases. Furthermore alternate method for disposal of waste plastic is also studied. And the results of this process are found to be better than other alternate methods which are used for the disposal of waste plastic.

*Key Words***:** *Hydrocarbons, catalytic, plastics, degradation, polymers, condensation, glycerin, Polystyrene.*

I. INTRODUCTION

Plastics play a pivotal role in modern society. From the vinyl siding on a house to the disposable beverage bottles sold in vending machines, plastics are ubiquitous. Nearly every modern product contains at least a few plastic components, yet synthetic plastics have only existed since the introduction of Bakelite in 1907.Before that point plastic materials had been used, but they were naturally derived. The most widely known of these natural materials is rubber. With the national focus of attention turning to reducing foreign oil imports and environmental impacts of human activities renewed interest has been placed into developing plastics from natural products [1]. Some background information is required before a discussion of the societal impacts of bio plastics can commence.

A. Basic Introduction to Plastics

Plastics have proliferated so readily throughout the modern world because of their versatility. Plastics can be flexible or rigid, brittle or resilient, clear or colored, and have many other useful properties. Some plastics are electrically conductive while others are excellent insulators. It is widely divergent properties such as these that allow a plastic to perform almost any role. In general plastics have a high strength to weight ratio that allows products made of plastics to be lighter and less bulky. Plastics are also less costly alternatives to metals and wood for many applications, such as packaging. The ability to add pigments directly to plastics instead of applying paint is also a benefit.

Plastics would not be as useful as they are without plasticizers. A plasticizer is a compound that makes another compound, usually a plastic, more pliable. Plasticizers also increase a plastic's ease of handling and resilience. The majority of plasticizers are esters, specifically, phthalates and adipates. Other types of plasticizers are citrates, epoxies, phosphate esters, polymerics, sebacates, azelates, and trimellitates. Phthalates are the most common plasticizers [3]. More than 300 plasticizers are known and between fifty and one hundred of those are currently used commercially. Some common plasticizing agents are di-2-ethyl hexyl phthalate (DEHP), disobey phthalate (DIDP), and diisononyl phthalate (DINP). PVC is the major product that utilizes plasticizers and it accounts for 95% of plasticizer use. Besides plastics, plasticizers are found in adhesives, cosmetics, and paints. Without plasticizers plastics would lose some of the properties that make them so useful.

B. Synthesis of Plastics

Before detailed syntheses of specific products can be discussed a general knowledge of polymer synthesis is required. In condensation polymers the monomers bond with the loss of a small molecule. If this small molecule is water, as it is in protein polymerization, then the reaction is called

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dehydration. Condensation polymers are also known as step-growth polymers. Addition polymers add one monomer at a time at the end of the polymer chain. The end of the chain that is growing will often have a reactive intermediate. There are three types of reactive intermediates that are found at the end of addition polymer chains. The first is a cation, which is a positively charged atom. The second is an anion, which is a negatively charged atom. The third option is a radical, which is an atom with a single non-bonded electron in its valence orbital. Addition polymers are also known as chain-growth polymers. When a polymer is made of 2 or more different monomers it is called a copolymer. Chain branching is caused by hydrogen abstraction where the free radical at the end of the chain in an addition polymer abstracts a hydrogen atom from the middle of the chain causing a branch to form at that point. This basic introduction to polymer synthesis sets the stage for the product syntheses that follow.

C. Nylon

Nylon, or more specifically nylons, since there are a variety of them, is some of the most common plastics in the world. Nylon is a thermoplastic normally produced as a fiber. It is widely used in the clothing industry as a substitute for silk. Nylon is prevalent to such an extent in the garment industry that a type of women's stockings is called nylons. Nylon is also used in injection molding, metal coating, and tubing. Nylon fabric dries quickly, washes well, and tends to hold its shape. It is also many times cheaper than silk. Nylon was the first synthetic fabric to be sold on the open market when it was released in 1939.Nylon's instant name recognition makes it a good example of a plastic [4].

D. Rayon

Rayon is a polymer that is neither fully synthetic nor natural. It is made from the cellulose in wood pulp but chemically treated to alter its properties. It has more in common with cotton than it does with nylon. Polymerization is unnecessary because the reactant, cellulose, is a polymer in itself. Rayon's only uses are as fabrics or absorbent materials. It directly competes against cotton in the fabrics industry and has a fairly low price, although, the cost is not as low as cotton. To sum up, Rayon can qualify as a biopolymer and as such deserves special consideration in this paper. Several non-chemical processing steps later, rayon fibers result [5].

E. Kevlar

Kevlar is a well-known polymer fabric noted for its strength. It is used in body armor and high-end sports equipment. It is also used in tires, brakes, and composite

materials. Kevlar's strength to weight ratio is very high. DuPont invented it in 1965. It is formed out of aramid fibers and retains flexibility despite its strength. Kevlar is synthesized in a simple one step reaction. Tere phthaloyl chloride is mixed with 1, 4-phenylenediamine in a solvent mix of HMPA and DMAC. The reaction is cooled to 3°C and kept under an inert atmosphere of nitrogen. After some waiting period the polymer can be filtered out. Kevlar is wet-spun from a hot solution of sulfuric acid containing high solids.

F. Polyvinyl Chloride

Polyvinyl chloride or PVC as it is commonly known is one of the most widely used plastics in existence. Varying the levels of plasticizers and other additives can make PVC soft and flexible, for things like toys and the vinyl seats in cars, or hard and rigid like vinyl siding and PVC water pipes. PVC is a thermoplastic so it can be melted down and recast once it has served its purpose. PVC is also commonly used as a rubber substitute [6].

G. Lexan

Lexan is a specialty plastic that is best known for its use in bullet resistant glass. Lexan is clear in its standard form, which makes it a good substitute for glass under harsh conditions. Lexan is impact resistant, abrasion resistant, weather resistant, and is resistant to many chemicals. It also behaves well when exposed to flame. Its impressive properties have led to its use in bomb resistant buildings, high end sports equipment like goggles and ice hockey masks, and airplane windows. Lexan has also seen use in storm-proofing commercial and government buildings. The characteristics of Lexan justify its high price in applications where strength and impact resistance are key.

H. Plexiglas

Plexiglas was one of the first plastics to be mass-produced. Its chemical name is poly (methyl Methacrylate). Plexiglas is a thermoplastic that competes directly against polycarbonates. It has good optical qualities making it a common material for aircraft windows and cockpits. It is lighter and stronger than glass. It is also shatter resistant. The production of Plexiglas totals several billion kilograms annually. Plexiglas is often used to replace glass in light fixtures and other places where its high strength and low cost are beneficial.

II. EXPERIMENTAL MEASUREMENTS

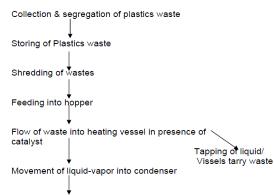To conduct the fuel test the following factors are taken for measurements.

- Properties of Bio-diesel
- Density/ Specific Gravity
- Cetane Number
- Viscosity
- Distillation characteristics
- Flash point
- Cold Filter Plugging Point (CFPP)
- Pour Point
- Cloud Point
- Aromatics
- Stability
- Oxidation Stability
- Thermal Stability
- Storage Stability
- Iodine Number and polyunsaturated methyl ester(C 18:3+)
- Water Content

A. Test Methods for Biodiesel

Lot of work need to be done to clearly understand the requirements, accuracy and precision, and applicability of these test methods for India. For India, as far as possible, use the current BIS specifications or modify them to suit the requirements. It is important to note that, as seen by the term " prEN" in several methods are under development or in proposal stage.

B. Process Technology
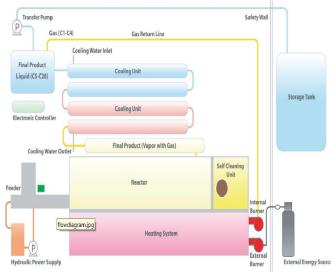
The process includes following steps;

Collection & segregation of plastics waste

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Storing of Plastics waste

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Shredding of wastes

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Feeding into hopper

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Flow of waste into heating vessel in presence of catalyst　→　Tapping of liquid/ Vissels tarry waste

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Movement of liquid-vapor into condenser

↓

Tapping of liquid fuel (as a product)

C. Mass Balance under Stable Operating Condition- Table-1

Mass Balance under Stable operating Condition with Municipal Plastics waste/Industrial plastics waste					
	MASS BALANCE- ZERUST FILM				
	TOTAL INPUT		TOTAL OUTPUT		
	Input Raw Material (KG)		Output Material (KG)		
Total	6100		5056		
Depolymerisation Efficiency	83.0%	As Crude oil	10%	As Sludge	7%	As Volatile Gases
% Conversion by Distillation	20%	42%	25%	10%	3%
	Naptha	Diesel	Refractory fraction	Residual sludge	Volatile losses
Overall Mass Efficiency%	72%				
Conversion Products	1 Ton polyolefins		220 L-Naptha / 420 L-Diesel 260 L- Furnace oil		

Figure-1

Polymer Energy System Flow Diagram

D. Properties of conventional & Alcohol Fuels
Table-2

Characteristics	Diesel	Gasoline	Methanol	Ethanol
Energy content (MJ/kg)	42.5	44.0	20.0	26.9
Heat of vaporisation (KJ/kg)		305		904
Kin Viscosity (mm^2/s)	4.01	0.6		1.5
Boiling point ^{o}C	140-360	37-205	65	79
Flash point ^{o}C	55-65	-40		13
Auto ignition temperature ^{o}C	230	300		366
Flammability limits (%gas in air)	0.0-5.6	1.4-7.6		3.3-19.0
Research octane no.	-25	87-98	106	107
Motor octane no.	-	80-9-	92	89
Cetane no.	45-55	0-5	5	5

III. RESULTS AND COMPARISION

The experimental apparatus for catalytic degradation of LLDPE and catalytic mixture consist of a semi-batch reactor made of borosilicate glass in which the reaction takes place; heated by a heating mental connected to a temperature controller. Prior to the reaction vacuum was created in the reactor to ensure that no oxygen is left there.

Polymer mixed with catalyst was charged into the reactor at the beginning and the reactor was heated up. The polymer catalysts ratio was also varied to know its effect on liquid yield. The ratio is shown in the table-3

Polymer catalyst ratio	Polymer mass (g)	Catalyst mass (g)	Total mass (g)
1:1	1.5	1.5	3.00
2:1	2.01	1.01	3.02
4:1	2.05	0.51	2.56
6:1	2.13	0.36	2.49
Catalyst 2			
1:1	1.52	1.52	3.04
2:1	2.04	1.02	3.06
4:1	2.26	0.56	2.82

Table-3 Polymer catalyst ratio

The overall mass of polymer and catalyst was kept between 2.5g to 3.5g. A constant set point for the controller was used throughout the 25 min. of experiment, which resulted in the following temperature profile in given in fig. I in first 10 min; a linear temperature increase was observed and then increased with slow rate for remaining 15 minutes.
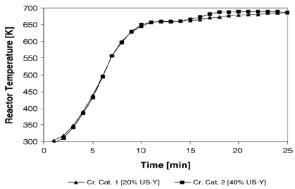

Figure-2 Graph between temperature achieved and time of reaction

The overall conversion, liquid yield and coke concentration obtained by cracking catalysts 1 and 2 are summarized in Table-4

Table-4 Overall Conversion of liquid yield by catalysts

Poly. cat. Ratio	Conversion (%)	Yield to liquid product (%)	Coke yield (%)	Coke Concentration
Catalyst 1				
1:1	98	66	2	2
2:1	99	76	1	2
4:1	99	89	1	4
6:1	99	73	1	6
Catalyst 2				
1:1	94	41	6	6
2:1	95	66	5	10
4:1	93	78	7	28

Cracking catalyst 1 could fully degrade the polymer samples in all cases, even at low values of overall content of active zeolite. No polymer remnants were observed and coke formed on catalyst was the only form of the polymer not

converted to volatile products. In terms of overall liquid yield, a maximum was observed around a ratio 4:1. In the same case of 4:1, the liquid yield was very close to 90%, which is an exceptionally high value observed by us. The low coke yields reflect upon the high conversion values reached. However, coke concentrations, the ratio of formed coke to catalyst mass, were higher, as higher polymers to catalyst ratio were applied. High conversion values around 78% was obtained with cracking catalyst 2 at all different polymer to catalyst ratios studied. Once again, all conversion values were above 90%.

The liquid yields were not so high when compared to cracking catalyst 1, but ratio 4:1 produced the highest value (89%). Obviously, we can say that the liquid yield is dependent on the specific ratio of polymer to catalyst ratio.

The liquid versus time graph is presented in Fig.6.1 for different polymer to catalyst ratios for commercial cracking catalyst 1 fort clearer interpretation of the results. It clearly indicate that ratio of polymer to catalyst 4:1 produces higher liquid yield (89%) as compared to the rest, as well as higher liquid yield during the complete experimental.
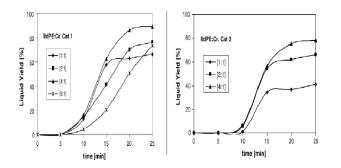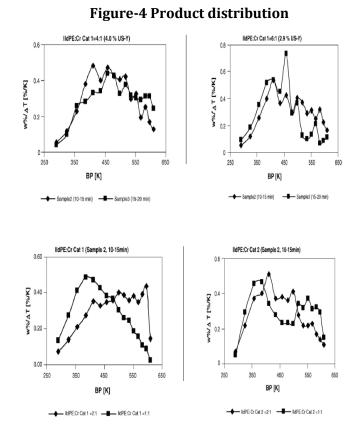

Figure-3 Graph between liquid yield and time taken for various polymers to catalyst ratio

For catalyst 2 a decrease in liquid yield is observed with the catalyst content for all reaction times. The Fig.6.2 suggests that the three exist a critical ratio of polymer to catalyst for maximum liquid yield.

Figure-4 Product distribution

Performance of catalyst for various proportions

Table-5 Typical analysis of gaseous product from

S.NO	COMPONENTS	QUANTITY in Wt %
1	Methane	6.6
2	Ethane + Ethylene	10.6
3	propane	7.4
4	propylene	29.1
5	Iso-butane	1.9
6	n-butane	0.9
7	C4 (unsaturated)	25.6
8	Iso-C5, n-C5	0.1
9	C5 +Higher	15.3
10	Hydrazen	2.5
11	Co/co2	<400ppm

process

Table-6 Typical analysis of liquid hydrocarbons obtained

S.NO	CARBON NO	QUANTITY IN Wt %
1	Up to C10	61.0
2	C10 to C13	2.4
3	C13 to C16	8.5
4	C16 to C20	4.1
5	C20 to C23	7.6
6	C23 to C30	16.4

Properties of crude oil obtained (when zeo lite type 5A is mixed with catalyst & kept in receiver and product is filtered.)

Table-7

PROPERTIES	REGULAR GASOLINE	FUEL EXTRACTED FROM WASTE PLASTIC
Colour Visual	Orange	Pale Yellow
Specific Gravity at 28 °C	0.7423	0.7254
Specific Gravity at 15 °C	0.7528	0.7365
Grass Calorific Value	11210	11262
Net Calorific Value	10450	10498
API Gravity	56.46	6065
Sulphur Content	0.1	0.002
Flash Point (Abel) °C	23.0	22.0
Pour Point°C	<-20°C	<-20°C
Cloud Point°C	<-20°C	<-20°C
Existent gum. Gm/m3	40	36
Reactivity with SS	Nil	Nil
Reactivity with MS	Nil	Nil
Reactivity with CI	Nil	Nil
Reactivity with Al	Nil	Nil
Reactivity with MS	Nil	Nil

CONCLUSION

A clear trend of liquid hydrocarbon formation was observed with the catalyst content during the catalytic degradations of polyethylene over the commercial cracking catalysts. An initial sharp increase in the liquid yield at low US-Y content is followed by a gradual decline at higher values this result in a maximum of liquid yield at ratio around 4:1 compared with a pure US-Y systems. Furthermore it is very clear from the above experiment that waste plastic can be converted into liquid fuel that can directly use as fuel but it will be better to use the as LDO and HSD for furnace heating etc. the process is very cheap as the catalyst can be recovered and used again and again.

Conversion of waste plastic into fuel will reduce dependence on fossil fuels as well as the one of the most critical problem can be solved. The process is 100% eco-friendly as nothing is left in the environment and getting rid

of plastic waste. Sulfur content in the fuel generated is less than 0.002%.

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BIOGRAPHIES

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