



Catalytic Cracking of Waste Plastic: Conversion of Plastics to Gasoline Fuel Using Zeolite Catalyst

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Abstract

In recent days fuel production from waste plastics has gained much attention because of the increasing number of generation of waste plastics and its non-biodegradability. Thermal cracking and catalytic cracking are typically used in the petrochemical industries for this recycling process. In thermal cracking it requires very high temperature and pressure (700-800⁰C & 70 atm). Catalytic cracking, in this term, is an effective way to degrade the long chain polymers into higher quality products at a lower temperature (500⁰C) and pressure. In this experiment, catalytic cracking method of waste plastics has been developed and demonstrated. The objective of this experiment is to produce gasoline fuel and observe its quality and quantity at different weight percentage of Zeolite. Three trial runs have been conducted using 7%, 10% and 15% mass fraction of Zeolite. As a result liquid oil was found in the products with mass fraction of 11%, 11% and 10% respectively. Property test of the derived fuel has also been conducted to investigate the fuel quality.

Keywords: Catalytic cracking, Plastic recycling, Plastic waste, Alternative fuel.

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1. Introduction

Plastic waste handling is one of the major problems that the developing countries are facing today. Plastics are so durable that they do not decay or cannot be entirely destroyed. As a result, great amounts of discarded waste plastic products accumulate and it has become a threat to our environment. The management of plastic waste is intended to decrease the environmental impact according to the following order- waste minimization, reuse, recycling, energy recovery, and land filling. Waste minimization and reuse are options with limited applicability. Hence, recycling and energy recovery are alternatives to be considered. Energy recovery by incineration seems to be a suitable solution that takes advantage of the high energy content of plastics, but presently is largely questioned because of the possible emission of toxic compounds such as dioxins, furans, etc. One of the prospective ways of the utilization of the waste polymers is catalytic cracking of higher molecular hydrocarbons (plastics) into lower molecular hydrocarbons which can be used as polymer energy. Cracking reactions are endothermic by nature, and the required heat and temperature can be reduced with catalysts. In such reactions, the most valuable fuel is obviously liquid fuel. Although gaseous products are useful too as their burning can contribute to the energy demand, but still excess gas production is not desirable. The use of catalysts allows the plastic degradation pathway to be modified with regard to pure thermal cracking. Initially, two positive effects are to be expected by the incorporation of a catalyst into the reaction medium. One is the reduction of the cracking temperature; and secondly, suitable control of the selectivity which enables the formation of more valuable products. Zeolite based catalysts are extensively used for higher hydrocarbon cracking process. Zeolites are three dimensional, crystalline structures having unusual and unique chemical properties which make them commercially attractive. They consist of a tetrahedral network of oxygen and silicon atoms where aluminium replaces some of the silicon to form aluminosilicates. The result is an extended passage of channels and cavities. It has crystal sizes in the approximate range of 0.2- 0.5 μ m and pore diameter of 7.4 \AA . It thermally decomposes at 793 $^{\circ}$ C [1]. A thorough and extensive experiment was carried out by setting-up of appropriate small scale pilot process to check the viability of fuel production from burning of plastics. The main scope of the work was to verify the gasoline production from burning of plastics due its importance in fuel consumption. Plastics were thermally cracked in presence of catalyst (Zeolite) which resulted in a product fuel that was combustible in nature. Important and necessary fuel tests were carried out to confirm the fuel as gasoline. Therefore, it can be a beneficial and constructive step for the energy sector by which the increasing demand of energy as well as environmental pollution can be minimized.

2. Theory of catalytic cracking of waste plastics to produce gasoline

Most of the studies reported as catalytic cracking of plastic use PE as starting material because it is the main polymer in plastic waste. The first work appeared in 1970s, mostly based on the use of Friedel-Crafts catalysts. Goodship [4] has described in detail the mechanism of PE degradation over AlCl_3 -based catalysts. Compared with thermal decomposition, the catalytic conversion of PE at 400 $^{\circ}$ C leads to higher conversions with significant changes in the product distribution, because the catalyst also promotes secondary isomerization reactions. Inches [6] has compared the thermal degradation of PE with catalytic cracking over amorphous silica-alumina and Zeolite catalysts. While thermal conversion of PE into volatile compounds starts at 400 $^{\circ}$ C, the catalytic decomposition causes a significant weight loss at temperatures below 200 $^{\circ}$ C and the polymer is almost

completely converted before reaching 400°C. The authors have also determined the activation energy of the PE degradation—a significant reduction being observed in the presence of the catalysts. In contrast with the high activation energy found for the thermal degradation (273 kJ mol⁻¹), catalytic degradation over Zeolites Y and REY (rare earth exchanged form of Zeolite Y) led to values of 57.3 and 41.0 kJ/mol. A significant decrease was also observed for silica-alumina materials, with activation energies nearly 120 kJ/mol. This effect was less significant when silica or alumina were used as catalysts, activation energies of 193.1 and 181.8 kJ/mol, respectively, being calculated. According to these results, the decrease in the activation energy of PE degradation appears to be correlated with the acid strength of the catalysts.

The mechanism and products of the PE catalytic decomposition over amorphous silica-alumina catalysts has been investigated by Sharma et al. [8], using a batch reactor under nitrogen atmosphere. Four fractions were recovered after the reaction— gases, liquids, degraded oligomer and degraded polymer. The authors propose a sequential mechanism to explain the catalytic PE degradation:



From an economic point of view, used plastic can be considered as both an important source of valuable chemicals, mainly hydrocarbons, and an energy source. The calorific value of most plastics is similar to that of fuel oils and higher than that of coals. Plastic wastes can therefore be viewed as potential fuels, when other alternatives of valorization are not possible.

Main concept of producing fuel from plastic based on the decomposition of polymers by means of heat, chemical agents and catalysts to yield a variety of products ranging from the starting monomers to mixtures of compounds, mainly hydrocarbons, with possible applications as a source of chemicals or fuels. Whole operation is done in absence of oxygen to inhibit the production of CO₂.

3. Materials and methods

3.1. Experimental equipments

The reactor used for this experiment is an insulated mild steel cylindrical vessel heated by two electrical heating coils to achieve a maximum temperature of more than 600°C.

The necessary provisions are made in the reactor for mounting the gadgets for measuring pressure, temperature and a collection of hydrocarbons from the reactor. Thermocouple along with a reader is set to measure the temperature rise. The heating coils are surrounded in the body of the circular reactor. Above it, necessary insulations of Asbestos fiber and tape are spiraled to reduce the amount of heat loss. The coils are electric, and there are connecting wires from the coils. To avoid any electric misfortune, the wires are connected in a series to the electric socket through a fuse. There is an outlet in the reactor directed to the condenser. A pressure gauge is appended on top of the reactor to measure the reactor pressure in psi unit.

The gaseous product from the reactor is passed through a mild steel double walled condenser with inlets and outlets for cooling water. The gaseous hydrocarbons at temperature of around 350°C are condensed to around

room temperature. In the experiment, a double pipe heat exchanger is used. A valve for releasing the heated gas from the reactor vessel is added at the inner pipe of the condenser. The whole portion is then welded to the reactor vessel. There are inlet and outlet pipes for cooling water streams. Counter-current flow system is used to cool the condensate.

Table 1: Size and specifications of reactor vessel

Sizing Parameters	Size
Inner Radius of Reactor Vessel	0.095 m (3.75 inches)
Height of Reactor	0.30 m (12 inches)
Volume of Reactor	0.009 m ³ (0.318 ft ³)
Outlet Pipe Outer Diameter	0.013 m (0.5 inches)
Radius of Upper Flange	0.17 m (6.75 inches)
Radius of Side Flange	0.17 m (6.75 inches)
Distance Between Two Flanges	0.006 m (0.25 inches)
Height of Reactor	0.30 m (12 inches)

Table 2: Size and specifications of condenser

Sizing Parameters	Size
Total Length of Condenser	0.76 m (30 inches)
Effective Length of Condenser	0.46 m (18 inches)
Distance between Inlet and Outlet	0.30 m (12 inch)
Water Streams	
Inlet and Outlet Pipe Outer Diameter	0.019 m (0.75 inches)

A temperature controller is attached with the reactor to keep a track of the temperature rise or fall inside the reactor. For this purpose, a thermocouple is affixed whose one end is put inside the reactor and the other end is connected to a thermocouple reader. The temperature range is around 0°C-999°C.

Two stainless steel electric heaters are spiraled around the body of the reactor to heat up the plastic for catalytic cracking. The power of individual heater is 3000 W which can heat up the plastic up to more than 600°C.

3.2. Experimental procedure

Three trials were carried out at three different mass fraction of Zeolite Y by employing two electric heaters and proper insulations described above. But before each trial, there were some initial and basic preparations.

The inside of the reactor vessel was cleaned up properly to avoid any moisture in it. The condenser was trialed by allowing the flow of water to check that all the streams were clear enough. Raw materials (polyethylene) along with Zeolite Y (catalyst) in the middle of the raw materials were packed densely inside the reactor. In order to secure leaks and losses of product a plate of Teflon was placed in between the two flanges. A collecting flask was kept ready to amass the product.

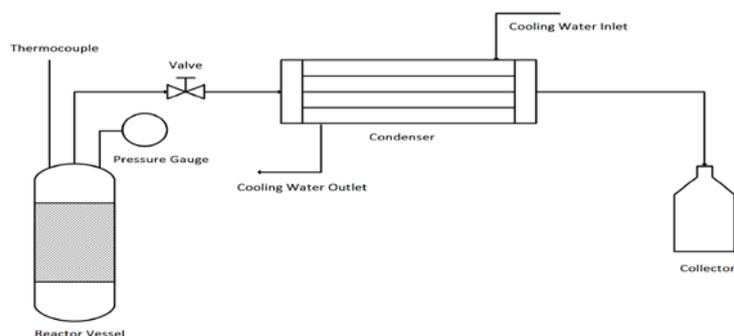


Figure 1: Process flow diagram of catalytic cracking of waste plastic

4. Results

Results of the three trials are listed in the following tables. Temperature was recorded periodically during every trial and from that data temperature vs. time graph was plotted. Fuel property test was conducted for the sample product collected from trial 1.

Table 3: Results of trial 1

Raw Materials	
Mass of Polyethylene	600 gm
Mass of Zeolite Y	42.4 gm
Percentage of Zeolite regarding feedstock	7%
Product Specification	
Liquid Oil	70.6 gm (11%)
Solid Residue as Char	102.8 gm (16%)
Wax	257 gm (40%)
Pyro Gas	212 gm (33%)
Color	Pale Yellow
Heating Procedure	Heating Coils
Heating Duration	40 minutes
Observation	With newly installed setup and appropriate heating system the trial gave good result. Sample was collected without any trouble.

Table 4: Results of trial 2

Raw Materials	
Mass of Polyethylene	600 gm
Mass of Zeolite Y	60 gm
Percentage of Zeolite regarding feedstock	10%
Product Specification	
Liquid Oil	72.6 gm (11%)
Solid Residue as Char	125.4 gm (19%)
Wax	264 gm (40%)
Pyro Gas	197 gm (30%)
Color	Dark Yellow
Heating Procedure	Heating Coils
Heating Duration	40 minutes
Observation	Insulations and heating coils have become wet due to contact with lost liquid and gaseous products from the previous trials.

Table 5: Results of trial 3

Raw Materials	
Mass of Polyethylene	600 gm
Mass of Zeolite Y	90 gm
Percentage of Zeolite regarding feedstock	15%
Product Specification	
Liquid Oil	69 gm (10%)
Solid Residue as Char	69 gm (10%)
Wax	276 gm (40%)
Pyro Gas	176.5 gm (40%)
Color	Dark Yellow
Heating Procedure	Heating Coils
Heating Duration	60 minutes
Observation	The performance of heater, its insulation and leakages have decreased to a considerable amount in this trial.

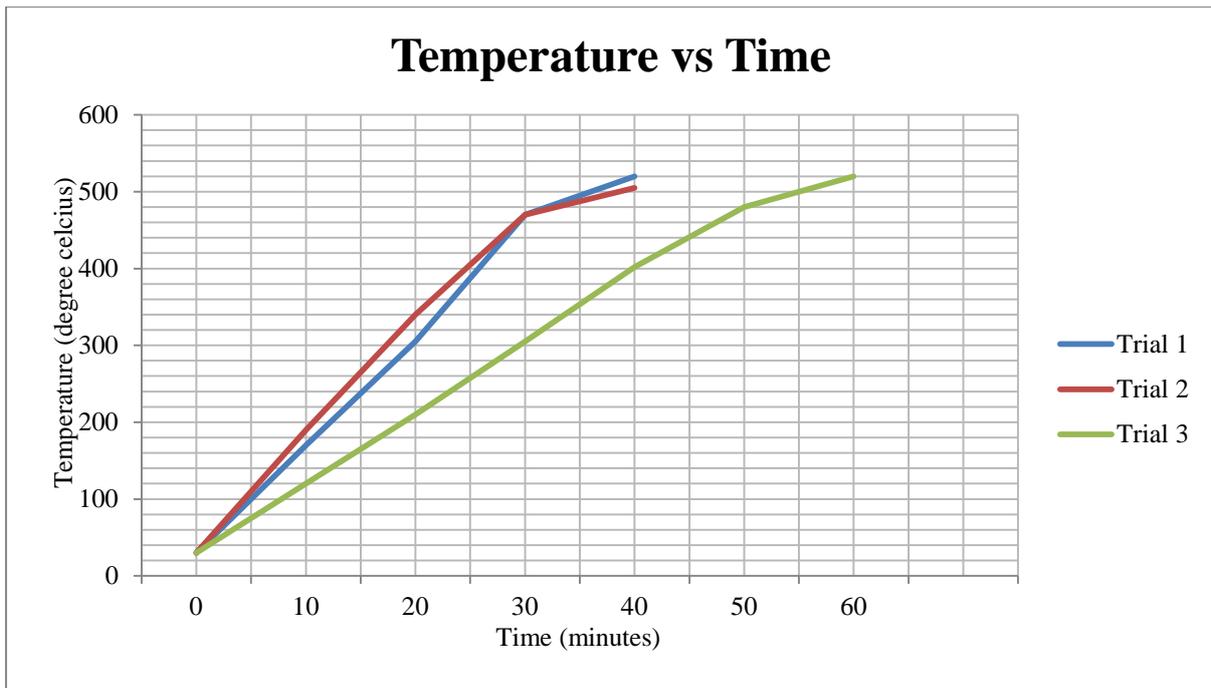


Figure 2: Plot of temperature vs. time for three trials

Table 6: Fuel property test

Parameter	Results	Regular gasoline
Color	Pale Yellow	Orange
Gross Calorific Value (cal/gm)	9784	10210
Net Calorific Value (cal/gm)	9998	10460
Pour Point (0C)	35	-6
API Gravity	62.56	56.46

5. Limitations

Losses in this experiment have been occurred enormously even if there were insulations. But such arrangement could not provide the entire equipments sufficient insulations against heat losses. Gases have been leaked through the joints of the nut-bolts, thermocouple and outlet connection points, and so have been oil. Time lag between two runs has become significant problems. The operation is continued in batch mode. As this is a high temperature process, the full experimental setup has become heated after each individual run. Then time is required to being cooled to reach atmospheric temperature. As a result of this, immediate dismantling of the equipment has not been possible and a portion of oil produced inside the reactor body have become solidified over time. Clogging has been a tremendous problem, cleaning of apparatus has been appeared as very difficult job. Due to clogging, sample collection has become more difficult after the first trial. Clogging has made rise of

pressure in various unwanted points (such as the joints of pressure gauge, thermocouple, valve etc.) rather than the outlet. As a result of this, sample loss has increased.

Gasoline stored in fuel tanks and other containers has, in time, undergone oxidative degradation and formed sticky resins referred to as gums. Such gums have been precipitated out of the gasoline and caused fouling of the various components of internal side of the reactor and pipeline which reduced the performance of the reactor and also made it harder to start them. In that case, relatively small amounts of various anti-oxidation additives should be included in end-product gasoline to improve the gasoline stability during storage by inhibiting the formation of gums. Other additives should also be provided in end-product gasoline, such as corrosion inhibitors to protect gasoline storage tanks and freezing point depressants to prevent icing.

The experiment has been carried out in batch process which creates a maintenance problem and a chance of losing materials. A good result can be obtained if it is possible to carry out the experiment in the continuous process. Moreover, only one type of Zeolite has been used for catalytic cracking in the experiment. But if it is possible to perform experiment by using other types of Zeolite, then the rate of conversions can be compared. In this way, appropriate type and condition of Zeolite can be identified.

6. Recommendations for future study

Some future recommendations based on the conducted experiment are proposed here-

- Although both liquid and powdered Zeolite Y have been involved in the experiment, quality of products can still be improved by using mixed plastic as raw material.
- Gas chromatography can be used to analyze the product gas for estimation of carbon chain. Liquid chromatography can also be employed to find out the range of hydrocarbon in liquid fuel.
- Product collection is not sophisticated in the experiment due to unavailability of well-designed equipment. A significant amount of gas is lost due to the unavailability of insulated gas collector. Product collection can be made far better to secure all the collected materials.
- Only one type of Zeolite has been used for catalytic cracking in the experiment. But if it is possible to perform experiment by using other types of Zeolite, then the rate of conversions can be compared. In this way, appropriate type and condition of Zeolite can be identified.
- The experiment has been carried out in batch process which creates a maintenance problem and a chance of losing materials. A good result can be obtained if it is possible to carry out the experiment in the continuous process.
- An extensive research can be carried out to find effective use of the chars (as waste byproducts produced from the experiment).

7. Conclusion

The percentage of oil production was found nearly same for different weight percentage of Zeolite. The fuel property test shows that the sample collected has properties quite similar to regular gasoline. Buekens [10] and

Goodship [4] both investigated that catalytic conversion of plastic starts at 400⁰ C. In this experiment, samples were collected at 40 - 60 minutes after the heating started and during that time the temperature range was found 450 – 500⁰ C.

Currently, it can be stated that the cracking of plastic waste constitutes a mature field of research with commercial opportunities and a promising future in the forthcoming years. The Zeolite Y catalyst can work well on plastic cracking as found from various researches. The fuel that is obtained from polyethylene cracking is mainly the mixture of hydrocarbon in the range of diesel and kerosene oil; and can be used as fuel as well as feed stock for industrial chemicals. The char produced can be used for reduction process and as an additive to road building material. The catalytic degradation of plastic to fuel is gradually gaining momentum and being adopted in different countries recently due to its efficiency over other process in all respects. In addition, this method would produce a substitute for the fossil fuel, so be an alternative source of energy. Depletion of non-renewable source of energy such as fossil fuel at this stage demands the improvement of this technique. This sets the future trends in plastics recycling as an Industry.

The selectivity towards particular products depends mainly on the choice of catalyst and reaction conditions. The study of the catalytic cracking of plastic waste has led to relevant scientific knowledge and to the development of innovative technologies. The large-scale application of these processes has been limited by economical and profitability reasons. Previous stages involve plastic separation from municipal waste and since different mixtures of products are obtained, end stages involve product separation processes. Up to now, it is hard to compete with the still cheap option of producing fuels from natural gas and crude oil than to produce from plastics. However, worldwide growing concerns about preserving our environment give plenty of room for imaginative ideas on how to scale up these processes to industry level.

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References

- [1] S. Hulse (2000). *Plastics Product Recycling: A Rapra Industry Analysis Report*. iSmithers Rapra Publishing. pp- 488. ISBN 978-1-85957-222-1.
- [2] DS Achilias, C Roupakias, P Megalokonomos, AA Lappas, EV Antonakou. "Chemical recycling of plastic wastes made from polyethylene (LDPE and HDPE) and polypropylene (PP)". *J Hazard Mater* 2007; vol. 149:536–42.
- [3] PL Beltrame, P Carniti, G Audisio, P Bertini. "Catalytic degradation of polymers: Part II - Degradation of polyethylene". *Polym Degrad Stab* 1989; vol. 26:209–20.
- [4] V. Goodship, (2009). *Management, Recycling and Reuse of Waste Composites*. Elsevier. pp- 108. ISBN 978-1-84569-766-2.

- [5] N.S. Akpanudoh, K. Gobin, & G. Manos, (2005). "Catalytic degradation of plastic waste to liquid fuel over commercial cracking catalysts: effect of polymer to catalyst ratio/acidity content". *Journal of Molecular Catalysis A: Chemical*, vol. 235(1), 67-73.
- [6] A. Inches, (2009). *The Adventures of a Plastic Bottle: A Story about Recycling*. Little Simon. pp- 102. ISBN 978-1-4169-6788-0.
- [7] J. Zeaiter, (2014). "A process study on the pyrolysis of waste polyethylene". *Fuel* 2010; vol. 89:474–80
- [8] B.K. Sharma, B.R. Moser, K.E. Vermillion, K.M. Doll, & N. Rajagopalan, (2014). "Production, characterization and fuel properties of alternative diesel fuel from pyrolysis of waste plastic grocery bags". *Fuel Processing Technology*, vol. 122, 79-90.
- [9] J. Scheirs, and W. Kaminsky, (2006). *Feedstock recycling and pyrolysis of waste plastics: converting waste plastics into diesel and other fuels*. J. Wiley & Sons. pp- 131. ISBN 978-0-470-02152-1.
- [10] A.G. Buekens, H. Huang (1998). "Catalytic plastics cracking for recovery of gasoline-range hydrocarbons from municipal plastic wastes". *Resources, conservation and recycling* vol. 23 (1998) 163-181
- [11] J.M. Arandes, I. Abajo, D. López-Valerio, I. Fernández, M.J. Azkoiti, M. Olazar, et al. "Transformation of several plastic wastes into fuels by catalytic cracking". *Ind Eng Chem Res* 1997; vol. 36:4523–9.
- [12] S.H. Shah, Z.M. Khan, I.A. Raja, Q. Mahmood, Z.A. Bhatti, J. Khan, et al. "Low temperature conversion of plastic waste into light hydrocarbons". *J Hazard Mater* 2010; vol. 179:15–20.