

Fuel from Waste Plastic

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CERTIFICATE

This is to certify that the dissertation entitled “Fuel from Waste Plastic” has been carried out by Kunjehkumar Virani, Dhruv Tank, Krupal Patel, Himalkumar Patel under my guidance in fulfillment of the degree of Bachelor of Engineering in Chemical Engineering (5th Semester) of Gujarat Technological University, Ahmedabad during the academic year 2016-17.

To the best of my knowledge, the matter embodied in the report has not been submitted to any other University/ Institute for the award of any Degree or Diploma.

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Keywords

PP – Polypropylene

PET – Polyethylene Terephthalate

PE – Polyethylene

LDPE – Low Density Polyethylene

HDPE – High Density Polyethylene

PS – Polystyrene

PVC – Polyvinyl Chloride

ABS - Acrylonitrile Butadiene Styrene

ZSM – Zeolite Socony Mobil

Pyrolysis,

MSW – Municipal Solid Waste

MPW – Municipal Plastic Waste

FCC – Fluid Catalytic Cracking

CSBR – Conical Spouted Bed Reactor

CFR – Continuous Flow Reactor

VGO – Vacuum Gas Oil

SCW – Supercritical Water

CW – Subcritical Water

PBD – Polybutadiene (Butadiene Rubber)

LCO – Light Cycle Oil

AIBN – Azobisisobutyronitrile

HCO – Heavy Cycle Oil

MAP – Microwave Assisted Pyrolysis

PONA – Paraffin, Olefin, Naphthene and Aromatic

USY – Ultrastable-Y

MCM – Mobile Crystalline Material

REY – Rare Earth Y

SA – Silica-Alumina ratio

FSM – Mesoporous Silica

SFC – Synthesized Fly Ash

TGA – Thermogravimetric Analysis or Thermal Gravimetric Analysis

HCl – Hydrochloric Acid

SAPO – Silico Aluminophosphate

MAPO – Metal Aluminophosphate

FUEL FROM WASTE PLASTIC / DESIGN ENGINEERING

ALPO – Alumino Phosphate

XPS – X-ray Photoelectron Spectroscopy

IR – Infrared

Electricity consumption is in KWh (if unit is not mentioned)

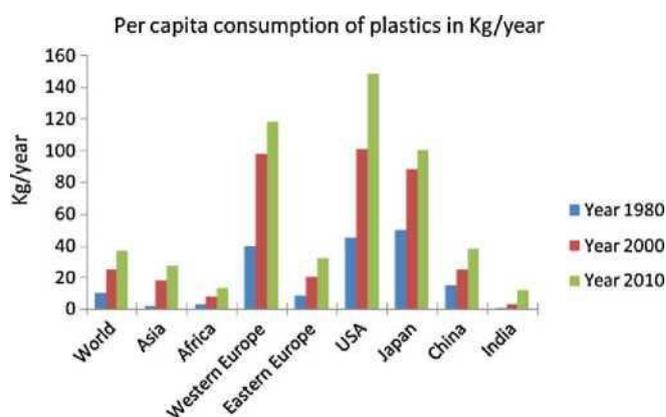
1. Abstract

Development and modernization have brought about a huge increase in the production of all kinds of plastic commodities, which directly generate waste due to their wide range of application coupled with their versatility of types and relatively low cost. Also the demand of plastics is ever increasing and has produced huge amount of plastics waste. Also both landfilling and incineration processes of plastic waste management system are identified as a source of pollutant gas emitters. So, idea of waste to energy recovery is one of the promising techniques used for managing the plastic waste. Plastics waste can be utilize for producing a fuel by the process called *pyrolysis*.

By the combination of reactor design and fair use of catalysts will lead to produce an effective fuel. In future this process play an important role because sustainable energy recovered from waste and easily obtainable raw materials. This process is pure eco-friendly. And by-product obtained in this process is also utilized for another purpose. We carried out experiments on this process and obtained 2.1 ml of pyrolysis oil through 17 plastic bag (pure LDPE).

2. Introduction

Plastics waste can be turned into a valuable alternative resource of energy production. According to the forecasts, the consumption of plastics is increasing at a rate of 4-5% annually. The recycling rates as well as the energy recovery of plastics have been increasing and it is wasting a lot of potential resources for energy recovery in the modern world. In reality about 7 yards of landfilling space to dump 1 ton of plastic wastes in the land. Since most of the plastics products are thrown out after single use it has been significantly contributing the accretion of plastic solid waste in earth. This is the reason why several different methods have been explored and applied to resolve the issue related to the polymer waste handling and disposal. From the very beginning of waste disposal activities, landfills dumping of waste of all tyres of biodegradable and non-biodegradable wastes as well as incineration of combustible wastes are considered the mostly adopted processes. The magnitude of the problem can be roughly estimated by examining several figures [1]. The total world waste of plastics in 2015 is 297 million of tonnes [2]. Since plastics are produced from petrochemical substances they have significant calorific values. Most of the plastics consumed plastics possess more calorific values than few of the mostly used fuels like coal and gas. That means the waste plastics can be used to recover energy.



[Fig. 2.1]. Per capita consumption of plastics [5].

[Table 2.1]. Heat Capacity comparison between various plastics and other materials [5].

Plastic material	Heat Capacity (MJ/kg)	Other materials	Heat Capacity (MJ/kg)
PVC	18	Heavy fuel oil	41
PP	46.4	Gasoline	44
PE	47	Coal	26
PET	46	Natural gas	36
PS	41	Milled peat	10*
ABS	35	Paper	17

*MJ/m³ at 0°C

Gasification of plastic wastes into synthesis gas has been proposed as one of these technologies, but it is very costly and requires the construction of large plants to be profitable. Cracking technologies toward transportation fuels (gasoline, diesel) and chemicals are more flexible and receive more attention, in a context of growing of prices of crude oil [3]. Therefore many process come in attention for conversion of plastic waste into fuel. Like, thermal cracking demands high temperature and its product require further processing for their quality to be upgraded, so the method is less desirable. On the other hand, catalytic cracking of plastic waste offers considerable advantages. It operates at considerably lower temperatures, since it reduce the activation energy of cracking. The use of catalyst will be more beneficial because it can lead to lower operating conditions of the cracking process. It requires lower operating costs as well [4]. Furthermore the catalyst allows the selectivity of the plastics conversion to be tailored so it can be targeted toward the desired products (e.g. gases, gasoline, or diesel) just by choosing adequately the acidity and pore structure of the catalyst [3]. The process or cracking hydrocarbon into low number of carbon is nothing but Pyrolysis. And in short pyrolysis can be upgraded by use of proper catalyst.

2.1 Current State and Prospects

Currently in the world there are many solid wastes are produced due to the human activities which are affecting the environment and as well as us and other very badly. Some of them are MSW (Municipal Solid Wastes), Industrial Solid Wastes. But the fuel produced from the MSW has more gaseous product than liquid product, where the fuel produced from industrial solid waste has more liquid product than gaseous product. In pyrolysis there is no pollution will be done, we will see this later. Currently in Industrial Solid wastes many hazardous and non-hazardous liquid and solid wastes produced in large quantities by regional industry are pyrolyzable. These includes solvents, coatings, treated wood, plastics, lubricants, agricultural chemicals and hazardous chemicals derived from the site remediation operations. Regional industry has a huge need for better, cheaper, and faster treatment, storage, disposal, and recycling, technologies, for its hazardous and non-hazardous wastes. Costs for managing these waste have risen sharply.

These circumstances should make pyrolysis increasingly attractive to industry. As an alternative to incineration, it offer lower costs without air emissions concerns or high-temperature process control challenges. Pyrolysis can be also integrated with the industrial waste exchanges. Among pyrolyzable wastes are solvents, other organic chemicals, oil and wax, plastics and rubber, textiles and leather, wood and paper, paints and coatings, unwanted hospital linens, diskettes, paints, and printed circuit board scrap. And for MSW, How much

material is now readily available for pyrolysis? Some specialized waste streams, such as automotive shredder fluff, municipal recycling facility rejected, and unwanted front-end material from incinerators, should be fairly readily available. Penetration into the second third of the 2.25 million tons of the pyrolyzable MSW materials not destined for recycling would establish pyrolysis as one of the region's anchor waste management technologies. In this role, pyrolysis would be the technology of choice for much of the raw MSW surplus recyclables engendered by adverse market conditions, and those currently incinerated material that lower incinerator efficiency. The product of pyrolysis can be used as fuel for electricity generation, industrial process heating, and transportation. Depending on the system chosen energy product are obtainable [7].

4. Empathy mapping

4.1 AEIOU Sheets

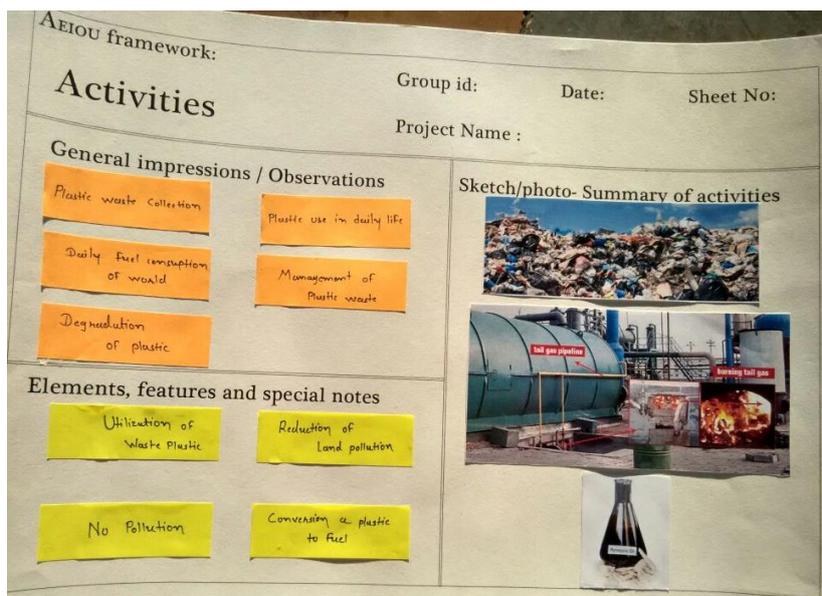
A – Activity

Activity involves our observation for the Plastic waste.

1. How it is?
2. How actually it is going on?
3. Why it is going on?
4. What is involved?

General Impression.

1. Plastic waste collection
2. Plastic use in daily life
3. Daily fuel consumption of world
4. Industry, Urban and Rural area involves in plastic waste
5. Management of plastic waste
6. Inherent toxicity condition



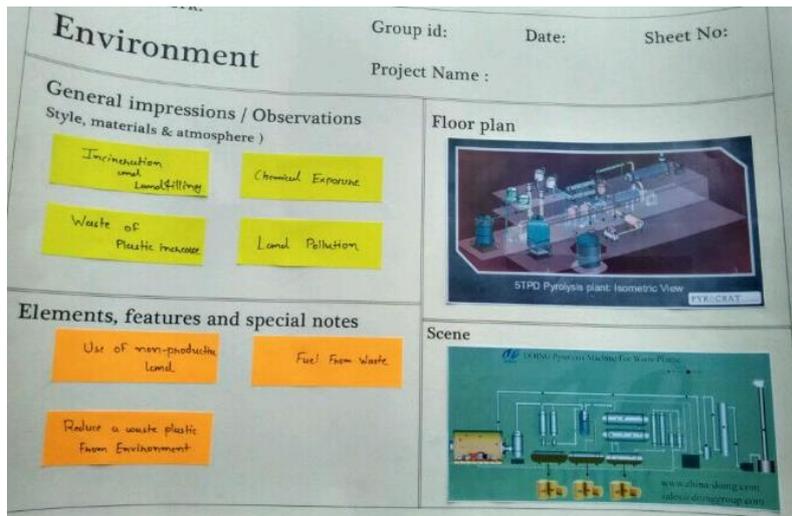
[Fig. 4.1]. Activity Sheet.

E – Environment

It includes the entire arena where the activity takes place. It involves the character and function of the overall space, of each individual's spaces and of shared spaces.

General Impression

1. Incineration and Landfilling
2. Waste of plastic increase
3. Chemical exposure
4. Land Pollution



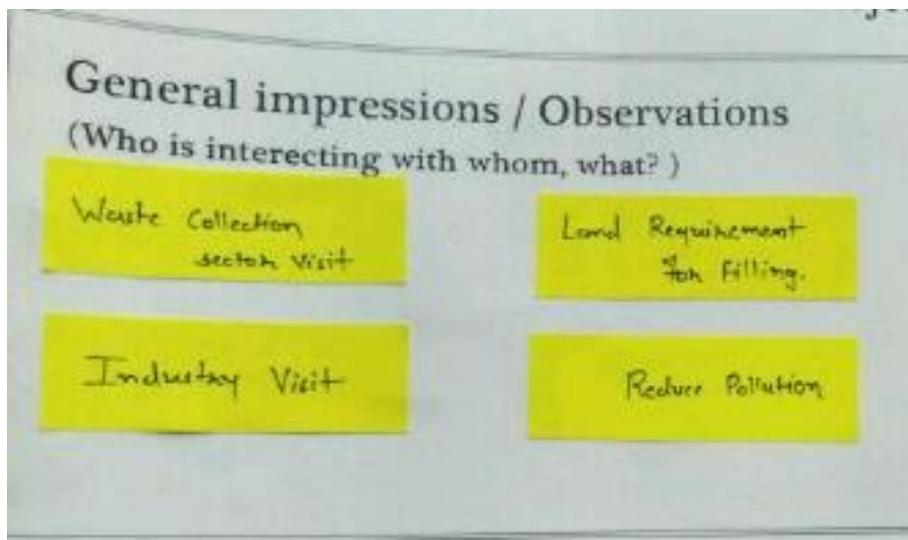
[Fig. 4.2]. Environment Sheet.

I – Interaction

It is the building blocks of activities. It involves nature of routine, interaction between people, interaction between people and objects in their environment and, across distance.

General Impression

1. Waste collection sector visit
2. Industry Visit
3. Land requirement for filling



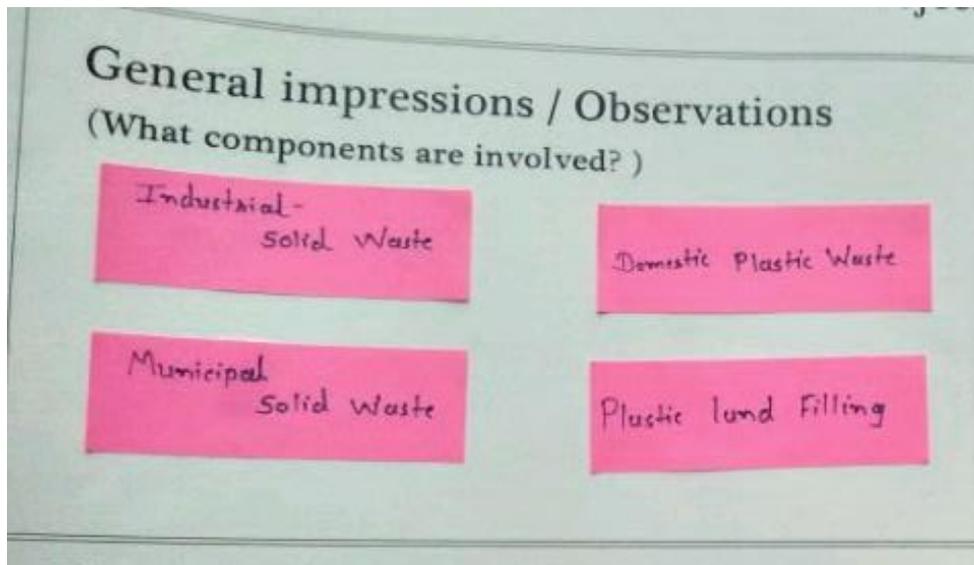
[Fig. 4.3]. Interaction sheet.

O – Object

These are building blocks of environment, key elements sometime put to complex or unintended use (thus changing their function, meaning and context). It involves the details about what are the object and people have in environment and how they relates to their activities.

General Impression

1. Very poor recycling
2. Industrial and Municipal Solid wastes
3. More demand for cheaper material



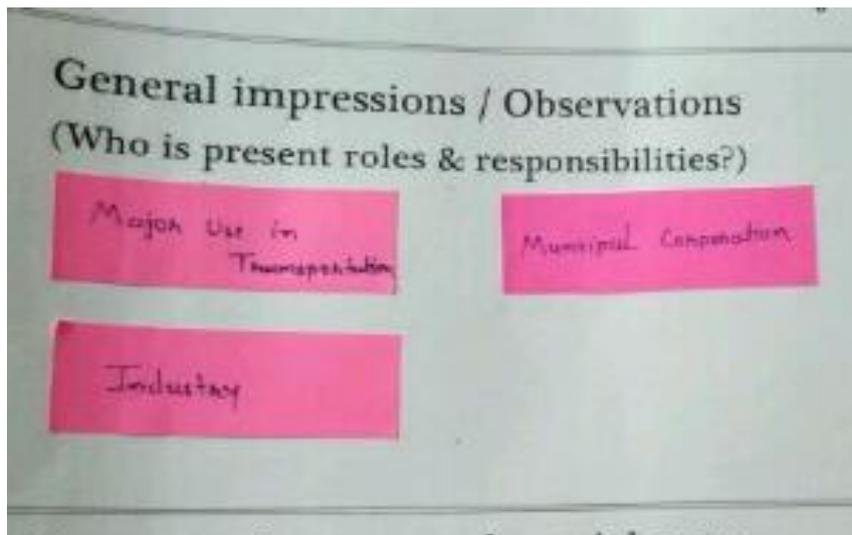
[Fig. 4.4]. Object Sheet

U – Users

Users are the people whose needs, behavior and preferences are being observed. It involves their identity, their roles and relationship as well as their values and prejudices.

General Impression

1. Major use in transportation
2. Industry
3. Municipal Corporation



[Fig. 4.5]. Users sheet.

5. Empathizing Canvas

Empathy mapping for design engineering.

Step 1: Identify the user.

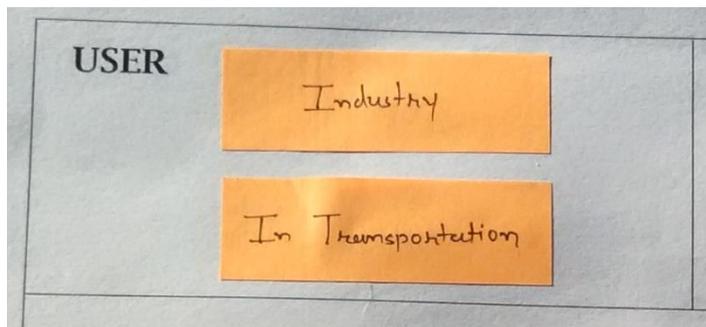
Step 2: Find all stakeholders.

Step 3: Find all activities related to the user and stakeholders.

Step 4: Write a four stories related on your user and subject to designed.

5.1 User

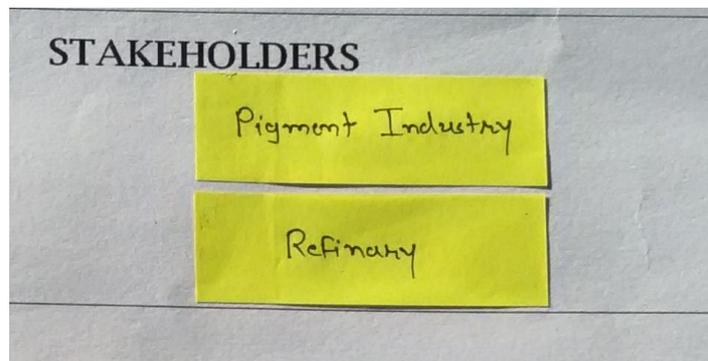
Who are the user ?



[Fig. 5.1] User section of empathizing canvas.

5.2 Stakeholders

Person, groups or organization that have direct or indirect stake in an organization because it can affect or be affected by the organization's action, objectives and policies.

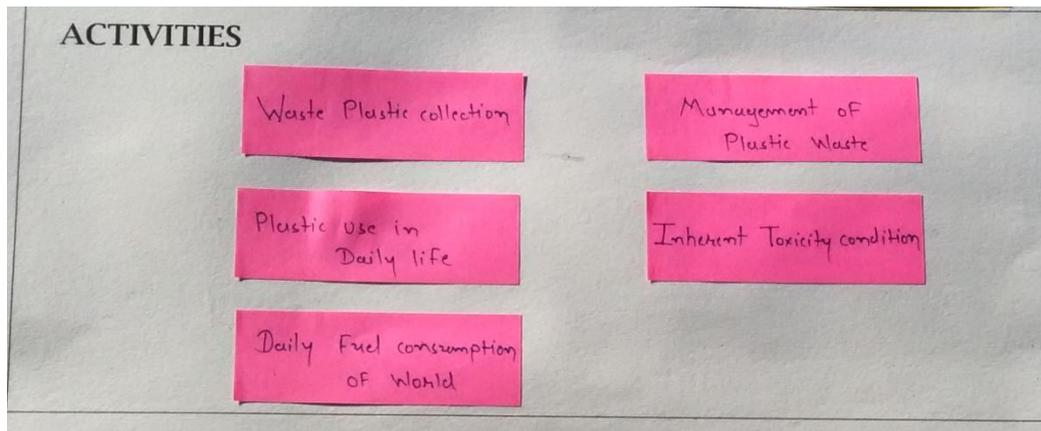


[Fig. 5.2]. Stakeholders section of empathizing canvas

In this project we have selected the study of Fuel from Waste Plastic used as alternative of a regular fuel.

5.3 Activities

The condition in which things are happening or being done and thing that a person or group does or has done.



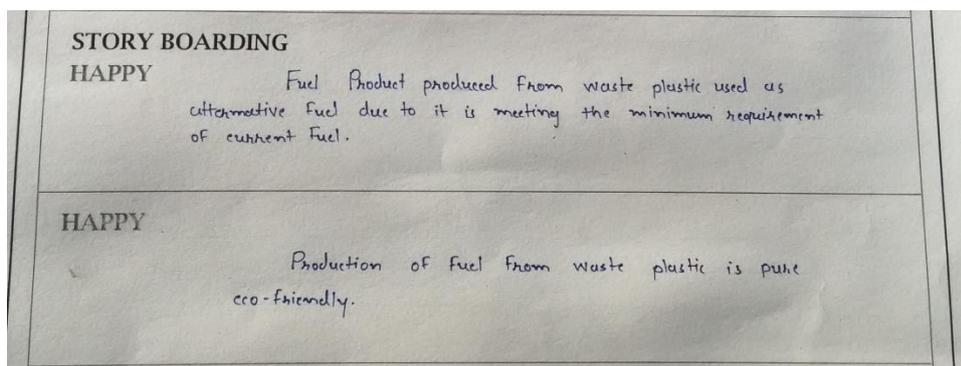
[Fig 5.3]. Activities section of empathizing canvas.

5.4 Story Boarding

In this part or section we written two happy and sad stories.

5.4.1 Happy Story

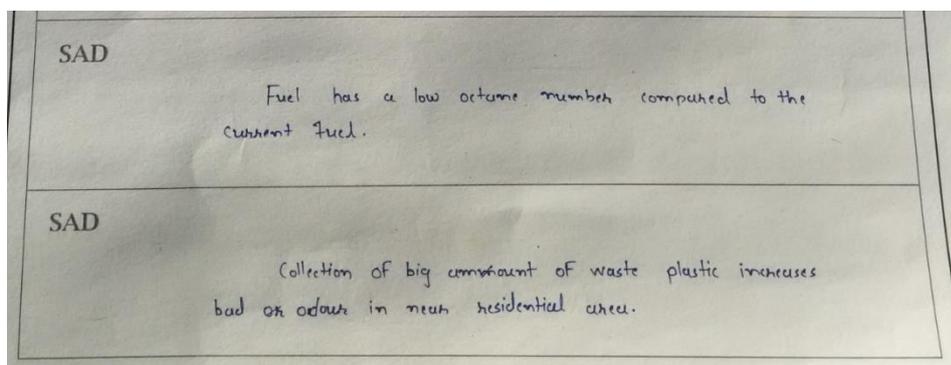
1. Fuel produced from waste plastic used as alternative fuel due to it is meeting the minimum requirement of current fuel.
2. Production of fuel from waste plastic is pure eco-friendly



[Fig. 5.4.1] Happy Story section of empathizing canvas.

5.4.2 Sad Story

1. Fuel produced from the waste plastics has a different color compared to the current fuel.
2. Fuel has a low octane number compared to the current fuel.



[Fig. 5.4.2]. Sad story section of empathizing canvas.

6. Ideation canvas

6.1 People

This involves people who are taking part in a study of Fuel from Waste Plastic.

1. Technician
2. Equipment Designer
3. Engineer
4. Labours
5. Garbage Collector

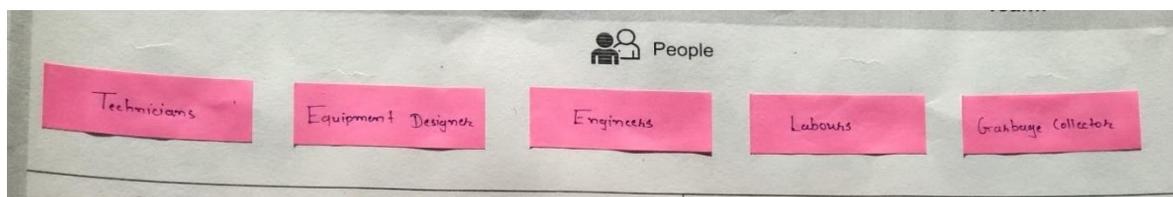
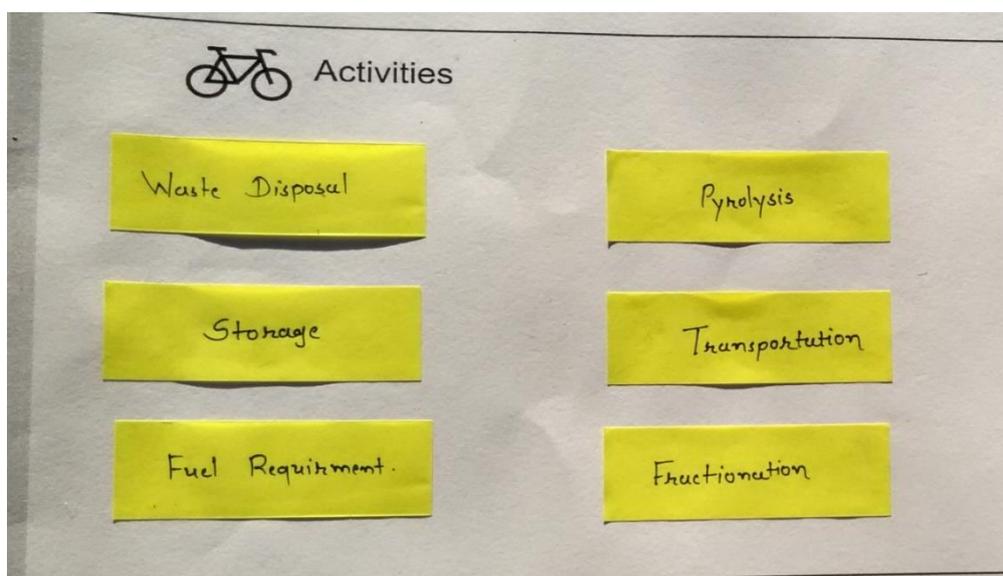


Fig. 6.1 People section of Ideation Canvas

6.2 Activities

This section has activities of all the people mentioned above in the “people” section of ideation canvas. What they may do in the study of Fuel from Waste Plastic is noted in the form of keyword.

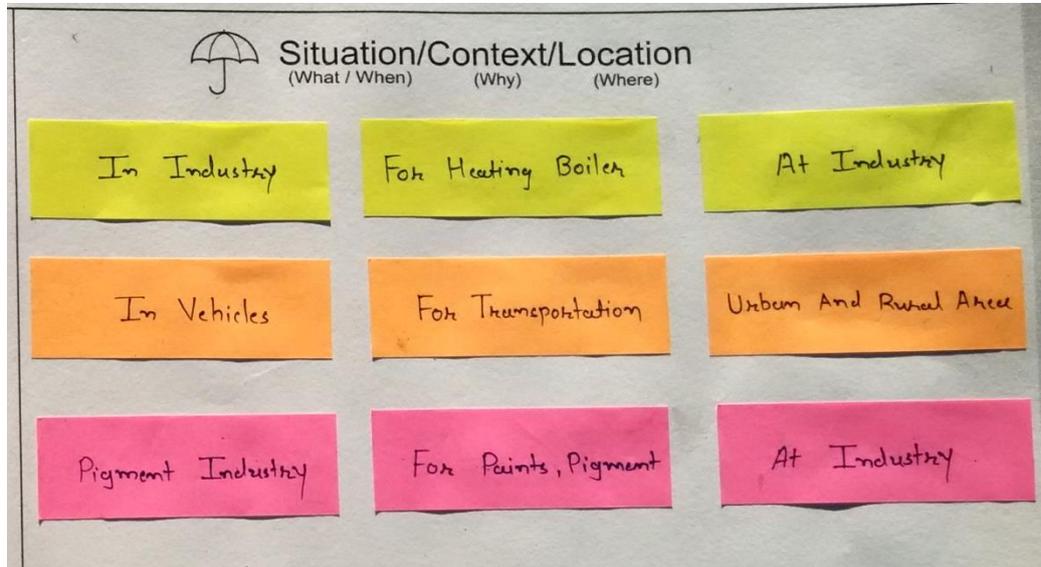
1. Waste Disposal
2. Storage
3. Fuel Requirement
4. Pyrolysis
5. Transportation
6. Fractionation



[Fig 6.2]. Activities section of ideation canvas

6.3 Situation/Context/Location

This section involves that mentioned detail of people and their activities is done in a particular time, like we need to find in which situation they have to do that activities.

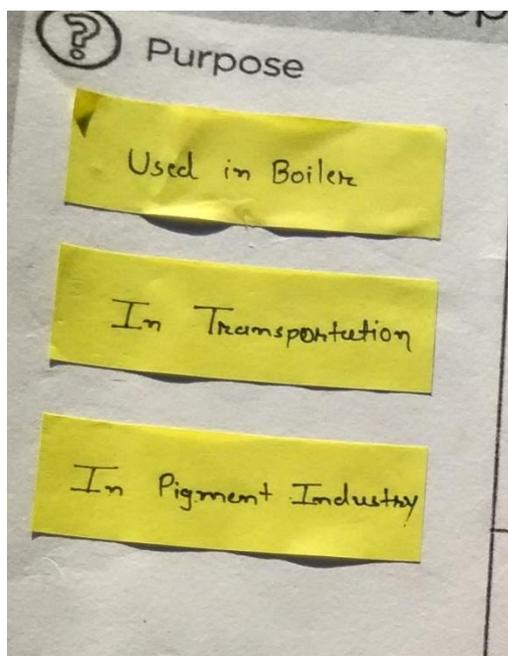


[Fig. 6.3]. Situation/Context/Location section of ideation canvas

7. PRODUCT DEVELOPMENT CANVAS

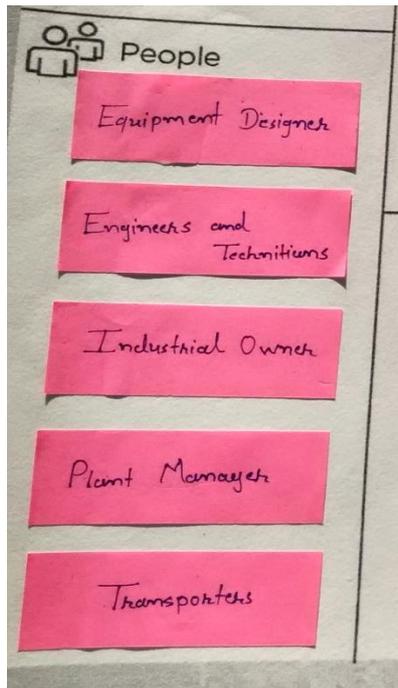
7.1 Purpose

Purpose of a study on Fuel from Waste Plastics



[Fig. 7.1]. Purpose section of product development canvas

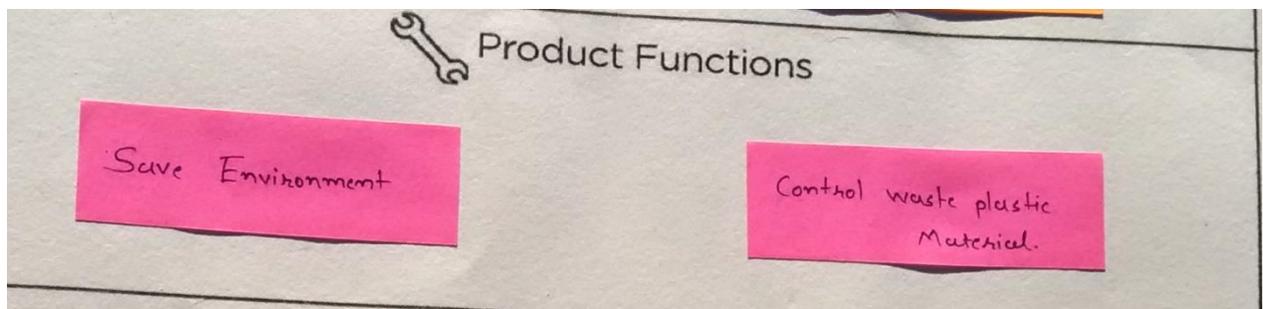
7.2 People



[Fig 7.2]. People section of product development canvas.

7.3 Product Function

This involves information about product function.

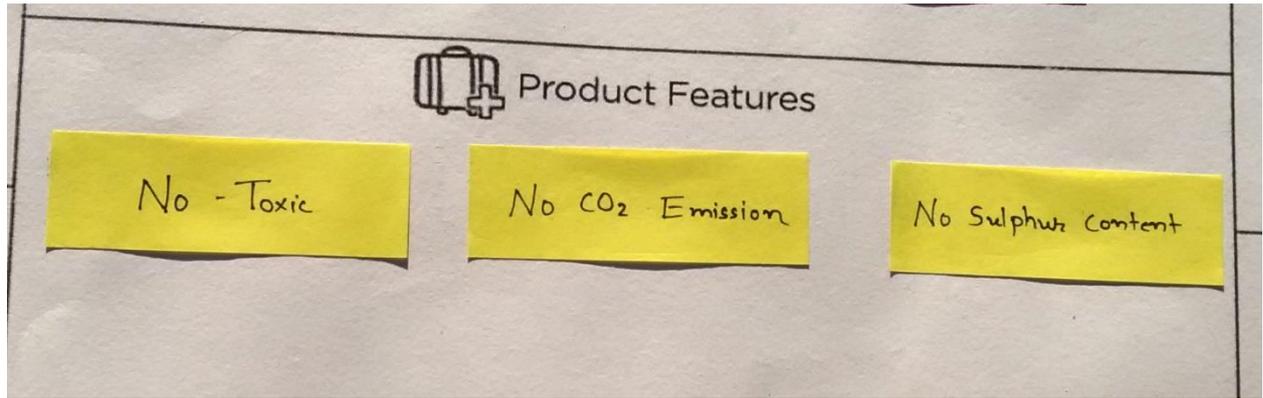


[Fig. 7.3]. Product functions section of product development canvas

7.4 Product Features

This contains details about features of the product.

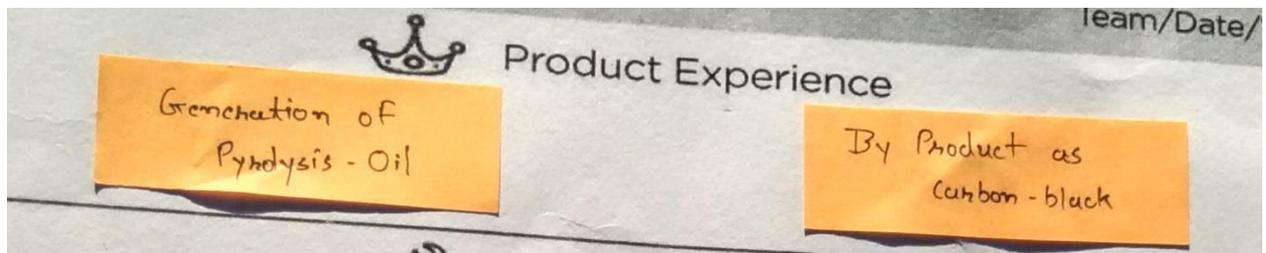
1. No toxic
2. No carbon dioxide emission
3. No sulfur content



[Fig 7.4] Product feature section of product development canvas

7.5 Product Experience

Experience of people while using this product what the product will do, main features of developed product.

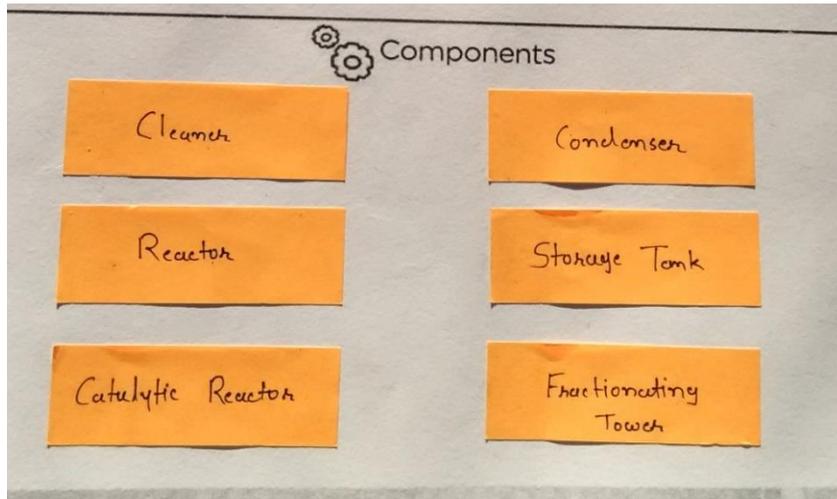


[Fig 7.5] Product experience section of product development canvas.

7.6 Components

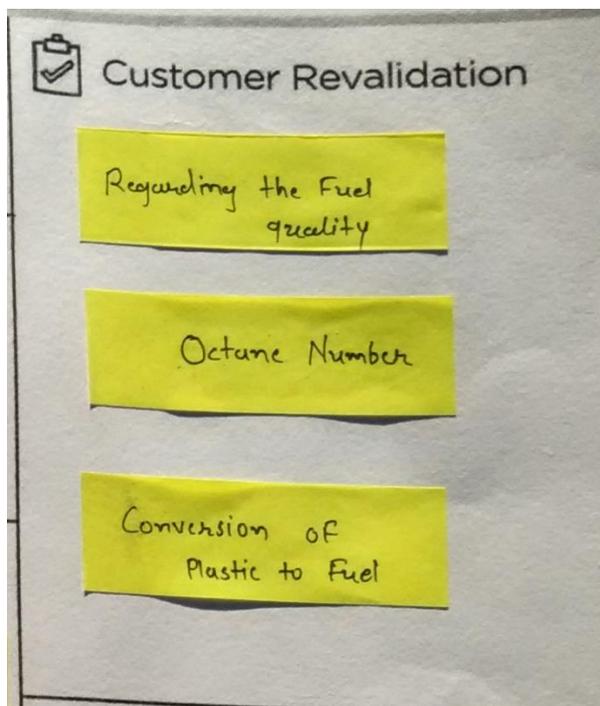
This involves the components for the development of the product.

1. Cleaner
2. Reactor
3. Catalytic Reactor
4. Condenser
5. Storage Tank
6. Fractionating Tower



[Fig 7.6] Components section in product development canvas.

7.7 Customer Revalidation



[Fig 7.7]. Customer revalidation section of product development canvas

8. Design of Process

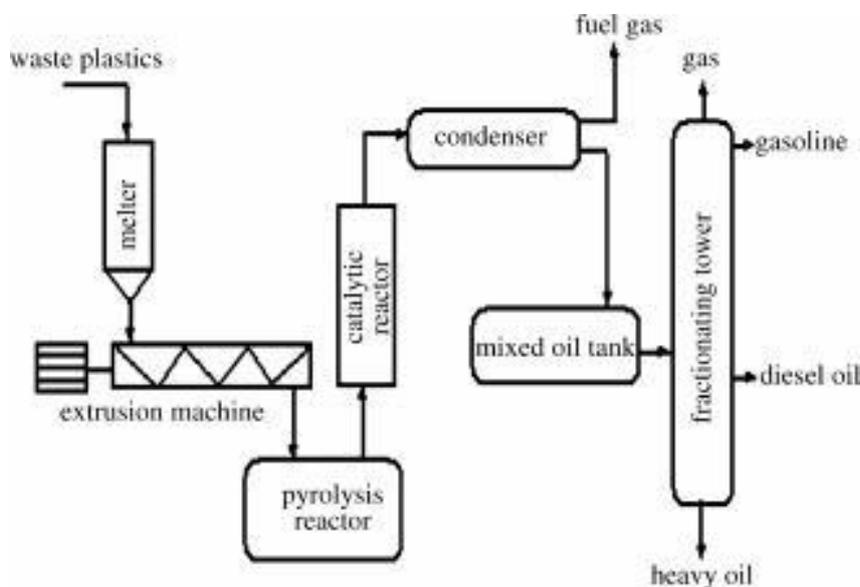
8.1 Principle of working

Pyrolysis is works on a principle of “Thermal-Catalytic Cracking”

“Long chain hydrocarbons are broken down into a simple molecules”.

In Pyrolysis process the long chain hydrocarbons (C_{200000} or more) are broken down into simpler molecules (C_{1-31}) at elevated temperature with or without use of catalyst in absence of oxygen.

8.2 Flowchart of process



[Fig. 8.2] Flowchart of thermal-catalyst cracking process.

In the process the Plastics wastes are first cleaned and then fed into the reactor where it will come in a contact with temperature of $300 - 475^{\circ}\text{C}$ and atmospheric pressure or the pressure which is slightly more than atmospheric pressure. In reactor plastic is converted into vapour form then come in a contact with catalyst in a catalytic reactor. After passing the catalytic reactor vapour goes in the condenser where it will be condensed to oil and other by-product will be also produce in the reactor like carbon-black, steel-wire, wax (those by-product can be by selecting on a proper catalyst). And the last oil produced is stored in the storage tank and go into fractionating tower where it will be divided into gas, gasoline, diesel, heavy oil and some other petrochemical products by the virtue of boiling point.

9. Cracking methods

1. Hydrocracking
2. Thermal Cracking
3. Catalytic Cracking

Hydrocracking

Hydrocracking of polymer waste typically involves reaction with hydrogen over a catalyst in a stirred batch autoclave at moderate temperatures and pressures (typically 423– 673 K and 3– 10 MPa hydrogen). The work reported, mainly focuses on obtaining a high quality gasoline starting from a wide range of feeds. Typical feeds include polyethylene, polyethylene terephthalate, polystyrene, polyvinyl chloride and mixed polymers, polymer waste from municipal solid waste and other sources, co-mixing of polymers with coal, co-mixing of polymers with different refinery oils such as vacuum gas–oil and scrap tyres alone or co processed with coal. To aid mixing and reaction, solvents such as 1-methyl naphthalene, tetralin and decalin have been used with some success. Several catalysts, classically used in refinery hydrocracking reactions, have been evaluated and include transition metals (e.g., Pt, Ni, Mo, Fe) supported on acid solids (such as alumina, amorphous silica–alumina, zeolites and sulphated zirconia). These catalysts incorporate both cracking and hydrogenation activities and although gasoline product range streams have been obtained, little information on effect of metal and catalyst, surface areas, Si/Al ratio or sensitivity to deactivation is quoted.

Thermal Cracking

Thermal cracking, or Pyrolysis, involves the degradation of the polymeric materials by heating in the absence of oxygen. The process is usually conducted at temperatures between 350 and 900 °C and results in the formation of a carbonized char (solid residues) and a volatile fraction that may be separated into condensable hydrocarbon oil consisting of paraffins, isoparaffins, olefins, naphthenes and aromatics, and a noncondensable high calorific value gas. The proportion of each fraction and their precise composition depends primarily on the nature of the plastic waste but also on process conditions. The extent and the nature of these reactions depend both on the reaction temperature and also on the residence of the products in the reaction zone, an aspect that is primarily affected by the reactor design. However, the thermal degradation of polymers to low molecular weight materials requires high temperatures and has a major drawback in that a very broad product range is obtained. Catalytic pyrolysis provides a means to address these problems.

Catalytic Cracking

In this method a suitable catalyst is used to carry out the cracking reaction. The presence of catalyst lowers the reaction temperature and time. In addition, catalytic degradation yields a much narrower product distribution of carbon atom number with a peak at lighter hydrocarbons and occurs at considerably lower temperatures. From an economic perspective, reducing the cost even further will make this process an even more attractive option. This option can be optimized by reuse of catalysts and the use of effective catalysts in lesser quantities. This method seem to be the most promising to be developed into a cost-effective commercial polymer recycling process to solve the acute environmental problem of plastic waste disposal.

10. Effect of reactor type on process

- Batch and semi-batch bed reactor,
- Fluidized bed reactor,
- Conical spouted bed reactor (CSBR),
- Fixed bed reactor,
- Two stages pyrolysis reactor,
- Screw kiln reactor,

Microwave assisted pyrolysis,
Pyrolysis in supercritical water, or
Fluid catalytic cracking (FCC) [8]

The type of reactor used determines mainly the quality of heat transfer, mixing, gas and liquid phase residence times, and the escape of primary products. A wide range of reactors have been used on a lab-scale in polyolefin pyrolysis. The reactor set-ups investigated so far under one of the following categories:

Batch reactor,
Semi-batch reactor

Continuous flow reactor (CFR), modifications or combinations of either of these. A common variable in batch and semi-batch operations is nitrogen which is used for the continuous removal of volatiles from the reactor vessel. The products are then collected by passing the vapors through a condensation system. Most are made out of Pyrex or stainless steel. A key disadvantage with this is the high reaction time observed. Furthermore, under batch operation, it seems that the potential of catalyst is minimized with similar product yields to thermal at similar conditions. From an industrial viewpoint, continuous reaction systems are preferred to batch set-ups for operational reasons [33, 34].

In fixed bed semi-batch reactor, polymer and catalyst samples are heated separately and reacted by vapor phase contact. Degraded polymer fragments are carried to the catalyst bed/mesh by a carrier gas, in most cases N_2 . Typically the catalyst bed is heated to a higher temperature than the polymer bed.

Riser simulator reactors are fluidized batch reactors, specifically designed to simulate similar conditions found in a catalytic riser reactor used in the FCC process. It is adapted for liquid phase catalytic reaction, in which heat from the catalysts could vaporize the melt polymer feed while simultaneously cracking the resulting hydrocarbons. During catalytic cracking, quartz sand is replaced by the respective FCC catalyst as packing material. Amongst the various catalysts investigated, FCCs produced the most decent liquid yields in polyethylene pyrolysis.

Unlike a batch reactor, a fluidized bed reactor is suited for pyrolysis because it provides very good heat and material transfer rates hence generating largely uniform products. However, the disadvantages are many and include: broad residence time distribution of solids due to intense mixing, attrition of bed internals and catalyst particles, difficulty in scale-up, defluidization problems, requires large amounts of catalysts, low liquid yields due to 'over cracking'.

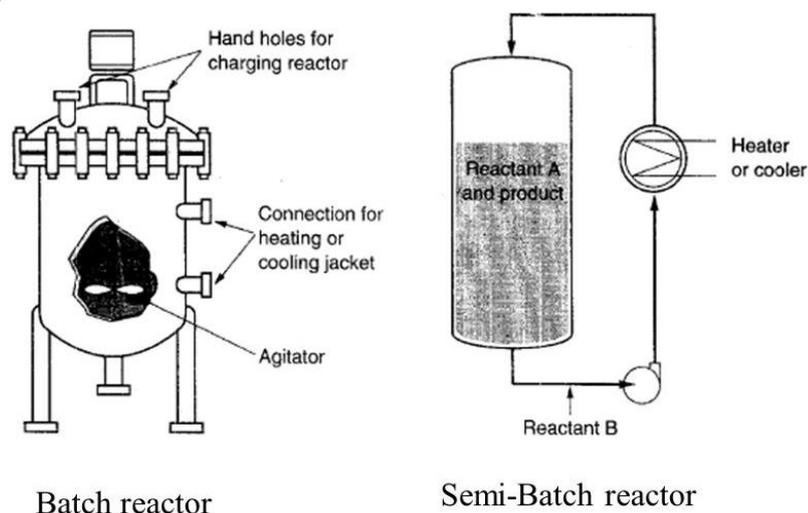
On the other hand, other continuous systems such as the three-step continuous flow pyrolysis process involving pre-heat, cracking reactor, and separation zone. In this method polymer is first pre-heated to a molten state in a CFR such as an extruder and driven into the reactor where it is further cracked at elevated temperatures.

[Table 10.1] Design of reactors and systems for polymer pyrolysis

Type of Reactor	Type of Material	References
Batch and semi-batch reactor	Mixture of LDPE and PP PE PP MSW and MPW	[35, 36] [37] [38,39] [40]
Fluidized bed reactor	LDPE and PP PVC MPW and MSW	[41] [42] [43]
Conical spouted bed reactor (CSBR)	Virgin LDPE Mixture of virgin LDPE, HDPE and PP	[44] [45]
Fixed bed reactor	PET PE	[46] [47]
Two stages pyrolysis reactor	Virgin LDPE	[20]
Screw kiln reactor	LDPE MPW	[48, 49] [50]
Microwave assisted pyrolysis	HDPE and toothpaste packaging HDPE waste, PP waste and tire PS waste from computer packing material Waste tire	[51] [52] [53] [54]
Pyrolysis in supercritical water	Residual oil and LDPE Heavy Oil	[55] [56]
Fluid catalytic cracking (FCC)	HDPE blended with gas vacuum oil (VGO) PB, PS, PS-polybutadiene (PBD) dissolved in light cycle oil (LCO) PS dissolved in benzene PE dissolved in toluene	[57] [58] [59] [60]

	LDPE dissolved in commercial VGO	[61]
	Cracking of HDPE in phenol	[62]

1. Batch and semi-batch reactor



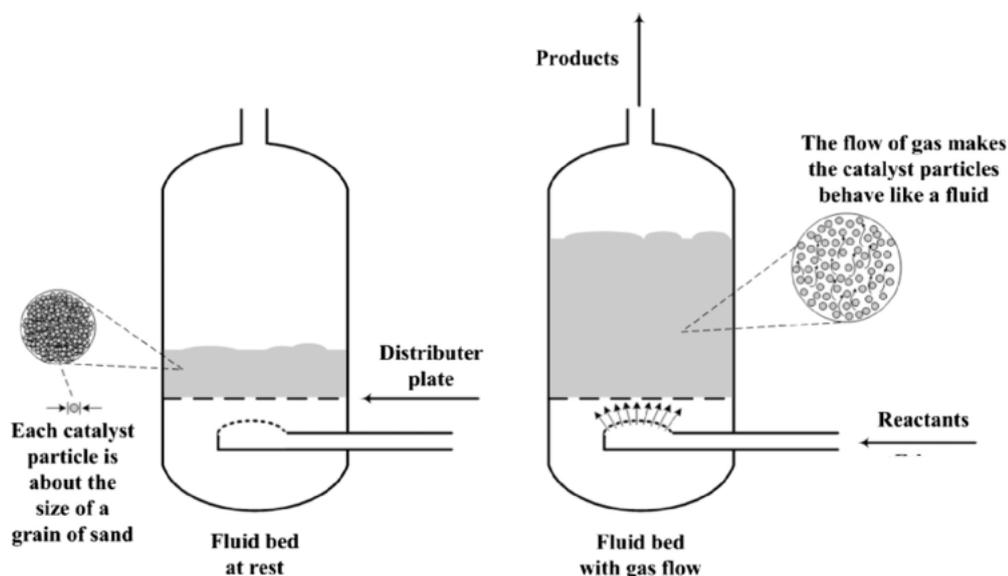
[Fig. 10.1] Batch and semi-batch reactor

In most researchers utilizes batch or semi-batch reactors for thermal and catalytic pyrolysis of virgin plastics, as well as consumer plastic wastes, as it is easy to control the process parameters. Some of the important parameters that were identified include reaction temperature, mass ratio of plastic:catalyst, and reaction time. The temperature used for the process ranged in 300-900 °C, and the reaction time 30-90 min [21, 29]. In case of catalytic pyrolysis, mass ratio of reactant:catalyst varied from 30:1 to 2:1 was used to increase the product yield and selectivity [21, 30]. This ratio used was based on the properties exhibited by the selected catalysts.

It is also possible to perform catalytic pyrolysis on polymer waste at low temperature [200-275 °C] [20]. The reaction was carried out in a locally manufactured reactor, with the volume of 1L. The reactor was added with a pressure valve. During the pyrolysis process, the production of condensable vapor and fuel gases exerted pressure on the pressure valve, and the valve opened at certain pressure to release these products into condenser and collection system. Thermal pyrolysis of LDPE bags at 275 °C produced 48.6 wt% of oil, 40.7 wt% gases and 10.1 wt% of char. This result was comparable to some thermal pyrolysis process in batch reactor [22] and fixed-bed reactor [81] in laboratories. Catalytic pyrolysis of the polymer waste using zeolite at 255 °C, on other hand, was able to produce 51.19 wt% of oil, 35.88 wt% of gases and 12.50% of waxes. The oil was identified to be a mixture of hydrocarbons in the range of kerosene and petrol, and could be used as fuel after upgrading. Further examination on the reaction conditions revealed that the exertion of pressure on the reaction system by the vapor and gases can be possible reason that increased the products yield at such low reaction temperature. Among the studies in catalytic pyrolysis of polymer, the one associated

with azoisobutylnitile (AIBN) as an initiator of plastic pyrolysis is worth mentioned. [82]. The use of AIBN produced higher conversion of HDPE, LDPE and PP when compared to thermal and even catalytic pyrolysis [17]. AIBN was also able to increase PET conversion compared to catalytic pyrolysis. It was deduced that AIBN forms radicals when heated, hence initiate pyrolysis via free radical mechanism. Due to low cost of AIBN (compared to other catalysts) and less harms it brings to the environment (it dissociated during pyrolysis, hence no problem of spent catalyst), the use of AIBN in pyrolysis is worth more attention in future studies.

2. Fluidized bed reactor



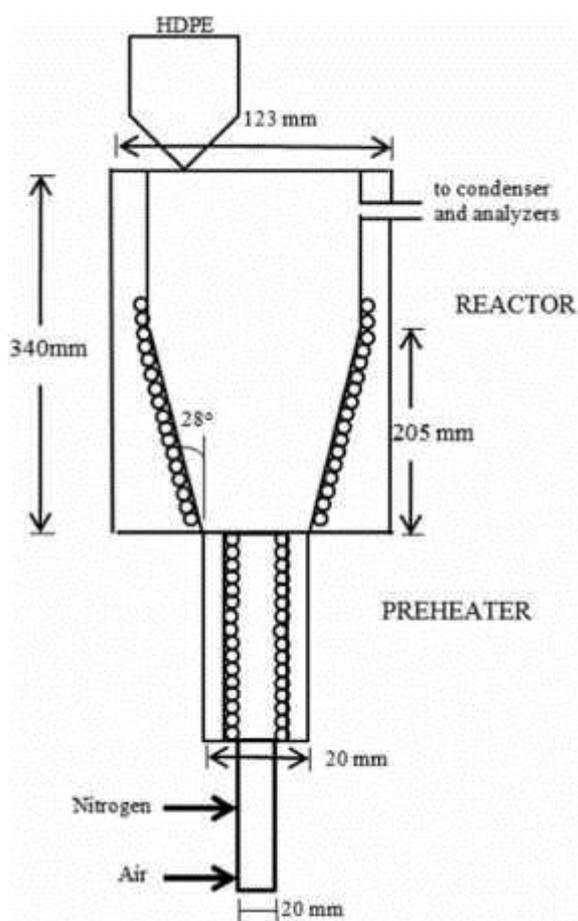
[Fig. 10.2] Fluidized bed reactor

Although pyrolysis of polymer waste in batch reactor is well studied, there is some drawbacks in its application in recycling industry [53]. It is more favorable to develop a continuous pyrolysis process, as it does not require frequent material charging and restarting the process. In addition, continuous pyrolysis process is also less labor-intensive. Trials were using fluidized bed reactors, due to several advantages they possess, including excellent mixing properties, as well as improved heat transfer from reactor to polymer, compared to batch reactors [46]. As polymer waste can be fed into reactor at constant temperature, it is possible to produce a narrower and more uniform spectrum of products by manipulating the residence time of polymer waste in the reactor [45]. It is also possible to periodically replace used catalyst with regenerated catalyst without halting the process [83]. However, care has to be taken to avoid bed defluidization, as this can easily when melted plastic stick on the fluidized bed.

Following the development of catalysts, thermal pyrolysis became less attractive in plastic waste recycling. Nonetheless, Marcilla and Gadcia [79] thermally cracked the LDPE-VGO blend in fluidized bed reactor to study its effect towards the products distribution. The sample, consisted of 2g of LDPE-VGO blend and 10g of sand, was pyrolyzed in 460g of sand at 500 °C. The proportion of LDPE and VGO were varied in the blend. From the result, the increase of LDPE percentage in the blend increased the

yields of dry gas and liquefied petroleum gas. The main components in the product gas were ethane and propene. It is important to realize that the temperature profile difference produced distinct effect on the products distribution, especially those from the pyrolysis of VGO oil. A decrease of the outlet temperature has significantly lowered the yield of heavy hydrocarbons. However, the effect became less significant with the increase of LDPE in the blend. Synergetic effect was not observed in this study, most probably due to the absence of catalyst which altered the reaction route. Thus, the experimental gas yield agreed with the theoretical yield, which was the addition of individual yield from LDPE and VGO respectively. The condensable products, on the other hand, showed a gradual decrease in yield with the increase of LDPE percentage in the blend. It is worth mentioned that without the use of catalyst, the pyrolysis of LDPE-VGO mixture could have the products yield comparable to the catalytic pyrolysis [77, 78]. When considering the reduction of costs in catalysts replacement and regeneration, this process might be feasible in term of economy. However, consideration from other aspects has to be taken into account.

3. Conical spouted bed reactor (CSBR)



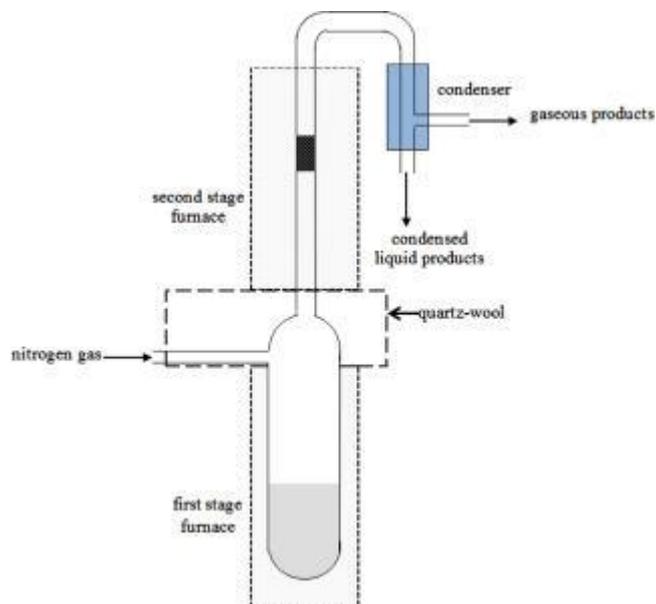
[Fig. 10.3] Conical spouted bed reactor

In order to avoid defluidization caused by melted plastic in the fluidized bed reactor, the use of CSBR was proposed, as the vigorous contact between different phases and collision between particles reduced the chance of particle agglomeration in the bed

materials. The extremely short residence time of polymer materials in CSBR is also important to avoid secondary reactions which lead to formation of coke precursor [53]. Another advantage of CSBR over other fluidized bed reactor is lower pressure drop. The schematic diagram of CSBR is showed in figure below.

When continuous thermal pyrolysis was performed on plastic waste at moderate temperature range in CSBR, waxes with high selectivity was reported [56]. The study on waxes produced from LDPE, HDPE and PP showed that they were rich in heavy cycle oil (HCO) fraction compared to gasoline fraction and light cycle oil (LCO) fraction. However, the percentage of the latter fraction increased with the pyrolysis temperature. It was also revealed that waxes that were produced at higher pyrolysis temperature has lower molecular weight compared to the waxes produced at lower temperature, irrespective to the type of plastic which they were produced from. This showed the existence of secondary and tertiary reactions during thermal pyrolysis, producing more hydrocarbons with shorter chains. The range of these short-chained products was also narrowed, results in lower pyrodipersity index. This observation demonstrated the ability of CSBR to produce wax with high selectivity at high temperature. On the other hand, the waxes produced at lower temperature were rich in paraffins, but the olefins content increased with temperature. The wax is suitable to undergo upgrading process in FCC units to produce gasoline, naphtha and other commercial hydrocarbons fractions.

4. Two-stage pyrolysis system

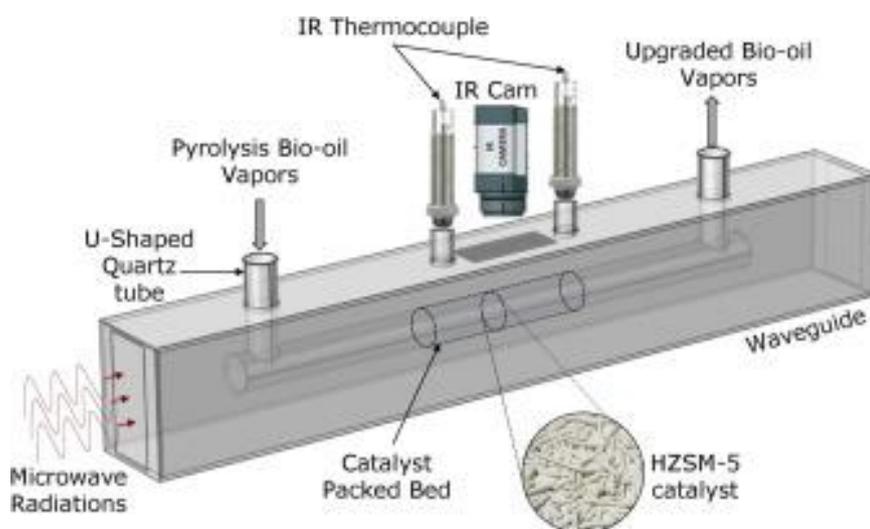


[Fig. 10.4] Two stage pyrolysis system

Despite of the advantages mentioned in the CSBR pyrolysis, the process tends to produce more wax rather than liquid and gaseous products. In order to improve pyrolysis performance associated with CSBR, a second reactor bed has been added to the existing reactor for further cracking of waxes from CSBR. This was able to produce gases and liquids with reported yields similar to other systems [84-85].

Another two-stage pyrolysis system was designed by Agaudo and Serrano [59], as shown in fig. In such design, the plastic waste was firstly melted and thermally cracked in the reactor at the bottom, and the vapor formed was then flown upwards and reacted with the catalyst on the fixed bed reactor. Such design avoided the direct contact of the catalysts with melted plastic, which causes several problems; difficulty in catalyst recovery after pyrolysis process, and rapid deactivation of catalyst when contacted with melted plastic, as well as impurities that are present. In such system, conversion of the polymer depended only on the temperature of the thermal reactor. Complete conversion of LDPE in such system was achieved in 475 °C, together with high liquid yield, with 16% product being grouped in light species, while 41% in gasoline fraction and 40% in diesel fraction. The use of HZSM-5 zeolites in the reactor was able to increase the cracking of gasoline to form more light species, due to the strong acidic sites that caused high rate of cracking. These studies demonstrated the feasibility of the two-stage thermo-catalytic reactors for the purpose of polymer pyrolysis to produce liquid products with the desired quality.

5. Microwave-assisted pyrolysis



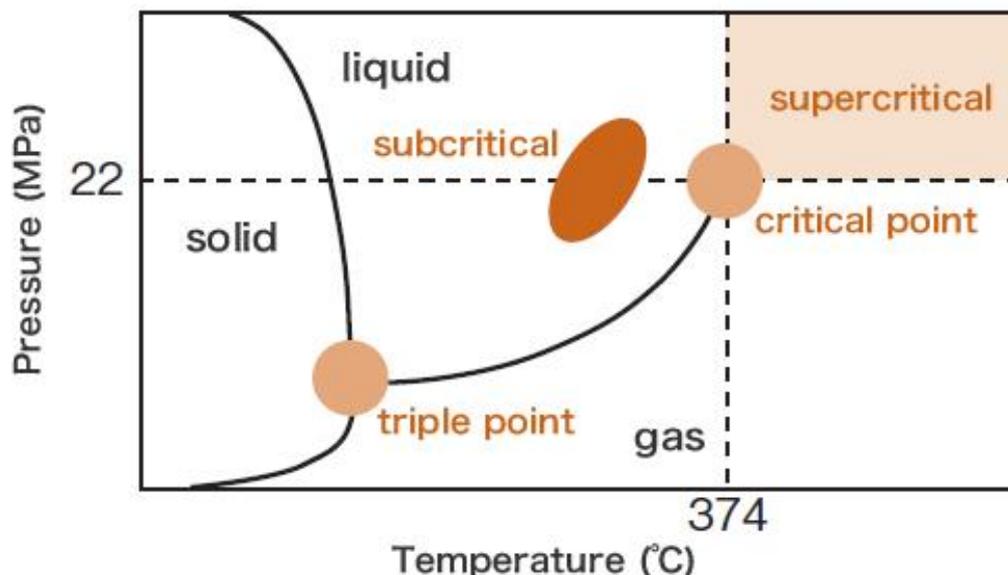
[Fig. 10.5] Microwave assisted pyrolysis system

Recently, microwave-assisted pyrolysis is receiving increasing attention from researchers, due to several advantages faster heating rate and cost effectiveness. One distinctive feature of MAP is the application of microwave power on polymer materials, which is converted into heat at fast rate. It is possible to raise the reaction temperature up to 1000 °C in a short period of time in MAP using microwave absorber, usually carbon material or metal [67]. The study of MAP started as early as 2001, when Ludlow-Parafox and Chase [65] pyrolyzed the HDPE and toothpaste packaging, which was a combination of aluminum and PVC. It was found that the increase in reaction temperature shortened the reaction time, but did not have much effect on the product distribution.

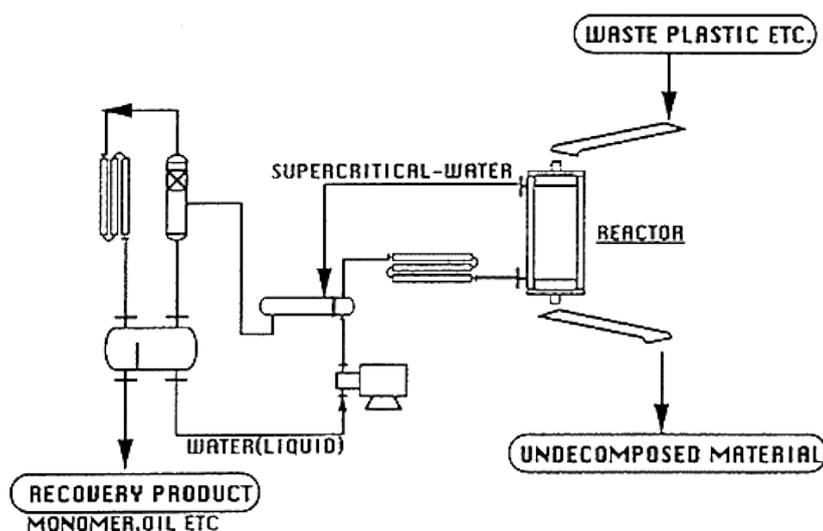
The shape of the absorbers plays important part in MAP, as it affects the amount of heat generated from the microwave.

Microwave-assisted co-pyrolysis of waste PS with coal was also reported to produce aromatic liquid products in narrow range, together with acetylene and hydrogen sulphide as a gaseous products [68]. Other than polymer waste, MAP can also be used to produce fuels from agricultural waste [86] and tire waste [69-71]. Although reviews on MAP different types of plastic waste, as well as the effect of catalysts in MAP. The effect of interaction of different types of plastic waste on the products distribution in MAP is also an important feature to be explored.

6. *Pyrolysis in supercritical water*



[Fig. 10.6.1] Supercritical and subcritical condition of water in phase diagram



[Fig. 10.6.2] Pyrolysis in supercritical water.

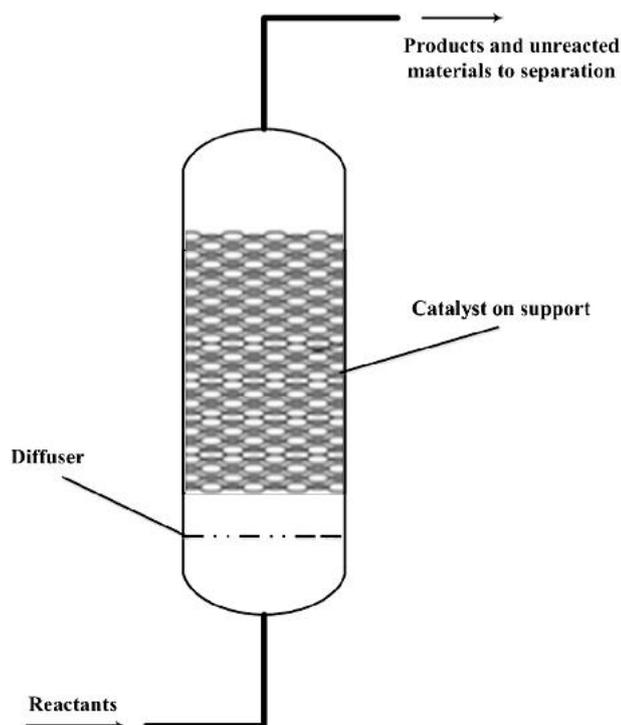
The use of sub-critical water (CW) system and supercritical water system (SCW), which are usually used in the cracking of heavy oil [89], was also attempted in plastic recycling, as supercritical water behaves as solvent and catalyst simultaneously in the

process [72, 90]. The small hydrocarbons molecules formed during polymer pyrolysis can easily disperse in SCW, hence the chance of subsequent condensation and coke formation is reduced [73, 91]. Excellent property of debromination was also discovered during pyrolysis of brominated polymer waste [92, 93]. The use of SCW in polymer waste pyrolysis also produce negligible amount of NO_x , SO_x and particulate emission [94]. On the other hand, the possibility of using CW and SCW system in polymer pyrolysis was also studied by Bai, Zhu [72]. During pyrolysis, the phase structure of residual oil/LDPE alternated between liquid/liquid/solid three-phase structure, partially miscible oil phase and water phase were in dynamic equilibrium, and LDPE was mostly suspended in the oil phase. In latter structure, oil containing saturates, aromatics and resins formed a continuous medium with CW or SCW. While asphaltene molecules were highly dispersed. At high water densities (liquid/solid phase structure), pyrolysis products from LDPE caused dealkylation of aromatic radicals that were produced from asphaltenes, hence the coke-inducing components were suppressed.

Another study on the similar process and system [73] revealed that extension of reaction time resulted in improved liquid product quality, but coke formation also increased. It was proposed that coke was formed from condensed asphaltenes, which existed in heavy oil itself, or formed from condensation of light oil fractions. Further data comparison revealed that coke formation seemed to be retarded at later reaction stage. Increased LDPE loading in co-pyrolysis also caused reduction in coke formation and increased aromatics formation. This is an evidence of LDPE as source of H in co-pyrolysis. Due to donation of H from LDPE to pyrolysis intermediates from heavy oil, condensation of the intermediates (that caused coke formation) can be suppressed. It was also found that release of LDPE oligomers was independent of heavy oil pyrolysis. However, the H-donating effect from LDPE can only occur with sufficient distribution of products from LDPE pyrolysis.

7. *Fixed bed reactor*

Fixed-bed reactor have been used in process industries. They contain catalyst, typically in pellet form, packed in a static bed. The gas is then passed through the bed, where the reactions are induced as the gases contact the catalyst. Originally, fixed-bed reactors were only commercially viable reactor type due to technological limitations. However, they also presented drawbacks mainly in the constraints existing in access to the catalyst material. Since the gas has to pass over the material the reaction is limited by the available surface area. This problem can be reduced by allowing more than one “bed” in the reactor for the gas to pass over, under and/or through. The catalysts in the fixed-bed reactors do not need to be as resilient, as they do not move in the bed. For the common situation encountered when a reaction process is exothermic, fixed-bed reactors demand cooling of the bed.

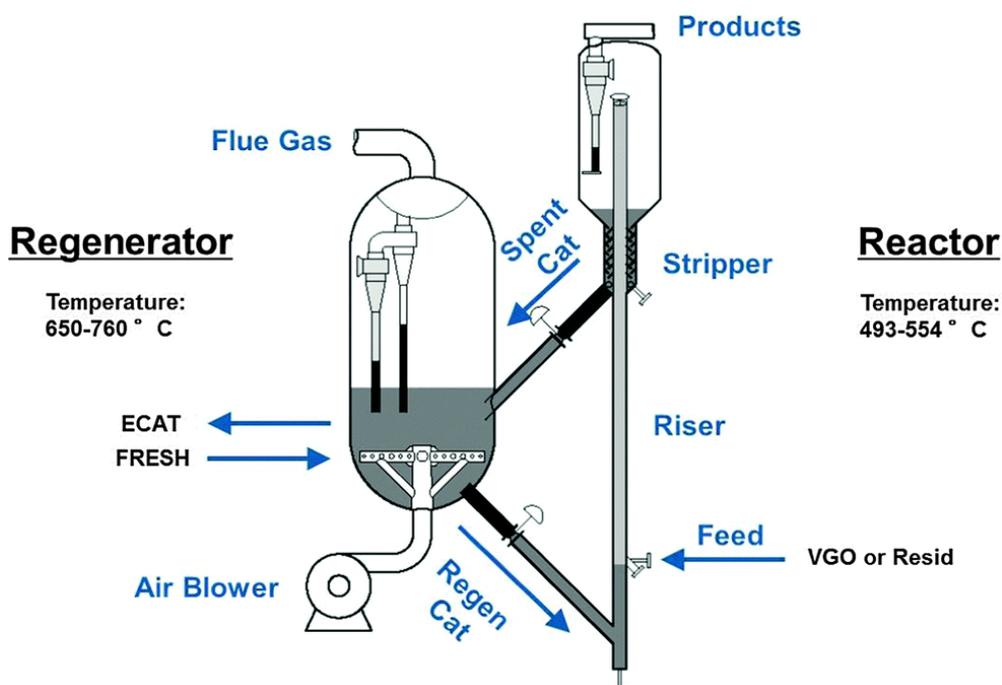


[Fig. 10.7] Fixed bed reactor.

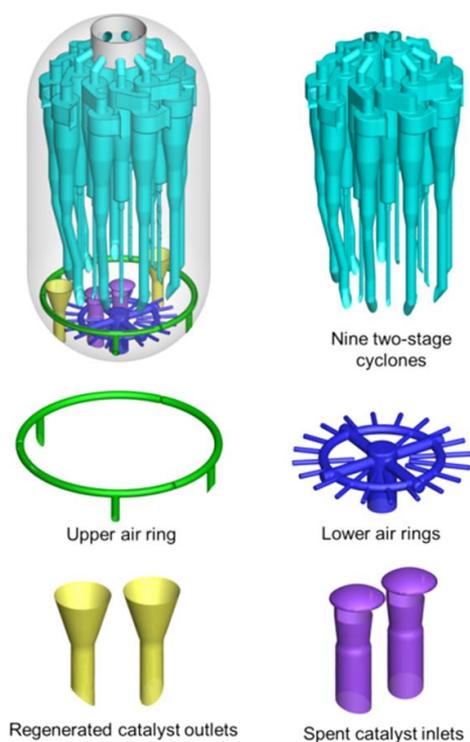
If the excess heat is not dissipated from the reactor bed, it could eventually lead to deterioration and deactivation of the catalyst material.

8. *Fluid catalytic cracking*

Following the development of pyrolysis technology, there is a need to develop continuous process for polymer pyrolysis before it can be applied in scalable production in the industries. However, one of the challenges faced is the continuous feeding of plastic waste in solid form into the reactor. In order to solve this problem, some researchers look into the possibility of dissolving plastic feed in suitable solvent, following by pyrolysis of the solution. Ng [74, 98] performed catalytic pyrolysis of the HDPE resin pellets dissolved in the vacuum gas oil (VGO), the conversion of HDPE was up to 77.4% (for 5 wt% HDPE concentration) and 52.4% (for 10 wt% HDPE concentration) respectively. It was also discovered that when the ratio of catalyst to oil increased, generally there was an increase in conversion and yield of products (dry gas, liquefied petroleum gas, gasoline, light cycle oil, heavy cycle oil and coke), although not in linear form. A synergistic effect was also observed in the pyrolysis of HDPE-VGO causing different conversion of VGO under the presence of HDPE, compared to the conversion of VGO alone under the same conditions.



[Fig. 10.8.1] Fluid catalytic cracking reactor side view.



[Fig. 10.8.2] Inner view of fluid catalytic cracking reactor

The rationale of investigating the plastic dissolution in solvent is to incorporate the tertiary recycling process in the fluid catalytic cracking (FCC) process in the petroleum refinery. In order to study the viability of this idea, Arandes and Abajo [75] dissolved PP, PS and PS-PBD in the light cycle oil (LCO) which is used in a commercial FCC unit. Almost complete conversion in thermal pyrolysis of the plastic was observed at 550 °C, where gases, gasoline and cokes were formed. PP tended to produce olefins and isoparaffins during the thermal pyrolysis, while thermal pyrolysis of PS produced

mainly styrene, together with small amount of ethylbenzene, toluene and benzene. The same observation was obtained for thermal pyrolysis of PS-PBD. On the other hand, catalytic pyrolysis using commercial catalyst produced almost the same products yields for PS and PS-PBD, with only minor difference with respect to certain products. Similar result was obtained when HZSM-5 [99] and HY zeolites [100] were used as the catalysts in the reaction. It was also discovered that the use of fresh catalyst in the reaction did not produce higher conversion compared to used catalyst, and higher acidity in fresh catalyst caused higher coke formation.

The possible effect of solvents used to dissolve plastic was studied by several researchers. It was shown that benzene did not react with polymer or decompose to form hydrocarbon molecules at temperature up to 550 °C [76]. On the other hand, when toluene was used as solvent, it disproportioned to form benzene and xylene. But did not react with polymer or its pyrolysis products [77]. Another study using phenol as solvent indicated that the polymer degradation was increased in the presence of phenol, as phenoxy radicals formed during pyrolysis enhanced the pyrolysis rate via free radical mechanism [80].

A more detailed study was carried out on the process mentioned above, but with different solvent [78], LDPE dissolved in vacuum gas oil (VGO) at 2% and 6% was catalytically cracked using two equilibrium catalysts, namely E-cat-M and E-cat-R. It was found that LDPE conversion increased with temperature, and did not change much with LDPE concentration. However, difference in pyrolysis behavior over different temperature suggested that the LDPE has higher activation energy compared to VGO. Analysis on different categories of products showed the increase of dry gas, LPG and gasoline yield at 10-12%. The coke formation also showed the same trend, however, it was limited to 7.7% for E-cat-R, and thus it should not affect the heat balance in the FCC unit, but a detailed study is required before it can be applied in a scalable production in the industry.

The advantages of using fluid catalytic cracking in polymer pyrolysis include [101]:

- a. Dissolution of plastic waste in the solvent increases its bulk density, hence reduce volume of the plastic waste prior to the process.
- b. The contaminants can be removed during the dissolution stage, hence the negative effect by these contaminants towards pyrolysis performance can be reduced.
- c. Separation of mixed plastic to different components is believed to be vital, as it is often reported that pyrolysis of single type of plastic is higher than that for mixed plastic. It is possible to separate mixed plastic waste to their components by using selective dissolution as introduced by Papaspyrides and Poulakis [101]. This is possible as different plastic can only dissolve in certain solvent at specified temperature range. This provides an alternative over manual sorting of plastic waste that require extra effort to separate by mechanical means (for example certain HDPE bottles that have caps or plastic label which are made of LDPE).
- d. Value added activities for petroleum refining companies that engaged in this type of plastic recycling.

However, some limitations are observed where large scale application of this method is considered:

- a. Pretreatment is needed to clear the contaminants in the municipal plastic waste. To ensure the efficiency of the process, the presence of the contaminants has to be minimized during the solvent recovery at the expense of other useful products that can be extracted from the solution.
- b. Since most solvents are volatile, dissolution process has to be done with extra safety measures.
- c. The reaction data and the kinematic models are not available yet, and this may cause considerable difficulties in reactor design.
- d. Since the use of solvent was observed to affect the pyrolysis mechanism, suitable solvent has to be selected to ensure positive influence towards the products yield and distribution.

[Table 10.2] Product yields for pyrolysis via different pyrolysis systems

Type of reactor and/or system	Type of materials	Parameters	Yield of gas (G), liquid (L), aqueous (A), wax (W) and solid (S)	Ref.
Batch and semi-batch reactor	Mixture of LDPE and PP	H ₂ , 400 °C, Ni/HZSM-5, 90 minutes	54% L.	[36]
	PE	460 °C, HZSM-5, 30 minutes	40% G, 55% L, 5% S	[63]
	Cleaned PP waste	360 °C, HZSM-5, reaction proceed until no products evolved	2% G, 92% L, 6% S	[64]
	PP	430 °C, 60 minutes	4.3% G, 80.7% L, 1% S	[39]
	PVC containing waste	1 dm ³ N ₂ /min, dechlorination at 300 °C using CaCO ₃ as dechlorination agent, then heating to 500 °C	36.6% G, 62.4% L, 1% S	[65]
	MSW	500 °C, HZSM-5, 57-72 minutes	20% G, 19% L, 17% W, 44% S	[40]
	MPW		35% G, 45% L, 21% S	
	MPW	500 °C, no-catalyst, 30 minutes	41.5%, 53% L, 5.5% S	[38]
	MSW rich in film		65.7% L, 26.5% G, 7.8% S	
	MSW rich in paper		26% G, 35.1% L, 12.4% A, 26.6% S	
	MSW rich in glass		25.6% G, 40.9% L, 33.5% S	
	MSW rich in film	440 °C, ZSM-5, 30 minutes	49.9% G, 41.5% L, 8.6% S	[65]
	MSW rich in paper		29.4% G, 25.5% L, 17.1% A, 28.1% S	
	MSW rich in glass		13.8% G, 39.2% L, 3.3% A, 43.7% S	

Fluidized bed reactor	LDPE and PP	680 °C, quartz sand fluidizing bed, product gas as fluidizing gas	42.8% G, 56.7% L, 0.5% S	[41]
	MPW	360 °C, MCM-41 as catalyst bed, 570 ml N_2 /min	87.3% G, 5.6% L, 7.1% S	[43]
	MPW	677 °C, 6.7 g N_2 /min, quartz sand as fluidized bed, no dechlorination agent	35.3%, 57.8%, 6.9%	[66]
	Mixed polymer	600 °C, hard burnt lime as fluidizing bed, 5 L stream/min	43% G, 49% L, 8% S	[67]
CSBR	HDPE	12 L N_2 /min, 500 °C, HY zeolite as catalyst bed, 1 g plastic/min	24.4% G, 72.56% L, 3% S	[68]
		N_2 , 650 °C, sand as fluidizing bed, 1 g plastic/min	18% G, 46% L, 36% W	[44]
	Mixture of virgin LDPE, HDPE and PP	11 L N_2 /min, 450-600 °C, sand as fluidizing bed, 1g plastic/min	100% W	[45]
Two stages pyrolysis system	HDPE (CSBR + thermal cracking)	CSBR: 5 L N_2 /min, 500 °C, sand as fluidized bed, 1 g plastic/min	CSBR: 1.5% G, 31.5% L, 67% W	[69]
		Cracking reactor: 900 °C	After thermal cracking: 41% G, 59% L	
		CSBR: 5 L N_2 /min, sand as fluidized bed, 500 °C, 1 g plastic/min	CSBR: 1.5% G, 31.5% L, 67% W	[70]
	MPW (Batch pyrolysis + catalytic cracking)	Cracking reactor: HZSM-5, 500 °C	After catalytic cracking: 41% G, 59% L	
		Reactor 1: 450 °C, 120 min.	After pyrolysis: not given	[71]
		Reactor 2: N_2 , 450 °C, no catalyst	After cracking: 18% G, 74% L, 8% S	
		MSW (pyrolysis in tubular reactor + batch catalytic cracking)	Reactor 1: 550 °C	After pyrolysis: 10.2% G, 67.3% L, 4.1% W, 18.4% S
Reactor 2: 450 °C, 45 min., FCC catalyst	After cracking: 9.7% G, 74.6%, 0.5% W, 15.2% S			
Microwave assisted pyrolysis	HDPE and toothpaste packaging	500 °C, reaction proceed till completion	19% G, 81% L, 100% recovery of metal	[51]
	HDPE waste	40 min, 500 °C	34.4% W, 56.5% L, 9.1% S	[52]
	PS waste	Temperature not specified, 10 min.	10% G, 88% L, 2% S	[53]
Pyrolysis in supercritical water	Residue oil and PE	420 °C, 20 min	90% L, 10% S	[55]
	Heavy oil and LDPE	420 °C, 30 min	85% L, 15% S	[56]

Fluid catalytic cracking (FCC)	PS dissolved in benzene	6.5 wt% polymer in benzene, FCC catalyst, 550 °C, retention time: 9 second	5.97% G, 94.03% L	[59]
	PE dissolved in toluene	2 wt% polymer in toluene, FCC catalyst, 500 °C, retention time: 3 second	10.2% G, 84% L, 4.8% S	[60]
	Cracking of HDPE blended with Phenol	400 °C, 5 hours	52.5% G, 43.5% L, 4% S	[62]
The term “solid” include solid residue, char and coke that remained after pyrolysis The term “aqueous” include water and hydrocarbons dissolved in it. All processes proceed in nitrogen atmosphere unless stated otherwise.				

11. Effect of catalyst contact mode

One may investigate the catalytic steps involved in polymer degradation by considering different mode of catalyst introduction to the polymer feed. Sakata et al. [17] investigated two modes of contact in the batch pyrolysis of polypropylene using various solid acids: “liquid phase contact” and “vapor phase contact”. For the catalytic degradation in the liquid phase contact, both catalyst and polymer are placed in the reactor and heated to the operating temperature. Whereas, with the vapor phase contact mode, the polymer is first thermally degraded into hydrocarbon vapors and then contacted with the catalyst. It has been observed that liquid phase pyrolysis retards the escape of evolving products, thus enhancing interactions and hydrocarbon vapors undergo further cracking in the vapor phase whereas the product yield in the liquid or melt phase contact is reported not to be differ significantly from that obtained by purely thermal degradation of polypropylene [25].

12. Effect of particle/crystalline size of catalyst on product distribution

The effect of catalyst particle size has only been sparsely studied in literature. You et al. [73] investigated the effect of particle size of zeolites on the catalytic degradation of polyethylene wax and found that whereas conversion decreased with particle size, product quality increased. Furthermore, particle sizes in the nano range have been investigated. Serrano et al. [74] reported conversions as high as 90%, temperature less than 350 °C for the cracking of polypropylene, LDPE and HDPE using nano crystalline ZSM-5. Aguado et al. [75] observed similar results in the batch pyrolysis of polypropylene and LDPE mixtures using nano HZSM-5. Based on these results, it can be deduced that nano-ZSM-5 catalyzed reactions result in very high gas yields in the range of $C_3 - C_6$ products, and apparently in much higher concentration than is observed with micro-sized ZSM-5. These nano-sized particles are so effective because of their increased surface area. Conversely, high surface area combined with a very small pore system poses great difficulty in achieving decent amounts of gasoline range products in the $C_5 - C_{12}$ range. So, the nano-catalyst selectivity to liquid products is also very limited [76]. This could be resolved by investigating the particle size effect with catalysts that are selective to gasoline range liquid products such as FCC catalysts.

13. Effect of feed composition (type of polymer) on the product yield and distribution

The primary pyrolysis products relates directly to the chemical structure and decomposition of the resin, and also to the mechanism of its decomposition (Purely thermal or catalytic). In general, the decomposition of polyolefin mixtures occurs roughly in the same range as their virgin counterparts (350–500 °C). However, waste polyolefin may degrade at slightly lower temperatures and achieve higher conversions than the respective virgin polyolefin [77]. As with

virgin plastics, the addition of catalysts in waste pyrolysis greatly influence product yields and conversion rates; however, the disparities between waste and virgin polyolefin pyrolysis lie mainly in the resulting product compositions [78]. It is clear that during pyrolysis, interactions between the different materials in a waste feed have a significant effect on the selectivity of specific liquid and gaseous product components. Pyrolysis of plastics yields liquid, gas and solid residue products. Liquid product yields greater than 82.5% and as high as 96% have been found for polyethylene and polypropylene 240 A.K. Panda et al. / Renewable and Sustainable Energy Reviews 14 (2010) 233–248 pyrolysis; however, these are obtained at high temperatures and within a reaction time of approximately one hour. Polyethylene and polypropylene decomposes in to a range of paraffin and olefins and the paraffin to olefin ratio decreases with increase temperature and time [25]. PONA distributions of FCC catalyzed decompositions show that the olefin yield far exceeds the yield of paraffins, naphthenes, or aromatics (PNAs) in the pyrolysis of polypropylene and HDPE. Lee et al. [79] also showed that the catalytic degradation of waste LDPE produced more paraffins and aromatics than those of waste HDPE and polypropylene. The pyrolysis of polyethylene and polypropylene is characterized by low monomer yield, whereas polystyrene mostly gives monomeric units as the main product. Polystyrene pyrolysis exhibits high yields of aromatics, as high as 97 wt% of liquid product [79]. This is attributed to the polycyclic nature of polystyrene and the thermodynamic challenge posed in converting cyclic compounds to aliphatic chains or alkene compounds. A closer look at the aromatic yield in many of these catalyzed reactions reveals that, the product selectivity is higher for benzene, toluene and ethyl benzene unlike in thermal pyrolysis, where the main product is styrene. Again, the results obtained in the thermal depolymerisation of polymethylmethacrylate are noteworthy since at 723 K, a 98% yield to the monomer has been reported. Mixture of polyethylene and polystyrene decomposes as usual in the case of polystyrene, with the pyrolysis yield somewhat more saturated, the polyethylene providing the required hydrogen. The decomposition of the polyethylene is somewhat accelerated by the presence of polystyrene [25]. This has been explained due to the radicals formed during polystyrene decomposition. The conversions of polyethylene and polypropylene are improved by polystyrene addition. Conversely, polystyrene decomposition seems to be immune to effects by either of the other polyolefins. Typically, polyethylene pyrolysis favors mostly the formation of paraffins; however, upon increasing its polystyrene or polypropylene content, the yield of aromatic and alkenic products is greatly enhanced, thus improving its octane value [80]. This clearly indicates the similarity and variance in the cracking mechanisms in different polyolefins.

14. Effect of catalyst loading

Ultrastable-Y Zeolite (USY),
Y-Zeolite,
Mordenite,
 β -Zeolite, or
ZSM-5 [5]

The use of catalyst loading in pyrolysis of plastics influences upon kinetics and mechanism, and hence, the product distribution, conversion increases with catalyst loading. The most commonly researched solid acid catalysts in plastic waste pyrolysis include molecular sieves, such as silica, alumina, zeolites and MCM-4.

Among the numerous kind of zeolites investigated in polyolefin pyrolysis, Beta, USY, ZSM-11, REY, Mordenite, ZSM-5 are most commonly used. Reports on the FCC process are also found in literature. Other catalytic material such as clays (montmorillonite, saponite), reforming catalysts, activated carbon, metal oxides, metal complexes and alkali metal carbonates or alkaline metal carbonates have also been tested for polymer degradation. The most common feature shared by the different zeolite catalysts are proper acid strength, pore size and pore structure. Generally, the level of the catalysts activity in polyolefin pyrolysis increases with increasing number of acid sites. Thus, zeolite based catalysts achieve higher conversion than non-zeolite based catalysts. The effect of some specific zeolite and other catalysts used by the different researchers for plastic pyrolysis is as summarized below.

The product distribution of the catalyst degradation of high density polyethylene on different zeolites yields hydrocarbons from C_3 to C_{15} . The structure of the zeolite framework has been shown a significant influence on the product distribution. Alkanes are the major products with US-Y, Y and Beta-Zeolite, whereas alkenes are the major products with mordenite and ZSM-5. The majority alkanes are reported to be isoparaffins, having a high octane number; this speaks for an increased fuel quality. A small amount of cycloproducts and aromatics are formed on all samples. This is an important advantage of catalytic degradation, as environment concern about aromatics grows and strict legislation for low levels of aromatics in fuels is under discussion [10].

The conversion of polyethylene to transportation fuel using *REY (Rare earth Y)* catalyst (7.8 Å size and 11.8 Å supercage) in addition to other acid and non-acid catalysts. REY is reported to best oil conversion, gasoline yield, and research octane number of gasoline. It is concluded that the performance of REY zeolite is attribute to its stability, adequate acidity, and relatively large pores into which oil molecules are allowed to penetrate [11].

The catalytic degradation of high-density polyethylene on *Ultrastable-Y* zeolite has significantly reduced the degradation temperature compared with pure thermal degradation in absence of catalyst. The product of the catalytic degradation were hydrocarbons in the gasoline range (C_3 to C_{15}) were the heaviest detected product. The majority of the products are isoparaffins, suggesting high octane number, speaks a high quality fuel as a product of a catalytic degradation process [12].

Thermal degradation on clinoptilolite showed high amount of residues, but the proton exchanged clinoptilolite showed practically no formation of residue. Pore volume is another important character for the further cracking of initially degraded fragments [13].

Pyrolysis of polyethylene using *ZSM-5* yields greater percentage of gaseous products than oil. This extraordinary and a unique larger intracrystalline pore channel structure of *ZSM-5* which helps in excellent catalytic efficiency on cracking, isomerization, aromatization. The larger intracrystalline pore channel structure allows more cracking of the heavy petroleum chemicals. In addition, *ZSM-5* possess a smaller pore diameter (5.4 – 5.6 Å) among zeolites. Since the initially degraded materials on the external surface of catalyst can be dispersed into the smaller internal cavities of catalyst, they can be further degraded to the

smaller size of gaseous hydrocarbons, leading to the remarkably high yield production of gaseous material [14, 15].

Mordenite is reported to enhance the rate of pyrolysis reaction, but it produce much greater fraction of (C_{11} to C_{13}) paraffins and greatest amount of coke explained due to its bottleneck crystalline structure [14].

With *silica-alumina* (SA), all of the polyethylene is found to be converted to liquid products with high yield (77-23 wt%) and without any wax production. The liquid products were distributed in the range of n- C_5 to n- C_{20} and mostly n- C_5 to n- C_{20} [16]. Silica-alumina also reported to increase the olefin content in oil product. The effect of silica-alumina SA-1 (SiO_2/Al_2O_3 ratios of 83.3/16.7) and silica-alumina SA-2 (SiO_2/Al_2O_3 ratios of 21.1/78.9) catalyst with different SiO_2/Al_2O_3 ratio also studied. The yield of liquid products was 68 wt% for SA-1 compared to 77 wt% for SA-2. With SA-1, liquid products were distributed in the range of equivalent carbon numbers of n- C_5 to n- C_{20} very similar to those of commercial gasoline. Therefore, the SA-1 catalyst degraded the polyethylene sample into much lighter hydrocarbon fuel oil than SA-2 catalyst. So it can be concluded that the yield and composition of the liquid products can be controlled by altering the SiO_2/Al_2O_3 ratio. As the SiO_2/Al_2O_3 ratio for SA-1 and SA-2 is different, both the acid strength and acid content of these catalysts may differ. Amorphous silica-alumina also shows a great activity on cracking polyethylene and polypropylene to lighter hydrocarbons [14].

Mesoporous silica (FSM) with acid sites is found to have faster rate of polymer degradation than that of non-catalytic thermal degradation and comparable to that over solid acid catalysts. This result is attributed due to the fact that mesoporous silica FSM, having arrays of uniform hexagonal pores of 2.7 nm accelerates the degradation of polymers, even though the FSM catalyst does not contain any significant acid sites. Again, when compared with non-catalytic thermal degradation, FSM not only accelerates the rate of degradation of polymers but also degrades the heavier waxy compounds into lighter liquid hydrocarbons [17].

Mesoporous aluminosilicate such as MCM-41 (Mobile Crystalline Material) suggest that it increases the product character and also reduces the reaction temperature [18]. HMCM-41 also leads to a high conversion of the plastic mixture because of its large pore size, which promotes the access of the polymer molecules to the acid sites [19]. Catalytic reforming over Al-MCM-41 generated a lower proportion of gaseous hydrocarbons and a higher yield of gasoline type condensable products, which was attributed to its weaker acid properties and larger pores dimensions. Catalytic conversion over this meso structured material showed a lower selectivity towards the formation of aromatic products but yield higher proportions of liquid isoparaffins and olefins. The composition of this oil fraction is comparable to commercial gasoline fuel [20].

FCC (Fluid catalytic cracking) catalysts usually have faujasite structure with a ration of Si/Al greater than 1.5. It is formed by the arrangement of truncated octahedra forming cages of 130 nm diameter, and the pore opening to these cages are 12-membered rings approx. 74 nm. The equilibrium FCC catalyst had good catalytic activity for producing light hydrocarbon liquids with carbon number $C_6 - C_{15}$. It is stated that C_2 and C_4 fractions are dominating mainly in gases on the cracking of polyethylene [21].

Activated carbon catalyzed plastics cracking yield normal alkanes and the amount of isoalkanes is very small. When Pt impregnated on activated carbon was tested, the aromatic yield is reported to reach as high as 50% of the plastics sample; it was suggested that this is due to a good combination of cracking and dehydrocyclization activities of the catalyst [22].

Synthesized fly ash catalyst (SFC) is found to decrease the decomposition temperature and the initiation time for pyrolysis and is more effective than some zeolite catalysts or no catalyst. For the pyrolysis of polyethylene, but the pyrolysis oil produced by SFC appeared to be creamy phase and is not in the full boiling point range of diesel. In case of paralyzing polypropylene by SFC, better oil is made for the alternative fuel oil which can be used without problem as commercial diesel oil [23].

The lead sulfide catalytic pyrolysis enables polyethylene to be converted into liquid, gas and wax with nearly 100% efficiency. As the char formation with lead sulfide is negligible therefore the catalyst can be used several times without treatment. No side products are associated with this method. The pyrolysis products mainly consists of paraffinic and olefinic compounds. Distillation data and other physiochemical tests for fuel oil show that, these oils are suitable to be used as fuel oil for different energy purposes [24].

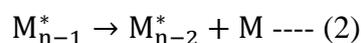
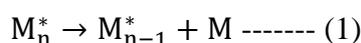
In pyrolysis process reactor type and catalyst selectivity is more recommended for obtain different yield. Pyrolysis process done without catalyst can also produce a fuel but the quality of the fuel is low and operating temperature is high, but when this process involve catalytic reaction yield quantity and quality can be changed easily as well as temperature and reaction time also considerably reduced. After the end of the reaction catalyst can be easily recoverable.

15. The hydrocarbon cracking mechanism

1. Mechanism for thermal degradation
2. Mechanism for catalytic degradation

Mechanism for thermal degradation

As a rule, the plastic pyrolysis follows complex routes that cannot be described by one or more chemical reactions, but still rather imperfectly by either empirical formulas featuring fractional stoichiometric coefficients or compressive systems of elementary reaction, i.e. reaction that really occurs as written. A detail study on the mechanism for the thermal decomposition of polymers is proposed by Cullis and Hirschler. The four different mechanisms proposed are: (1) End-chain scission or unzipping, (2) Random-chain scission/fragmentation, (3) Chainstripping/elimination of side chain, (4) Cross-linking. The decomposition mode mainly depends on the type of polymer (the molecular structure).The following Table 15.1 describes the reaction pattern of different thermoplastics where first three types of mechanism is being followed. This has been shown as below.



Eqs. (1) And (2) represent the thermal degradation and Eq. (3) represents the random degradation route of the polymers pyrolysis. The fourth type of mechanism i.e. cross linking often occurs in thermosetting plastics upon heating at high temperature in which two adjacent 'stripped' polymer chains can form a bond resulting in a chain network (a higher MW species). An example is char formation.

Mechanism for catalytic degradation

Garforth et al. have investigated catalytic degradation of polyolefins using TGA as a potential method for screening catalysts and have found that the presence of catalyst led to the decrease in the apparent activation energy. Different mechanisms (ionic and free radical) for plastic pyrolysis proposed by different scientists are as given below. Reaction occur by carbonium ion chemistry includes different steps such as H-transfer, chain/beta-scission, isomerisation, oligomerisation/alkylation, aromatization which is influenced by acid-site strength, density and distribution. Solid acid catalysts, such as zeolites, favor hydrogen transfer reactions due to the presence of many acid sites. The acid strength of solid acids is characterized by both Bronsted and Lewis acid sites; however, the presence of Bronsted acid sites has been observed to support the cracking of olefinic compounds. A study of the Bronsted and Lewis acid sites in polyolefin cracking has been reviewed by several authors . Furthermore, in the case of crystalline solid acids, the majority of the acid sites are believed to be located within the pores of the material, such as with zeolites. Thus micro-porosity of porous solid acids is an important feature in assessing the level of polyolefin cracking over such catalysts. The carbonium ion mechanism of catalytic pyrolysis of polyethylene can be described as follows.

1. Initiation
2. Depropagation
3. Isomerization
4. Aromatization

Initiation

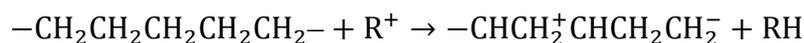
Initiation may occurs on some defect sites of the polymer chains. For instance, an olefinic linkage could be converted into an on-chain carbonium ion by proton addition:



The polymer chain may be broken up through β -scission.



Initiation may also take place through random hydride-ion abstraction by low-molecular-weight carbonium ions (R^+).



The newly formed on-chain carbonium in then undergoes β -scission as shown in Eq. (3).

Depropagation

The molecular weight of the main polymer chains may be reduced through successive attacks by acidic sites or other carbonium ions and chain cleavage, yielding an oligomer fraction approximately ($\text{C}_{30} - \text{C}_{80}$). Further cleavage of the oligomer fraction probably by direct β -

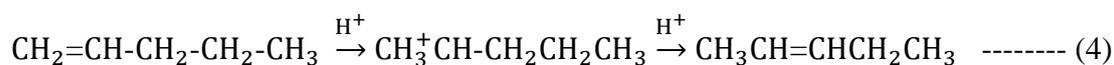
scission of chain-end carbonium ions leads to gas formation on the one hand, and a liquid fraction (approximately ($C_{10} - C_{25}$)) on the other.

[Table 15.1] Mode of thermal decomposition of different thermoplastics and products.

Resin	Mode of thermal decomposition	Low temperature products	High temperature products
PE	Random chain rupture (involves random fragmentation of polymer along polymer length, results in both monomers and oligomers)	Waxes, paraffin oil, α -olefins	Gases and light oils
PP	Random chain rupture	Vaseline, olefins	Gases and light oils
PVC	Chain-stripping (Side chain reactions involving substituents on the polymer chain i.e. elimination of reactive substituents or side groups (HCl) on the polymer chain, chain dehydrogenation and cyclization)	HCl (<300 °C), Benzene	Toluene (> 300 °C)
PS	Combination of unzipping and chain rupture, forming oligomers	Styrene and its oligomers	Styrene and its oligomers
Polymethyl methacralate	Unzipping (Cracking is targeted at chain ends first, and then successively proceeds down the polymeric length, results in monomer formation)	Monomer Methyl methacralate	Less Methyl methacralate, more decomposition
Polytetrafluoro ethylene	Unzipping	Monomer tetrafluoro ethylene	
PET	B-Hydrogen transfer, rearrangement and decarboxylation	Benzoic acid and vinyl terephthalate	
Polyamide 6	Unzipping	Caprolactum	

Isomerization

The carbonium ion intermediates can undergo rearrangement by hydrogen or carbon atom shifts leading to a double-bond isomerization of an olefin:



Other important isomerization reactions are methyl group shift and isomerization of saturated hydrocarbons.

Aromatization

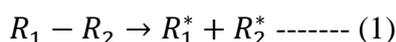
Some carbonium ion intermediates can undergo cyclization reactions. An example is when hydride-ion abstraction first takes place on an olefin at a position several carbons removed from the double bond, the result being the formation of an olefinic carbonium ion:



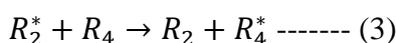
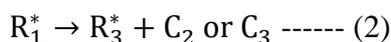
The carbonium ion could undergo intramolecular attack on the double bond: Such reactions provide a route to cyclization and formation of aromatics.

Sekine and Fujimoto have proposed a free radical mechanism for the catalytic degradation of PP using Fe/activated carbon catalyst. During degradation, methyl, primary and secondary alkyl radicals are formed, and by hydrogen abstractions and recombination of radical units, methane, olefins and monomers are produced. The various steps in catalytic degradation are shown below. In initiation step, random breakage of the C–C bond of the main chain occurs with heat to produce hydrocarbon radicals. In propagation, the hydrocarbon radical decomposes to produce lower hydrocarbons such as propylene, followed by β -scission and abstraction of H radicals from other hydrocarbons to produce a new hydrocarbon radical. Disproportionation or recombination of two radicals is termination reaction. During catalytic degradation with Fe/activated charcoal in H_2 atmosphere, hydrogenation of hydrocarbon radical (olefin) and the abstraction of the H radical from hydrocarbon or hydrocarbon radical generate radicals, enhancing degradation rate. In a reaction temperature lower than 400°C or a reaction time shorter than 1.0 h, many macromolecular hydrocarbon radicals exist in the reactor, and recombination occurs readily because these radicals cannot move fast. However, with Fe/Activated Carbon in H_2 atmosphere, these radicals are hydrogenated and therefore recombination may be suppressed. Consequently, it seems as if the decomposition of the solid product is promoted, including low polymers whose molecular diameter is larger than the pore size of the catalysts.

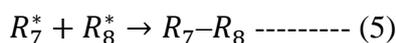
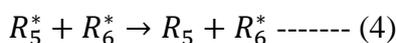
Initiation:



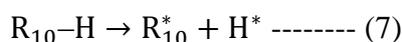
Chain reaction:



Termination

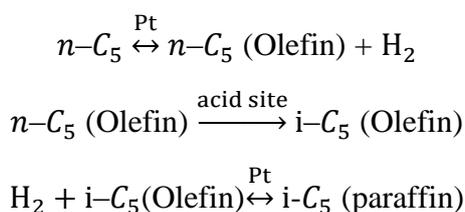


In presence of Fe/Activated Carbon + H_2 :



Wall et al have studied the catalytic degradation of waste plastics and have found that when these polymers have been heated above 380°C , they undergo depolymerisation and

degradation by a free radical chain reaction. Plastic degradation in presence of a reforming catalyst is explained differently. The reforming catalysts are said to be bifunctional, in view of the two kinds of active sites playing different roles. The metallic sites catalyze hydrogenation and dehydrogenation reactions, while the acidic sites on the support catalyze isomerization reactions. A proper combination of these two functions can promote a variety of reforming reactions such as isomerization where straight-chain paraffins are isomerized to branched-chain molecules, dehydrocyclization where straight-chain paraffins are converted to cycloparaffins, and dehydrogenation in which naphthenes are dehydrogenated to aromatics; the octane numbers of gasoline-range hydrocarbons are improved without changing their carbon numbers. The most commonly used reforming catalyst is Pt/SiO₂-Al₂O₃ with about 0.5 wt% Pt only. The following overall reaction scheme for n-pentane isomerization illustrates the reforming reactions [5].



16. Waste plastic to fuel conversion through non-zeolite catalysts

[Table 16.1] Waste plastic to fuel conversion through non-zeolite catalysts.

Type of Mixture	Plastic	Process	Temp. (°C) and Pressure	Catalysts	Time (min)	Solvent / light gas cleaner	% Fuel yield	Remarks	Ref.
Mixed Plastics	50 gm PS + 20 gm PVC	TCD	200-430	5 wt% ZnO	201	0.5N NaHCO ₃ + 0.2N AgNO ₃	50.08% (C ₃ – C ₃₂) (0.86 gm/ml)	Cl content is high in PVC that left as residue. Electricity consumption is 0.433 KWh	[81]
Mixed Plastic	50% waste plastic (LDPE, HDPE, PP, PS mixture) + 50% tire	TCD	250-430	2 wt% Fe ₂ CO ₃	270	0.5N NaOH + 0.25N NaHCO ₃ + 0.25N AgNO ₃	47.4% (C ₃ – C ₂₀) (0.78 gm/ml)	Higher residue (37.7%) due to other contents in tire and PS that cannot converted into fuel. Electricity Consumption 0.711 KWh	[82]
Mixed Plastic	LDPE, HDPE, PP, PS mixture	TCD	200-400	20 wt% ZnO	258	0.25N NaHCO ₃ + 0.25N AgNO ₃	87.19% (C ₃ – C ₃₆) (0.77 gm/ml)	Plastics were cut into pieces of 2-3 mm size. Electricity consumption 6.25 KWh	[83]
Homogeneous	HDPE	CD	400	Cat 1. (7% SO ₃)			34.31% oil +	Fixed bed reactor.	[84]

			(Heating rate is approx. 20 °C/min)	And Cat 2. (3.5% SO ₃) Modified Zirconium Catalysts.			65.68% gas (with Cat 1.), and 53% oil + 46.98% gas (with Cat 2.)	The sizes of plastic and catalysts were 125-150 μ and 75-100 μ respectively. Oil composition with Cat 1 is more of aromatic type which is favorable with gasoline. The oil yielded by Cat 2 is olifinic (65%) which is good for industrial uses.	
Homogeneous	LDPE	Catalytic Pyrolysis	175-400 And Atm. Pressure	1g (20 wt%) CaC ₂	60		69.73% fuel oil + 30.07% gas + 0.2% char	Batch reactor, Optimal liquid yield was found at 350 °C	[85]
Homogeneous	Waste PP	Catalytic Pyrolysis	400-550 (10 °C/min) Batch reactor made of stainless steel	Kaolin clay (SiO ₂ 43.12% + Al ₂ O ₃ 46.07% + Fe ₂ O ₃ nil, + MgO 0.027% + CaO 0.030% + ZnO 0.0064% + K ₂ O 0.01% + TiO ₂ 0.74%) Catalyst to plastic ratio (1:2, 1:3, 1:4, 1:6, 1:10, 1:20, 1:40)			87.5 wt% liquid (754 kg/m ³) + 11.75 wt% gaseous + 0.75 wt% residue	The highest yield of oil (87.5 wt%) was obtained at ratio of plastics to catalyst 3:1 at 500 °C. The catalysts could be reused for several times and reduces the activity after 4 times of reusing due to decomposition of carbon and wastes over the catalyst's surface.	[86]
Homogeneous	HDPE	Catalytic Cracking	381-427	Al ₂ O ₃ (HDPE:Catalyst = 7:1)		Nitrogen Gas	Conversion efficiency 65.4% (89.6%)	Semi-batch reactor with about 50% efficient electric heating system.	[87]

							liquid + 10.4% wax)		
Mixed Plastic	Polyolefins (HDPE, PP)	Clemeni Processes	419-428	Alloy based molten metal bed (59-61 wt% of Tin + 38.4 wt% of Lead + 1 wt% of Impurities) Of 8 gm/cc And melting Temperature of 183-185 °C			93.31 wt% liquid (~10 mol% light wax, and ~50 wt% light gasoline) + 6.69 wt% gaseous hydrocarbons	No solid residue was found at the end of the conversion process. Products can be treated to produce transport grade fuel or directly used in electricity generation. The amount of aromatic hydrocarbons in liquid yield is lower than other reactors.	[88]
Homogeneous	LDPE film	Catalytic Pyrolysis	550 °C (10 °C/min)	NiMo/Al ₂ O ₃ (2.72 wt% Ni + 13.16 wt% Mo + 84.12 wt% Al ₂ O ₃) Plastic to catalyst ratio = 20:1		The reactor was completely purged with dry nitrogen to remove air	Conversion efficiency is 93.8% (85.3 wt% liquid + 8.5 wt% gaseous + 6.2 wt% solid residue), Liquid fraction's heating value is 10,810 Cal/g, which is higher than that of fuel oil	Batch reactor. Through the pyrolysis occurs in absence of oxygen, the presence of catalyst reduces the degradation temperature and increases the fraction of liquid yield.	[89]

17. Experiments in Laboratory

17.1 Experiment material and apparatus table

We carried out an experiment in the laboratory of organic chemistry. Raw material and catalyst used in the process is as follow.

Name	Description
Raw Materials	17 Plastic bags (pure LDPE)
Catalyst	Regenerated Y-Zeolite

Reactor	Experiment done in Cooker.
Temperature	180 – 210 °C (measured when cooker is removed from stove)
Pressure	Atmospheric
Condition	In the absence of air while thermal cracking process.
Time	3 hours and 20 minutes
Heat Source	Gas Stove
Room Temperature	31 °C

[Table 17.1]. Experimental setup and raw material.

17.2 Description about an experiment

An experiment with a purpose of obtaining a sustainable fuel from waste plastics is carried out in the Textile Processing Lab of Sarvajanic College of Engineering & Technology, Surat by our team in the overall time of 3 hours and 20 minutes. The Data shown in the table of section 5.1 is the primary condition for the process. The pressure of the process is maintained atmospheric throughout the experiment and experiment carried out with elevation of temperature from the room temperature. In the experiment we used 17 plastic bags as a raw materials (plastics bags has material of pure LDPE) and catalyst Y-Zeolite (Regenerated catalyst at temperature of 465 °C using a one stage process. Due to one stage regenerated catalyst the activity and effectiveness of cracking quality and conversion rate will slightly differ or may be slight slower from original catalyst.) Experiment carried out in Cooker made of aluminum. A Cooker is fitted on the stove worked as a chamber. The condition in the experiment is there should be no air.

In the thermal cracking process we just heated the cooker contain only plastic using gas stove more than 200 °C. We get a fuel on the form of wax. This fuel cannot be used in general due to its solid form. So in the second case we did experiment using thermal-catalytic process. In this process we put the catalyst and raw materials in one test tube and heated it until/unless the gas is evolved and condensed. In this process we kept the condition of absence of oxygen or air during the process until we get a liquid form of plastic and it stop evolving the white fumes. When temperature more goes higher cracking will be higher and due to present of catalyst cracking will be efficient and temperature condition will be goes lower. When it start evolving gas, gas will be further cracked by the catalyst which is in the wall of test tube. And then after condensing the fuel we get the liquid fuel which is stable at room temperature. In the process necessary step is that we must have to heat the mixture in the absence of oxygen or air until/unless the white fumes disappears and whole plastic material turn into liquid form. When it will turn into liquid form it will stop evolving white fumes for some time, in this time catalyst cracking takes place and gas was evolved but we have not considered it in our experiment. (LDPE cracking yields liquid (less) and gas (more) also but in the presence of ZSM-5 catalyst, cracking in the presence of USY Zeolite (Ultra Stable Y-Zeolite) or Y-Zeolite yields more alkane rather than product more means using this catalysts we get liquid product in more amount in the comparison of other.) The fuel obtained via this process contain pale yellow color and slightly bad smell.

18. Result and analysis of an experiments

18.1 *Process yields table*

Name	Yield	Stability at room temperature	Carbon molecule range.
Thermal Cracking only	<ol style="list-style-type: none"> 1. Fuel in the wax form at room temperature. 2. Carbon black at the end. 3. Gas evolved. (Not measured in the process.) 	Solid form cannot be used as a fuel.	High range carbon molecule.
Cracking thermally and catalytically	<ol style="list-style-type: none"> 1. Fuel in the liquid form at room temperature. 2. Carbon black at the end. 3. Gas evolved. (in small amount, Not measured in this process) 	Yields a liquid product more. It is stable at room temperature.	Carbon molecules are in low range.

[Table 18.1]. Process yields according to type of cracking

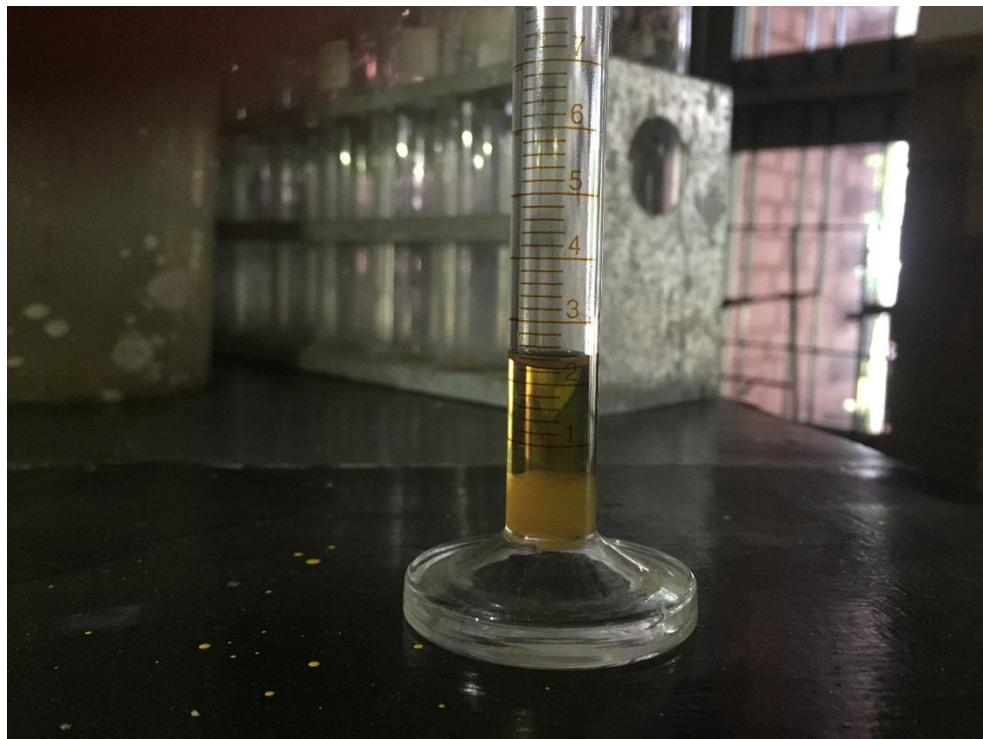
18.2 *Specification of Fuel (thermally and catalytically cracked)*

Name	Description
Colour	Pale Yellow
Phase	Liquid
Smell	Slightly bad smell.
Reactivity with <i>Al</i>	Nil
Reactivity with <i>Cl</i>	Nil
Reactivity with <i>Cu</i>	Nil
Flash Point	Not Measured
Kinematic Viscosity	Not measured
Acidity	Not measured
Pour point	Not Measured
Water Content	Nil
Sulphur content	Not measured (But fuel obtained from plastic contains negligible amount of Sulphur content compared to gasoline or diesel)
Density	Not measured
Ash Content	Not measured

Gross Calorific Value	Not measured
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[Table 18.2] Specification of fuel (contains basic only)

18.3 *Picture of fuel*



[Fig. 18.1] Picture of fuel obtained.

18.4 *Analysis through an experiment*

A. *Catalyst Deactivation*

As the process goes on the catalyst's deactivation will start rapidly. Consider the reaction takes place in the fixed bed reactor. Hence, in this type of reactor catalyst will be placed in a static place so due to cracking pore structure of catalysts will be closed by carbon molecule and it will lead to rapid deactivation of catalyst. Deactivated catalyst will decrease the conversion rate and quality of fuel considerably. So as a solution we must have to pass fresh catalyst in the process. We have to take care that over cracking should not be done because it is also one of the major cause of lower quality of fuel.

B. *With and Without Catalysts.*

In the first case we did process and got result. The results shows that the yields obtained via this is in the solid form however it has pale yellow color and it has a bad smell as observed in the second case. But yield obtained in the first case is not stable at room temperature due to incomplete or partial cracking had done. As we know that long number of carbon molecule chain is in the solid form. As the carbon number decreases the phase goes from solid to liquid and liquid to gaseous. If the yield contains low number of carbon molecule number in a chain says 15 to 30 or 35 (approx.) it is in the

liquid form. Means that product in the first case contain the higher carbon molecule chain, also low quality.

In the second case we did process and got result. The result shows that the yields obtained via this is in the liquid form with a pale yellow color and slight bad smell. But it is in the liquid phase that means due to presence of catalyst the cracking is higher and carbon molecule in the chain is as said above fitted. This fuel also contain high quality compared to case one.

C. *Different catalyst, yields different product*

In first case process was done using spent catalyst. So it resulted that at the time of condensing the gas it will form a liquid as well as few amount of solid fuels (wax form.) and take more time. We have to double use of catalyst for get complete fuel. Due to spent catalyst it was did cracking more than without catalyst process. But yield lower quality with lower conversion ratio.

In second case process was done using Regenerated catalyst. So it resulted that at the time of condensing the gas it will form only liquid rather forming a solid fuel as shown in above case one. And conversion ratio is not much considerable. But time is less than above process. This will lead to lower by product also.

19. Deactivation of Zeolite Catalysts

19.1 *Introduction to deactivation of zeolite catalysts[90]*

Deactivation of catalysts is of considerable importance in catalysis because most of the catalysts show a loss of activity with time. In the last decade, research activities on this subject have been intense and concerned primarily with chemical, kinetic, modeling, and regeneration of catalyst aspects. In these, deactivation due to poisoning, fouling, sintering, solid-state reactions, and vapor transport mechanisms were discussed, with the emphasis on chemical and kinetics aspects, modeling of deactivation process in a single particle to a catalytic reactor, methods of preventing or slowing deactivation, and regeneration schemes of catalysts. Zeolite catalysts received much attention and importance in petroleum refining and chemical industry due to their unique *shape-selective properties*. Interest in medium-pore zeolites has grown in recent years, both at academic institutions and in industrial research laboratories as evidenced by the exponential growth of publications dealing with the fundamental and applied aspects of zeolite catalysis. Zeolite catalysts are no longer laboratories curiosities; rather they have emerged as an important class of commercial catalysts for a number of chemical processes. New class of zeolite catalysts such as silico aluminophosphate (SAPO), metal aluminophosphate (MAPO), and alumino phosphate (ALPO) are reported to be active and highly selective catalysts for skeletal rearrangement reactions of olefins, paraffins, and aromatics. Most zeolitic catalysts are complex composites of two or more components. The role of these components can be directly catalytic, as in the case of the zeolite component or an active metal. Other components can act as stabilizing agents or metal supports, or simply contribute to the physical nature of the composite catalyst. During use, these components may undergo change, often in the form of an interaction with other components in the catalysts,

which can result in a loss of activity and a change in selectivity (solid-state transformation or loss of crystallinity). In the case of metals, they can migrate from their original locus of incorporation. Such as within the zeolite, to another component of catalyst and agglomerate, losing a good portion of their catalytic activity (sintering), the catalytic nature of zeolitic component can also change; for example. There may be a shift in the acid strength distribution (poisoning of acid sites). The pores of zeolite crystal can be blocked by the formation of carbonaceous deposits due to side reaction which can also result in loss of activity (coking).

Thus, the loss in activity of zeolite catalysts may be caused by:

- Formation of coke, which will accumulate on the surface or blocking pores.
- Selective adsorption of undesirable agent which poisons the active sites.
- Sintering, which changes the structure and the surface area of the catalyst.

Today zeolite catalyst application has expanded well beyond the boundaries of traditional petroleum refining and zeolites have already found application in synthetic fuels production, NO_x abatement, production of fine chemicals, and intermediates. Therefore, improvements of the catalytic processes require highly efficient catalysts exhibiting a good resistance to deactivation. In the past decade a tremendous effort has been focused on zeolite catalysts due to their high acidity and to their peculiar channels or cavities. Catalyst selectivity, resistance to deactivation, and aging are major features of zeolite catalysts. Catalyst deactivation is industrially a very important problem. In zeolite catalysts, the deactivation feature is related to mass transfer and diffusion limitations. Diffusion inside the zeolite channels is still not well understood and the general diffusion laws do not apply since the size of the channels is in the same range as those of hydrocarbon molecules. This corresponds to “configurational diffusion” and intracrystalline and intercrystalline diffusion govern the selectivity and activity of the catalyst. It has been reported that coke formation in hydrocarbon reactions is a shape selective reaction and that coking tendency (and aging rate) is an intrinsic property of the zeolite pore structure. Further, it has been observed that large-pore zeolites deactivate rapidly whereas medium-pore zeolites inhibit coke formation and deactivate slowly in hydrocarbon reactions. There are numerous modifications of zeolites in respect of the number and strength of acid centers, isomorphous substitution. And doping with metals to suit the requirement of a desired reaction such as high selectivity and stability. A fundamental understanding of the deactivation process with the modification of zeolite structure will enable more efficient use of the existing catalysts as well as give design criteria for a new class of zeolite catalysts. The role of diffusion in such catalysts to predict their shape selectivity is lacking in the literature, and this needs to be analyzed. In this report an overall analysis of the zeolite deactivation phenomenon is presented, in order to examine the chemical phenomenology of deactivation, the role of zeolite structure (size and shape) and location of active sites affecting selectivity during deactivation, the effects of diffusion and their influence on shape selectivity, and the design of zeolite catalysts. The various deactivation models proposed to involve pore blocking and site blocking due to deactivation process are examined to ascertain the role of blocking in the selectivity of zeolite catalyst. The application of surface science techniques to examine the changes in the zeolite surface leading to fundamental understanding of the factors controlling catalytic activity, selectivity, and stability has been examined. Finally, this paper examines the methodology of regeneration of deactivated catalysts, especially that of the medium-pore zeolite.

19.2 *Relation between zeolite structure and deactivation*[90]

19.2.1 *Pore/Channel System*

Zeolites are crystalline inorganic polymers based on a framework of XO_4 tetrahedra linked to each other by the sharing of oxygen ions, where X may be trivalent (e.g., Al, B, Ga), tetravalent (e.g., Ge, Si), or pentavalent (e.g., P). The crystal structure of a zeolite is defined by the specific order in which a network of tetrahedral units are linked together. In A, X, and Y zeolites, four- and six-membered rings are joined together and they form a cubic octahedron referred to as a sodalite unit. These sodalite units are connected by oxygen bridges between the six-membered rings, forming a hexagonal prism (zeolite X and Y). These arrangements leave in the framework, cages with 8 (zeolite A) or 12 (zeolite X, Y) oxygen membered windows which determine the pore structure.

In the *mordenite* framework, TO_4 tetrahedra are arranged to form five-membered rings; these are joined to form five chains and the chains are linked to form the crystal. This arrangement of TO_4 led to a framework with two families of tubular elliptical pores having 12 and 8 oxygen membered windows, respectively.

In ZSM-5, the framework is formed from five-membered oxygen rings (pentasil family zeolite) linked together to form the building unit of eight five-membered rings. These units are joined through edges, forming chains. The chains are linked to form sheets, which are linked together to form the three-dimensional framework. In the ZSM-5 family, the framework consists of two intersecting channels with 10 oxygen membered rings. In ZSM-5, one channel system is straight and the other sinusoidal, whereas in ZSM-11 the two channel systems are straight. Zeolites with more than one pore system are classified according to their largest accessible pore. Zeolites are often classified according to their silica-to-alumina ratios. Generally, the higher is the silica-to-alumina ratio, the more thermally stable is the zeolite. Zeolite with silico-alumina ratios greater than 10 are typically classified as high-silica materials. Among all the zeolites, ZSM-5, which has bidirectional intersecting channels, has received the most attention as a potential catalyst in number of chemical processes. It serves as a prime example of the uniqueness of medium-pore zeolites in catalysis. Figure 1 depicts a schematic view of the ZSM-5 channel system. ZSM-5 has two types of openings, one a nearly circular (0.54 x 0.56 nm) opening and the other an elliptical opening (0.51x 0.55nm). The size of these openings determines the shape-selective properties of these catalysts. Another important structure feature of medium-pore pentads (like ZSM-5) is the absence of large supercages with small-size windows as present in other types of zeolites. ZSM-5 has uniform pores, which is believed to be major factor in its unusual shape-selective properties. Molecules larger than the size of the channel do not form, with the exception perhaps at the intersections.

19.2.2 *Types of deactivation in zeolites*

Catalyst deactivation has been divided into various types according to the deactivation mechanism. The general classification can also be equally applied to zeolite catalysts.

a. Coking

The formation of coke is the most important example of deactivation by fouling in zeolite catalysts. In commercial cracking units the formation of carbonaceous residues block the pore system and covers the reaction sites, leading to deactivation. Zeolites are known to

exhibit high catalytic activity toward coke formation over the temperature range 300-400 °C. Although coke formation from hydrocarbon reactions on acid catalysts has been reported, the origin and nature of coke have been studied less extensively. Aromatic hydrocarbons present in the feed or produced during the reaction act as a main source for coke formation. Bulky aromatic compounds formed in the large-pore zeolites such as Y cannot easily escape and condense to form coke resulting in rapid deactivation. Medium-pore zeolites, such as ZSM-5, are unique in that they inhibit coke formation while admitting large molecules such as monocyclic aromatics. Another important aspect of coking in zeolite catalyst is the effect of coking on the diffusional properties of zeolites. Exterior surface coking is known to modify the diffusional characteristics and/or the activity of ZSM-5 zeolites. Coking results in increased diffusional resistance which is believed to be responsible for increased selectivity in certain types of reactions such as xylene isomerization. The problem of diffusional reactions in coked catalysts has been studied using the Monte Carlo approach and effective medium approximation. The site at which the coke formation takes place in ZSM-5 is not well understood. Different types of coking phenomenon such as surface coking, pore blocking, and external/internal coke have been described in the literature. It is important to ascertain the role of acidity (strong acid sites vs weak acid sites) in the coking phenomenon.

b. Poisoning

Deactivation of zeolites due to poisoning can be caused by strong chemisorption of some impurity, normally contained in the reacting mixture. Zeolites are known to be poisoned by nitrogen bases present in the feed or by metal contaminants such as vanadium, copper, and nickel which would accumulate to a high level on the zeolite. These metals are known for their dehydrogenating and hydrogenolysis catalytic properties. Small impurities of sulfur compounds such as mercaptans, thiophenes, etc., present in the feed stream may deactivate the catalyst.

c. Solid-states reactions

Solid-state reactions which cause a change in the chemical nature of the constituents of the catalyst or a change in phases lead to deactivation of the catalysts. In zeolite catalysts, phase transformation from the crystalline to the amorphous phase can lead to collapse of crystalline structure and thereby make the catalyst completely deactivated.

d. Sintering

Sintering is a process of deactivation which results in loss of metal surface area and is of considerable importance for the metal zeolite catalysts. The metal component is generally introduced in the zeolite either by ion exchange or impregnation. The active metal is maintained in a high degree of dispersion within the zeolite matrix when introduced via ion exchange. Many noble metals like Pt, Pd, Rh, and Ru are introduced via ion exchange in the zeolite matrix. The highly divided metal engaged in zeolites possesses interesting catalytic properties for a number of reactions such as hydrogenation, dehydrogenation, hydrocracking, and isomerization. The physical state of the metal in the zeolite framework describes the catalytic properties of these catalysts. It is, therefore, important to maintain the catalytic activity by minimizing the sintering and poisoning of the metal phase.

19.3 Zeolite deactivation by coking[90]

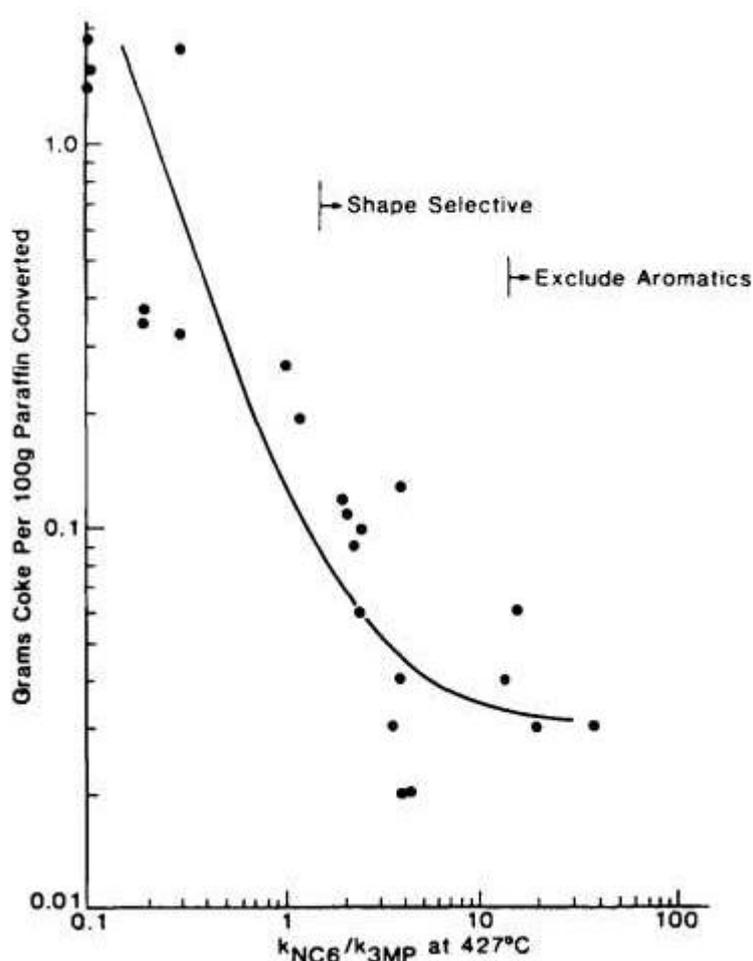
Deactivation of acid zeolite is mainly due to the formation of carbonaceous products, which occurs during all transformations of organic compounds. It has been proved that the coking process is determined by the acidity and zeolite pore structure. As an example, the cooking rate is 50 to 1000 times lower on the small or intermediate pore size zeolites than on those with larger pores. The coke composition depends mainly on the space available for its formation; coke will be polyaromatic and very heavy if the reactions leading to its formation are not limited by steric constraints (Y zeolites), whereas it will be less aromatic and more olefinic in the other cases of intermediate pores (ZSM-5). The aging rate of a zeolite is also determined by its pore structure. As in the case of porous catalysts, deactivation can occur in two ways, namely site coverage (active sites poisoned by coke adsorption) or pore blockage (active sites inaccessible to reactants). However, with zeolites, since their pore sizes are close to those of organic molecules, pore blockage will be more likely than with amorphous catalysts. This is why the structure is one of the most significant parameters of zeolite deactivation. To clarify the significance of two-way deactivation (pore blockage and site coverage), HY-zeolites were studied for cracking of n-heptane. Polyaromatic molecules are rapidly formed near the strongest acid sites. The smaller molecules limit the access of reactant to acid sites without completely obstructing them, while the larger ones totally prevent the access. In general, molecules which have fewer than 8 aromatic rings occupy one supercage, whereas larger molecules formed at higher content occupy two supercages.

The effect of coke on acidity and the role of the acid site on coke formation also play a major role in deactivation. In ZSM-5, which has so far received little study, the lower density of its acid sites is partly responsible for its reduced coking activity. The steric constraints exerted by its porous network on the formation of the bulky intermediates of coking also play a significant role. To show this steric effect, a strongly dealuminated HY-zeolite which has lower site density has a coking rate 10 times greater than that of ZSM-5 because of the availability of the pore space in Y-zeolite for coke formation. It has been established that ZSM-5 contains very strong Bronsted acid sites which are associated with framework aluminum atoms. The density of such sites in ZSM-5 is low in comparison with other zeolites, and the distribution of sites throughout the zeolite can be non-uniform. The slow deactivation of ZSM-5 during methanol conversion is attributed to the buildup of nonvolatile hydrocarbon residues (coke), which block access of reactant molecules to the active sites.

The deactivation modes of three different zeolites-H-mordenite, ZSM-5, and HY-were studied by Magnoux et al. during n-heptane cracking. For HY-zeolites, polyaromatics with alkyl groups are rapidly formed initially on the very strong acid sites. As soon as they attain a certain size (more than 3 aromatic rings) their migration becomes very slow and these molecules obstruct the pore entry (=8Å) of the supercages, limiting the penetration of n heptane (4.3Å). For ZSM-5, deactivation is initially due to coverage of acid sites located at channel intersections by alkylaromatics with 1 or 2 rings; later on bulkier molecules form extremely slowly, either on the external acid sites or more likely by growth of the coke molecules located on the acid sites near the external surface that can obstruct the pore. This formation of coke on the external surface has already been observed during the conversion of methanol into hydrocarbons. Deactivation of H-mordenite is essentially due to pore blockage.

[Table 21.3.1] Relationship between coke yield and pore size.

Zeolite	Pore Size (nm)	Coke yield (g/100 g paraffin)
Y	0.72	2.2
Mordenite	0.7*0.67	0.3
ZSM-5	0.54*0.65	0.4



[Fig 21.3.1] Coke yield vs shape selectivity paraffin conversion over acid zeolite catalysts.

A comparison of coke origin and yield between ZSM-5 and mordenite is given in Table 21.3.1. At low aluminum density, aromatics and paraffin contribute equally to coke formation in these two structures despite the order of magnitude differences in coke yield. When the Al content of ZSM-5 is increased, the aromatic contribution to coke drops; this means that more Al represents more catalytic sites, more paraffin cracking, more carbonium ions, and hence a greater paraffin contribution to coke. With the mordenite structure, more Al represents more adsorption of aromatics, and because of the large pores, a greater probability that when reactions occur to produce coke, they will involve these adsorbed aromatics.

The evidence indicates that coke formation in zeolite catalysts is a spatially demanding reaction and, as such, is particularly sensitive to zeolite pore structure. Factors such as SiO_2/Al_2O_3 ratio,

temperature, charge stock, and crystal size can significantly perturb the behavior within any isostructural sequence of framework compositions.

a. Origin and nature of carbon deposits

Zeolite catalysts exhibit high catalytic activity for the formation of coke which poisons the acid sites and blocks the pore system. In order to study the problem of zeolite deactivation by coking, the chemical identity and origin of the coke deposits must be better understood. This entails fundamental investigation of the coked catalyst surface on a molecular level.

The site of coke formation and the nature of the coke formed on ZSM-5 have received relatively little consideration. Different views have been expressed in the literature:

- DeJafue et al. suggested that coke forms on the external surfaces of the ZSM-5 crystals causing pore mouth blocking and deactivation.
- Magnoux et al. reported that while coke initially forms on the external surfaces, an internal coke later forms by polymerization of small olefins.
- Langner found that coke is monoaromatic and forms within the pores.
- X-ray diffraction suggested that some coke must be formed in the channel system of ZSM-5 because diffraction patterns of ZSM-5 structure were distorted.
- Sexton et al. using XPS, distinguished coke formation on the external and the internal surfaces. They provide data which supported the finding that coke fills the channel system initially before any significant amount of surface coke is formed. Up to 8% coke, there is no evidence for external coke formation. From 8% to 12% coke, one or two monolayers of external carbon are deposited as internal coking continues. Above 15% coke, the channels are filled and the external surface accumulates further coke.

In an *in situ* Fourier transform infrared spectroscopy investigation of coke formation on HY-zeolite cracking catalysts, two types of active sites are proposed for the formation of coke. One site consists of the Bronsted acid hydroxyl groups present after low-temperature calcination of the zeolite. The second type of site involves a sort of synergism between strong Bronsted acid hydroxyl groups and neighboring Lewis acid cationic sites, formed after high temperature calcination. This dual-site mechanism for coke formation suggests that the active sites of the dehydroxylated sample are produced through an inductive effect of Lewis acid site on the remaining supercage hydroxyl groups. The composition of the coke on the zeolite catalyst exhibits a distinct aromatic character, suggesting that the route to coke formation always proceeds through aromatic precursors.

Recently, Karger and Bolding investigated coke formation over a series of dealuminated mordenites using an *in situ* IR spectroscopy for dealkylation/disproportionation of ethylbenzene as a reaction test. They found that coke formation is strongly influenced by the Bronsted acidity of the zeolite catalysts. In the case of conversion of ethylbenzene, the rates of coke formation and deactivation increase with increasing acidity of the acidic sites. Deactivation of the zeolite is more likely due to partial pore blocking than to site poisoning or consumption of the active OH groups. The sensitivity of the dealuminated mordenite catalysts to coke formation increases with their Si/Al ratio, most probably due to an increase in the strength of their acidic sites.

19.4 *Poisoning in zeolite catalysts[90]*

Deactivation due to metal poisons is important in the case of heavy hydrocarbon feeds such as resid cracking. Nickel and iron act as co-catalysts that create undesirable dehydrogenation activity, whereas vanadium is not as active a dehydrogenation catalyst as nickel but has sufficient mobility to react with zeolite to destroy its crystallinity and porosity. Sodium is another metal poison commonly found in heavy hydrocarbon feeds. Sodium neutralizes acid sites, thereby reducing activity. It also reduces the thermal and hydrothermal stability of the zeolite, accelerating its deactivation at the high temperatures of the reactor. Zeolite catalyst acidity is affected by the chemisorption of basic compounds containing nitrogen, as well as compounds containing oxygen or sulfur. This results in catalyst deactivation. However, in some cases, simple heating of the catalyst in an inert atmosphere to desorb these poisons will restore activity. Ammonia has been a widely employed poison/probe molecule in investigation of sites in zeolites. NH_3 Poisoning has been reported to be completely reversible in zeolite Y. Phosphorous is also reported to interact with Bronsted acid sites in ZSM-5 zeolites, resulting in acid site poisoning. Sulfur is known to be a severe poison for most metal catalysts because sulfur compounds are strongly chemisorbed on the metal surface. Metal-zeolite catalysts are active for a number of chemical processes such as hydrogenation, hydrocracking, oxidation, dehydrogenation, and isomerization.

19.5 *Solid-state reactions[90]*

Zeolites can undergo phase transformation when subjected to high temperature in the presence of water vapor during regeneration. The thermal stability of zeolites depends strongly on the silica-to-alumina ratio and can be improved by aluminum extraction from the framework (dealumination). Dealuminated zeolites are resistant to collapse and are referred to as stabilized zeolite or ultrastable zeolites. Loss of crystallinity resulting in deactivation in zeolite catalysts is generally avoided during reaction/regeneration by operating reactor/regenerator temperatures below their thermal decomposition temperatures. ZSM-5 zeolites generally have high Si/Al ratios and therefore have high thermal stability. The thermal and chemical stability of zeolites has been reviewed. Zeolite-X, which has a relatively low silica-alumina mole ratio of about 2.5, undergoes irreversible deactivation when it is cyclically hydrated and dehydrated at elevated temperature. It is believed that in zeolites, the deactivation is caused by hydrolysis of tetrahedrally coordinated aluminum in the zeolite framework and corresponding loss of acid sites originally associated with aluminum. In case of composite catalysts such as catalytic cracking catalysts, zeolitic component is combined with a binder such as oxides of silica, alumina, or clays. These binders are used primarily to impart physical strength to the zeolite catalyst particle so that it can withstand the rigors of handling and use in process applications. The binder or matrix possesses good thermal and hydrothermal stability and resistance to chemical attack. The interaction of zeolitic component with the matrix at high temperature can also result in the changes in structure and activity. The composite zeolite may deactivate due to migration of alkali or alkaline earth metals from the binder to the zeolite. It has been found that at low temperature (600-750°C), deactivation is dominated by matrix changes, while deactivation at higher temperatures (750-900°C) is dominated by loss of crystallinity of the zeolite component.

Aluminum insertion through a soluble aluminum (Al) species by reaction with SiOH groups of highly siliceous ZSM-5 is reported to increase ion-exchange capacity and Bronsted acidity.

Thus, solid-phase transformations may become advantageous in zeolite catalysts. Delmon et al. reviewed the role of chemical transformations of solids in deactivation of catalysts. The review covered the aging and deactivation phenomena which are related to true chemical transformation of heterogeneous catalysts.

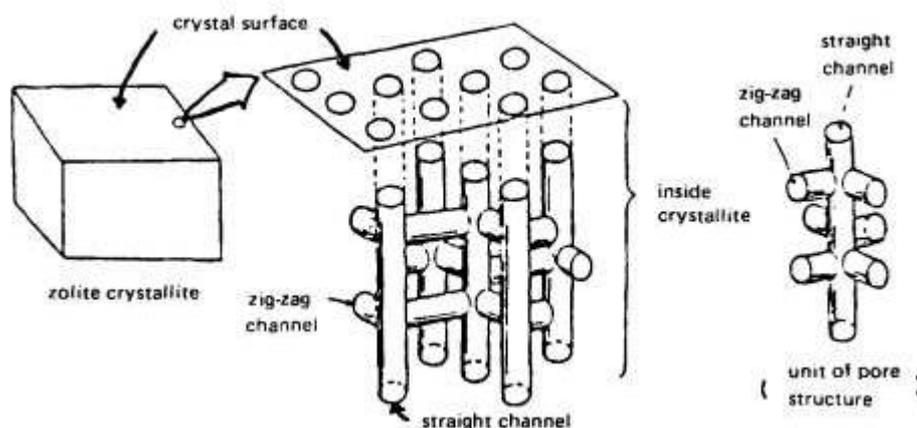
19.6 Mechanism and model for coke build up[90]

a. Mechanism

The presence of coke, highly unsaturated hydrocarbons produced by unwanted side reactions and strongly adsorbed on the catalyst, is known to decrease the activity of the catalysts. Two possibilities of deactivation in zeolite catalysts have been proposed:

- If the coke molecule is adsorbed on an active site (responsible for reaction), the catalyst loses activity because the site has been taken out of circulation. This is termed as site or surface blocking.
- On the other hand, the presence of coke molecules adsorbed on the pore walls/cages/channels increases the resistance to mass transfer inside the catalyst pellet, decreases the concentration of reactant in the fluid phase above an active site, and thereby decreases the rate of reaction. This is termed deactivation by pore blocking. Phenomenologically the effective diffusivity of the reactant inside the zeolite is affected.

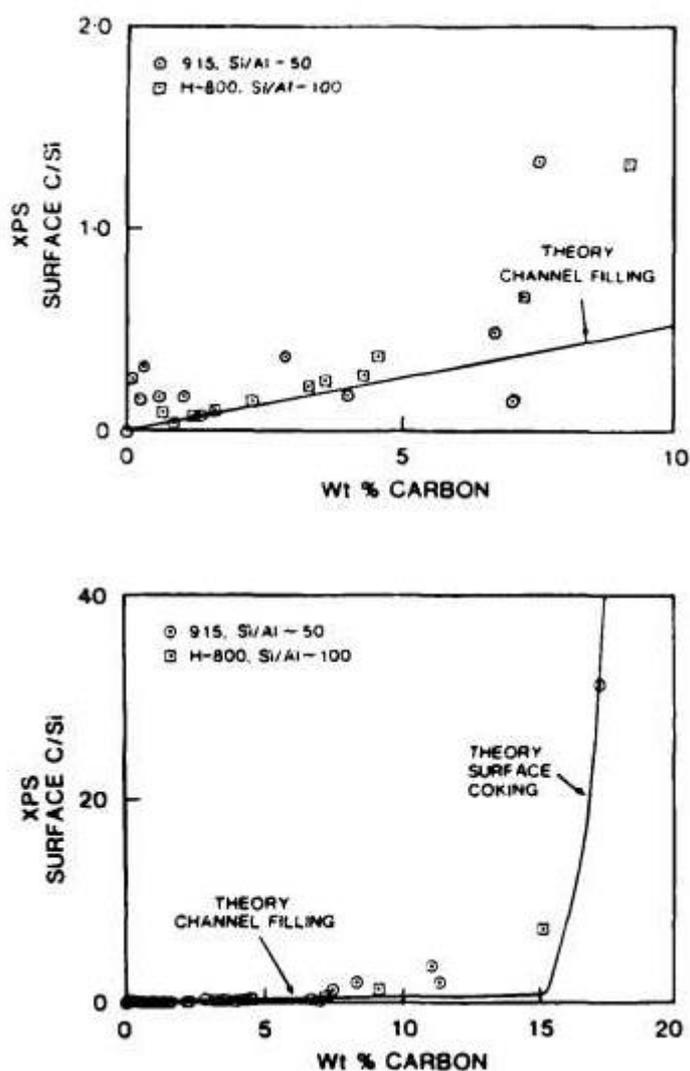
Aromatic carbonaceous residues are deposited mostly on the surface of the crystallite. A schematic diagram of H-ZSM5 showing channels and crystallite surface is shown in Fig. 21.6.1.



[Fig. 21.6.1] Schematic representation of pore structure in HZSM-5 zeolite structure

In HZSM-5 zeolites, (a) coke is formed mainly inside the crystallite; (b) coke is deposited mainly on the outer surface of the crystallite. The site of coke formation and the nature of coke formed on ZSM-5 have received relatively little consideration. The two effects (pore blocking and surface blocking) are not mutually exclusive; both or neither could be significant under appropriate conditions. Some data on zeolite deactivation show a rapid initial loss of activity caused by direct site suppression followed by a slow decrease probably caused by choking of

the pores. It is important to know which phenomenon is the predominant one causing deactivation by coking. The distinction between intracrystalline coke and surface coke was made by measurement of molecular self-diffusion data of methane and propane in coked catalysts. The intracrystalline self-diffusivity of absorbed molecule was found to be independent if the coke was deposited on the external surface whereas intercrystalline coke caused a severe reduction in the diffusivity value. The XPS technique is also employed to distinguish coke formation on the external surface and on the internal crystalline surface. The C/Si ratio increases linearly with intercrystalline coke formation and exponentially when external coke forms, as shown in Fig. 21.6.2.



[Fig. 21.6.2] Measured C/Si ratio by XPS versus wt% coke.

So, from above we can conclude that The coking phenomenon in zeolite is a complex process which depends on structure and acidity of zeolite. A realistic model to represent the zeolite deactivation due to coking should be proposed incorporating the effect of coking on effective acidity.

20. Applications

- a. In transportation as an alternative of current gasoline or diesel when further processed and treated.
- b. For heating purpose in industries.
- c. For Jet Fuels.[3]
- d. Carbon Black (as a by-product) used in the pigment industry.
- e. Gas (mainly contained methane) used for operate reactor or for sell.

21. Advantages and Drawbacks

- a. Fuel produced via pyrolysis process should be further treated in the fractionating tower.
- b. Gasoline from pyrolysis oil has a low octane number (octane number shows the quality of fuel, if it will high fuel has a high quality, if it is low fuel is of low quality).
- c. Diesel obtained from this process can be used instead of regular diesel because its meet the minimum requirement of regular diesel.
- d. Pyrolysis oil is more and more demanded in the industry due to its low cost.
- e. Its production is eco-friendly.
- f. Capacity to complete recycle of plastics.
- g. Unskilled person can also operate pyrolysis plant.

Pyrolysis oil from plastics has a very low amount or negligible amount of sulfur content compared to the regular fuel.

22. Economic and ecological aspects of catalytic pyrolysis of plastic

The new technologies and economics have come to play an important role in plastics recycling. As described in previous section, plastic recycling principally refers to recovery, which is divided into material recycling and energy recovery. Material recycling is again divided into mechanical and feedstock recycling. The choice between these methods will depend on the types of plastics waste, the relative ease/difficulty in total or partial segregation from other plastics and/or other waste materials, ecological and cost aspect involved in the process. While determining economic boundary conditions of plastics recycling, it is necessary to make a distinction between: (i) mechanical recycling to the same or similar applications, (ii) mechanical recycling to new areas of applications, (iii) incineration and energy recovery, cement kilns, incineration for power generation, (iv) feedstock recycling to form different products like conversion to monomer, fuel, reducing agent in blast furnace for the production of iron, gasification and liquefaction.

Worldwide, mechanical recycling is the most preferred and accepted method of plastics recycling. However, it includes a wide variety of processing techniques and a broad range of processing methods requires lot of energy, which increase the cost depending on the degree of contamination. After collection of the portions that can be recycled by mechanical recycling, there remain numerous very small, heavily contaminated articles or cross-linked products or products contaminated with hazardous substances. Heavily contaminated plastics waste collected from domestic waste stream can be utilized by energy recovery from waste incineration plants. Cost of this system of recovery is considered highest among all the alternatives. Again, incinerator design and operation depends upon the type of waste to be incinerated and another important factor to carry out this process is to minimize the harmful

emissions. Non-adherence to these two basic principles caused serious failures of various incineration activities in the 1980s raising doubt about the effectiveness of this process itself. Feedstock recycling would be a better alternative from cost and ecological aspects. As the cost of feedstock recycling even in the best case of large-scale plants may be similar (as high as) to the cost for incineration and energy recovery and does not produce harmful emission if designed properly. Again this process is complementary to mechanical recycling since it is less sensitive to unsorted or uncontaminated plastic waste and enlarges the overall recycling capacities for large waste quantities to be supplies in future. This is also important today from the global warming point of view and the operator in a developing country is able to cash on the carbon credit as there is reduction in dependence on fossil fuels [26].

Extensive research has been carried out on catalytic pyrolysis of plastics using different catalysts and the process has also been materialized in different countries.

In the early 1990s BP Chemicals, first tested technology for feedstock recycling, using a fluid bed cracking process. Research on a laboratory scale was followed (1994) by demonstration at a continuous pilot plant scale (nominal 50 kg/h) at BP's Grangemouth site, using mixed waste packaging plastics. The technology was further developed with some support from a Consortium of European companies (Elf Atochem, EniChem, DSM, CREED) and from APME. In 1998, BP Chemicals, VALPAK and Shanks & McEwan, set up a joint project (POLSCO), to study the feasibility of a 25,000 tonnes/y plant, including logistics infrastructure for supplying mixed plastics from Scotland. The process involves initial cleaning of waste plastics to remove the non-plastic impurities and heating them in a fluidised bed reactor operating as 500 8C, in absence of oxygen. Lime absorber is used to remove the HCl produced due to the presence of polyvinyl chloride. The different type plastic that has been used includes polyethylene, polypropylene, polyvinyl chloride, polyethylene terephthalate and styrenic polymers. The hydrocarbon products (85% yield) can be fed directly to petrochemical plants or to gasoline without further purification [25].

Veba oil developed a commercial process, operating in a temperature range of 350–450 C and requiring a high hydrogen partial pressure (50–100 bar) using a liquid phase reactor. The technology was realized in the coal-to-oil plant at Bottrop, with a capacity of 40,000 tonnes annually doubled at the end of 1995 [25].

A large pilot plant, with a substantial capacity of 15,000 tonnes/ y, was started up in Ludwigshafen in 1994 by the BASF in which plastic waste is converted into petrochemical products using a tubular cracker reactor [25].

A plant operating according to the Hamburg University pyrolysis process was built at Ebenhausen, Germany with a capacity of 5000 tonnes/y. This process was developed by W. Kiminsky in 1883 in which pyrolysis is carried out in an externally heated fluidised bed reactor containing sand [25].

The first report of turning plastic wastes into oil came in 2001 from the People's Daily, China's English language newspaper. An oil refinery in Hunan province had succeeded in processing 30,000 tonnes of plastic wastes into 20,000 tonnes of gasoline and diesel oil that satisfied the provincial standards. Wang Xu, who built the refinery in 1999, started experimenting with waste plastic processing in the 1980s, and later teamed up with Hunan University doctoral tutor Zeng Guangming who gave him scientific advice on decomposing plastic wastes. In the 1980s, Illinois microbiologist Paul Baskis in the United States modified the process to produce a

lighter, cleaner oil, but failed to convince investors until 1996, when a company called Changing World Technologies began development with Baskis to make the process commercially viable [27]. Again, the plants with a capacity of 1000 tonnes/annum have been running nearby many cities in China [28].

Environmental Technology Systems Ltd is a U.K. company, incorporated in 2003, which now has the rights to acquire a proven Chinese technology to convert waste plastics into gasoline and diesel fuels produce 2000 tonnes/annum of fuel oil (roughly, half petrol and half diesel) from 2740 tonnes of waste plastics. The balance is 410 tonnes of combustible gas which is used to provide heat for the process. The sole by-product is 330 tonnes of 'slag'. The process is continuous and can handle all plastics including polyvinyl chloride and no pre-sorting is required. The plastic is shredded prior to being passed into the feed-hopper and the process uses non-pressurised modular catalytic reactor running at moderate temperatures of 350–400 °C [29] converts plastic feed into 73% fuel oil, 15% gas and 12% inert ash residue (mainly dirt introduced with the waste). The fuel oil can be burned immediately to produce heat or electricity or it can be fractionated into roughly equal parts transport grade diesel and high-octane gasoline that is lead and sulphur-free. The Technology is "clean". There is no odour. There are no gaseous emissions or liquid effluents beyond modern petrochemicals practice. The eco-friendly processing plants produce high quality fuels, which meet or exceed current industry standards for transport grade fuels [30].

In India, a zero-pollution industrial process to convert non-biodegradable and mostly non-recyclable plastic waste into liquid hydrocarbons has been set up at Butibori industrial estate, Nagpur in 2005 by Prof. Alka Zadgaonkar. The Zadgaonkar's Unique Waste Plastic Management & Research Company plant devours a whole range of plastic waste from discarded carry bags to mineral water bottles and broken buckets to polyvinyl chloride pipes, polyethylene terephthalate bottles, even acrylonitrile butadiene styrene plastic material used in the making of computer monitors and TV sets, keyboards, etc. and converts it 100% into liquid hydrocarbon fuels (85%) and gases (15%). This is the World's first continuous process for plastic recycling to liquid fuel [31, 32].

Enviro-Hub the waste management and recycling firm announced the construction of Singapore's first US\$ 50 million plastic-to-fuel plant which converts waste plastic into useable fuels and gases. It is building the world's first large-scale, commercial plastic-to-fuel plant. This process is based on patented technology imported from India, for which Enviro-Hub now holds an exclusive license, heats waste plastic with a special catalyst that breaks it down into 85% diesel, 10% liquid petroleum gas and 5% coke [33].

23. Future works

The present issues are the necessary scale up, minimization of waste handling costs and production cost and optimization of gasoline range products for a wide range of plastics mixtures or waste. The further task are

1. To constitute the standards for process and products of post-consumer recycled plastics and to adopt the more advanced pyrolysis technologies for waste plastics, referring to the observations of research and development in this field. The pyrolysis reactor must be designed to suit the mixed waste plastics and small-scaled and middle-scaled production.

2. More attention should be pay to exploring the recycling and pyrolysis of waste PVC and the optimization of operational conditions of pyrolysis for waste plastics to abate the generation of toxic substances like dioxins and PCBs.
3. A novel and more efficient catalyst ought to be studied for the process of pyrolysis which would be cheaper, obtainable on commercial scale and should be regenerated back.
4. Process integration through pinch analysis would help reducing the capital investment and also the operating cost and thus would enhance the economic viability of the process.
5. A more sophisticated mechanism of catalytic pyrolysis should be explored to improve the process further.

24. Conclusion

Fuel have been found effectively produced from plastic waste as an alternative of regular fuel. Corrosive content, overall reaction time and temperature is reduced with a proper use of catalyst. So, the thermo-catalytic process can be industrially or nationally sponsored to reduce solid polymer waste from environment. Alternative fuel production can effectively reduce the fuel import load of any nation producing more plastics wastes.

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