



Review Paper

Study of catalysts used in pyrolysis of plastic for enhancing gasoline fraction – A Review

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Abstract

Plastics are usually synthetic or semi-synthetic polymers with high molecular mass and can be moulded onto solid objects of different sizes and shapes. Plastics are with limitless numbers of useful characteristics, and colours, and are easy to manufacture. Plastics have major applications in the field of automotive, building constructions, medical devices, electrical and electronics, industrial machinery, Packaging etc, because of the wide spread of plastic use plastic become an integral part of our life. Once the plastic is discarded it becomes waste and it acts as a pollutant. Accumulation of plastic waste in the environment affects human as well as wildlife habitats on earth. The main disadvantage of plastic waste is that it takes around 500 years to decompose. Recycling waste plastic using the pyrolysis process can be beneficial as it converts waste into energy. Pyrolysis is the endothermic irreversible thermochemical degradation and decomposition of complex long-chain organic polymer molecules into units of simple short-chain compounds at temperatures greater than 300^oC in the absence of atmospheric oxygen, with or without the application of pressure. The liquid product is oil-like material and has properties similar to diesel as plastics are originally petroleum-based products. To make pyrolysis more effective by using a catalyst which can be lower the temperature and enhance the efficiency of the reaction to produce liquid oil with characteristics of gasoline or diesel.

Keywords: Plastic Recycling, Thermoplastics, Pyrolysis, Catalyst, waste to energy.

Introduction

Plastic Polymers are major contributors to waste and plastic products consumption in different forms of products continuously increases the generation of plastic waste. Two common types of plastics are Thermoset and Thermoplastics depending upon behavior with temperature. Remolding under the application of heat is the property of plastic that make thermoplastic useful for a larger variety of purposes in different applications. Products produced with recycled plastics are not of same quality so the pyrolysis and thermo-catalytic conversion is viable solution for plastic waste management. The problem of plastic waste management and increasing world demand for fuel or energy can get solved by the conversion of plastic waste to energy. The fuel obtained by the pyrolysis process is sulfur-free and also exhibits characteristics of fossil fuel.

Thermal Cracking: (pyrolysis and Liquefaction)

Thermal cracking process solely in presence of Nitrogen gas (N₂) is known as pyrolysis and when process is undergoes in the presence of hydrogen (H₂) gas it is known as liquefaction. Pyrolysis is the safe way to produce liquid fuel from waste plastic which can be used alone or mixing with other fuel as transportation grade fuel¹.

Products produced from the pyrolysis of plastics are gas, liquid and char among them liquid oil is desired product. Most plastics contain very high volatile content. As the volatile matter increase the yield of oil in the pyrolysis process is also increases so plastic waste pyrolysis would be a beneficial technique². The pyrolysis process uses thermal energy for long-chained polymer molecules to break down into small chain molecules. By controlling the heat flow and pressure of the reaction smaller molecules can be obtained³. Conversion of waste plastic into fuel represents recovery of organic content of polymeric waste in the form of valuable petroleum products is the most sustainable way for protection of environment⁴.

Conventional plastic waste management method such as incineration generates toxic nitrogenous compounds and gases such as CO and CO₂ which produces greenhouse emission. The fact that the dioxins are not able to be produced as the process of pyrolysis takes place in the absence of oxygen so not needed Flue gas clean up⁵. Pyrolysis of plastic is beneficial in the environmental, economical and operational aspects⁶.

Pyrolysis: Pyrolysis of plastic generates products in the form of fuel for energy. The 3 different routes for pyrolysis are hydrocracking, Thermal Pyrolysis and catalytic Pyrolysis.

Hydro cracking: Involves the cracking of large polymer molecules into smaller hydrocarbon molecules in the presence of hydrogen that can be used as fuel for energy. The reaction takes place with hydrogen over a catalyst, and typically use of batch stirred reactor under conditions of 150-400⁰C and 3-10 Mpa hydrogen. This process is boost using catalysts which consist of structural support like Silica- Alumina, Zeolites etc coated with transition metal elements such as Pt, Fe, Mo and Ni by decreasing the temperature and reaction time which make reaction more effective⁷.

Thermal Pyrolysis or non catalytic Pyrolysis: Is the process in which plastic degradation is carried out at higher temperature ranging from 350⁰C-900⁰C using energy from heat under anaerobic condition. Thermal Pyrolysis is endothermic process, which required very high temperature for breaking down Plastic Polymers like PS, PP, and Polyethylene etc. Fuel which converted from plastic at higher temperature is containing large range of hydrocarbon chain which is not suitable for replacement of petroleum or diesel. Liquid product obtained from thermal pyrolysis needs to further refining to get useful as motor engine oil and achieve Octane/Cetane rating. As the temperature increases formation of gaseous product increases while the yield of liquid fuel decreases⁷. Dependence on temperature and residence time of pyrolytic fraction was studied which shows temperature has a great influence on benzene and methane production and longer residence time increases production of tar⁸. To overcome problems faced by thermal pyrolysis the term catalytic pyrolysis is important.

Catalytic Pyrolysis: Catalysts are substances that modify the rate of a chemical reaction without themselves being changed or consumed in the process and without affecting the overall thermodynamics of the system. The use of catalysts in the pyrolysis of plastic waste to obtained maximum yield in less reaction time is known as catalytic Pyrolysis. One of the main purposes of catalytic pyrolysis is to shorten the carbon chain length of the products and thus to decrease the boiling point of the products. Catalytic Pyrolysis is a process in which the addition of catalyst lowers the activation energy which significantly reduces the time and temperature required to completion of the reaction. Utilization of catalyst increases the conversion rate of the large variety of polymer at a significantly lower temperature than non-catalytic thermal pyrolysis. Various kinds of catalysts are used to improve the pyrolysis process of plastic waste overall and to enhance process efficiency⁷.

Catalyst

Catalysts have a very critical role in promoting process efficiency and reducing the process temperature and time which enhances the efficiency of reaction for targeting specific reaction. Different kinds of catalysts are used to improve the pyrolysis process of plastic waste. A wide range of catalysts have been employed in plastic pyrolysis processes, but the most extensively used catalysts are ZSM-5, zeolite, Y-zeolite, FCC, and MCM-41⁹.

Catalysts are of 2 types according to their phases are homogeneous and heterogeneous.

Homogeneous Catalyst: A catalytic system in which the substrates for a reaction and the catalyst components are in one phase, most often the liquid phase. The separation process is become easier due to the difference in phase with a heterogeneous catalyst which is in solid form, so heterogeneous catalysts are dominantly used in the catalytic pyrolysis procedure⁶. Apart from that, some research was conducted using homogeneous catalysts having Lewis acids such as AlCl₃, metatrichloroluminates meltsand organic ionic liquids. Catalytic pyrolysis of PE with AlCl₃ and electrophilic complexes at 370⁰C generated a high gas yield of 88 % as compared to thermal pyrolysis which was required 400⁰C and got a lower yield of 40%. Gaseous products are obtained predominantly are isobutane and Isobutene. The hydrocarbon heavier the C5 was not significantly obtained¹⁰. Ionic liquids as catalysts in pyrolysis of polymers have selectivity very high towards lighter alkane hydrocarbons. To separate the product of the reaction from ionic catalysts techniques such as solvent extraction or any physical separation process are useful¹¹. Catalytic systems over ionic liquids are gaining increased attention worldwide as benign solvents for green chemistry processes due to their low volatility and ease of product separation¹².

Heterogeneous Catalyst: A catalytic system in which the substrates for a reaction and the catalyst components are in different phase. The most common types of catalysts used are the nano-sized acidic zeolite catalysts, with the most effective at pyrolysis being Y-Zeolite, HZSM-5, H-ultrastable zeolite which is act as FCC catalysts. Microporous crystalline structure is with a pore size smaller than 1 nm and the narrow size distribution of zeolite permits the shape selectivity. The large external surface area and acidic nature of zeolite catalyst generate higher selectivity to shorter chained hydrocarbons. This catalyst shows better performance than amorphous silica-alumina & mesoporous MCM-41. Mesoporous catalysts like MCM-41 tend to produce heavier hydrocarbons. Silica alumina catalysts have a lower surface area and larger pore size and also have lower acid strength as compared to zeolite tend to produce bulkier hydrocarbons.

Zeolite Catalysts: Zeolites are primarily divided into 2 types Natural and synthetic Zeolites.

Natural Zeolites : are non porous made up from volcanic glass and saline water at temperature 300- 350K and pH more than 13 which requires hundreds of years.

Synthetic Zeolites: are porous with high exchange capacity. They are prepared by heating soda ash, feldspar and china clay.

Catalytic property of Zeolite: To compensate (negative) charge on Zeolite, some hydrogen ions H⁺ are present which

results acidic property of Zeolite and also responsible for catalytic property of Zeolite. Catalytic cracking due to various reactions like isomerization, dehydrogenation, hydrogen transfer, condensation, cyclization, alkylation and dealkylation occurs in the channel of Zeolite. Long chain hydrocarbons present in the oil can easily enter into the Zeolite channels and broke down into smaller chain hydrocarbons. Zeolite is also known as cracking catalyst. Zeolites are microporous structures composed of Aluminium, Silicon and Oxygen. They have a honeycomb-like structure which gives them a large surface area and acts as a shape-selective catalyst. Aluminosilicate with a 3-dimensional network of silicates in which some silicon atoms are replaced by aluminium atoms gives Al-O-Si Framework with cavities and channels, where cations reside. The ion exchange capabilities and open pores are the main characteristics of these catalysts. Zeolite catalysts have a different ratio of $\text{SiO}_2/\text{Al}_2\text{O}_3$ that determine their reactivity and also affect the end products of the pyrolysis process. Zeolites catalysts having high acidity are more active in the cracking process, hence increasing the production of light olefins and decreasing the heavy fractions. The acidity of these catalysts affects the production of liquid oil from the pyrolysis of plastics wastes. The higher the acidity, the lower will be the production of liquid oil¹³. The key features of zeolite catalysts are pore size, pore distribution and acid strength¹⁷. Narrowed carbon chain $\text{C}_{10} - \text{C}_{28}$ were obtained using Zeolite catalyst also significant yield of aromatic compounds mainly naphthalene and D-limonene achieved which indicates the product obtained is like fuel products¹⁴.

General Formula: $\text{M}_{x/n}[(\text{AlO}_2)_x(\text{SiO}_2)_y]m\text{H}_2\text{O}$ where M- Na^+ / K^+ / H^+ / Ca^{2+} / Mg^{2+} x/n - Valency of Cation, m-no. of water molecule, examples of some Zeolite are as follows.

ZSM-5 General Formula: $\text{H}_x[(\text{AlO}_2)_x(\text{SiO}_2)_{96-x}]16\text{H}_2\text{O}$ (sieve and molecular polarity 5).

Different catalyst studies

Zeolite X and Zeolite Y are types of Zeolite are distinguished from each other on the basis of silica to alumina ratio. Zeolite X has silica to alumina ratio between 2 to 3 whereas Zeolite Y has more than 3. ZMS-5, ZSM-12, ZSM-22 and HZSM 5 are different types of zeolite with different pore sizes and applications. In addition to the chemical properties geometrical features of catalyst plays an important role in selection of product¹⁵.

It was Studied catalytic degradation of HDPE with different types of Zeolites having a difference in their porosity is BEA, FAU, MWW, MOR and MFI Zeolites¹⁶. Study shows that in the determination of degradation activity of zeolite acidity and pore size are not major factors but the pore shape of zeolite is play an important role in catalytic activity during degradation. The highest activity is seen with using MFI and BEA Zeolites due to the bent pore shape, which inhibits carbon deposition. FAU zeolite catalyst is with largest pores intensified mass transfer in process and also increases the yield of liquid product. MWW zeolite catalyst enhances the yield of shorter chained hydrocarbons due to large recurrent spaces which cause slow diffusion. This proves that the pore shape can affect the catalytic activity as well as product selectivity. MOR zeolites are rapidly blocked with even a small amount of carbon deposit, resulting in poor.

Due to difference in pore size, Surface acidity and area of Y Zeolite and ZSM-5 catalyst high yield of aromatic compound found with Y- Zeolite 29¹⁷. Suitable combination of surface acidity and porous structure needed in favorable production of oil for mixed plastic pyrolysis¹⁸.

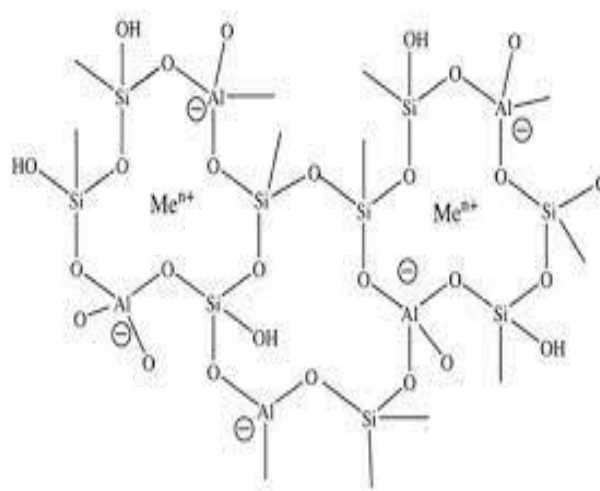
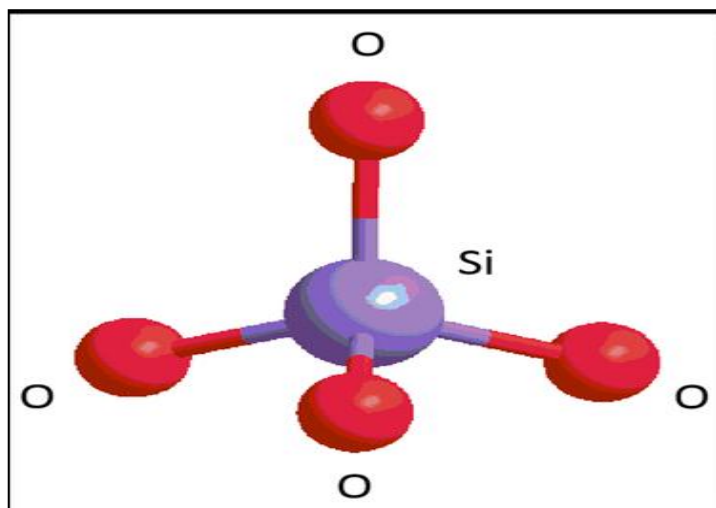


Figure-1: Zeolite 3 D structure and Al-O-Si frame work with cavities.

Table-1: List of shape selective catalyst with activity in plastic pyrolysis¹⁶.

Catalyst and structure	Si/Al ratio	Surface Area M ² /gm	Pore size	Temp.	Plastic Type	Result
BEA Zeolite: bent pore shape	13	690	Below 0.2µm	380-410°C	HDPE	Highest activity is seen
FAU Zeolite: largest pores	6.7	490	Around 0.5µm			yield of liquid product is increased
MWW Zeolite : coral shape, large recurrent spaces	10	420	Can't define			Yield of shorter chained hydrocarbons enhanced
MOR Zeolite : large but linear pore	10	410	1.5-2µm			Poor conversion
MFI Zeolite : bent pore shape,	25	390	Around 0.5µm			Highest activity is seen

GCMS study shows that around 99% of aromatic compounds are found in liquid oil produced from catalytic or thermal pyrolysis using Polystyrene as a raw material. Further refining makes the product more suitable for use as fuel.

Styrene, ethylbenzene, toluene and benzo (b) triphenylene are the major compounds found in pyrolysis oil, among all these Styrene is the major compound¹⁹.

An experiment was carried out to study the thermal and catalytic pyrolysis of different types of plastics using natural and synthetic zeolite as a catalyst. catalytic pyrolysis of polystyrene (PS), polypropylene (PP), polyethylene (PE) and their mixtures in different ratios at 450°C and 75 min. PS plastic waste resulted in the highest liquid oil yield of 54% using natural zeolite and 50% using synthetic zeolite catalysts. Mixing PS with other plastic wastes lowered the liquid oil yield. All mixtures of PP and PE resulted in higher liquid oil yield than the individual plastic feedstock using both catalysts. The liquid oils produced have high heating values (HHV) of 40.2–45 MJ/kg, which was similar to conventional diesel. The liquid oil has the potential to be used as an alternative source of energy or fuel production¹³.

Zeolite ZAA or activated Zeolite is used in the experiment for catalytic pyrolysis of HDPE and Polystyrene in a 1:1 ratio. Pyrolysis is carried out using a reactor with 3 level separators which separates oil fractions from heavy to light oil. The range of temperature was 200°C to 400°C. The total conversion was 97.2% from which 55.17% was found in the top separator having gasoline (C5-C10) hydrocarbons. According to physio-chemical studies, it is shown that all the fractions have properties of kerosene, diesel or gasoline²⁰.

Both catalysts ZSM-5 zeolite and Red Mud in the pyrolysis of mixed plastic wastes have been studied. ZSM-5 is a commercial catalyst while red mud is scarcely used. ZSM-5 is very active in plastic pyrolysis which promotes smaller molecular weight and higher aromatic compounds at 440°C and also promoted gas production. On the other hand, red mud requires a higher temperature than ZSM-5 but shows a noticeable application in plastic pyrolysis. Components like Fe₂O₃ and TiO₂ of Red mud are responsible for hydrocracking or hydrogenation reaction taking place. Red mud also can consider a solid acid catalyst which is an inexpensive by-product of the alumina industry and

can be reused. Red mud shows good hydrogenation activity as well as cracking activity²¹.

Conducted comparative study on HZSM-5 and Y type Zeolite using pure Polyethylene for determination of deactivation behavior and activity. Using catalyst high yield of oil obtained at the expense of wax. Oils obtained by the degradation with H-ZSM-5 were distributed between C₄ and C₁₀, predominantly between C₅ and C₆. The module of H-ZSM-5 seems to have little influence on the product distribution. In the case of HY 8 zeolite, the distribution of oils was slightly shifted to hydrocarbons with higher numbers of carbon, compared with the case of H-ZSM-5²².

The Comparative study on ZSM-5 and Y zeolite catalyst on polyethylene shows both increases yield of gas and decrease the oil yield with increasing temperature from 400°C–600°C. Influence of both the catalysts markedly increases the yield aromatic compounds in derived pyrolysis oil¹⁷.

PZSM-5 catalyst which is chemically modified catalyst of HZSM-5 with orthophosphoric acid is suitable for decomposition of PP and PE. The PZSM-5 catalyst, with a lower acidity and a greater steric effect than HZSM-5, catalyzed the formation of condensable products, with a higher amount of toluene and less of xylenes²³.

Pelletized form of the bentonite clay as a catalyst in pyrolysis of plastic wastes such as PS, PP, LDPE and HDPE was successfully studied that oil with higher calorific value can be produced GC MS and FTIR results are shown that oils obtained from PS had dominantly aromatic hydrocarbons in gasoline range (C5–C9), while PP, LDPE and HDPE had longer aliphatic hydrocarbons making the oil suitable for use in diesel engines. The high acidity of the catalyst (low SiO₂-Al₂O₃ ratio) of bentonite catalyst pellet as compared to the other less acidic catalyst make it more active in cracking which shows no formation of wax²⁴. Study of catalytic pyrolysis of mixed plastic using Fe-, Ti-, Zr- and Al-pillared clays using bentonite as basic raw material is carried out. Among this catalyst Fe-PILC is showing high oil yield with excellent selectivity towards diesel fraction and also high yield of H₂ gas due to its moderate acidity and higher BET surface area¹.

Using catalyst CAT-2 the liquid yield is lowered while the yield of a gaseous product increases showing hydrocarbon distributions towards a lower molecular weight (C7-C12) range with cracking at a lower temperature. The higher proportion of PP increases the gasoline range fraction²⁵.

If only zeolite is used as a catalyst gaseous product yield is increases whereas the high content of oil produced with the use of MCM-41 catalysts. As pore size provides the shape selectivity acidity provides the catalytic activity. Si-Al ration in MCM-41 is 4 and in ZSM-5 is 20, reducing in Si-Al ration increases the surface acidity by increasing the aluminum concentration.

MCM-41 acidity was useful in pyrolysis for cracking polyethylene to liquid hydrocarbon. In two-stage pyrolysis use of MCM-41 and ZSM-5 in a layered system can be useful in enhancing the production of gasoline with higher liquid yield⁹. MCM-41 is promising material as catalyst for catalytic conversion of Polymeric waste into liquid yield. As MCM-41 has weaker acidity than that of Zeolites. MCM-41, a mesoporous aluminosilicate found more active than amorphous $\text{SiO}_2 - \text{Al}_2\text{O}_3$ due to presence of higher surface area and uniform mesoporosity²⁶.

Zeolite as catalyst in pyrolysis of Multi layered plastic with polyolefin based mixed plastic waste will be feasible to obtain consistent oil quality and quantity²⁷.

CuCO_3 as a catalyst plays an important role in reducing the temperature of the reaction up to 390°C and also HDPE deformation was seen due to the formation of CuO carbenium. 94% of liquid fuel yield was observed using 5% CuCO_3 ²⁸.

An increase in gasoline fraction was observed with the use of Y – Zeolite catalyst and an increase in Diesel fraction was observed with MgCO_3 catalyst. MgCO_3 is act as an inexpensive basic catalyst²⁹.

Mesoporous silica (KFS-16-kanemite derived folded silica) which was synthesized having uniform hexagonal pore of around 3.6nm in size accelerate the degradation of HDPE to liquid hydrocarbon even though catalyst is not contain any acid site³⁰.

Use of 5-10% dolomite as catalyst in pyrolysis of different plastics enhanced the low molecular weight component concentration in liquid fuel which increases the calorific value of fuel³¹.

Over the past two decades, a large number of results on catalytic pyrolysis process for plastic have been reported. A wide range of catalysts such as ZnO , MgO , CaCO_3 , CaC_2 , SiO_2 , 4 Al_2O_3 , 4 $\text{SiO}_2 - \text{Al}_2\text{O}_3$, 4 ZSM-5 zeolite, 6–8 kaolin, red mud, CuCO_3 and FCC have been used. A study carried out using Coal Fly Ash (CFA), Basic CFA derived Zeolite (NaX/CFA) and acidic CFA

derived Zeolite (HX/CFA) is carried out. Due to stronger acidity HX/CFA shows more selectivity towards lower hydrocarbons than other³².

In his experiment successfully proves kaolin clay is efficient catalyst for the conversion of PP waste into gasoline/ diesel/ kerosene range products using pyrolysis³³. Kaolin clay is increases yield of oil and also the rate of reaction. As kaolin clay is abundant in nature so its commercial application in degradation of plastic becomes useful as it reduces the cost of process¹. Kaoline clay as catalyst also gives maximum yield using HDPE plastic waste at $400^\circ\text{C} - 500^\circ\text{C}$ ³⁴.

Wide range of basic and acidic catalyst like silica, calcium carbide, magnesium oxide, zinc oxide, alumina and homogenous mixture of silica alumina was used for polyethylene conversion. A comparative Study carried out Shows SiO_2 has maximum efficiency and CaC_2 is better on the basis of reaction time for conversion of LDPE in optimum conditions. The results also indicate the oxide containing catalysts are best suited for selective conversion into polar and aromatic products while CaC_2 shows selective conversion into aliphatic products³⁵.

Reforming Catalyst: The most commonly used reforming catalyst was $\text{Pt/SiO}_2 - \text{Al}_2\text{O}_3$ with about 0.5% wt Pt only. Catalyst which is based on transition metals supported on silica – alumina is known as reforming catalysts. These catalysts are bifunctional, as they have two active sites which plays different role. Metallic sites catalyze hydrogenation/ dehydrogenation reaction while acidic site on the support catalyze isomerization reaction. Proper combination of these both functions can promote variety of reforming reactions and having highest selectivity towards aromatic products³⁶. To increase octane number with catalyzation reaction platinum catalysts supported on silica-alumina and alumina is widely used in degradation of polyethylene. When reforming catalysts are applied for plastic cracking the alumina based acidic sites acts as FCC catalyst while metal sites acts as dehydrocyclization and isomerization reaction and shows higher selectivity in production of aromatic compounds which was already demonstrated by Uemichi Y.³⁷

Activated carbon catalyst: Activated carbon catalyst has high cracking and cyclization activities in the degradation of polyethylene to produce aromatic hydrocarbons in significant amounts. Activated carbon catalyst was effective for the formation of n-alkanes and aromatics. It was studied that activated carbon impregnated with Pt, Fe, MO, Zn, Co, Ni or Cu showed a higher catalytic activity for the formation of aromatics than that of the metal-free catalyst. Among them Pt and Fe ate most effective with activated carbon as support. Yield of aromatic increased from 45% to 60% with use of metals like Pt, Fe, Mo with activated carbon catalyst. Benzene was produced as main aromatic component with using Pt containing catalyst while toluene is the main aromatic product with using Fe, Mo containing catalysts^{37 38}.

Table-2: List of conventionally used catalyst in plastic pyrolysis and their results.

Catalyst	Temperature	Plastic Type	Result		Ref.
Natural Zeolite/ Synthetic Zeolite	450°C for 75 min	Polystyrene (PS), Polypropylene (PP), Polyethylene (PE) and their mixtures in different ratios	Liquid oil yield of 54% with natural and 50% with synthetic zeolite. Mixing of PS with other plastic wastes lowered the liquid oil yield. All mixtures of PP and PE resulted in higher liquid oil yield than the individual plastic feedstock using both catalysts.		13
Natural Zeolite/ Synthetic Zeolite (Zeolite type SDUSY, hydrogen form, aluminium oxide)	450°C for 75 min	Polystyrene (PS)	Liquid oil yield of 54% with natural and 50% with synthetic zeolite while thermal pyrolysis 80% liquid		19
Zeolite ZAA	350°C for 90 min	HDPE + Polystyrene (1:1)	Total conversion 97.2% gasoline 55.17% using 3 level separator apparatus at 200- 400°C		20
CAT – 2 Zeolite	460°C heating rate 10°C/min	PP, LDPE PP+LDPE (PP in lower proportion)	Liquid yield	With catalyst 58% 51% 68% without catalyst 86% 96% 62%	25
ZSM 5	440°C	Mixed plastic	40.4 wt% gases and 56.9 wt% liquids		21
	500°C		17.7 wt% gases & 79.3 wt% liquid		
Red Mud	440°C	Mixed plastic	58.4 wt% gases and 39.8 wt% liquids		
	500°C		34 wt% gases & 89.2 wt% liquid		
HZSM-5	290°C-430°C	PE	21.6 wt% gases and 72.2 wt% liquids		22
			41.3 wt% gases and 57.0 wt% liquids		
Y Zeolite	290°C-430°C	PE	Liquid 70% Gases 21% Lighter hydrocarbons		
PZSM-5	50°C-250°C	PP, PE	Liquid 67% Gases 26%		23
MCM-41 + ZSM-5	500°C heating rate 10°C/min	HDPE	Liquid: PP-43.3%, PE-34.6% PP – gas products contains 89% of C3 product		9
MCM-41	400°C for 30 min	HDPE LDPE PP	Total Conversion	HDPE: 35.2% LDPE: 67.6% PP: 41%	26
SiO ₂ - Al ₂ O ₃	400°C for 30 min	HDPE LDPE PP	Total Conversion	PE: 9.2% LDPE: 34.4% PP: 47.9%	
ZSM-5	400°C for 30 min	HDPE LDPE PP	Total Conversion	HDPE: 96.4% LDPE: 95.4% PP: 11.3%	
HMCM-41	375°C for 30 min	PS	Total Conversion	82%	
HZSM-5	375°C for 30 min	PS	Total Conversion	75%	
Bentonite Clay	500°C for 10 min	PSPP LDPE HDPE	Without catalyst 85.6–89.5%	With catalyst 86.6-90.5%	24
Fe - PICL (modified pillared bentonite clays)	300°C for 5/ min increased to 500°C for 30 min	Mixed Plastic	97.72% gasoline with aromatic contents of 95.85% Oil yield is around 80-83%		18
Al - PICL			Oil –79.3% Gas -18%		
Ti - PICL			Oil – 68.2% Gas -30.8 %		
			Oil – 62.8 %		

			Gas -34.2 %	
Zr- PICL			Oil – 62.1 % Gas – 36.7 %	
kaolin clay	400 ⁰ C- 550 ⁰ C	PP	Liquid – 87.5 % Gas - 11.75 %	7
CuCO ₃	390 ⁰ C	HDPE	2% CuCO ₃ : 90% 5% CuCO ₃ : 94% 8% CuCO ₃ : 92%	Without catalyst : 85% 28
Y Zeolite	430 ⁰ C	HDPE	75% liquid crude oil	29
MgCO ₃	450 ⁰ C	HDPE	80% liquid crude oil 86.2% liquid crude oil without catalyst	
KFS 16 B	430 ⁰ C	HDPE	More than 80% Liquid oil	30
CaMg(CO ₃) ₂	400 ⁰ C-450 ⁰ C	HDPE, LDPE, PP	More than 80% Liquid oil	31
NaOH	450 ⁰ C	HDPE	81% liquid and 19% gas yield, no wax	14
Huzy Zeolite	450 ⁰ C	HDPE	Highest yield of Gases 73%	
H Beta Zeolite	450 ⁰ C	HDPE	Highest yield of Gases 81%	
Coal Fly Ash	450-480 ⁰ C	PFR (Packaging plastic film residue made up of PE)	HX/CFA highly selective toward lower hydrocarbon	32
NaX/CFA				
HX/CFA				
CaC ₂	350 ⁰ C for 1h	Waste PE	70 % liquid yield	35
SiO ₂	350 ⁰ C for 3 h		79% liquid yield	
MgO	350 ⁰ C for 2 h		66% liquid yield	
Al ₂ O ₃	350 ⁰ C for 2 h		62% liquid yield	
SiO ₂ – Al ₂ O ₃	400 ⁰ C for 3 h		68% liquid yield	
ZnO	400 ⁰ C for 3 h		65% liquid yield	

Table-3: List of catalyst with their Physio- chemical Properties.

Catalyst	Si/Al ration	Structure	Surface Area M ² /gm	Pore size	Ref.
Natural Zeolite	9.2	Nano-micro size	3.231	8.34 Å	13
Synthetic Zeolite	5.1	Microporous	900	24.65 Å	
ZSM 5	50	Microporous	412	Nearly 100 -300 nm	21
Red Mud lower acidity	Si–O–T units	Meso-microporous material	27.49	Some nanometer	
MCM-41 Highly acidic	4	Mesoporous	799	3.95nm	9
ZSM-5	20	Microporous	266	5.2 nm	
MCM-41	42.7	Mesoporous	1327	2.9 nm	26
SiO ₂ -Al ₂ O ₃	35.6	Amorphous	261	40-110 nm	
ZSM-5	31	Microporous	362	0.55 nm	39
HMCM-41	42.7	Mesoporous	1327	2.8 nm	
HZSM-5	31	Microporous	362	0.55	

Bentonite Clay	0.94	Mesoporous	47	10.9 nm	34
KFS 16 B	∞	Mesoporous	900	3.6 nm	30
Huzy Zeolite	5.2	Micro-Mesoporous	660	-	14
H Beta Zeolite	300	Micro-Mesoporous	620	-	
Fe – PICL (modified pillared bentonite clays)	-	Microporous	215	26.2	18
Al – PICL	-	Microporous	2018	18.3	
Ti - PICL	-	Supermicropores - large mesopore	280	22.5	
Zr- PICL	-	Microporous	201	20.9	
kaolin clay	0.94	Mesoporous	23	-	33

Conclusion

Catalytic pyrolysis with suitable catalyst offers lower reaction time and temperature. The catalytic pyrolysis process also demonstrates the ability to produce products of similar composition to motor fuel. The most used catalysts are Zeolites (eg. HZSM-5, HY), mesoporous catalysts like MCM-41 and silica –alumina.

Depending upon pore size catalysts are gets divided into macroporous and microporous category. During pyrolysis process of plastic macroporous catalyst favors liquid and microporous catalyst favors gas products.

Catalyst like Zeolite having internal crystalline structure and higher BET Surface area increases the catalytic activity which increases the gaseous yield and decreases liquid yield.

Acid base catalyst shows more cracking with increase in production of gases and decrease in liquid product. Acidic catalyst removes impurities from liquid product.

Reforming catalyst in which metals are doped on acid base catalyst is enhances the catalytic activity and also perform dual function.

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