



Methods for chemical conversion of plastic wastes into fuels and chemicals. A review

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Abstract

Plastics are utilized in various materials that are useful in everyday life. As the usage of plastics increases, the disposal of plastic materials has become a major issue, calling for recycling methods. Here, we review the different methods to recycle plastics, with focus on catalytic cracking. We present catalysts, cracking mechanisms, and we compare the various treatment methodologies. Several attempts were made by researchers to increase the efficiency of the cracking process using different catalysts and reactors. Many studies reveal high quality products are obtained by catalytic cracking, which consumes low energy and produces lesser residues when compared to other treatment technologies.

Keywords Plastics · Catalytic cracking process · Mechanisms · Catalyst · Reactors

Abbreviations

PET	Polyethylene terephthalate
PS	Polystyrene
PP	Polypropylene
HDPE	High-density polyethylene
LDPE	Low-density polyethylene
PVC	Polyvinyl chloride
HZSM-5	Hydrogen zeolite Socony Mobil-5
MCM-41	Mobil Composition of Matter No.41
Al–Al ₂ O ₃	Alumina-supported aluminum oxide
PE	Polyethylene
AMF	Alumino silicate mesostructured foam

FCC	Fluid catalytic cracking
RON	Research octane number

Introduction

Today, plastics play a significant part in all over the world because that is useful in making different kinds of products. In the area of textile, packaging and consumer electronics, plastics are most important. The essential element of plastic is a polymer. Polymer is a Greek word that represents many parts. Due to the significant demand in the field of farming, packing materials, vehicles, electronics and in other applications, the plastics are manufactured in large quantities. The production rate of plastics and their products was increased this year when compared to previous years. During the year 2015 to 2016, the production of plastics was increased by about 13 million tons (Kehinde et al. 2020). Half of the plastic products are disposed of on the roadsides because they are single-use plastic products. It is a typical practice that plastics are not disposed into the waste bins properly for additional processing, recovery, landfill site; they are carelessly disposed of which was difficult for waste collection. Plastic waste is not only an issue for human life or wildlife but also a major concern to the government (Reddy et al. 2014). The best solution for this problem is to recycle plastic waste. By recycling the plastics, more amount of energy can be conserved, and it reduces the greenhouse gas emissions

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and safeguards the resources. Throughout the world, the most demanding research area is generation of fuel from plastics. The composition of the fuel depends upon the type of plastics, temperature and atmospheric conditions. Plastic waste is generally impacted by manmade fibers such as polyethylene terephthalate (PET), polystyrene (PS), polypropylene (PP), high-density polyethylene (HDPE), low-density polyethylene (LDPE) and polyvinyl chloride (PVC) (Sulyman et al. 2016; Sandin and Peters 2018).

In the consecutive section, the characteristics of various plastics, different methods employed for recycling of plastics were explained. In addition to that, mechanism involved in plastic cracking, the behavior of different catalysts and reactors performance were also presented in this review.

Polyethylene terephthalate

Polyethylene terephthalate (PET) is a crystalline form of thermoplastic material. The properties of PET are toughness, strength, abrasion, chemical resistance and low moisture absorption. PET is generally simple to reuse, and therefore, it is mostly used as a packing material and primarily in projector, films (Zhao et al. 2018). To degrade PET efficiently, hydrolysis process is used either in the presence of acid or base. Ethylene glycol and terephthalic acid combined to form PET. 1 kJ (Kg K) is the thermochemistry of PET. When PET undergoes the pyrolysis process, terephthalic acid, benzoic acid and carbon dioxide (CO₂) are formed, which leads to global warming (Ahmad et al. 2015b). The pyrolysis oil obtained from PET contains heteroatom in the range of 0.1–15% which indicates the impurity of the product (Wang et al. 2019a, b). PET contains a cyclic compound of oligomers from dimer to pentamer. Based on the type of PET, the cyclic compound will be between 0.06 and 1% (Hahladakis et al. 2018). Generally, PET is easy to recycle because breaking of polymer chain is possible even at very low temperature. Hence, this type of plastic waste can be recycled for a greater number of times until it turns to unusable.

High-density polyethylene

Among different types of polyethylene (PE), high-density polyethylene (HDPE) is the one highly used. It is non-biodegradable and takes hundreds of years to decompose. HDPE has a linear chain without any side branches and more crystalline. Compared to LDPE, HDPE is stronger, stiffer, robust, brittle, and costly but possesses high physical stress. It is widely used in food containers, kitchenware, toys and furniture. The composition of HDPE is about 83.9% of carbon, 14.9% of hydrogen (H₂) and 0.74% of oxygen (Sharma et al. 2014). Environmental impact produced by this type plastic is high because HDPE is

used in various applications. Therefore, proper recycling of HDPE is essential.

Low-density polyethylene

Low-density polyethylene (LDPE) has side branches where the chains are not packed loosely in the form of crystallites. This is the major difference between LDPE and HDPE. The addition of comonomers in the main chain of the PE leads to a decrease in the density which is known to be LDPE. The process called stirred autoclave or tubular routes is used for manufacturing LDPE. It is generally used as an electrical insulator and as packaging films, bottles and tanks. The density of PE ranges from 0.910 to 0.925 g/cm³ (Jordan et al. 2016). LDPE is poorly resistant to CO₂, oxygen but acts as a resistance for water vapor (Goswami and Mangaraj 2011). Because of its simple structure, LDPE is very easy to produce and mostly used for making different types of bags, but recycling is challengeable.

Polyvinyl chloride

Polyvinyl chloride (PVC) is a thermoplastic material that has high strength, used for making pipes, wires and cables. It is white, fragile strong material and feasible in powder form or granules. Most of the researchers have detailed that it is broadly used plastic material (Sadat-Shojai and Bakhshandeh 2011). Based upon its characteristics, it is classified into two forms. They are plasticized and unplasticized. Plasticized material is mostly used for packaging because of its very good surface properties. Unplasticized material is widely used in construction materials such as wall claddings also in window frames. Different recycling methods are available such as incineration, composting, landfilling, mechanical recycling and chemical recycling, of which only mechanical and chemical recycling methods are mostly favorable for recycling PVC (Kameda et al. 2010). At present, the recycling of PVC is increasing compared to other plastics materials.

Polystyrene

Polystyrene (PS) is a manmade polymer aromatic hydrocarbon from the monomer called styrene. It is simply brittle and can be either in foam form or in solid form. Since the cost of PS is low, it is mostly preferable in making drinking cups, light fittings, kits for aircraft. Some electronic waste plastic materials contain PS which is not easily recyclable (Beigbeder et al. 2013). It is resistant to acids and alkalis, and hence, its usage is high for packaging and electronic

products but soluble in both toxic and non-toxic solvents (Yang and Yang 2012). In addition, PS is a poisonous plastic even when a limited quantity of PS is burned, it may cause visual problems, because of the inhalation of toxic chemicals released from PS, sometimes lead to vomiting, especially for young children which can cause very serious issues. Brems et al. (2011) have found out that when PS undergoes the pyrolysis process, the rate of degradation is low and hence it has become a great compete for environmental conservers.

Polypropylene

Polypropylene (PP) is a flexible plastic which is widely used in various applications such as in TV, computer cabinets, car components and small machine parts. It is available in both film and fiber form. A very important distinctive feature about PP is that it appears effortlessly crystalline. PP has poor conductivity of electricity, good chemical resistance and very hard which cannot be easily breakable and it also behaves like elastic. When PP is blended with HDPE, the brittleness of HDPE increases (Wang et al. 2019a, b). Plastic wastes are not homogeneous in which different recycling methods are favored and recycled products are obtained. For an instance, Gu et al. (2016) reported that recycled PP contains a high amount of ash content and hence PP is generally used as a packaging plastic. Recycling of PP is prominent nowadays because of its environmental threat created by improper disposal and conceived to be economically viable.

Effects of disposal of plastics

Current natural and wellbeing impacts are identified with plastics which are still inadequately inferred, however, possibly extensive. Ecological contamination by plastic debris is broadly considered as destined natural stress particularly in the oceanic environment and creates negative effects on the wildlife (Alabi et al. 2019). Environmental impacts due to disposal of plastic wastes include entrapment and spoilage of environment for animals and absorption of hazard, transfer of biological systems to a new environment, sewage blockages which results in breeding mosquitoes and various health issues such as deposition in the human parts, creating problems in respiratory systems, lymphatic system, circulatory system, etc. (Lamb et al. 2018; Setala et al. 2014; McCormick et al. 2016; Virsek et al. 2017; Feng et al. 2017). The effects of plastic disposal depend mainly on the characteristics and the composition of plastic material. The characteristics of different polymers used in the previous studies are listed in Table 1.

Terrestrial birds and animals get affected, especially because of macro-plastics. Most of the plastic wastes get disposed in underdeveloped countries. The chemicals released

from the plastics which was disposed of in the ground, cause soil pollution. *Pseudomonas* and *Flavobacteriia* break up the nylon material led to the emission of methane (CH_4) gas which is responsible for global warming (Jambeck et al. 2015; Ganguly and Choudhary 2018). The chlorinated plastics can drain out harmful synthetic compound into the soil that gets contaminated in the groundwater or pollute the surrounding aquatic ecosystem. Generally, an average of about 8 million tonnes of plastics are disposed of inside the ocean annually (Jambeck et al. 2015). Owing to the ingestion of polymers in marine, various organisms such as turtles, sea-birds, fishes and mammals lead to the reduction of reproduction, movement, feeding and even cause death also. The major gas released on the burning of plastic is CO_2 which will not allow the heat radiation to emit outside from the atmosphere. Even some of the heavy metals, polychlorinated biphenyl and furans are also released into the atmosphere. Particularly, the types of monomers and the type of additives are capable of the suspected health risks. As per the size, shape and polymer type, the effects will vary (Dris et al. 2015). The size of the plastics less than 5 mm is known as microplastics which are being perceived as one of the utmost dangers to the marine environment over the entire world (Laskar and Kumar 2019). These plastics also cause serious threat to the human beings: it disrupts the reproduction and may get contaminated with blood (Padervand et al. 2020). Microplastics and nanoplastics are generally utilized in various fields, such as semiconductors, beauty care products and drug transporters. It has now become an ordinary utilization for the creation of various materials (Ruan et al. 2018). After ingestion of food by the marine organisms, contamination occurs by the microplastics that lead to public health risk. Moreover, chemical additives that are combined with plastics during its production process, such as phthalates, bisphenol, polybrominated biphenyl which are weakly bonded with the plastics can easily relocate from plastics to air, water, soil and get contaminated with tissues. Hence, these contaminants are considered to be toxic to the environment (Andrady 2011; Hermabessiere et al. 2017; Horton et al. 2017; Lithner et al. 2011; Rodrigues et al. 2019). The toxicity of plastics is an issue globally from individual to a group of people. The frequent deposition of plastic items in various water bodies including lakes, streams and so on which upsets the natural flow, restricts fish reproduction and diminishes other organisms (Proshad et al. 2018). Additionally, plastic bags are mostly used for packing food materials which can cause serious health issues because due to chemical reaction that takes place in the plastic materials may release carcinogenic agents into the atmosphere (Adane and Muleta 2011). To decrease these effects on the environment, the littering of plastics should be reduced. It can be done by using the strategies such as reduce, redesign, reuse and

Table 1 Characteristic of different polymers used in previous studies

	Proximate analysis					Ultimate analysis					References
	Moisture	Volatile matter	Ash	Fixed carbon	Carbon residue	Carbon	Hydrogen	Nitrogen	Sulfur	Oxygen	
Plastic material	0	99.90	0.01	0.09	0.20	83.10	11.77	0.14	0.16	–	Ahmad et al. (2015a)
	–	93.7	0	6.3	–	90.8	7.1	0.1	0	2	Suriapparao et al. (2020)
PP ^a	0.15–0.18	95.08–97.85	1.99–3.85	0.16–1.22	–	–	–	–	–	–	Sharma et al. (2014)
											Miandad et al. (2016)
											Sajdak et al. (2015)
											Aydinli and Caglar (2010)
	0.00–0.30	95.08–100	0.00–9.00	0.00–1.22	–	85.1–86.50	12.90–14.40	0.00	0.00–0.5	0.00–0.20	Yu et al. (2014)
											Pinto et al. (2016)
											Chen et al. (2017)
											Zhou and Yang (2015)
	–	–	–	–	–	85.18	14.54	0.02	–	0.26	Wang et al. (2019a, b)
	0.16	–	4.45	1.62	–	83.65	14.27	0.67	0.1	0.15	Hakeem et al. (2018)
HDPE ^b	0.00	98.57–99.81	0.18–1.40	0.01–0.3	–	–	–	–	–	–	Sharma et al. (2014)
											Ahmad et al. (2013)
	0	100	0	0	–	80.58	13.98	0.60	0.080	5.19	Singh et al. (2018)
	0	100	0	0	–	85.93	14.07	0	–	0	Chen et al. (2020)
	–	99.44	0.52	0.04	–	85.42	14.30	–	0.04	0.16	Xu et al. (2020)
	1.74	58.56	31.11	8.59	–	–	–	–	–	–	Syamsiro et al. (2014)
HDPE waxes	–	–	–	–	–	83.80	14.90	1.30	–	–	Rodriguez et al. (2019)
Virgin HDPE	0	100	0	0	–	84.95	14.30	0.55	–	0.20	Singh et al. (2018)
LDPE ^c	0.3	99.6–99.7	0.0–0.40	0.0	–	–	–	–	–	–	Aboulkas et al. (2012)
											Miandad et al. (2016)
	0.46–0.61	86.83–91.75	0.00–0.02	7.77–13.17	–	–	–	–	–	–	Zannikos et al. (2013)
PET ^d	0.00–0.46	88.61–91.75	0.00–0.02	7.77–11.39	–	–	–	–	–	–	Xiong et al. (2015)
											Pinto et al. (2016)
	0.25–0.30	99.50–99.63	0	0.12–0.20	–	–	–	–	–	–	Anash et al. (2016)
PS ^e	–	99.5	0	0.5	–	89.5	8.5	0	0	2	Abnisa and Daud (2014)
											Park et al. (2012)
	0.00–0.30	97.85–99.80	0.00–1.99	0.12–0.24	–	86.40–92.70	7.40–8.50	0.00–6.10	0.00–0.10	0.00–1.30	Suriapparao et al. (2020)
											Dorado et al. (2015)
											Melendi-Espina et al. (2015)
	–	–	–	–	–	91.92	7.89	–	–	0.19	Zhou and Yang (2015)
											Wang et al. (2019a, b)

Table 1 (continued)

	Proximate analysis					Ultimate analysis					References
	Moisture	Volatile matter	Ash	Fixed carbon	Carbon residue	Carbon	Hydrogen	Nitrogen	Sulfur	Oxygen	
PE ^f	–	–	–	–	–	80.5	15.5	0.08	–	3.90	Zhou and Yang (2015)
	0.00–0.30	98.87–99.80	0.00–0.99	0.04–0.20	–	80.50–85.40	14.30–15.50	0.00–0.30	0.00–0.30	0.03–3.90	Sajdak and Muzyka (2014)
											Yu et al. (2014)
											Zannikos et al. (2013)
											Zhou and Yang (2015)
PVC ^g	–	–	–	–	–	84.59	14.24	0.05	0.03	1.09	Wang et al. (2019a, b)
	0.00–0.80	92.14–98.57	0.00–1.40	0.03–7.86	–	–	–	–	–	–	Xiong et al. (2015)
											Park et al. (2012)

PP^a, polypropylene; HDPE^b, high-density polyethylene; LDPE^c, low-density polyethylene; PET^d, polyethylene terephthalate; PS^e, polystyrene; PE^f, polyethylene; PVC^g, polyvinyl chloride

recycle. Mostly used strategy to reduce the environmental threat and depletion of resources is recycling.

Technologies available for the recycling of plastics

Various treatment methods are available to convert plastics to valuable products like mechanical recycling, chemical recycling, Landfill, Incineration. But nowadays, chemical recycling methods are mostly preferred since it produces high-quality oligomeric compounds, low molecular weight compounds, fuels, etc. Chemical treatment methods like thermal cracking, catalytic cracking process and some of the recently developed techniques like microwave-assisted pyrolysis process, plasma pyrolysis process were also depicted in this review. Percentage yield obtained by different recycling methods is presented in Table 2.

Hydrocracking process

The addition of H₂ to the cracking process is known as the hydrocracking process. The H₂ used in this process improves the quality of product yield. It works between the temperature range of about 375–500 °C under the atmospheric pressure of about 70 atm approximately (Ragaert et al. 2017). The catalyst along with the H₂ is utilized for the cracking of plastics to reduce the temperature in operating conditions and to extend the product yield. The high quality of liquid with a smaller number of olefins was also obtained using this process. However, Munir et al. (2017) detailed a report and stated that under high temperature, the kind of catalyst has insufficient dominance on the process. Initially, the plastics waste should be pyrolyzed; after that, the liquefaction process will take place. The obtained liquid from that process passed over the catalytic bed (Solis 2020). The major disadvantages of this process are expensive H₂ (Ragaert et al. 2017), and it is not suitable for PVC cracking because of its poisoning effect (Solis 2020).

Gasification process

Gasification is one of the thermochemical processes used to produce hydrocarbons and syngas which contains carbon monoxide (CO), CO₂, CH₄ and H₂. The most important product is the formation of syngas. Steam, air, or oxygen is used as an oxidizing agent (Trippe et al. 2011) in temperature range of about 800–1200 °C (Shahabuddin et al. 2020). Nearly 21 to 50% of oxygen usage in the gasification process, yield syngas with a higher heating value (Arena 2012). For different models of plastics, researchers have examined the gasification process. Bai et al. (2019) encountered the problem of using PS, in the batch reactor for the gasification

Table 2 Percentage yield obtained by different recycling method

	Recycling technique	Plastic material used	Catalyst used	% Yield			References
				Gas%	Liquid%	Solid%	
1	Thermal cracking	HDPE ^a	No catalyst used	13	84	3	Kumar et al. (2011)
2	Hydrocracking	Polyolefins	HZSM-5	13	1	13	Liu et al. (2021)
			HY	73	20	6	
			Al-MCM-41	11	9	68	
			WO ₃ /ZrO ₂	23	23	31	
3	Plasma gasification	Mixture of plastics	No catalyst used	Syngases: CO-26.5 H ₂ -44.6 N ₂ -29.9	–	–	Mazzoni et al. (2017)
4	Catalytic pyrolysis	HDPE ^a , LDPE ^b	Fly ash	24.16	50.84	25	Nalluri et al. (2021)
		PE ^c	H-Beta	95.7	2.4	1.9	Zeaiter (2014)
5	Plasma pyrolysis	PE ^c	No catalyst used	10.9	–	–	Aminu et al. (2020)
6	Pyrolysis	HDPE ^a	No catalyst used	44.8	53.5	1.7	Zeaiter (2014)
7	Two stage pyrolysis (Pyrolysis + Catalytic pyrolysis)	HDPE ^a	Al-MCM-41	18	74	8	Wong et al. (2015)
8	Microwave-assisted pyrolysis	HDPE ^a	No catalyst used	19	81	–	Wong et al. (2015)

HDPE^a, high-density polyethylene; LDPE^b, low-density polyethylene; PE^c, polyethylene

process. It was reported that the performance of plastic degradation was improved by increasing the process temperature and time. The various reactions were carried out during this process, especially endothermic and exothermic processes. Besides CO and H₂ as mentioned earlier, the syngas and impurities like hydrogen sulfide (H₂S), nitrogen oxide (NO_x), ammonia (NH₃) and some alkaline deposits are also formed during this process (Dudynski et al. 2015; Ruiz et al. 2013). But in this technique, pure oxygen is suitable only for a large amount of feedstock (Arena 2012) and oxygen must be separated from air; hence, air separation unit is required which is very high cost. An oxidizing agent, oxygen under pure condition should be used but leads to high operation costs (Lopez 2018).

Plasma gasification process

This process converts solid waste into useful energy using external power to heat the system and leads to higher conversion of plastics due to its higher temperature nearly about 15,000 °C. This is known as the allothermal process. An electric arc produced from the plasma torch is mostly used as an external source in this process (Arena 2012). Here also, syngas is produced from the solid state of organic matter. Except for radioactive materials, most of the materials such as plastics are broken down into an elemental form (Sanlisoy and Carpinlioglu 2017). Based on the plasma discharge, it is classified as direct current, radiofrequency or microwave (Tang et al. 2013). When compared to the conventional gasification process, the product obtained from this process has high quality. This process is not mostly preferred because a

high amount of electric current is required. Approximately, 15 to 20% of power output is required for 1200–2500 MJ/ton of waste (Lombardi et al. 2012).

Thermal cracking process

The pyrolysis process or thermal cracking is used to convert mixed plastics to fuels, monomers and chemicals. The foremost appropriate energy recuperation process is pyrolysis which is recovered from plastic. Sometimes, thermal cracking is also called as thermochemical transformation process mostly applicable for the wastes which get diverted from landfills. It is considered to be a more manageable process when compared to the gasification process. In contrast to the mechanical recycling method, this alternative method for the heterogeneous combination of plastics increases the adaptability of the method concerning raw materials used. (Vermeulen et al. 2011). The degradation mechanism of pyrolysis process on cracking of plastics is very difficult to understand; hence, the same process in the presence of catalyst is mostly preferred (Miskolczi and Nagy 2012; Lopez-Urionabarrenechea et al. 2012). Pyrolysis is a very easy method and financially not suitable when it is used in large-scale development (Ragaert et al. 2017). Another major issue is that, on pyrolyzing solid plastic waste containing polyvinyl chloride, leads to the formation of hydrogen chloride and hence the resulting products from this process cannot be used as a petroleum feedstock (Sadat-Shojai and Bakhshandeh 2011).

Plasma pyrolysis

The plasma pyrolysis process takes place at higher temperatures, and it is considered to be a suitable method for plastic waste treatment. In this plasma pyrolysis process, the wastes get heated at a very high temperature of about 1000 °C using plasma torches (Chen et al. 2015). This process takes place very rapidly and gets converted to CO, H₂, CH₄, acetylene (C₂H₂) and other hydrocarbons (Puncochar et al. 2012). In this process, an oxidizing agent is supplied and rapid heating will take place. A high volume of solid waste such as plastics can be reduced effectively using this technique (Tang et al. 2013). Appropriate plasma selection is the major problem of this technology (Dave and Joshi 2010) and also suitable for mixed waste and requires power (Puncochar et al. 2012).

Microwave-assisted pyrolysis

The microwave-assisted pyrolysis process involves the transfer of heat from the microwave to the plastic by conduction. Microwave heating supplies the heat to the plastic material equally without any deviation (Suresh et al. 2021). The conversion of electromagnetic radiation to thermal energy takes place in this process by the involvement of absorbent as the dielectric element. The distribution of heat is even throughout the plastics and reaches high conversion because the rate of heat transfer is high (Arshad et al. 2017). The primary feature in this process is that the heating of plastics without direct contact. Until now, this process was carried out in a small scale. (Aishwarya and Sindhu 2016). Numerous investigations have reported that the rate of heat transfer is very high (Motasemi and Afzal 2013; Lam and Chase 2012). This process operated at a high temperature compared to the conventional pyrolysis process permits higher polymer breakdown. The transfer of energy in absorbent is considered to be unusual in this technique (Arshad et al. 2017). The dielectric material has different heating efficiency and lacks information about its properties, and hence, this process is most preferable at the laboratory-scale level (Sharuddin et al. 2016).

Catalytic cracking process

Catalytic cracking is the main method for splitting plastics to produce low molecular weight valuable products. It is a tertiary recycling process. The most broadly utilized method for the production of fuel from plastic is the catalytic cracking process. This process can be used to treat the polymer which enhances the efficiency of energy which is based on the reactors, temperature, type of catalyst and feed material used. The presence of catalyst in cracking process influences both the product structure and the formation of desired product with numerous advantages

(Jahnavi et al. 2020, Kumar et al. 2015). The optimum ratio of PP and catalyst was identified by Panda and Singh (2011), and they mentioned that as the catalyst feed ratio changes, the product obtained also varied. The increase in yield of oil was obtained up to the ratio of 3:1 (polymer to catalyst). Roozbehani et al. (2014) correlated the product dispersion attained by breaking of HDPE in catalyst presence and absence. The liquid product formed was increased till 450 °C. But after 450 °C, it was observed that the formation of liquid product was reduced in this process, whereas for the non-catalytic process the yield of the liquid product increased.

The presence of acid sites inside the catalyst act as an important part of this method. In the thermal cracking process, the breaking of the polymer chain will take place at high temperature. This problem can be overcome by the catalytic cracking process because the temperature of the reaction decreases, enhancement the product generation rate occurs and the formation of undesired reaction is inhibited (Ma et al. 2016). Henceforth, it is cheaper than the thermal cracking process. Percentage yield obtained by cracking of plastics using different catalysts is given in Table 3. The majority of work in the plastic cracking process was done using unmixed catalyst because of the presence of contaminants in the blended plastic materials (Almeida and Marques 2016). In this process with a suitable catalyst, the conversion may occur; even 100% and nearly 86 to 92% of oil can also be obtained (Sahu et al. 2014). The pretreatment of waste plastic should be done to overcome the problems such as deactivation of catalyst and blockage of cavities inside the catalyst (Ragaert et al. 2017). Due to coke arrangement in the interior part of the catalyst causes this kind of issues. As a result of secondary reactions taking place in the catalytic process, mainly organic materials get struck into the micropores and block the active sites of the catalyst (Renzini et al. 2011). Hence, 2 to 50-nm-pore-size diameter catalyst was preferred to overcome this problem (Obali et al. 2011). The highest conversion can be achieved in this process, only if there is proper contact between catalyst and plastic. When compared to other techniques, the use of catalyst in cracking of plastic materials increases the selectivity, reduces the operating temperature, increases the conversion and improves the quality of fuel (Panda et al. 2010). The recycling processes of distinctive plastic refuse are depicted in Fig. 1.

Mechanisms of the catalytic cracking process

Various researchers have studied reaction mechanisms for the catalytic cracking process. The response of the catalyst on the splitting of the network structure of polymer results in

Table 3 Percentage yield obtained by catalytic cracking of plastics

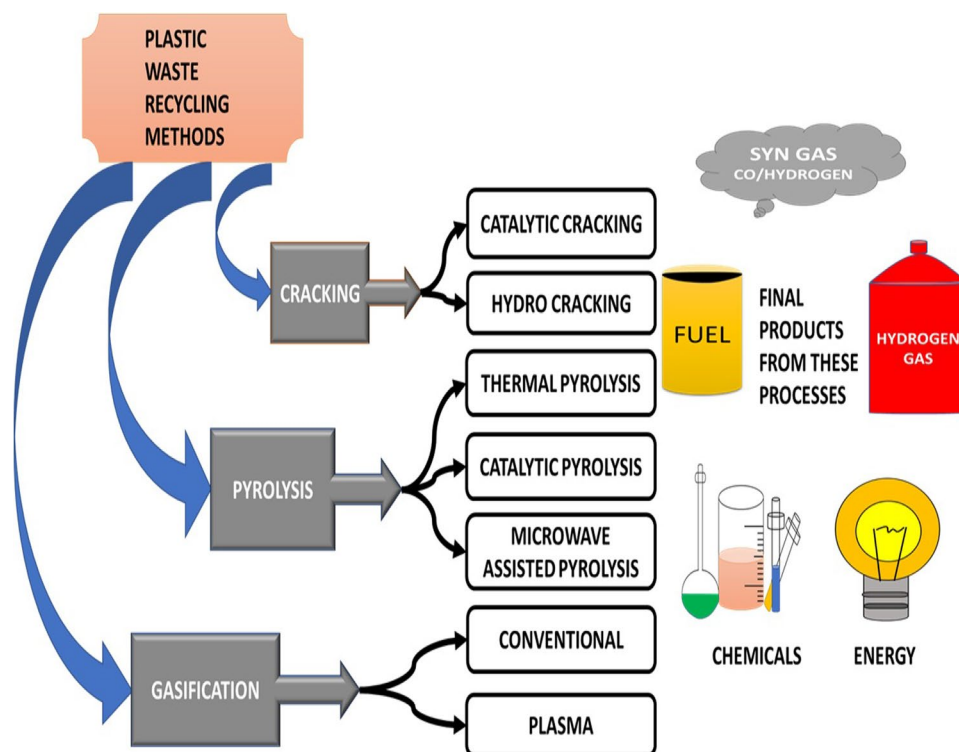
Plastic material	Catalyst used	% Yield				References
		Gas%	Liquid%	Solid%	Residue%	
LDPE ^a	HZSM-5	70.7	18.3	0.5	–	Devasahayam (2019)
	CAC1	24	73.1	2.9	–	Zhang et al. (2019)
	CAC2	25.5	70.4	4.1	–	Zhang et al. (2019)
	CAC3	25.9	61.6	2.5	–	Zhang et al. (2019)
	CAC4	29.7	64.7	4.6	–	Zhang et al. (2019)
	CAC5	29.5	65.1	5.4	–	Zhang et al. (2019)
	CAC6	30	66.5	3.5	–	Zhang et al. (2019)
HDPE ^b	HZSM-5	72.6	17.3	0.7	–	Devasahayam (2019)
	ZSM-5	63.5	35	1.5	–	Devasahayam (2019)
	Zeolite Y (powder)	27	71.50	1.5	–	Kumar et al. (2011)
	Zeolite (pellet)	17.5	81	1.5	–	Kumar et al. (2011)
	Modernite (pellet)	18.50	78.50	3	–	Kumar et al. (2011)
	Silica alumina (powder)	21	78	1	–	Kumar et al. (2011)
	Alumina (powder)	15.90	82	2.10	–	Kumar et al. (2011)
	CuCO ₃ (2%)	9.66	90	–	0.34	Singh et al. (2018)
	CuCO ₃ (5%)	5.64	94	–	0.36	Singh et al. (2018)
	CuCO ₃ (8%)	7.45	92	–	0.55	Singh et al. (2018)
	Ni/Z	68.27	30.74	–	1.10	Sriningsih et al. (2014)
	HZSM-5	5	90	–	5	Sarker et al. (2011)
	GAS OIL + HDPE	FCC-ECAT (C/O ratio = 2)	38.7	53.9	7.4	–
FCC-ECAT (C/O ratio = 4)		46.2	48.9	4.9	–	Lovas et al. (2017)
FCC-ECAT (C/O ratio = 6)		43.3	49.1	7.6	–	Lovas et al. (2017)
FCC-ECAT (C/O ratio = 12)		38.7	50.4	10.9	–	Lovas et al. (2017)
PP ^c	Zeolite beta (Si/Al ratio = 30)	33.1	17.4	–	49.5	Wanchai and Chaisuwan (2013)
	Zeolite beta (Si/Al ratio = 60)	27.5	15.4	–	57.1	Wanchai and Chaisuwan (2013)
	Zeolite beta (Si/Al ratio = 90)	27.3	16.9	–	55.8	Wanchai and Chaisuwan (2013)
	Kaolin (1:1 catalyst plastic ratio)	16.24	69.75	14.01	–	Hakeem et al. (2018)
	Kaolin (1:2 catalyst plastic ratio)	17.06	72.52	10.42	–	Hakeem et al. (2018)
	Kaolin (1:3 catalyst plastic ratio)	18.67	79.85	1.48	–	Hakeem et al. (2018)
	Kaolin (1:4 catalyst plastic ratio)	21.52	76.49	1.99	–	Hakeem et al. (2018)
PS ^d	Cu	6.07	93.93	–	0	Adnan et al. (2014)
	Al ₂ O ₃	13	87	–	0	Adnan et al. (2014)
	AC	15.53	84.47	–	0	Adnan et al. (2014)
	Silica alumina (plastic /catalyst ratio = 5)	1.4	88.2	–	10.3	Moqadam et al. (2015)
	Silica alumina (plastic /catalyst ratio = 10)	3.3	84	–	12.7	Moqadam et al. (2015)
	Silica alumina (plastic /catalyst ratio = 20)	3.9	82.7	–	13.4	Moqadam et al. (2015)
	Silica alumina (plastic /catalyst ratio = 30)	6.2	78.8	–	15	Moqadam et al. (2015)
PE ^e	Zeolite Y	26.8	71	2.2	–	Kassargy et al. (2017)
	Waste plastics (PE,PP,PS)	13.5	1.4	–	85.1	Lin et al. (2010)
	ZSM-5	88.3	3.4	–	8.6	

LDPE^a, low-density polyethylene; HDPE^b, high-density polyethylene; PP^c, polypropylene; PS^d, polystyrene; PE^e, polyethylene

more or less the same mechanism for the splitting of hydrocarbons present in crude oil. Catalytic cracking reaction undergoes either addition of carbon atoms, when catalyst acts as a Bronsted acid or in the case of Lewis acid acts as a removal of a hydride ion from plastic. During the initial cracking process, fragments are formed which was broken

away and converts to CH₄, ethane, propane in the presence of active sites of the catalyst. Primary fragments which were unstable undergo further deterioration process (Kumar et al. 2011). The catalytic cracking mechanism takes place through carbenium ions (an ionic mechanism). Elordi et al. (2012) stated that C₂₀ hydrocarbons and their distribution

Fig. 1 The recycling processes of distinctive plastic refuse



such as C_2 – C_4 light olefins, C_4 light alkanes, C_5 – C_{11} light liquid fraction and C_{12} – C_{20} heavy liquid fraction were formed by the catalytic cracking mechanism of HDPE.

In the presence of cobalt carbonate ($CoCO_3$) catalyst, the depolymerization of waste HDPE produced light olefins. The $CoCO_3$ catalyst breaks up into cobalt oxide (CoO) because of heat inside the reactor which undergoes the carbenium pathway in the course of breaking of hydrocarbon, leads to form light olefins (Singh 2018). When disorder breaking of hydrocarbon takes place, polymer end chain scission reaction will occur in cracking process which yield waxes, distillates and light hydrocarbons. This mechanism is basically in consideration of catalyst acid sites, which results in PET and PP degradation (Coelho et al. 2012; Almeida and Marques 2016). Murata et al. (2010) have mentioned that both random chain and end chain scission reaction was carried out by silica and alumina catalyst. Especially, on degradation of polyolefins, silica and alumina catalyst undergo carbenium mechanism because it is an electrophilic catalyst. Hydrogen Zeolite Socony Mobil-5 (HZSM-5) catalyst has smaller pores where the reaction mechanism was controlled by beta scission reaction on cracking of HDPE. This mechanism inhibits the bimolecular reaction to occur in the catalyst openings (Kumar et al. 2011). On cracking of polyolefins, two steps were carried out: (1) classical bimolecular mechanism and (2) proteolytic mechanism. These are the two carbocation mechanisms carried out in the cracking process (Artetxe et al. 2012). Rodriguez et al. (2020) reported HDPE

waxes cracking by using a catalyst with vacuum gas oil leads to the formation of carbenium ion and beta scission reaction took place. This carbenium ion undergoes an oligomerization process to raise the catalyst action.

Adnan and Jan (2014) reported that acidic type of catalyst for degradation of PS, the proton in the phenol ring gets affected and produced the carbenium ion. Beta scission and H_2 transfer will take place and leads to the formation of secondary cation and styrene monomer. Similarly, Kunwar et al. (2016) summarized that the acidic catalyst provides proton to produce carbenium polymer, but basic catalyst yield carbocation ion by accepting a proton from the polymer. As mentioned earlier, beta scission takes place and leads to the formation of light molecular weight compounds. Mainly the catalyst which was prepared from zeolites such as beta catalyst, HZSM5, Mobil Composition of Matter No. 41 (MCM-41) enhances the cracking mechanism, i.e., carbocation mechanism and improve the H_2 transfer (Elordi et al. 2011). Castano et al. (2011) discussed thermal cracking followed by catalytic cracking of plastics. In this report, a catalytic cracking mechanism took place for waxes that were formed from the thermal cracking of plastics. Since the waxes were paraffinic, protonated cyclopropane was formed after it reached the active sites of the zeolite. Similarly, Wong et al. (2016) summarized the same as mentioned by Castano et al. (2011) that waxes formed by thermal cracking undergo a carbocation mechanism and leads to form diesel and gasoline range

products by the presence of acid sites within the catalyst (Wong et al. 2016).

Even in the catalytic pyrolysis process, the cracking mechanism plays a major role. Adnan et al. (2015) reported that on increasing the alumina-supported aluminum oxide ($\text{Al-Al}_2\text{O}_3$) catalyst for cracking of PET, the formation of gaseous product gets increased and decreased the liquid products. This is due to the factor that there is an increment in acid sites because the feed catalyst ratio accelerated and the reaction mechanism changed. Zhang et al. (2013) also stated that on cracking of polyolefins using HZSM-5 catalyst, large amount of gaseous product formed in the range of C1–C5. Initially, in this cracking process, beta scission comes forth in the outer covering of the catalyst acid sites and hydrogen transformation occurred which produced the gaseous hydrocarbon in the range of C3–C5 and oligomerization, cyclization, isomerization reaction took place which produced the C3 to C5 olefins. Lee and Park (2018) have undergone degradation of PP and PE by two catalysts with the size of less than 50 nm such as desilicated beta along with that aluminosilicate mesostructured foam (AMF). As mentioned earlier, two mechanisms will be carried out in the catalytic pyrolysis process like carbenium and free radical mechanism. But in this study, it was reported that the carbenium mechanism is the rearrangement of carbocations which was carried out on catalytic pyrolysis process for cracking of PE and PP using AMF catalyst. Shah et al. (2014) correlated the degradation activity of alumina catalyst by fusing alumina in different metals for degradation of PS. Impregnation of alumina with metals showed good yield since the number of acid sites was increased based on impregnation because Lewis acid site in the catalyst underwent beta scission reaction by removing the hydride ion from PS which was present in the benzylic position. Two catalysts with different compositions showed different degradation mechanisms of HDPE; they are zirconium catalysts with different sulfate composition such as 7% of Sulfito (SO_3) and 3.5% of SO_3 . This study reported that the yield of gaseous products is high in zirconium which contains 7% of SO_3 . This is due to a high amount of acid content present in the catalyst and leads to end chain scission reaction and formed high amount of gaseous product, whereas in 3.5% of SO_3 catalyst does not produce any aromatic compound because it prevents the aromatization reaction and enhances the olefinic compound formation (Muhammad et al. 2012). In another report, an aromatization reaction for zeolite catalyst was improved by adding Zinc (Zn) species. Therefore, the rate of conversion was also increased (Lerici et al. 2013). On cracking of LDPE using zeolite catalyst, the initiation of cracking mechanism took place in two forms. First mechanism is the initiation process that occurs at the weaker portion of LDPE chains, that is, carbenium ions, that is formed by the addition of protons, and second mechanism is the beta scission reaction.

Another way of the initiation may occur by removing the hydride ion from LDPE by using carbenium ions (Sriningsih et al. 2014). Even activation energy of the cracking process also varied based on the mechanism. This variation was clearly stated by Corma et al. (2012) that, in the absence of a steam, protolytic cracking mechanism with an activation energy of about 18.3 kcal/mol and for beta scission reaction, the activation energy was about 14.7 kcal/mol was determined, whereas in the presence of steam, the activation energy decreased by 14.9 and 13.7 kcal/mol. Especially zeolite catalyst started the carbenium mechanism on breaking of high atomic weight hydrocarbons. The initiation and propagation step in the mechanism plays a major role in production distribution (Hou et al. 2019). Therefore, the main characteristics of products can be outlined from the mechanism of ionic reaction in the presence of catalyst.

Catalysts

In the catalytic cracking process, catalyst reduces the process temperature and energy consumption and increases the product yield and product quality. The catalyst amount plays an important role in the degradation of plastic and product distribution. The catalysts are also used in the thermal cracking process to decrease the temperature of the process for cracking and to produce hydrocarbons without any further treatment methods (Obali et al. 2012). The factors concerning catalyst, which influence the cracking performances, are: the presence of acid sites in the catalyst, pore size, volume and configuration of catalyst (Chandrasekaran et al. 2015). When the catalyst pore size increases, the hydrocarbon undergoes further degradation and form a valuable low molecular weight compound. Catalysts with a large surface area may have a small pore size and vice versa. Catalyst can be mixed directly with the plastic through liquid phase contact and indirectly through the vapor phase contact. Catalysts are utilized to improve the distribution of product and selectivity particularly, based on car powers and chemicals utilized in petroleum industries (Miandad et al. 2017). This can be achieved even by using low-cost catalyst also. Hence, various researches were performed on the cracking of plastics utilizing distinctive sorts of low-cost catalysts like zeolites (Castano et al. 2011; Zeaiter 2014; Ramya et al. 2015), silica alumina (Moqadam et al. 2015), mesostructured catalyst (Liu et al. 2013) and investigated the mechanism of cracking process and its efficiency.

Zeolite

Zeolites are crystalline materials that have high thermal stability and hence particularly used for the cracking of

hydrocarbons. Zeolite materials are broadly utilized in catalytic cracking and petroleum industries. The quality of products was improved, especially obtained from the catalytic cracking process. The acid-based catalyst has higher efficiency than the less acidic catalyst. Hence, the pore size of the catalyst and acidity are the important factors in this process. The strong acid catalyst such as zeolites showed higher production of fuels and synthetic chemicals especially in catalytic cracking of polyolefin waste materials. The primary catalyst used in fluid catalytic cracking (FCC) reactor was zeolite. Based upon the topology of zeolite, the size of the micropores in it varies between 0.4 and 1 nm range (Serrano and Aguado 2012) and favors hydrogen exchange reaction because of the availability of numerous acid sites, which was characterized by Lewis and Bronsted (Almeida and Marques 2016). Other types of zeolites such as Y-zeolite, X-zeolite, modernite, clinoptilolite, HZSM-5 and zeolite- β were also used for the cracking of plastics. Natural zeolites are also used for the cracking process because of its low cost. According to Miandad et al. (2019), the natural zeolite catalyst property was increased by thermal activation and acid activation so that the yield of products gets increased.

In some papers, transition metals were also added with the zeolites to improve the yield of products. Particularly, the higher yield of conversion of plastics can be obtained by the contact area of catalyst and plastics. In any case, the pore size less than 1 nm of zeolites, blocked the entrance of many atoms into the acid sites placed inside the channels and constrained the application of catalysts for splitting of plastic wastes. This case could be resolved by mesoporous catalysts such as HMCM-41 and HZSM-5. Recently, many metals like Cu^{2+} , Mg^{2+} , Ni^{2+} packed with zeolite influence the pore size and surface area of the zeolite which is most essential in cracking process. Addition of metals to the catalysts decreases the reaction temperature and improves the product yield (Fadillah et al. 2021).

Zeolite Y

Zeolite Y is an acidic catalyst that leads to higher productivity of products in comparison with low acidic catalysts such as silica and alumina. Cleetus et al. (2013) have stated that oil produced from plastics by zeolite Y has high octane number which can be used mostly in high-performance gasoline engines. Ajibola et al. (2018) showed that the liquid fuel contains carbon in the range of C_8 – C_{29} which was aromatic and aliphatic that can act as an alternate for fossil fuel. In the pyrolysis process, the yield of liquid oil from catalyst zeolite Y was only about 46.7%; hence, in order to increase the yield, the zeolite was used with the combination of aluminum hydroxide, sodium silicate, metakaolin. The product yield due to this technique was similar to common fuel such as gasoline and diesel oil (Eze et al. 2020). Zeolite Y

catalysts have proved that it has the efficiency to produce a rich source of chemicals, liquid fuels by cracking of plastics. Especially, high fraction of gaseous products can be produced by zeolite Y catalyst due to its high acidity.

ZSM-5 Zeolite

ZSM-5 is a catalyst which showed the best performance in catalytic cracking of plastics because of its microporous crystalline structure and strong acidic property. The pore size of the catalyst is $5.4 \times 5.6 \text{ \AA}$ with three-dimensional pore structure and permits an expanded breaking of bigger atoms, past the Si/Al with a high proportion that prompts the development in heat dependability and causticity (Almeida and Marques 2016). In the breaking of long-chain paraffin, another sort of high silica zeolite is used. This zeolite is called ZSM-5 and is utilized to improve octane number. Additionally, to increase one research octane number (RON), 5% of ZSM-5 is added to the catalyst (Fahim et al. 2010). Out of all zeolite materials mentioned above, this catalyst was considered to be suitable for cracking of hydrocarbons, alkylation and isomerization because of its size, shape, pore structure and surface area. To produce olefins from hydrocarbons, cracking process using steam was mostly preferred. But this process has various disadvantages such as operates at high temperature and large amount of CO_2 emission occurs. So, these problems can be overcome by using tridimensional structure of HZSM-5 zeolite (Rahimi and Karimzedehe 2011).

In cracking of PE, HZSM-5 showed higher conversion because of its acidity. Therefore, acid sites present in the catalysts are most important when compared to other factors. Coelho et al. (2012) modified the acidity of ZSM-5 by the ion-exchange method. In this method, the sodium cations replaced the protons present in the catalyst. After this modification, three types of HZSM-5 catalyst were obtained. But acidity of the obtained catalyst was reduced due to the addition of sodium metal to the catalyst. Hence, it was proved that sodium metal influences the acidic property of the original ZSM-5. Deactivation of ZSM-5 occurs because of dealumination of the ZSM-5 system and the coke stored on the outer surface of the catalysts which is considered to be an issue for modern applications (Paphawong et al. 2020). Figueiredo et al. (2016) examined the performance of nanocrystalline HZSM-5 was synthesized by seed-assisted method for catalytic cracking of LDPE. This kind of zeolite has a larger surface area similar to the heterogeneous catalysts used for the cracking of polymers. Nearly greater than 60% of olefins at $380 \text{ }^\circ\text{C}$ were produced which can be used as feedstocks for petroleum industries. Ma et al. (2013) stated that ZSM-5 catalyst synthesized using glucose showed good acidity and good hydrothermal stability when compared to conventional mesoporous catalyst Al-MCM-41.

Ji et al. (2017) discussed different approaches to process the execution of ZSM-5 catalyst. This study clearly showed that on increasing the catalyst performance, the acidity of catalyst, diffusion length and pore size also changed. The nanosized ZSM-5 catalyst improves the cracking process if it has a shorter diffusion length, whereas hierarchical zeolites catalyst prepared using post-treatment method and template method enhances the mesoporous structure which was also described. Sarker et al. (2011) reported that degradation under a high-temperature condition of HDPE was carried out by an HZSM-5 catalyst with the size of 3 to 5 μm which produced the gaseous product by degrading plastics in the range of C_1 – C_4 . Among all the zeolite catalysts, HZSM-5 catalyst was best because of its pore size with a specific structure and their higher activation (Sadrameli 2016).

Zeolite beta catalyst

Similar to other zeolites, beta catalyst is also acidic in nature and large pore crystalline aluminosilicate material and has large 12 membered ring pore openings. It has a particular pore structure and also used in other processes such as hydroforming and FCC processes. The distinctive processes used for producing beta catalyst are dry gel, fluoride method and xerogel method. In some research papers stated that the synthesis of beta catalyst also plays a major part in the degradation process. Renzini et al. (2011) synthesized zeolite beta catalyst from amorphous xerogels which introduced high transformation nearly 40–60% and great selectivity 60–70% toward C_5 to C_{12} hydrocarbons. On cracking of LDPE, the yield of hydrocarbons increases by increasing the number of cycles of contact between plastic and catalyst.

On cracking of PP, HDPE, LDPE, by using the catalyst of about 400 $^\circ\text{C}$, zeolite beta revealed a higher yield of gasoline compared to HZSM-5 because of its large pore size about 12 rings 0.55×0.55 and 0.76×0.64 nm channels which were proved by Serrano and Aguado (2012). Likewise, another study specified that Ni/H Beta catalysts produce 55% of gasoline as the main constituents during the aromatization process (Ishihara 2019). This catalyst also acts as an additive due to its faster deactivation when compared to ZSM-5. Deactivation of catalysts is the major issue faced during the cracking of plastics. Lericci et al. (2013) discussed zeolite beta catalyst behavior on LDPE cracking and proved that its performance was similar to thermal cracking because the formation of gaseous hydrocarbon was decreased and liquid hydrocarbons formed about 59%. The size of 10 nm H-beta nanocrystalline zeolite was able to degrade HDPE in the liquid phase. At -4 $^\circ\text{C}$, liquid products collected contain C_7 to C_{12} hydrocarbons (Burange et al. 2015). Also, this catalyst can be utilized as a support in cracking process because it has high surface area.

Mordenite

Mordenite is one of the types of zeolites that has mesoporous aluminosilicate crystalline structure. It consists of O, Si and Al atoms present inside the framework and inside the pores, water molecules are also present. A large pore volume is present with a one-dimensional pore system (6.7–7 \AA) and linked with tiny side pockets of (2.6–5.7 \AA) (Tamizhdurai et al. 2019). Zeolites are normally surrounded by a kaolin matrix that has not significant pores, which affects the cracking activity of catalyst. Similarly, the microporous pattern of zeolite Y reduces the usage of feed material because of pore active sites. Diffusional confinement is caused to the product and feed materials also leads to the formation of undesired secondary reactions.

Thus, pore characteristics of zeolites were improved by using the mesoporous material, nanosized zeolite, piled zeolite and ultra-large pore zeolite. Hence, some hierarchical structures were developed to increase the catalytic activity of zeolites. Ishihara (2019) has prepared mordenite zeolite based on this technique. Y zeolite was added to pre-synthesized mordenite which was arranged beneath aqueous conditions of about 170 $^\circ\text{C}$ around 21 h similarly hydrothermal reaction was carried out at 90 $^\circ\text{C}$ for 8–21 h. Because of the interpolation of hierarchical technique, the life of the catalyst and conversion are increased.

MCM-41

MCM-41 is a mesoporous material used as a catalyst or catalyst support in the cracking of plastics. The activation energy for degradation of HDPE is high when compared to silica alumina and HZSM-5 catalyst. Pore walls and pore sizes of the catalyst are about 1–2 nm and 2–5 nm. It overcomes the limitation of diffusional constraints (Socci et al. 2019). To reduce the fuel pore point, this kind of catalysts is preferred. Tamizhdurai et al. (2019) stated that for isomerization of hydrocarbons, MCM-41 was used which is supported by palladium (Pd). Al-MCM-41 can be prepared by hydrothermal and sol-gel methods. Each method showed different acidic strength in the order of $\text{Al-MCM}_{\text{hy}} > \text{Al-MCM}_{\text{sg}}$ catalysts having Si/Al atomic ratios (37–52) (Serrano and Aguado 2012). Similarly, a recent study reported that cracking of HDPE showed the lowest conversion of about less than 5% weight, when compared to other conventional zeolites such as beta zeolite (Ishihara 2019). Chandran et al. (2020) have reported that by using MCM-41 for cracking of mixture of plastics, the yield of gases is about 82.4% and 84.15%. Ratnasari et al. (2017) used staged catalyst for cracking waste plastics. The yield of oil was nearly about 83.15 weight %. Hence, the MCM-41 (mesoporous catalyst) exhibits phenomenal dispersion of heavier particles. A newly modified MCM-41 catalyst that was coated with Fe–Ni bimetal was

utilized to increase the production of oil to 49.9% and also reduced the bromine level in the product to 2.3% (Fadillah et al. 2021).

Bentonite

Bentonite is a broadly disseminated clay product, also glassy volcanic ash or tuff that is chemically altered. Increasing the loading of bentonite, it prompts an increment in the breaking of high molecular chains. Particularly, on cracking a mixture of PE and PP using bentonite 83.5% of gasoline was yielded (Goad and Ali 2017). There are different types of bentonites based on the dominant element like calcium, sodium, potassium and aluminum. The sodium and aluminum were used as a base material in bentonite for converting the waste plastic into fuel. Yan and Mao (2010) showed that this catalyst is also used as a binding material to extract the hybrid catalyst. This binder will hold the hybrid catalysts unbending and pressurized. Recently, at 500 °C, the speed of the pyrolysis process increases and produced up to 89% of liquid product by using calcium bentonite (Olivera et al. 2020).

Silica and alumina

It is a white powdery catalyst and has a large number of pores, which is mostly suitable for catalytic reaction. The performance of silica and alumina catalyst was analyzed by various researchers. Silica and alumina catalyst was mostly used in the thermal catalytic cracking process because it benefits the formation of products at low temperature. Owusu et al. (2017) studied silica-alumina catalyst effects in the pyrolysis process and investigated the action of polymers which was strongly manipulated by catalysts. The impact of silica and alumina on breaking of PE, PP and polyolefin was analyzed by Murata et al. (2010). They reported that the catalyst breaking effect was verified by a decrement in the molecular weight of the liquid product obtained and acid strength of the active sites which affects the division of degraded products (Murata et al. 2010). This catalyst also acts as an acid supporter for some of the metals such as molybdenum, cobalt, nickel and tungsten in the catalytic cracking process.

Panda and Singh (2011) compared the product distribution on the degradation of PP using kaoline and the catalyst, silica alumina. The oil yield was increased on using those two catalysts because of the presence of acid sites and the surface of the catalyst. The residence time also decreased due to these catalysts in the pyrolysis process. On comparing those two catalysts silica and alumina catalysts showed good product distribution. Moqadam et al. (2015) have examined that on increasing the PS and silica- alumina ratio the yield of liquid product was decreased but increased the formation of residues. At the minimum amount of catalyst, the

conversion of PS reached a maximum of 410 °C. From the above report, it was proved that role of the catalyst is most important in the catalytic cracking process.

From the above study, it depicted that, to recycle the plastics in a proper manner, role of catalyst is essential because the catalyst follows a different pathway of reaction to produce high-quality products. Therefore, depending upon the structure of pores, regeneration efficiency, costs and stability, suitable catalysts are chosen for plastic cracking.

Reactors and their operating conditions

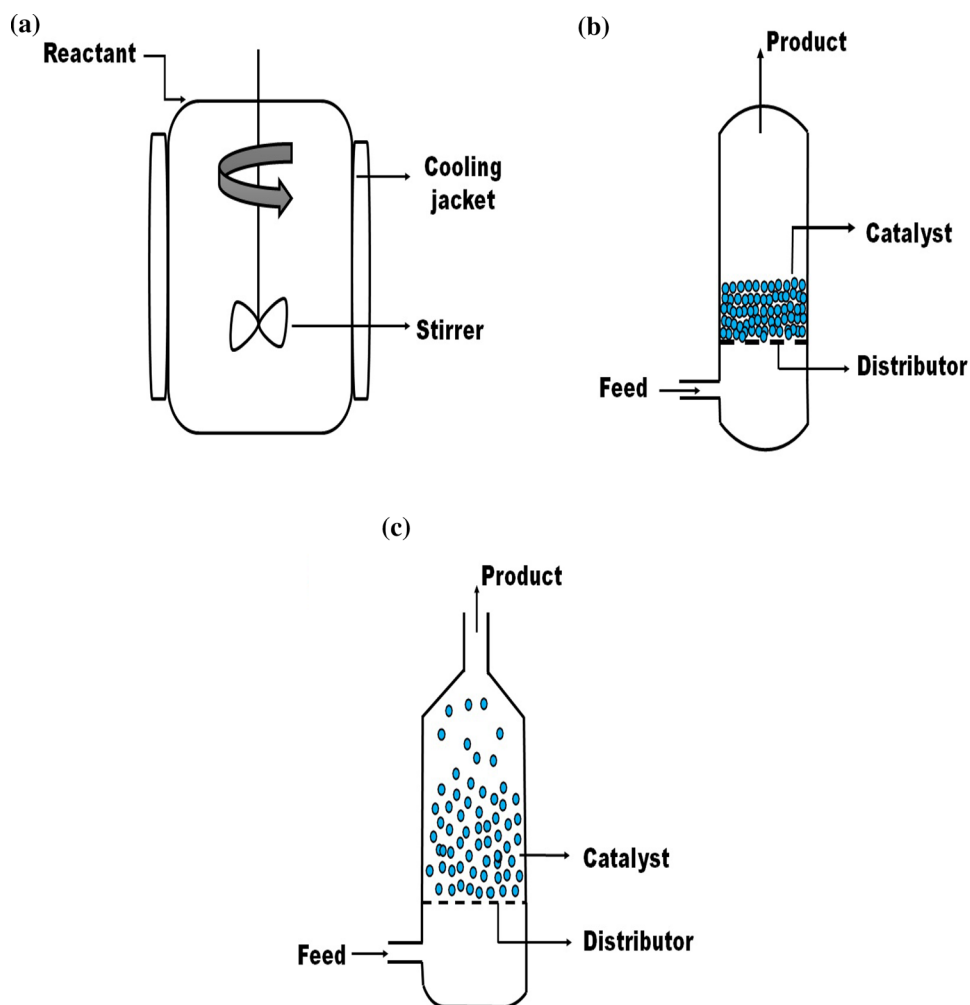
Batch reactor

Batch reactors are loaded up with the media, and no product gets included or expelled until the end of the reaction. It is used under static and as well as in mixed conditions where the stirrer is fixed. Different types of plastics were degraded using a batch reactor. Sakaki et al. (2014) have mentioned that on the degradation of HDPE 67% of liquid was produced. Renzini et al. (2011) have mentioned that two types of catalyst were used such as HZSM-5 and H- β zeolite in the batch reactor and compared their performance on cracking of LDPE. Figueiredo et al. (2016) showed that nitrogen is purged in a batch reactor at 40 ml/min to confirm that atmosphere is inert and to remove the unstable product. To monitor the enhanced activity of the mesoporous catalyst for cracking of LDPE, HDPE and PP, batch reactor was used. Hence, this type of reactor is used even for cracking of mixture of plastics. On cracking of PE and PP by using silica and alumina catalysts in a batch reactor, different degradation effects were determined, whereas on using a continuous flow reactor, the degradation effects for both the plastics were same (Murata et al. 2010). Even though this reactor is very simple to design and controls the parameters very easily, it is not mostly preferred for continuous process because frequent restart and feed charging is needed. Thus, selecting the type of reactor is very essential in the catalytic cracking of plastics. The diagrammatic representation of batch reactor is shown in Fig. 2a.

Semi-batch reactor

Most of the plastics were degraded catalytically using a semi-batch reactor. It is similar to the batch reactor but semi-batch allows partial filling of reactants. The main advantage of using a semi-batch reactor is that simple design maintains the reaction parameters and high yield of liquid product. Gulab et al. (2010) degraded HDPE plastic waste using zeolite catalyst in the semi-batch pyrex reactor. To remove volatile compounds from the reactor, nitrogen was added at different flow rates such as 50, 10 and 5 ml/min to contrast

Fig. 2 Utilization of reactors for plastic catalytic cracking: **a** batch reactor; **b** fixed bed reactor; **c** fluidized bed reactor



the execution of the reactor. But increasing the carrier gas flow rate in a semi-batch reactor leads to the evaporation of liquid product. This research proved that 10 ml/min of carrier gas in a semi-batch reactor was acceptable to keep away from liquid product evaporation.

Muhammad et al. (2019) used the pre-degradation technique for cracking of LDPE using H-Y Zeolite in a semi-batch pyrex reactor with the capacity of 0.2 L. The reactor is purged with 100 ml/min of nitrogen for about 15 min. This pre-degradation technique improves the contact time between catalyst and polymer. Similarly, various researches have used semi-batch reactor for cracking of LDPE. The mixture of plastics was degraded to obtain volatile hydrocarbons and was performed in a semi-batch reactor using a silica-alumina catalyst. This reactor was identified to be useful for the production of gasoline, 35% of ethylbenzene from a mixture of plastics namely LDPE, PP, HDPE (Sakaki et al. 2014). So, the product distribution control mainly depends upon the combination of type of plastic and reactor used. In a semi-batch reactor, a large number of samples and particle

size nearer to conditions used in the industries can also be treated.

Fixed bed reactor

It is the first type of reactor used economically, where activated natural or synthetic catalysts were employed. An uninterrupted flow is used to feed the material and mostly catalyst can be fed in the form of pellets, small lumps, or in the form of layers. The jet fuels from LDPE were done by Zhang et al. (2017) using catalytic microwave-assisted degradation in the course of the hydrogenation process. The volatile matter from the microwave degradation of plastic underwent the packed bed reactor made up of quartz material of 15 mm inside diameter which was loaded with ZSM5 catalyst to increase the yield of liquid. Zeolite catalysts were surrounded by matrix material which leads to low degradation. It was realized that the performance of catalytic cracking in the reactor gets influenced if the matrix and zeolite base is fixed independently. When the matrix was placed at the top and zeolite are placed at the bottom in the fixed

bed, the reactor showed higher action and selectivity (Ishihara 2019). Artetxe et al. (2012) executed the degradation of HDPE in two steps, pyrolysis followed by catalytic cracking to increase the olefin yield. Fixed bed inline reactor which is made up of stainless steel was used in the second step for cracking of plastic using HZSM-5 zeolite. In both, the steps, low residence time was used and this fixed bed reactor limits the formation of secondary reactions and yields the light olefins by 62 weight%.

Renzini et al. (2011) examined the catalyst deactivation like ZSM5 and beta zeolites used for degradation of LDPE plastic using this reactor. It includes quartz material of about 9 mm internal diameter and 300 mm height, where nitrogen is purged with 25 ml/min. The study of the conversion of dissolved plastic waste was very less in the case of catalytic cracking. Wong et al. (2017) performed the degradation of dissolved LDPE (dissolved in benzene) using a fixed bed reactor which is made up of stainless steel. In this study, the catalyst went through the bed in a downflow direction and nitrogen is passed for about 120 ml/min. So, on comparing a normal reactor with a fixed bed reactor, a good breaking of plastic material is observed and high yield of fluid is obtained. Most economically suitable reactor is considered to be fixed bed due to low operating and maintenance cost. The diagrammatic representation of the fixed bed reactor is shown in Fig. 2b.

Fluidized bed reactor

Fluidized bed reactor increased ongoing applications due to their various benefits which includes their mixing properties, better transfer of heat to the polymer from the reactor when compared with the batch reactor. Additionally, the replacing of catalysts can be easily achieved with a regenerated catalyst in a fluidized bed reactor without stopping the process. Heat and mass transfer limitations may take place in fixed and batch reactors. To overcome this issue, fluidized bed reactor was preferred. This reactor can hold homogeneous temperatures and compositions throughout the process. Al-harashshah et al. (2019) mentioned that on degrading PVC in fluidized bed, the operating condition plays a major role because it alters the final product. Various studies have investigated the cracking of polyolefin using ZSM5 catalyst to obtain light olefin and gasoline fraction with low aromatic hydrocarbons (Artetxe et al. 2012).

Vyas et al. (2016) have done cracking of PP using zeolite, ZSM5, red brick, sludge picking liquor in fluidized bed reactor with different ratios of feed to catalyst 1:1 to 5:1. Out of this, ZSM5 showed good conversion of PP to the liquid product at the temperature range of 420–510 °C in the ratio of 3:1. It revealed that mass and heat transfer limitations are based on the reactor and its working conditions. Nowadays, the application of fluidized bed for plastics recycling

is increasing on account of good mixing ability, high rate of heat transfer from reactor to plastic and possible to substitute the catalyst without process termination. The fluidized bed reactor diagram is shown in Fig. 2c.

Conclusion

Recycling plastics becomes most important because it gives the best solution for waste management and energy production. The recycling of plastic is considered to be the first step in plastic waste management. Especially, chemical recycling is found out to be the best solution for treating household plastics and for mixed plastics. This study established seven treatment technologies, and a comparative study is also performed. Most researchers revealed that the catalytic cracking process is a promising technology that can minimize the adverse consequences in the environment occurring due to plastic. The type of catalyst and usage of reactors play a vital role in the catalytic cracking process based on which the performance of recycling and selectivity of the product gets improved. Since there is a necessity of fuel and plastic waste management, the recycling method which gives more efficiency is preferred. Though various researches were made based on the recycling of plastic, this study exposes the importance of low-cost catalyst usage in plastic treatment and reveals that catalytic cracking process is the best suitable method for high fuel yield and waste management. The major challenge in this process is choosing a suitable catalyst that has high porosity, high acidic property and regeneration of the catalyst. For synthesizing such kind of catalyst, more literature study and technical development are needed.

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