

ADVANCES IN CATALYSIS FOR PLASTIC CONVERSION TO HYDROCARBONS

*A technical investigation commissioned by the members of the
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RESEARCH & SCOPE

Continuous rise of plastic demand, led to increase in generation of plastic waste. Around 60% of the plastic enter the environment as plastic waste.

It is worth mentioning that polymers/waste plastics display a wide range of chemical structures which makes the depolymerization technically difficult and the task gets even more complicated due to presence of mixed streams in wastes.

This report discusses the recent developments in catalytic processes for the conversion of plastic into hydrocarbons. Other scope items addressed in this report include:

- ✓ Catalytic pyrolysis processes that involve conversion of long chain polymeric molecules into small molecular weight hydrocarbons, in the presence of catalyst, under inert atmosphere.
- ✓ Hydrocracking of plastic that involves cleavage of carbon-carbon bond of heavy plastic molecules (high boiling) into lighter molecules (low boiling) in the presence of hydrogen with successive or simultaneous hydrogenation of unsaturated molecules.
- ✓ Recent advancements in catalyst development for hydrocracking such as zeolites, sulfated zirconia, mesoporous catalyst, aluminosilicates, and bifunctional catalysts.
- ✓ Recent trends regarding composite catalyst synthesis for product selectivity, that effectively increases the conversion of plastic at comparatively lower reaction temperatures.
- ✓ Metathesis reaction and its applications in depolymerization of polymers/plastics.
- ✓ Recent literature for depolymerization of waste plastic mainly used when macromolecules are reduced to monomer units without major changes in chemical compositions or petrochemical materials which can later be used for production of chemicals.
- ✓ Other approaches used for degradation/depolymerization of plastic wastes such as bioprocesses, reductive depolymerization and co-processing techniques.

The massive increase in plastic production over the last few decades has resulted in a gigantic amount of plastic waste, that necessitates the need for economical and environmentally friendly methods for plastic waste management.

INDUSTRY DRIVERS

Plastic footprints are considered as more challenging than carbon footprints.

Plastic recycling methods are considered as alternative for plastic waste management.

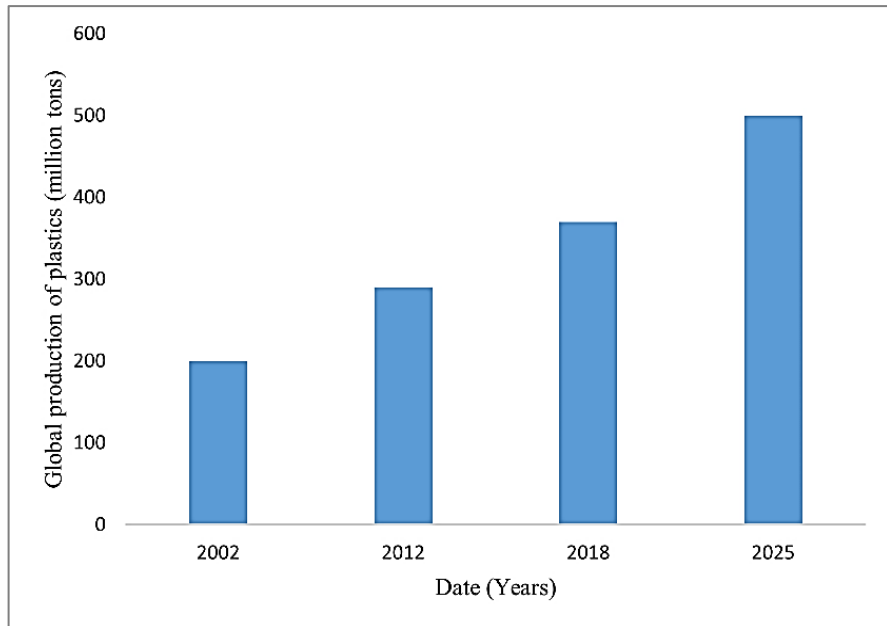


Figure 1: Growth trend of plastic production. Source: Bai et al., 2019; Geyer et al., 2017

- ✓ Investigation into different options for plastic waste management revealed that most of the waste plastic is disposed of by sending it to landfill sites.
- ✓ Production of plastic has increased at annual growth rate of 8.4% since 1950. In 2018, annual plastic production was 360 million tons and is estimated to reach at 500 million tons by 2025
- ✓ Continuous disposal of plastic to landfill site is a serious environmental concern. Interaction of plastic with groundwater and toxic substances of landfill sites can produce toxic leachate, causing deterioration of surrounding land.
- ✓ Waste plastic ending up in oceans make huge plastic garbage patch such as great pacific garbage patch that is a risk for aquatic animals
- ✓ Plastic demand is mostly comprised of HDPE (High density polyethylene), LDPE (Low density Polyethylene), PP (Polypropylene), PET (polyethylene terephthalate), PU (polyurethane), PS (polystyrene), and PVC (polyvinyl chloride)

According to a statistic established by the US Environmental Protection Agency (EPA), 75.5% of all generated plastic waste ended up in landfilling, 15.7% is utilized for energy recovery and only 8.7% of plastic is recycled for the year of 2018

FOCUS ON: PLASTIC WASTE DISPOSAL METHODS

RECYCLING

Plastic recycling divides into four categories according to the standard D5033-(2000) of American Society of Testing and Materials (ASTM).

Primary Recycling (ASTM I) - mechanical reprocessing of scrap plastic to make the plastic product of the same type/properties. It is a recycling technique of low cost and simple operation. It requires plastic waste of high quality, clean, uncontaminated, and single type. An example is the production of new PET bottles from waste PET bottles.

Secondary Recycling (ASTM II) - mechanical reprocessing of the scrap material to make product of lower quality/properties than that of virgin plastic. It includes series of material recycling processes such as reduction of size using shredders, granulators, crumblers, followed by segregation, cleaning, drying, palletization, and extrusion.

Tertiary Recycling (ASTM III) - comprised of technologies for recovery of valuable chemical intermediates such as liquid, gas and solid from plastic waste, that is considered as resource recovery. It includes thermolysis and chemolysis methods. Thermolysis is divided into three types: (1) Pyrolysis, (2) Hydrocracking, and (3) Gasification.

Quaternary Recycling (ASTM IV) - energy recover from non-recyclable or economically unprofitable waste plastic by incineration, as calorific value of some of the plastics are found to be close to the crude oil derivatives.

DEGRADATION

A series of degradation processes that results in conversion of plastic waste into low molecular weight oligomers, dimers and their by-products including CO₂, water, or methane. Microbial degradation of plastics is very popular due to complete degradation, low energy consumption, and environmentally friendly. The plastic that people uses are mostly non-biodegradable, therefore, many advanced pre-treatments are performed to increase the degradability of plastics by microorganisms. Major pre-treatments techniques are Photodegradation, Biodegradation, Thermal Degradation and Mechanochemical degradation.

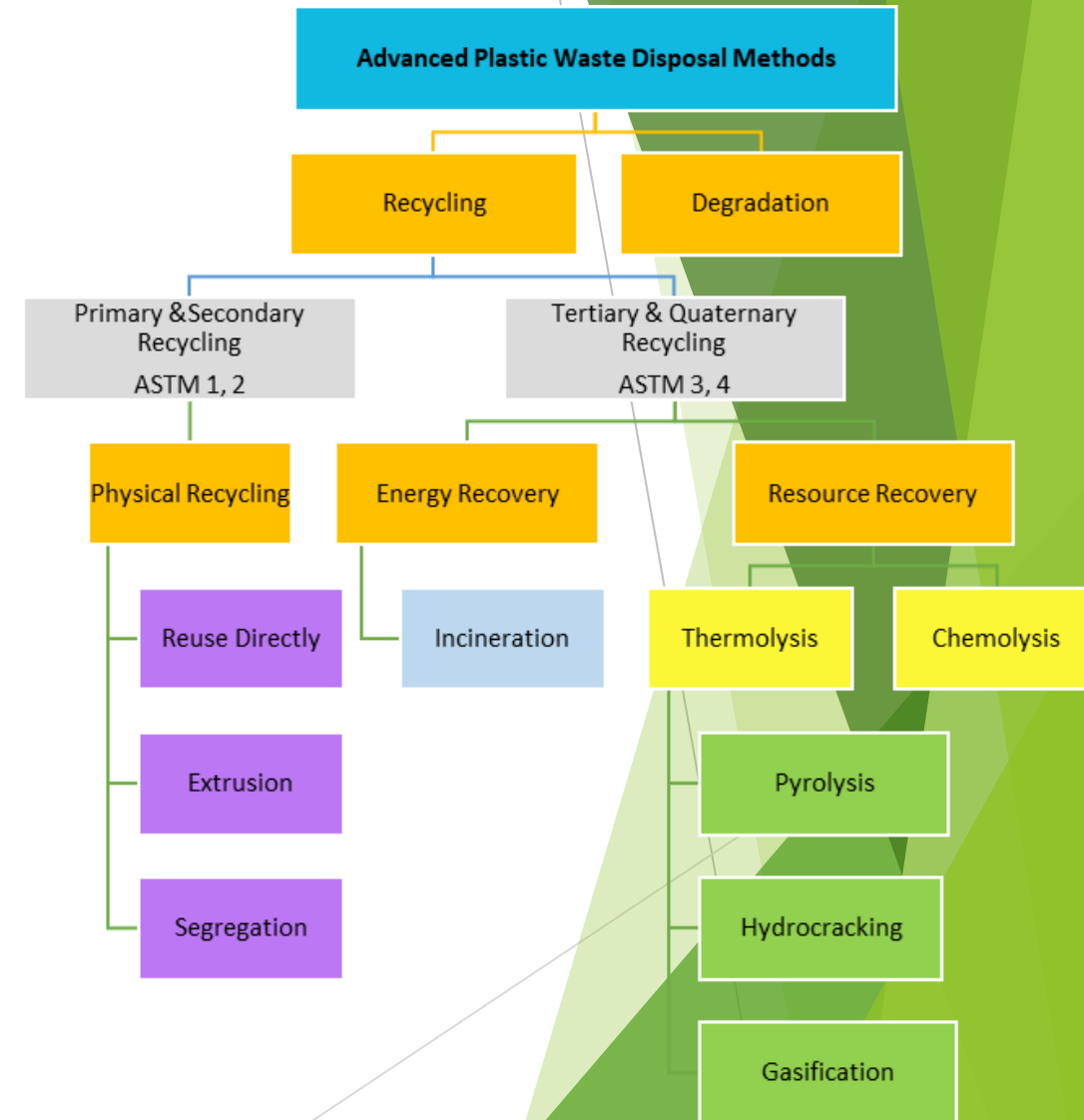


Figure 3: Classification of currently reported advanced NPW disposal methods. Source: Zhang et al., 2020

ADVANCES IN CATALYTIC PYROLYSIS

Pyrolysis of plastic involves cracking of long chain, high molecular weight polymeric molecules into smaller molecular weight molecules in an inert atmosphere at a temperature ranging from 300-800°C. It is an advantageous process more so than that of thermal pyrolysis as it results in the formation of smaller hydrocarbon molecules from long chain polymeric macromolecules at comparatively lower reaction temperature with higher selectivity.

- ✓ **The use of catalysts in plastic pyrolysis can promote:** Cracking reactions at lower temperatures which results in lower energy consumption and lower operational cost. Catalysts can yield higher desirable products & higher quality, increase product selectivity and leads to faster cracking of reactions that result in smaller residence time. Catalysts in pyrolysis require less reactor volume, preventing the formation of undesirable products and the formation of products that are primarily comprised of cyclic, aromatic, and branched hydrocarbons.
- ✓ Catalytic pyrolysis of polyolefins can yield liquid products with low boiling point ranges
- ✓ Municipal plastic waste is composed mostly of high-density polyethylene (HDPE), low-density polyethylene (LDPE), polystyrene (PS), polyethylene terephthalate (PET), Poly vinyl chloride (PVC) and Polypropylene (PP). Polyolefins (PE, PS, and their copolymers) are most widely used thermoplastics that make up 60-70% of municipal solid waste.
- ✓ PVC in MPW is not desired for the catalytic pyrolysis as it results in the emission of hydrogen chloride, which can cause corrosion in the pyrolysis reactor, and it also produce organochlorides in fuel yield. The presence of chlorine in fuel is very harmful and is highly undesirable.
- ✓ Furthermore, PET could be mechanically recycled to obtain fibers used in carpets, clothes, and bottles. The quality of the mechanically recycled PET is also high that is comparable to virgin PET. PET could easily be converted into its monomers such as terephthalic acid (TPA), dimethyl terephthalate (DMT), bis(hydroxyethylene) terephthalate (BHET), and ethylene glycol (EG) through depolymerization. Hence, PET, and other special polymers should be mechanically separated from the municipal plastic waste feed before treating it for chemical pyrolysis.
- ✓ HDPE, LDPE, PP and PS are the most suitable waste plastics for catalytic pyrolysis economically and are abundantly available in municipal plastic feed as well. However, due to limitations of available sorting techniques, sometimes it is not feasible technically and economically to separate PET and PVC from MPW mixture and therefore, few researchers also included PET and PVC in their mixed plastic feed mixture for investigating catalytic pyrolysis study to make the research more comprehensive.

Pyrolysis occurs by depolymerization process caused by elimination of small molecules, random cleavage, or chain scission. Various valuable products are produced as the result of plastic pyrolysis in the form of gas, liquid oil, and char. It has an advantage over other processes such as incineration and plasma arc gasification with lower net operation cost and annual capital cost.

ADVANCES IN HYDROCRACKING

Plastics that are most suitable for hydrocracking are the same as that of pyrolysis, therefore HDPE, LDPE, PP, and PS are the most suitable plastic to be used for hydrocracking process and exist abundantly in municipal plastic waste (MPW). Hydrocracking of plastic waste is a process that involves cleavage of carbon-carbon bonds of heavy plastic molecules (high boiling) into lighter molecules (low boiling) in the presence of hydrogen with successive or simultaneous hydrogenation of unsaturated molecules.

Compared with pyrolysis, hydrocracking has many advantages: (1) High quality liquid fuel, yields highly saturated fuel and no additional hydrogenation step is required, (2) Produces petrochemicals by adding processes for further cracking of hydrocracked product such as steam cracking, (3) Produces hydrocarbon product with better selectivity of gasoline (C₅-C₁₂) range hydrocarbons, (4) Yields product with low quantity of coke that prolong catalyst life as well as produces reduced amounts of olefins, (5) Requires lower process temperatures, (6) Reduced amount of aromatics are produced in hydrocracking process, as compared to pyrolysis (that produces higher quantity of benzene and xylene while pyrolyzing plastics containing benzene ring such as polystyrene. Additional hydrotreatment steps is required for pyrolysis oil upgrading).

- It affects hydrotreating, therefore produces hydrocarbon product with significantly reduced quantities of heteroatoms such as chlorine, bromine, and fluorine that may exist in waste plastic
- Hydrocracking process increases mass and heat transfer efficiencies then that of pyrolysis process: that has limitation for mass and heat transfer
- No toxic product such as dioxins are produced or survive in this process
- Cracking and *hydrogenation* are complementary reactions, as cracking is endothermic reaction while hydrogenation is an exothermic reaction thereby saves energy

PET could be included in hydrocracking process; however, it is a good candidate for mechanical recycling, and it produces least quantity of liquid by thermal degradation. For the two-stage liquefaction technique, PVC could also be included and dechlorination step is performed at the first step.

Hydrocracking of plastic generally occurs in the presence of a bi-functional catalyst in a stirred batch autoclave reactor under high hydrogen pressure, and moderate temperature conditions. Typical hydrocracking process temperature are in the range of 300-450°C, and hydrogen pressure is in the range of 2-15MPa. Plastic is washed, dried, and shredded into small pieces before conveying it into the reactor with catalyst, given a certain residence time under certain temperature and hydrogen pressure. Few researchers found 2 MPa of hydrogen pressure as most optimized one for obtaining high yield conversion of plastics by providing good mass transfer and hydrogen solubility in molten plastic.

Hydrocarbons in the range of C1-C22 are mostly reported in the product obtained from catalytic hydrocracking of plastic, that contain gasoline (C5-C12), naphtha (C5-C11), kerosene (C10-C16) and diesel (C13-C18).

FOCUS ON: LIQUEFACTION TECHNIQUES FOR HYDROCRACKING

Hydrocracking process for plastic can be performed by direct liquefaction or two stage liquefaction.

- ✓ Two stage liquefaction includes initial step comprised of pyrolysis, catalytic pyrolysis or hydrocracking and final step includes hydrotreatment for the improvement of final liquid product. Although the two-stage liquefaction technique is not cost effective, however it yields liquid with reduced quantities of heteroatoms (Cl, S, N, etc.).
- ✓ Further, low quantity of coke is produced in this performing plastic hydrocracking with coal, technique that consequence less catalyst deactivation. Reduced quantities of olefins are produced, allowing the liquid yield to be directly use in automobile engine. PVC containing feed, dechlorination could be performed in initial step to avoid the presence of chlorinated compounds in the final stage.
- ✓ Few researchers also investigated the co-processing of plastic with other co-feeds, by biomass, VGO, oil residue, wax, tetralin, and long chain alkanes. Co-processing is a good processing technique for increasing the plant capacity and economizing it.
- ✓ Narayanaswamy et al. invented a process configuration involving pyrolysis, hydrocracking, hydroalkylation and steam cracking to integrate different processes from start to end with plastic waste as a feed and petrochemicals as a product. The process is designed for making pyrolysis product suitable according to the feed specification of steam cracker as it may contain, paraffins, iso-paraffins, aromatics, naphthenes, olefins and organic chlorides in hundreds of ppm that are found unfit to be used directly in steam cracker.
- ✓ The waste plastic feed selected for this integrated process is comprised of PP, PS, LDPE, HDPE, PVC, PVDC (polyvinylidene chloride), co-polymers, waste tires, PET, PBT (polybutylene terephthalate).

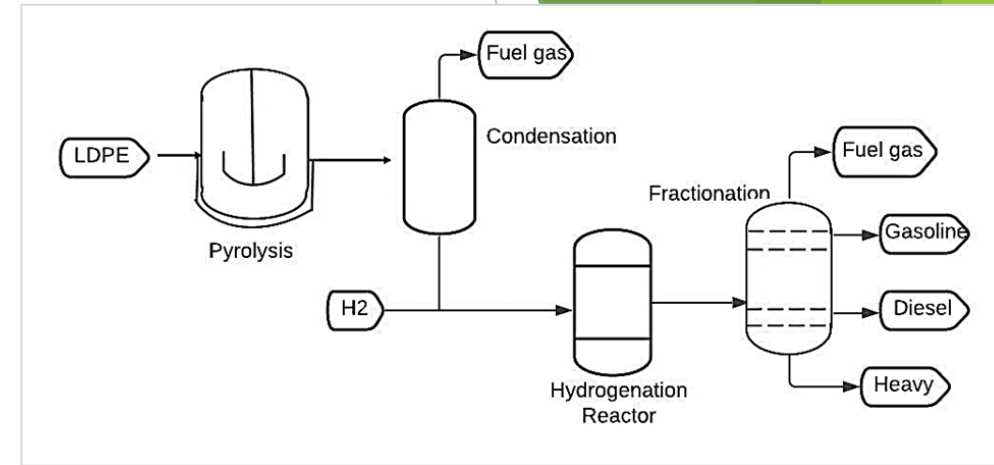


Figure 6: Two stage liquefaction technique. Source: Gala et al., 2020

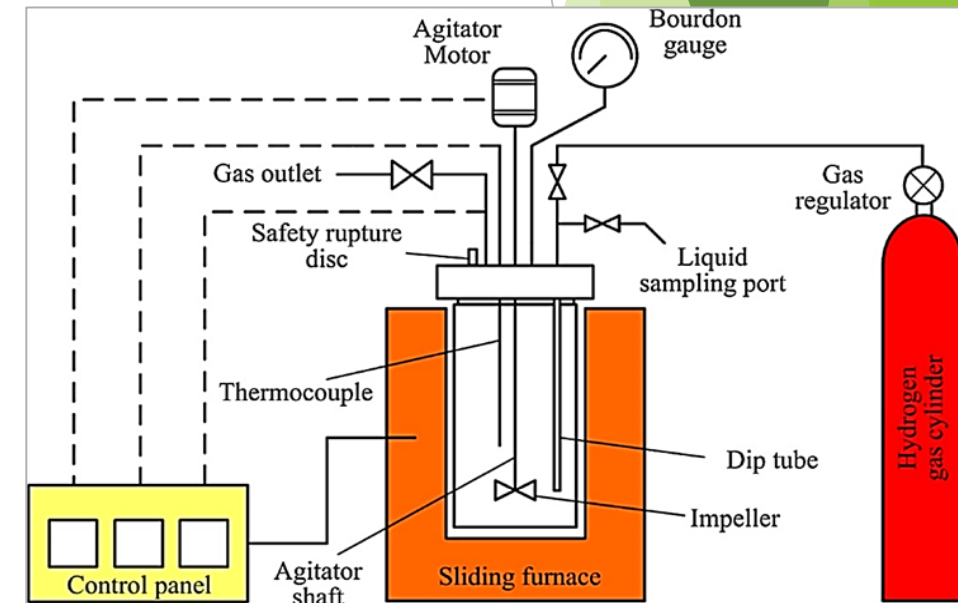


Figure 7: Typical hydrocracking set up (Direct Liquefaction). Source: Munir et al., 2018a

ADVANCES IN ALKANE METATHESIS

Alkane metathesis is basically a novel catalytic technique to transform two alkane molecules into its lower and higher homologues. The transformation of alkanes remains a difficult challenge because of the relative inertness of the carbon-hydrogen and carbon-carbon bonds. Alkane metathesis development brought new concept of alkane reactivity and production of lower and higher alkane molecules.

- ✓ The reaction was first reported on silica-supported tantalum hydride (J. M. Basset et al., 2010). In that reaction, saturated linear and branched chains were rearranged to longer and shorter saturated molecules (paraffins).
- ✓ Metathesis is a bimolecular double displacement reaction involving the exchange of bonds between the two reacting chemical species.
- ✓ It is a kind of organic synthesis where carbon compounds from very simple and small molecular weight to very large, complex macromolecules and even natural products may be synthesized.
- ✓ In metathesis, double bonds are broken and made between carbon atoms in ways that cause atom groups to change places with the assistance of special catalyst molecules.
- ✓ Metathesis reactions are generally reversible, and, with the right catalyst system, equilibrium can be attained in seconds, even with high substrate to catalyst ratios (104).

Various Categories of Metathesis Are Reported Such As:

- ✓ Metathesis of olefins is the reaction in which the molecules of olefins are formally fragmented at their double bonds and new hydrocarbons (olefin molecules) result by recombination of fragments originating from different molecules.
- ✓ Ring opening metathesis polymerization (ROMP) is a process of one or more cyclic olefins transformation to polymer catalyzed by metal carbene compounds.
- ✓ Ring-closing metathesis (RCM) is a variant of the olefin metathesis reaction in which alkylidene compounds are exchanged to form a ring. The most common catalysts for this reaction are complexes of molybdenum or ruthenium.
- ✓ Enzyme metathesis (EM) is a bond reorganization of an alkene and an alkyne in the presence of catalyst.
- ✓ Cross-metathesis (CM) involves the intermolecular reaction of two alkene units in the presence of a metathesis catalyst.
- ✓ Alkane metathesis (AM) is a class of chemical reaction in which an alkane is rearranged to give a longer or shorter alkane product. It is like olefin metathesis, except that olefin metathesis cleaves and recreates a carbon-carbon double bond, but alkane metathesis operates on a carbon-carbon single bond.

ADVANCES IN DEPOLYMERIZATION

Huge increases in generation of waste plastic pave a road map towards various eco-friendly and waste management recycling approaches and depolymerization is one of those. The term depolymerization is mainly used when macromolecules are reduced to monomer units without major changes in chemical compositions or petrochemical materials which can later be used for production of chemicals. Various processes are reported to date for depolymerization of plastics which are listed below:

✓ **Oxidative depolymerization** - involves the breakdown of macromolecules by the action of oxygen on the substrate. For instance, in 2005, Phinyocheep et al. reported the oxidative depolymerization of epoxidised natural rubber catalyzed by performic acid generated in situ by the reaction of hydrogen peroxide and formic acid.

✓ **Glycolysis Depolymerization** - is the molecular degradation of polymer (especially PET) by glycols ((CH₂OH)₂), in the presence of trans-esterification catalysts, where ester linkages are broken and replaced with hydroxyl terminals.

✓ **Methanolysis Depolymerization** - the depolymerization reaction in the presence of methanol. Methanolysis is applicable to polymers with heteroatoms in their backbone and cannot be used to break C-C bonds.

✓ **Hydrolytic Depolymerization** - the reaction with water where the water molecules lead to cleavage of chemical bonds within a plastic material. The solvolysis processes is broader term used to incorporate cleavage agents such as methanolysis, glycolysis, hydrolysis and ammonolysis etc. Ether, ester and acid amide bonds can be cleaved this way.

✓ **Hydrogenolysis Depolymerization** - a chemical reaction mostly carried out in the presence of catalyst in which chemical bonds in an organic molecule are broken down with the simultaneous addition of a hydrogen atom to the resulting molecular fragments.

Table 1: Reported Literature for Oxidative Depolymerization

Polymer/ plastic	Reagent and conditions	Catalysts	Product	Yield or conversion	References
multilayer and coloured PET plastic waste	alkaline hydrolysis 60 : 40 vol% EtOH : H ₂ O 80 °C, 20 min	5 wt% NaOH	terephthalic acid (TPA) and ethylene glycol	95 %	(Ügdüler et al., 2020)
poly-(bisphenol A carbonate)	THF as solvent 200 °C Reaction time 6 hrs	Clinochlore (natural clay mineral)	Bisphenol A	99%	(Quaranta et al., 2021)
PET	-	Acidic ZSM-5	TPA	-	(Kang et al., 2020)
Polycarbonate	140 °C 3 hours n(H ₂ O)/n(PC) = 3:1 and n(Cat.)/n(PC) = 0.1:1	1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) based ILs.	Bisphenol A	97 %	(M. Liu et al., 2018)
Aliphatic Polyamides (PA 66, PA 1010, PA 11, and PA 12)	For PA 66: 200 °C Reaction time 10min long chain Pas: 200°C Longer reaction time	Acidic conditions (HCl as catalyst) HCl/amide mole ratio of 1.5 to 2.5 depending upon PAs.	Respective monomers	-	(Češarek et al., 2020)

FOCUS ON: CATALYST FOR DEHALOGENATION OF DEPOLYMERIZATION PRODUCTS

The process comprised of contacting the mixed plastics with a zeolites' catalyst in a pyrolysis unit to produce a hydrocarbon product comprising a gas phase and a liquid phase and separating the hydrocarbon product into a hydrocarbon gas stream and a hydrocarbon liquid stream, wherein the hydrocarbon gas stream comprises at least a portion of the gas phase of the hydrocarbon product. The catalyst helps to simultaneous dehalogenate the pyrolysis products.

- ✓ The catalytic effects of CuAl layered double hydroxide (CuAl-LDH) on dechlorination and carbonization of polyvinyl chloride (PVC) during pyrolysis were reported with high efficiency. The results showed that the addition of CuAl-LDH accelerated the dehydrochlorination and promoted the char formation of PVC.
- ✓ In another study, Chen et al reported pyrolysis of computer casing plastic waste containing brominated flame retardants (BFRs) in a two-stage vertical quartz tube reactor using iron and nickel metals modified MCM-41 catalysts. Various catalysts with different ratios of Fe and Ni were evaluated to study their catalytic performance. 20%Ni/MCM-41 catalyst gave maximum the pyrolytic yield of oil and gas (49.9 wt% and 13.8 wt% respectively).
- ✓ The reported bimetallic catalysts also exhibited remarkable effect on eliminating bromine from pyrolytic oil. Researchers reported that a higher amount of Fe in the catalyst is beneficial for the debromination efficiency.

Table 2: Catalysts for Dehalogenation of Depolymerization Products

Plastic	Depolymerization / conversion technique	Catalyst	Dehalogenation process	References
Mixed Plastic	pyrolysis	zeolite catalyst	dechlorination	Stanislaus et al., 2020
PVC	pyrolysis	CuAl layered double hydroxide (CuAl-LDH)	dechlorination	Y. Chen et al., 2018
Computer casing plastic waste	pyrolysis	iron and nickel metals modified MCM-41 catalyst	debromination	T. Chen et al., 2020
PVC	Degradation	superheated steam and metallic oxides such as CaO, Fe ₃ O ₄ , SiO ₂ , Al ₂ O ₃ , Ca(OH) ₂ , MgO catalyst/adsorbent	dechlorination	Nishibata et al., 2020
PVC	Hydrothermal treatment	cupric ion (Cu ²⁺)	dechlorination	(Ma et al., 2021)

CONCLUSIONS & FUTURE CHALLENGES

- ✓ Catalytic pyrolysis of plastic waste is an efficient and sustainable process to convert most energy from plastic waste into liquid oil, gas, and char.
- ✓ Future development for plastics processing will rely on two approaches to polymer recycling:
 - ✓ The design of depolymerization catalysts
 - ✓ The development of recyclable polymers for targeted applications.
- ✓ Catalytic depolymerization offers routes to convert polymers via depolymerization of polymers to monomers or other small molecules, valuable hydrocarbons, such as BTX. Thus, chemical recycling can in principle be achieved by depolymerization of plastics to recover the constituent monomers, which can (after purification) be re-polymerized.
- ✓ Polymers display a wide range of chemical structures, thus making the depolymerization of plastic waste a technically difficult task that is complicated further due to mixture of waste streams. Additionally, additives have made it difficult to selectively depolymerize waste plastics to useful/value added chemicals.
- ✓ Depolymerization is extremely slow under moderate reaction conditions and therefore catalyst development is needed.
 - ✓ Catalysts for depolymerization should be inexpensive processes competitive with virgin material prices, stable to air, moisture, and organic or metal salt contaminants and effective in heterogeneous mixtures with high selectivity for polymer to monomer conversion.
- ✓ Concurrent with the development of depolymerization catalysts and new recyclable materials, mechanical sorting methods in recycling plants and decontamination processes must continue to be improved. Then, chemical depolymerization processes can be applied to pure starting materials, and precious monomers can be recovered.
- ✓ Hydrocracking is a promising technique for producing high quality liquid fuel from plastic waste.
 - ✓ Type of plastic feed is first thing to be considered. HDPE, LDPE, PP, and PS are the most suitable plastic feed for this process; however, PET could also be included in this process.
- ✓ If realized, the future for end-of-life treatment of plastics will change dramatically, materials will be kept out of landfills, and the relationship between plastics and the environment will certainly improve.

The development of cost-efficient chemical recycling methods signifies considerable economic and scientific opportunities.

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