

Recent Advanced in Green Chemical Methods for the Degradation and Upcycling of Polyethylene Waste

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Abstract—Polyethylene is one of the most widely used synthetic polymers, but its high chemical stability and resistance to degradation have resulted in the accumulation of large quantities of plastic waste. Conventional recycling approaches often face limitation related to material quality, energy consumption, and economic feasibility. Catalytic chemical upcycling has emerged as a promising strategy for converting polyethylene waste into valuable chemical feedstock and products. This review provides an overview of recent advances in catalytic approaches for the chemical upcycling of polyethylene with emphasis on hydrogenolysis, hydrocracking, catalytic pyrolysis and oxidative transformation particular attention is given to the role of catalyst composition, active site, reaction condition, polymer chain activation and product selectivity. The formation hydrocarbon and other cleavage of c-c bond is also discussed, Furthermore, the advantages and limitation of different catalytic system are compared to identify factors influencing conversion efficiency and selectivity. Current challenges, including high energy requirements, catalyst deactivation complex product distributions and difficulties in process scalability, are highlighted. Finally potential research direction toward more selective energy efficient, environmentally sustainable polyethylene upcycling technologies are discussed. This review aims to provide a comprehensive understanding of catalytic strategies for transforming polyethylene waste from an environmental burden into useful chemical resource.

I. INTRODUCTION

Polyethylene is one of the most extensively used synthetic polymers because of its low cost. Chemical resistance, light weight nature, and versatile mechanical properties. It is widely employed in packaging materials, containers films household products, agricultural application and numerous industrial products. However, the same chemical stability that makes polyethylene useful also makes it

highly resistance continuous accumulation of polyethylene waste has become important environmental challenge.

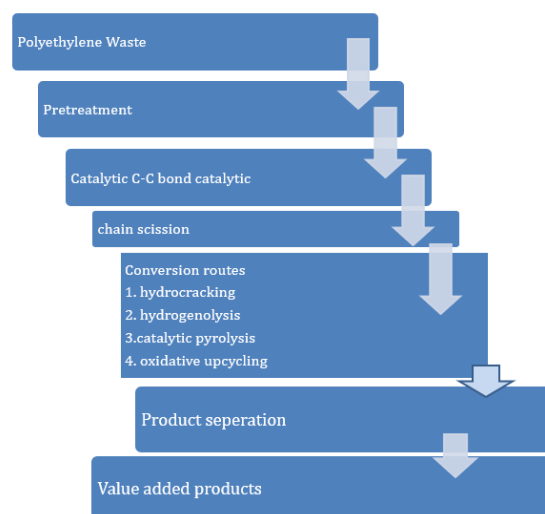


Figure1 General concept of catalytic chemical upcycling of polyethylene waste into value added chemical products.

Conventional approaches for managing polyethylene waste mainly include landfilling, incineration, mechanical recycling and limited forms of chemical recycling. Mechanical recycling can reduce the demand for virgin polymers, but repeated processing may affect the physical properties of the resulting materials. Chemical upcycling has emerged as a promising approach in which polymer chain are transformed into smaller molecules or higher value products rather than simply being converted into materials of similar quality. Catalysts play a particularly important role in this process because they can influence polymer activation carbon-carbon bond cleavage, selectivity, reaction temperature and product distribution. Depending on the reaction pathway and catalytic system, polyethylene can potentially be

converted into hydrocarbons, liquid products, waxes, oxygen containing compounds or other valuable chemical feed stocks. Recent research has explored several catalytic strategies for polyethylene conversion, including hydrogenolysis, hydrocracking, oxidative degradation, catalytic pyrolysis and other emerging approaches. Different catalyst system including metal-based catalysts, supported catalysts, zeolite-based materials and multifunctional catalytic system have been investigated to improve conversion efficiency and product selectivity. However, challenges such as high energy requirement, catalyst deactivation, complex product mixtures, process scalability and separation of products continue to limit the practical implementation of these technologies. Therefore, a systematic understanding of the catalytic pathway used for polyethylene upcycling is essential for developing more efficient and environmentally sustainable processes. This review discusses recent advance in catalytic chemical upcycling of polyethylene with particular emphasis on catalytic system, reaction mechanism, operating condition, major product and factor controlling product selectivity. The review also highlights current limitation and research gaps and discusses future opportunities for developing efficient and greener roots for converting polyethylene waste into value added chemical resources.

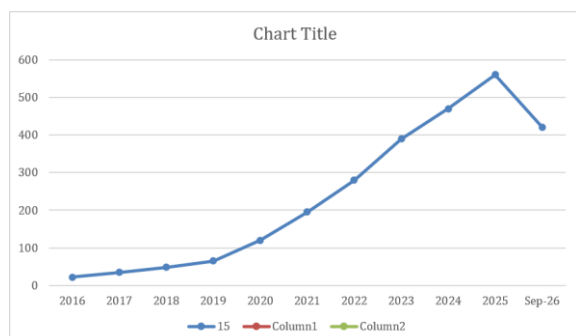


Figure 2- publication trend in catalytic upcycling of polyethylene and polyolefin waste based on the selected literature database.

II. POLYETHYLENE STRUCTURE PROPERTIES AND TYPES

2.1 Structure of polyethylene

Polyethylene is a thermoplastic polymer composed of repeating ethylene units. It is produced by the

polymerization of ethylene ($\text{CH}_2=\text{CH}_2$), Resulting in a long hydrocarbon chain with the general repeating unit $(-\text{CH}_2-\text{CH}_2-)_n$. The polymer backbone consists primarily of carbon- carbon (C-C) and carbon-hydrogen bonds(C-H). The absence of polar functional groups and high stability of the C-C backbone contribute significantly to the chemical resistance of polyethylene.

The physical and chemical properties of polyethylene are strongly influenced by its. Molecular weight, Degree of branching, crystallinity and molecular architecture. Depending on the polymerization conditions and catalyst system, polyethylene chain can exhibit different degree of linearity on and branching. These structural differences are responsible for the formation of different grades of polyethylene with distinct mechanical, thermal and processing characteristics.



2.2 Properties of polyethylene

Polyethylene possesses several properties that make it suitable for a wide range of commercial and industrial application it generally exhibits low density, good flexibility, high chemical resistance, moisture resistance, electrical insulation properties and relatively good mechanical strength. Its resistance toward water and many common chemical particularly useful and packaging and storage applications.

However chemically stability polyethylene also creates a major challenge for waste management. The polymer backbone contains strong C-C and C-H bond and lacks easily hydrolysable functional groups consequently polyethylene undergoes very slow natural degradation under ordinary environmental conditions. Thermal and catalytic processes are therefore being investigated to selectively activate and cleave the polymer backbone for chemical recycling and upcycling.

2.3 Types of polyethylene

Polyethylene can be classified into different types according to its chain architecture, density degree of branching and method synthesis the major type includes LDPE, HDPE, LLDPE, UHMWPE.

2.3.1 LDPE (Low density polyethylene)

LDPE contain a relatively high degree of short and long chain branching. This structure reduces chain

packing and crystallinity resulting in a flexible and relatively low-density material. LDPE commonly used in films, bag, coatings, and flexible packing.

2.3.2 HDPE (High density polyethylene)

HDPE possesses a predominantly linear molecular structure with relatively low branching. The chain can pack more efficiently, giving HDPE higher crystallinity, density, stiffness and mechanical strength than LDPE. It is widely used for bottles, containers, pipes and rigid packaging.

2.3.3 LLDPE (Linear low-density polyethylene)

LLDPE has mainly linear backbone with controlled short chain branching, commonly introduced through copolymerization with α -olefins. It combines flexibility with relatively high tensile strength and is extensively used in films, packaging and industrial applications.

2.3.4 UHMWPE (Ultra molecular-weight polyethylene)

UHMWPE has an exceptionally high molecular weight and exhibits outstanding wear resistance, toughness and chemical resistance. It is used in specialized engineering and biomedical applications.

Type	Structural characteristics	General properties	Common application
LDPE	Highly branched chain	Flexible, low density, relatively low crystallinity	Films, bags, packaging
HDPE	Mostly linear chain	High density, stiffness, crystallinity	Bottles, pipe, containers
LLDPE	Linear chain with controlled short branching	Flexible with good strength	Films, packaging
UHMWPE	Extremely long polymer chain	Very high wear resistance and toughness	Engineering and biomedical application

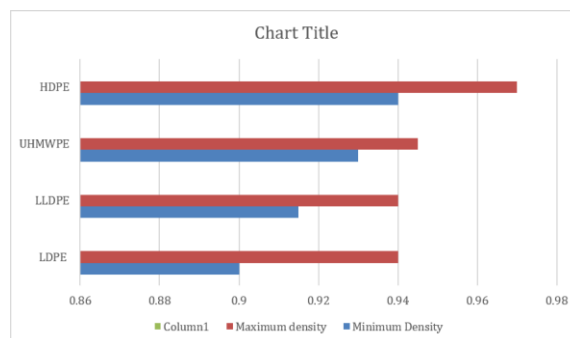


Figure 3- comparison of different polyethylene density.

III. ENVIRONMENTAL IMPACT OF POLYETHYLENE WASTE

Polyethylene is widely used in packaging agricultural films, containers, household product and industrial application. Its highly durability and resistance to chemical and biological degradation make it useful during its service life, however these same characteristics create significant challenges after disposal. Large quantities of polyethylene waste can persist in the environment for long period, particularly when waste collection, recycling and disposal system are inadequate.

3.1 Accumulation of polyethylene waste-

The continuous production and consumption of polyethylene product have resulted in substantial amount of post-consumer and postindustrial plastic waste. Improper disposal can lead to the accumulation of plastic materials in landfills, terrestrials, river and marine ecosystem. Because polyethylene is light weight and resistance to degradation, it can remain in the environment and gradually fragment into smaller plastic particles.

3.2 Formation of micro plastic

Environmental weathering of polyethylene through sunlight, oxygen, mechanical abrasion and temperature fluctuation can cause fragmentation of larger plastic materials into smaller particles including micro plastic.

3.3 Effects on terrestrial and aquatic ecosystem-

Polyethylene waste can physically interfere with terrestrial and aquatic systems. Larger plastic material may cause ingestion or entanglement hazard for

wildlife, while smaller particles can interact with organism and sediment. Polyethylene particles may also provide surface on which other environmental contaminants and microorganism can accumulate potentially altering their transport and distribution.

3.4 Environmental and climate concern

The life cycle of polyethylene is associated with the consumption of fossil derived resources and energy. Disposal through uncontrolled burning can release carbon containing gasses and potentially hazardous combustion products depending on the condition and consumption the waste. Landfilling, meanwhile does not recover the chemical value contain with in the polymer.

3.5 Limitation of conventional waste management

Mechanical recycling is an important approach for managing polyethylene waste but repeated processing can lead to changes in material properties, while

contamination and mixed plastic stream can make sorting and recycling more difficult. Landfilling and incineration also have important limitation. These challenges have increased interest in chemical recycling and chemical upcycling, where polyethylene is transformed into useful hydrocarbon or other chemical feed stocks.

3.6 Need sustainable polyethylene management

The environment persistence of polyethylene highlights the need for improved waste management strategies. Chemical upcycling offers an attractive complementary approach because it aims not merely to dispose of or remelt the polymer but to recover its carbon content as useful chemical products. It particularly catalytic processes can facilitate selective C-C bond cleavage and potentially convert polyethylene to valuable products under controlled reaction condition.

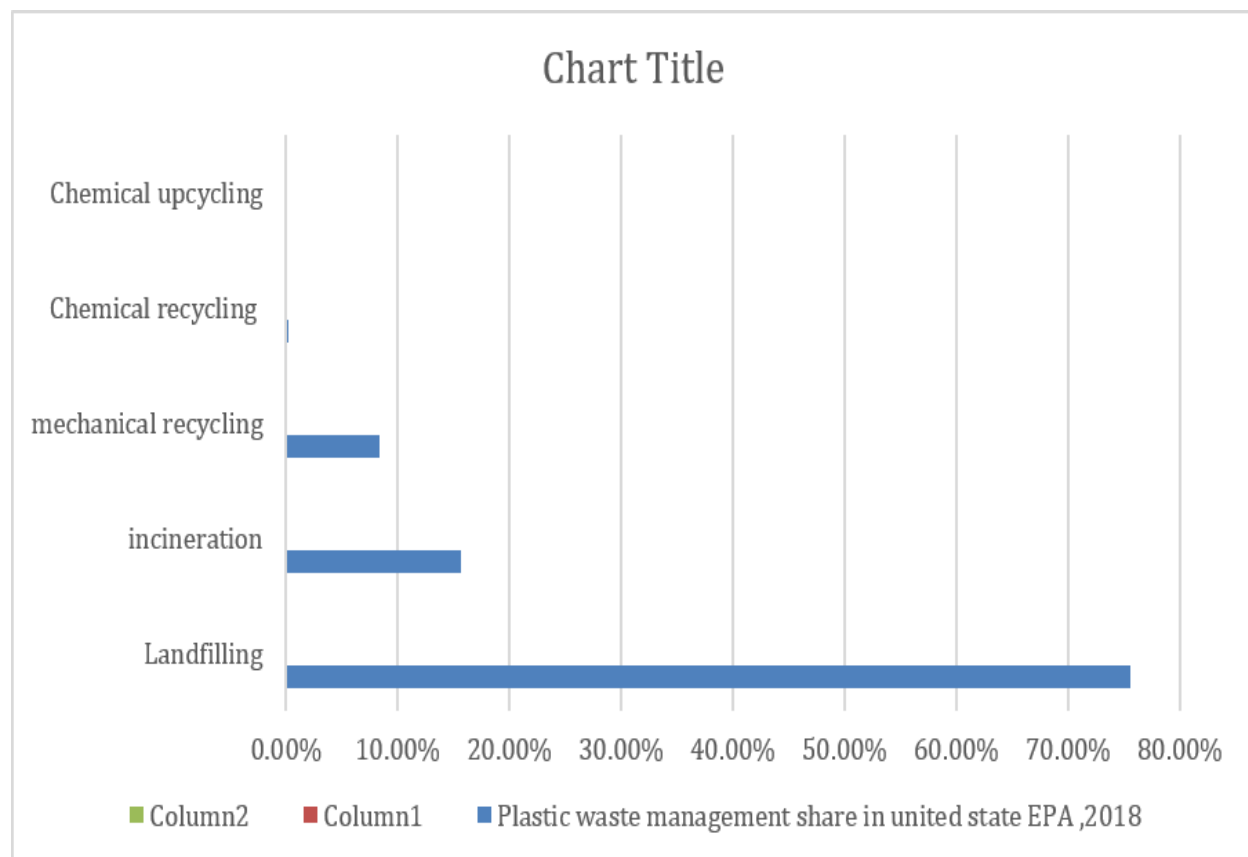


Figure 4- Comparison of selected polyethylene waste management pathway based on reported waste management data for the specified region and year.

IV. CHEMICAL UPCYCLING OF POLYETHYLENE

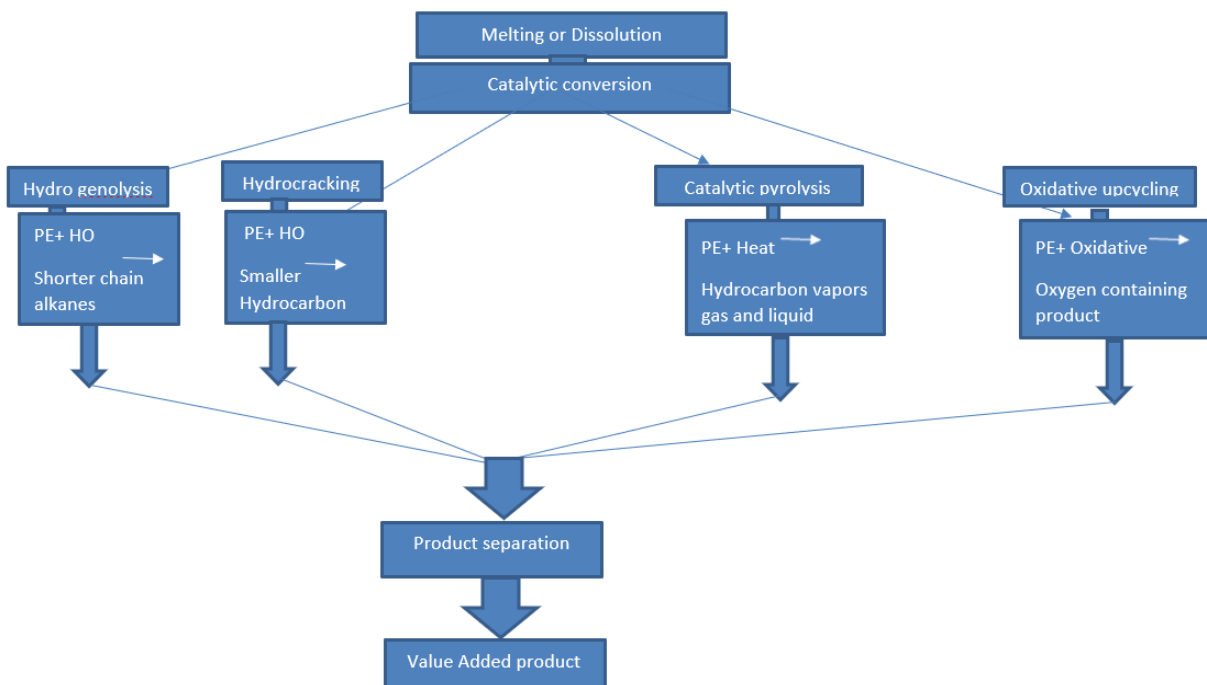


Figure 5- Major catalytic chemical upcycling pathway for polyethylene waste

Chemical upcycling of polyethylene refers to the conversion of polyethylene waste into useful chemicals, fuels, or other valuable products through controlled chemical transformation. Unlike conventional mechanical recycling, which generally preserved the polymeric nature of the material chemical upcycling aims to alter the molecular structure of PE and recover its carbon content in the form of smaller or chemically functionalized molecules. This approach has attracted considerable attention as a potential strategy for reducing plastic waste while simultaneously recovering chemical value from discarded polymer.

4.1 principle of chemical upcycling

The main challenges upcycling in the chemical transformation of polyethylene is the presence of a chemically stable hydrocarbon backbone consisting primarily of strong C-C and C-H bonds. Selective activation of this bond is therefore essential for converting long polymer chain into useful product. In catalyst upcycling catalyst facilitate the activation and cleavage of polymer chain and can influence the molecular weight and composition of the resulting products. Depending on the catalyst and reaction

condition polyethylene can undergo hydrolysis, hydrocracking, pyrolysis oxidation or other chemical transformation.

4.2 Chemical recycling versus chemical upcycling

Chemical recycling and chemical upcycling are related but distinct concepts. Chemical recycling generally focused on recovering chemical building block or feedstock from waste polymers, whereas chemical upcycling emphasis the production of higher value or useful product from waste material.

For polyethylene, complete depolymerization into the original ethylene monomers is challenging because of the structure or stability of the polymer. Consequently, many current approaches focus on controlled chain cleavage to produce hydrocarbon within desired molecular weight ranges or other useful chemical intermediates.

4.3 Major chemical upcycling approaches

Hydrogenolysis: Hydrogenolysis involves the cleavage of C-C bond in the presence of hydrogen and a suitable catalyst acidity and metal functionality are important factor controlling the reaction pathway,

Hydrocracking: Hydrocracking combines hydrogenation and C-C bond cleavage. It can convert long polyethylene chain into shorter hydrocarbons, including liquid range products. Catalyst acidity and metal functionality are important factor controlling the reaction pathway.

Catalyst pyrolysis: In catalyst pyrolysis, polyethylene is thermally decomposed in the presence of catalyst generally under oxygen free conditions. Catalyst such as zeolite-based materials can influence cracking reaction and product distribution depending on the catalyst and operating condition gaseous, liquid, aromatic compound may be generated.

4.4 Oxidative upcycling

Oxidative approaches introduce oxygen containing functional group into polyethylene derived molecules. Controlled oxidation can produced oxygenated compound such as alcohol, ketones, aldehydes and carboxylic acid containing products. A major challenge is achieving controlled oxidation without excessive degradation or undesired product mixture.

4.5 Role of catalyst

Catalyst is central to polyethylene chemical upcycling because they can lower the energy barrier associated with polymer chain activation and improve reaction selectivity. Catalyst performance depends on factor such as active metal, support material, acidity, particle size, surface properties and interaction between active sites. Bi functional catalyst containing both metallic and acidic sites are particularly interesting because different active site can perform complementary steps such as hydrogenation and C-C bond cleavage. Designing catalyst with controlled active site environment may therefore help achieve better conversion and product selectivity.

4.6 Factor affecting chemical upcycling

The efficiency of polyethylene upcycling depends on several parameters

Polyethylene structure: LDPE, HDPE, and LLDPE can show different reaction behaviors.

- Catalyst composition Determines activity and product selectivity.
- Catalyst loading Influence the interaction between polymer and catalyst.

- Temperature strongly affects conversion and product distribution.
- Reaction time longer reaction time may increase conversion but can also promote secondary reaction.
- Hydrogen pressure particularly important in hydrogenolysis and hydrocracking.
- Solvent and reaction medium Can influence heat and mass transfer.
- Polymer molecular weight and crystallinity Affect accessibility of polymer chains to catalytic sites.

V. CATALYST USED IN POLYETHYLENE UPCYCLING

Catalyst plays a central role in the chemical upcycling of polyethylene because the polymer contains strong and chemically stable C-C and C-H bonds. Efficient catalytic system can facilitate polymer chain activation, C-C bond cleavage, Hydrogenation, oxidation and rearrangement reaction thereby controlling the molecular weight and chemical composition of the products.

5.1 Metal based catalyst

Transition metal such as Ru, Pt, Pd, Ni and Rh have been investigated extensively for polyethylene conversion. This metal can activate hydrogen and facilitate hydrogenation-dehydrogenation reaction as well as C-C bond cleavage.

Ru- Ruthenium catalyst is particularly important in hydrogenolysis because of their strong activity toward C-C bond cleavage in the presence of hydrogen. Supported Ru catalyst can converted polyethylene into shorter chain hydrocarbon with product distribution depending strongly on reaction condition and catalyst properties.

Pt and Pd Pt and Pd are also effective catalyst for hydrogenation related transformations. Their high catalytic activity can promote controlled reaction involving polymer derived hydrocarbons, although their relatively high cost can limit large scale application.

Ni Ni has received considerable attention as a comparatively inexpensive alternative to noble metals. Ni-based can promote hydrogenation and C-C bond cleavage and therefore have potential for more economically viable catalytic system.

5.2 Supported metal catalyst

Supporting an active metal on a solid material can improve catalyst dispersion, stability and accessibility of active sites. Al_2O_3 , SiO_2 , activated carbon, TiO_2 and zeolite materials.

The interaction between the metal and support can significantly influence catalytic activity. Small and well-dispersed metal particle may provide more accessible active site, while the acidity or surface properties of the support can influence cracking and product selectivity.

5.3 Zeolite based catalyst

Zeolite are microporous crystalline aluminosilicate material with tunable acidity and well-defined pore structure. Their acidic site can promote C-C bond cleavage and hydrocarbon cracking during catalytic conversion of polyethylene.

Commonly investigated Zeolite material included HZSM-5, HY, And H-beta. Their pore structure and acidity can influence the formation of gaseous, liquid, and aromatic products. Zeolite based system are particularly relevant to catalytic pyrolysis and cracking process.

5.4 Bi functional catalyst bifunctional catalyst contains two types of catalytic functionality, commonly metallic site and acidic site. The metallic components can facilitate hydrogenation and dehydrogenation, while acidic site can promote C-C bond cleavage and rearrangement.

5.5 Bimetallic catalyst

Bimetallic catalyst contains two different material whose combined properties may provide advantages over individual metals. The second metal can modify the electronic structure. Dispersion, surface properties, or reaction pathway of the primary active metal. Examples include combinations based on Ni, Pt, Pd, Ru, Co, and other transition metals.

5.6 Metal Oxide catalyst

Metal oxide such as TiO_2 , CeO_2 , ZrO_2 , and various mixed oxides can provide acidic, basic, redox or oxygen storage properties. These characteristics make them useful in oxidative transformation and other catalytic approaches for polymer conversion.

The surface structure, oxygen vacancies, oxidation state, and acid base properties of metal oxides can

influence the activation of polyethylene-derived intermediates and the formation of oxygen-containing products.

5.7 Emerging catalytic materials

Recent research is increasingly focused on catalyst with precisely controlled active sites, including single atom catalyst, highly dispersed metal catalyst, nanostructure material and multifunctional catalytic system. This material may provide improved atom efficiency and better control over reaction pathways.

5.8 Catalyst selection and future development

An ideal catalyst for polyethylene upcycling should provide high conversion, high selectivity, low energy consumption, long term stability, resistance to poisoning, easy recovery and recyclability.

Future catalyst development should therefore move beyond simply maximizing conversion and should focus on controlling the exact product distribution. Designing catalyst with tailored active site optimize metal-support interaction reducing the use of critical and expensive metal and developing recyclable heterogeneous catalysts could significantly improve the practical potential of polyethylene chemical upcycling.

VI. REACTION MECHANISM

Reaction mechanism of long hydrocarbon chain containing strong C-C and C-H bonds. The chemical upcycling of PE therefore requires activation of these relatively inert bonds followed by controlled cleavage of the polymer backbone. Depending on the catalytic system and reaction environment, different pathway such as hydrogenolysis, hydrocracking, catalytic pyrolysis and oxidative transformation can be employed.

6.1 C-C bond activation

The first important step in polyethylene upcycling is the activation of the polymer backbone. The strong C-C bond of PE normally requires substantial energy for cleavage. A suitable catalyst provides an active surface where polymer chain interacts with catalytic sites, lowering the energy barriers for bond activation.

1. 1st step metal coordination and C-H activation (Oxidative addition) $-\text{CH}_2-\text{CH}_2- + [\text{M}] \rightarrow -\text{CH}_2\text{CH}(\text{M})(\text{H})-$

2. Step β -hydride elimination $-\text{CH}_2\text{CH}(\text{M})(\text{H})- \rightarrow -\text{CH}=\text{CH}- + [\text{M}](\text{H}_2)$
3. Step migratory insertion (C-C bond cleavage)-
 $\text{CH}=\text{CH}- + [\text{M}] \rightarrow -\text{CH}(\text{M})-\text{CH}_3 \rightarrow -\text{CH}=\text{M} + \text{CH}_3-\text{R}$
4. step Reductive elimination (Regenerate catalyst)-
 $\text{CH}=\text{M} + \text{H}_2 \rightarrow -\text{CH}_3 + [\text{M}]$

The reactive fragments generated during this process can subsequently undergo hydrogenation, beta-scission, rearrangement or other reactions depending on the catalytic environment.

6.2 Hydrogenolysis mechanism

Hydrogenolysis is one of the important catalytic routes for PE upcycling. In this process hydrogen participate in the cleavage of C-C bonds.

The simplified pathway can be represented as

1. Step- Dissociative adsorption H_2 on metal surface
 $\text{R}-\text{CH}_2-\text{CH}_2-\text{R}' + 2[*] \rightarrow \text{R}-\text{CH}=\text{CH}-\text{R}'_{(\text{ads})}$
 $\text{H}_2-2[*] \rightarrow 2\text{H}_{(\text{ads})}$
2. Step Surface dehydrogenation and C-C bond cleavage
 $\text{R}-\text{CH}=\text{CH}-\text{R}'_{(\text{ads})} \rightarrow \text{R}-\text{CH}_{(\text{ads})} + \text{R}'-\text{CH}_2_{(\text{ads})}$
3. Step Surface hydrogenation
 $\text{R}-\text{CH}_{(\text{ads})} + \text{H}_{(\text{ads})} \rightarrow \text{R}-\text{CH}_2_{(\text{ads})}$
 $\text{R}'-\text{CH}_2_{(\text{ads})} + \text{H}_{(\text{ads})} \rightarrow \text{R}'-\text{CH}_3_{(\text{ads})}$
4. Step Product desorption
 $\text{R}-\text{CH}_2_{(\text{ads})} + \text{H}_{(\text{ads})} \rightarrow \text{R}-\text{CH}_3_{(\text{gas})} + [*]$
 $\text{R}-\text{CH}_3_{(\text{ads})} \rightarrow \text{R}-\text{CH}_3_{(\text{gas})} + [*]$

A metallic catalyst such as Ru, Pt, Pd, or Ni can activate molecular hydrogen on its surface. The polymer chain interacts with the metal surface, followed by C-C bond cleavage and hydrogen addition to the resulting fragments. The final products are generally shorter hydrocarbon.

6.3 Hydrocracking mechanism

Hydrocracking generally involve two complementary catalytic function. Hydrogenation/dehydrogenation on metallic sites and C-C bond cleavage on acidic sites.

1. Step Metal site dehydrogenation: $\text{R}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{R}' + (\text{Pt}) \rightarrow \text{R}-\text{CH}_2-\text{CH}=\text{CH}-\text{R}' + \text{H}_2$
2. Step Acid site protonation: $\text{R}-\text{CH}_2-\text{CH}=\text{CH}-\text{R}' + \text{H}^+(\text{Zeolite}) \rightarrow \text{R}-\text{CH}_2-\text{CH}^+-\text{CH}_2-\text{R}' + (\text{Zeolite})^-$
3. Step- β -Scission: $\text{R}-\text{CH}^+-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{R}'' \rightarrow \text{R}-\text{CH}=\text{CH}_2 + \text{CH}_2^+-\text{CH}_2-\text{R}''$
4. Step Hydride transfer and metal site re hydrogenation: $\text{CH}_2^+-\text{CH}_2-\text{R}'' \rightarrow \text{CH}_3-\text{CH}_2-\text{R}''$ (Shorter fuel alkane)

The polymer derived intermediate undergoes cracking on acidic sites stabilizes the resulting fragments bi functional catalysts are therefore particularly useful for this pathway.

6.4 Catalytic pyrolysis mechanism

In catalyst pyrolysis, polyethylene is heated in the absence of oxygen. Thermal energy generates reactive species within the polymer chain which undergo chain scission and secondary reaction.

1. Step Thermal hemolytic initiation: $\text{R}-\text{CH}_2-\text{CH}_2-\text{R}' + (\text{Heat}) \rightarrow \text{R}-\text{CH}_2^* + \text{CH}_2-\text{R}'$
2. Step- Radical propagation and β -scission: $\text{R}-\text{CH}_2-\text{CH}_2^* \rightarrow \text{R}^* + \text{CH}_2=\text{CH}_2$ (Ethylene / propene)
3. Zeolite, Oligomerization and Cyclization: $\text{N C}_2\text{H}_4/\text{C}_3\text{H}_6 \rightarrow \text{Cyclohexane/ Cyclohexane intermediate}$
4. Dehydrogenation to BTX: $\text{Cyclohexane intermediate} + -3\text{H}_2 \rightarrow \text{C}_6\text{H}_6 / \text{C}_6\text{H}_5\text{CH}_3$

Depending on the catalyst and reaction conditions the product may include.

- Light hydrocarbons
- Liquid hydrocarbons
- Wax like products
- Olefins
- Aromatic compounds

6.5 Oxidative upcycling mechanism

Oxidative upcycling follows a different pathway in which oxygen containing functionalities are introduced into the polyethylene derived carbon skeleton.

A simplified sequence is

1. Step Radical initiation- (O_2 and Metal catalyst MN/CO): $\text{R}-\text{CH}_2-\text{CH}_2-\text{R}' + \text{M}^{3+} \rightarrow \text{R}-\text{CH}^+-\text{CH}_2-\text{R}' + \text{M}^{2+} + \text{H}^+$
2. Step- Oxygen Addition: $\text{R}-\text{CH}^+-\text{CH}_2-\text{R}' + \text{O}_2 \rightarrow \text{R}-\text{CH}(\text{OO}^*)-\text{CH}_2-\text{R}'$
3. Step- Hydrogen abstraction and hydrogen peroxide formation: $\text{R}-\text{CH}(\text{OO}^*)-\text{CH}_2-\text{R}' + \text{R}-\text{CH}_2-\text{R} \rightarrow \text{R}-\text{CH}(\text{OOH})-\text{CH}_2-\text{R}' + \text{R}-\text{CH}^+-\text{R}$
4. Homolytic O-O Cleavage and Alkoxy radical β -scission
 $\text{R}-\text{CH}(\text{OOH})-\text{CH}_2-\text{R}' \rightarrow \text{R}-\text{CH}(\text{O}^*)-\text{CH}_2-\text{R}' + \text{OH}$
 $\text{R}-\text{CH}(\text{O}^*)-\text{CH}_2-\text{R}' \rightarrow \text{R}-\text{CHO} + \text{CH}_2-\text{R}'$
5. Final oxidation to dicarboxylic acid: $\text{HOOC}-(\text{CH}_2)_n-\text{COOH}$ (eg- adipic acid, succinic acid)

Depending on the oxidant and catalyst, oxidation can generate functional group such as -OH, -C=O, -COOH

This transformation can convert relatively inert hydrocarbon chain into more chemically useful molecules. However, controlling the extent of oxidation is important because excessive oxidation may lead to unwanted degradation and complex product mixtures.

6.6 Factor controlling the reaction pathway-

Several parameters influence the mechanism and product selectivity

1. Catalyst composition and active site structure
2. Metal dispersion and particle size
3. Acidity of the catalyst
4. Temperature
5. Hydrogen pressure
6. Reaction time
7. Polyethylene molecular weight
8. Degree of branching and crystallinity
9. Polymer to catalyst ratio
10. Presence of additive and contaminants

VII. VALUE ADDED PRODUCTS FROM POLYETHYLENE

Catalytic upcycling can convert polyethylene waste into a range of useful products by controlled cleavage and functionalization of its polymer chain. Depending on the catalyst and reaction conditions, the major products include.

- Liquid hydrocarbons: Gasoline and diesel range hydrocarbon.
- Light hydrocarbons: Short chain alkanes and alkenes.
- Wax fractions: Useful in lubricants, coatings, and related application.
- Aromatic compounds: Such as benzene, toluene and related hydrocarbon through catalytic cracking.
- Oxygenated chemical: Alcohol, ketone, aldehydes, and carboxylic acid through acid through oxidative upcycling.
- Chemical Feedstock: Hydrocarbon and intermediates that can be further used for synthesis of new chemicals and material.

VIII. RESULT AND DISCUSSION

The literature analysis shows that catalytic chemical upcycling provides promising routes for converting polyethylene waste into value added hydrocarbon and chemicals. Among the reported approaches, hydrogenolysis, hydrocracking, catalytic pyrolysis and oxidative upcycling are the major routes investigated for PE conversion.

The catalytic performance is strongly influenced by PE structure catalyst composition, catalyst support temperature reaction time, hydrogen pressure and catalyst to polymer ratio. Metal catalyst such as Ru, Pt, Pd and Ni are widely studied for hydrogenolysis and hydro conversion while acidic zeolites and bi functional metal acid catalyst are commonly used for cracking and aromatization. Literature studies indicate that appropriate catalyst design can improve C-C bond cleavage and controlled product distribution toward liquid hydrocarbons, lighter hydrocarbons, waxes, aromatics, and oxygen containing chemicals. However higher selectivity toward the desired product because severe reaction condition may promote secondary cracking and gas formation.

Catalyst deactivation, high energy requirements, noble metal cost limited selectivity and difference in selectivity and differences in experimental condition remain important challenges. In addition, most studies use relatively clean model PE, whereas real post-consumer plastic contain additives and contaminants, that can affect catalytic performance.

IX. CURRENT CHALLENGES AND RESEARCH GAP

9.1 Major challenges

- High energy requirement: Many process require high temperature and pressure increasing energy consumption.
- Low product selectivity: Different C-C bond may break simultaneously. Producing complex mixture of hydrocarbons.
- Catalyst deactivation: Coke formation poisoning, sintering and deposition of impurities can reduce catalytic activities.
- Expensive catalyst: Noble metal such as Ru, Pt, and Pd provide high activity but can increase process cost.

- Mass transfer limitation: The high molecular weight and viscosity of molten PE can restrict contact between polymer chain and catalytic active site.
- Real world plastic waste: Additives, pigments, fillers, and contamination can negatively affect catalyst performance.
- product separation: Complex product mixture may require additional purification steps.
- Scale-up result obtained at laboratory scale may not directly translate to industrial scale processes.

9.2 Research gap

Despite rapid progress, several important research gaps remain.

- Development of low cost and highly selective catalyst that can replace expensive noble metal system.
- Design with catalysts with controlled active sites for selective C-C bond cleavage.
- Operation under mild reaction conditions to reduce energy consumption.
- Improve catalyst stabilities and recyclability during repeated reaction cycles.
- Better understanding of structure activity relationship between PE type, Catalyst structure and product distribution.
- Treatment of mixed and contaminated plastic waste rather than only pure laboratory grade PE.
- Mechanistic studies using advanced analytical techniques to understand reaction intermediate and pathway.
- Industrial scale up and techno economic assessment to determine commercial feasibility.
- Life cycle assessment (LCA) to verify the actual environmental benefits of different upcycling routes.
- integration with renewable hydrogen and renewable energy for developing more sustainable catalytic processes.

X. CONCLUSION

Catalytic chemical upcycling of polyethylene represents a promising strategy for transforming persistent plastic waste into value-added hydrocarbons and functional chemicals while promoting a more circular carbon economy. This review highlights the

significant roles of hydrogenolysis, hydrocracking, catalytic pyrolysis, and oxidative upcycling in controlling polymer-chain scission and product formation. Catalyst composition, support characteristics, polyethylene structure, and reaction conditions collectively govern conversion, selectivity, and product distribution. Despite substantial advances, challenges related to catalyst cost, deactivation, energy demand, product selectivity, and the complexity of real post-consumer waste continue to limit large-scale implementation. Future research should therefore prioritize earth-abundant and recyclable catalysts, mild and selective reaction conditions, real-waste feed stocks, and integrated techno-economic and life-cycle assessments. Such developments are essential for translating laboratory-scale catalytic upcycling into sustainable and scalable polyethylene waste valorization technologies.

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