THERMOCHEMICAL PROCESS MODELING OF PLASTICS FOR WASTE MANAGEMENT

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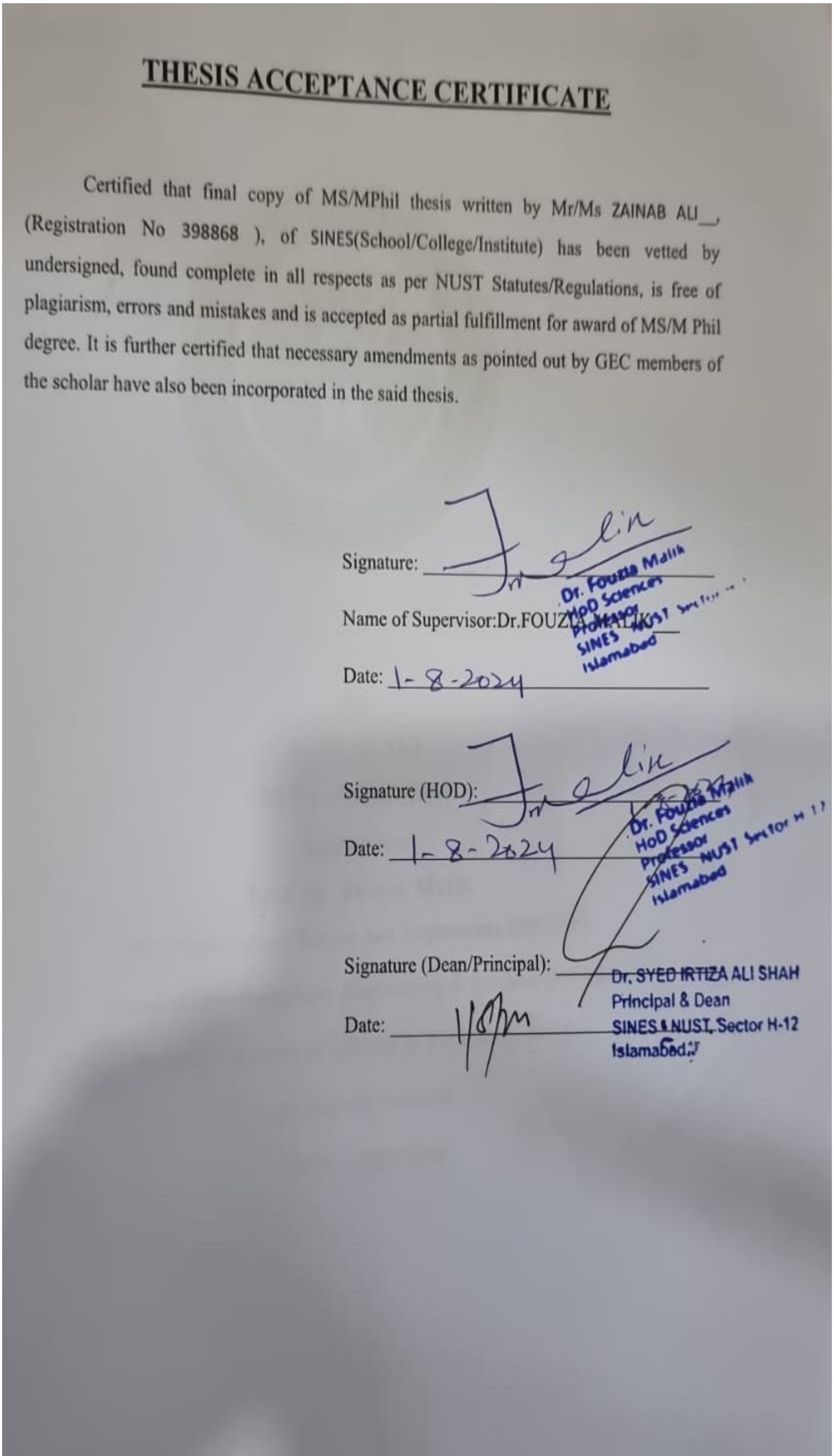

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A thesis submitted to partially fulfill the requirements of the degree of MS in Computational Science and Engineering (Stream: Computational Chemistry)

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Dedicated to my esteemed parents, Mr. RAJA GHAZANFAR ALI SHUJAH and Mrs. KOUSAR for their unconditional love & support.

Statement of Originality

I hereby declare that the research for my thesis, "Thermochemical process modeling of plastic waste materials for waste management" was completed by me at the School of Interdisciplinary Engineering and Sciences (SINES), National University of Sciences and Technology (NUST) under the supervision of Dr. Fouzia Malik. I solemnly affirm that all the information, data, and findings presented in this thesis are authentic and have not been submitted for any other academic degree or certification. To the best of my knowledge, this is my original work, and it is free from any plagiarism or academic misconduct.

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ZAINAB ALI

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List of Abbreviations

PET	Polyethylene terephthalate
PVC	Polyvinylchloride
PP	Polypropylene
PP	Polyethylene
PS	Polystyrene
EPA	Environmental Protection Agency
HLC	Henry’s law constant
WS	Water solubility
BCF	Bio-concentration factor
EPI-Suite	Estimation program interface-Suite
ADF	Amsterdam modeling suite
DFT	Density functional theory
LDA	Local density approximation
GGA	Generalized gradient approximation
ABSM	Abraham solvation model
HOMO	Highest occupied molecular orbital
LUMO	Lowest unoccupied molecular orbital
FMO	Frontier molecular orbitals

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Abstract

Plastic is valuable for its versatility, durability, and affordability, serving many purposes across industries and daily life. Its lightweight nature and moldability make it indispensable in packaging, construction, healthcare, and countless other sectors. However, despite its utility, the pervasive use and disposal of plastic have led to severe environmental consequences. Plastic pollution badly effect ecosystems, wildlife, and human health, as non-biodegradable plastics stays in the environment for hundreds and thousands of years, leaching harmful chemicals and disrupting natural habitats. Thermochemical processes offer a promising solution to address the escalating challenge of plastic waste management. This study investigates the thermochemical processing of five major types of plastics: PP, PET, PVC, PE, and PS. Each plastic variant presents distinct thermodynamic properties and chemical compositions, which are essential considerations in their effective conversion. The detrimental environmental impact of plastic pollution underscores the urgent need for sustainable waste management strategies. -Despite the critical importance of plastic waste management, an integrated study encompassing the environmental fate properties, optimization of plastics remains and comprehensive gasification studies specific to the diverse array of plastic polymers using Cao sorbent is lacking. This research work aims at structure-based toxicity assessment of various plastics by employing a dual methodology approach *i.e.,* through monitoring these pollutants in the environment and computing their electronic & molecular behavior for assessing their distribution, bioaccumulation, and aquatic toxicity and exploring active sites responsible for molecular interactions which contribute to their toxicity. Herein, the environmental fate of these plastics is monitored by calculating their bioconcentration factor (log BCF), biodegradation probability (BIOWIN 3), Henry's law constant (HLC), soil adsorption coefficient (Koc), Octanol-water partition coefficient (log Kow), atmospheric oxidation (Aopwin), and water solubility (WS) using Estimation Program Interface (EPI) Suite. Moreover, DFT calculations are performed to explore & compare their chemical reactivity and toxicity through triple zeta (TZ) basis set, GGA, and BLYP functional. Furthermore, this research extends to address the dual bed air-steam gasification using Cao as a sorbent for enhanced production of energy.

1. Introduction

1.1 Plastic Waste

For over 50 years, plastic has played a significant role in improving people's living [1]. However, the use of these plastic products has led to an ongoing global problem with plastic trash pollution. Most of these plastic wastes are now disposed of by being dumped into landfills or burned in incinerators along with other solid trash as shown in figure 1.1 [2]. Electronic garbage has become a significant problem for experts in recent years due to how frequently it is discarded worldwide. Analysis indicates that 44.7 million tons of e-waste were produced in 2016, and it is anticipated that, with an annual growth rate of 3-4%, that number will rise to 50.2 million tons by 2021. E-waste is made up of many components that include glass and polymers [3]. Additionally, polymers include macromolecules like plastics, cellulose, rubber, and wax that are made up of smaller components called monomers and are roughly divided into three types according to their genesis natural, synthetic, and semisynthetic molecules. Synthetic polymers called plastics are made of a variety of synthetic/semisynthetic organic molecules that are pliable and can be molded into a variety of solid substances [4].

Since the first synthetic plastic was made in New York in 1907, polymers have played a significant role in everyday human existence. Plastics are used in every aspect of daily life, including clothes, transportation, telecommunications, footwear, and packaging materials that make it possible to convey a variety of foods, beverages, and other items. Furthermore, the practical use of plastics in a variety of commercial, industrial, and agricultural activities is accelerated by their advantageous characteristics, such as their affordability, minimal upkeep needs, lightweight nature, stability, degradation resistance, transparency, decreased contamination, better insulation from electricity, excellent thermal properties, and design adaptability when compared to other solid substances [5].

Figure 1.1 Plastic litter in a natural habitat, highlighting environmental concerns [5].

1.2 Global plastic waste production:

Plastic has been the most frequently used material in the world during the past 60 years as a result of its extensive use in a variety of applications. With annual worldwide consumption exceeding 260 million tons, plastic currently makes up nearly 10% of all garbage produced [6,7]. According to the survey, around 370 million metric tons of plastic were produced globally in 2019. Of these, 36.4% are estimated to be burned; a comparable percentage (36.4%) is forecast to be thrown into landfills or excreted into the environment and just 27.2% will be utilized for recycling. These predictions clearly foresee the incorrect management of plastic wastes caused by improper recycling or reuse of these materials, which ultimately results in plastic wastes contaminating land, freshwater, and oceans across the world. Plastics have a ubiquitous presence in marine trash due to their lightweight, durable nature, with subsequent effects on the natural environment and all living things [8,9].Effective waste management falls under the category of upstream responses. Currently, preventative measures to lessen the plastic wastes expelled to the environment(upstream responses) and strategies to mitigate their impact after they are discharged into the environment (downstream responses) are considered vital instruments for combating the growing problem of global plastic waste. The recycling of plastic waste, on the other side, has several drawbacks, one of which contributes to the item's monetary appeal [10-15].

1.3 Classification:

The process of polymerization involves the joining of individual molecules (or "mers") through chemical processes to form macromolecules having a long chain structure that possesses characteristics that are different from those of the initial molecules. Polymers are classified as rubber or elastomers, plastics, and fibers based on their characteristics and nature as shown in Figure 1.2. So, the right amount of pressure, heat, or some external force is used to shape macromolecules(plastics) created by

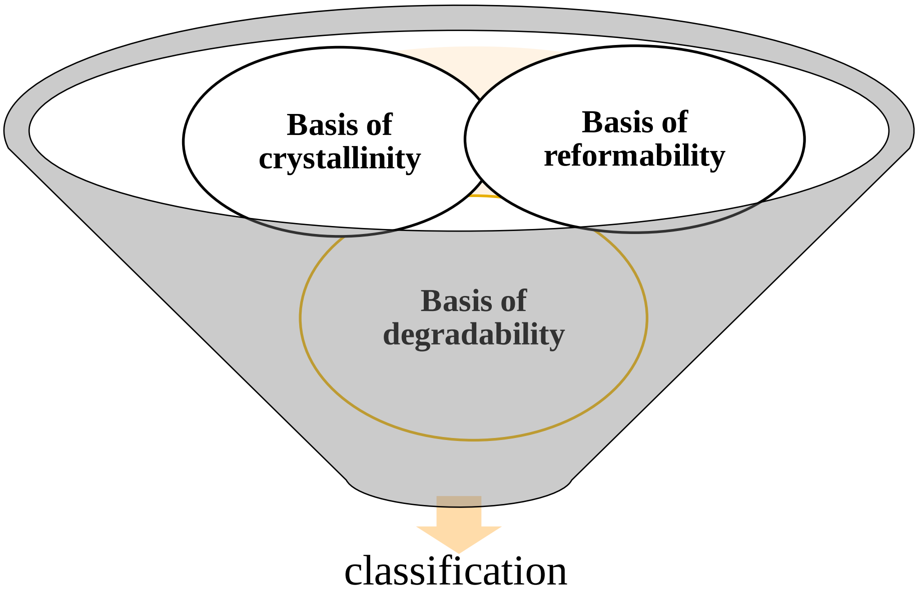


Figure 1.2 Classification of plastics [16].

1.3.1 Based on re-formability

Plastic is classified into two main types as thermosetting and thermoplastic plastics.

Thermoplastics and thermosetting polymers

Thermoplastics are made of long chains of molecules linked together through weak Van der Wall forces. Once created, they may be repeatedly bent into various forms by applying heat until they shed their individuality. They have low melting points and low tensile strength while thermosetting polymers do not come back to their original position as they exhibit cross-linked structures polyethylene, polypropylene, polystyrene, and polyvinyl chloride [23]. Thermoplastic and thermosets polymers are favored in biomedical applications for their mechanical properties, chemical stability, and versatility. Plastics, with attributes like ease of processing and sterilization susceptibility, find use in coating medical devices, creating novel biomedical tools, and facilitating accurate diagnostics. The main distinction between thermoplastics and thermosets lies in their structural changes at specific temperatures [24].

1.3.2 Based on the degree of crystallinity and molecular structure

Plastic is classified into Amorphous and crystalline or semi-crystalline based on their molecular structure.

Amorphous and crystalline or semi-crystalline:

Amorphous polymers lack a well-defined and ordered structure at the microscopic scale, with polymer chains exhibiting a more random arrangement and lacking the long-range order seen in crystalline polymers. This absence of a distinct repeating pattern imparts a certain randomness to their properties, such as a gradual softening over a temperature range. In contrast, crystalline polymers feature a highly ordered and repetitive three-dimensional arrangement of polymer chains, forming a crystal lattice that imparts a distinct, repeating pattern on the microscopic scale. Crystalline polymers often exhibit sharp melting points and clear X-ray diffraction patterns, contributing to enhanced mechanical properties like higher strength and stiffness. Examples of amorphous polymers include certain thermoplastics like polystyrene, while crystalline polymers include polyethylene and polypropylene [25].

1.3.3 Based on the degradability

Biodegradable and non-biodegradable

Biodegradation refers to alterations in the chemical composition of plastics induced by biological processes, including enzymatic activities. Plastics undergoing such changes are termed biodegradable, while those resistant to decomposition by bacterial action are classified as non-biodegradable. [26]

1.4 Physical properties of commonly used plastics

Plastics are broken down into seven groups based on their ability to be recycled. In under mentioned table 1.1 PET (polyethylene terephthalate), HDPE (high-density polyethylene), PVC (polyvinyl chloride), LDPE (low-density polyethylene), PP (polypropylene), PS (polystyrene), and 'other'. Polybutylene terephthalate, polycarbonate, polylactic acid, acrylic, acrylonitrile, butadiene styrene, multi-layered mixed polymers, and nylon are included in the "other" group [25].

Table 1.1 Recyclability of diverse groups of plastics [25].

polymers	**Recyclability percentage**	Recyclable
PE	46%	yes
PP	16%	yes
PS	16%	yes, but not common
PVC	7%	yes, but not common
PET	5%	yes
Acrylonitrile-Butadiene-Styrene	5%	yes
Other Polymers	5%	yes/no

1.5 Consequences of plastic buildup on the environment and human health

The 2020 survey indicated that 195 different countries produced 400 Mt of plastic garbage, and 8.8 Mt of that debris was found to be discharged into the ocean. The largest source of organic contaminants, heavy metals, chemicals, and pathogens is plastic debris. Furthermore, the hydrophobic nature of plastics facilitates their interaction with other contaminants. Many chemicals are added to plastics throughout the manufacturing process to change their characteristics, including phthalates, biphenyl-A, and flame retardants, which are harmful to both human and animal health and primarily impact the hormonal systems. In addition, the hazardous moieties frequently undergo cross-linking that can lead to cancer and reproductive problems as shown in figure 1.3.

1.5.1 Crisis Unveiled: Plastic Waste's Symbiotic Peril with Human Expansion

The symbiotic relationship between plastic waste distribution and expanding human populations is evidenced by rising demands for plastics and their products. Indiscriminate disposal leads to environmental pollution, impacting natural aesthetics, aquatic life, and urban sewage systems.

Plastic-laden occupational and residential environments threaten terrestrial ecosystems, with additives leaching into soil and water, persisting for extended periods. Microplastics and synthetic fibers endure in soils, and chlorinated plastics release toxins, while microbial plastic biodegradation emits methane, a potent greenhouse gas. Water pollution stems from the presence of 165 million tonnes of oceanic plastics, impacting marine life and ecosystems. Air pollution results from landfill decomposition and burning, releasing carbon dioxide and methane, exacerbating global warming. Plastics' pervasive impact on both water and air quality underscores the urgency of mitigating their environmental consequences. [26]

1.5.2 Microplastic Menace: Disrupting Soil Ecosystems and Microbial Dynamics

The intricate balance of soil ecosystems, orchestrated by a diverse microbial community, faces escalating disruption from plastic pollution, particularly microplastics (MPs). Soil, a complex habitat formed by minerals, organic matter, and interconnected pores, serves as a vital arena for essential processes directed by microorganisms. Human-induced impacts such as intensive agriculture and climate change have already altered soil structure and microbial composition. The emerging threat of microplastic pollution exacerbates these challenges, disturbing the delicate interactions between plants, soil, and microorganisms. Microplastics infiltrate the ecosystem, acting as microbial hotspots and causing shifts in community dynamics. These disruptions manifest in altered soil structure, hindered plant development, and perturbed microbial activity. Plastic's influence extends beyond the visible, impacting core processes like carbon sequestration and nutrient cycling. Recognizing the pervasive impact of plastic on soil underscores the imperative for extensive research and robust mitigation strategies to safeguard the resilience and functionality of this critical environmental domain [27].

1.5.3 Navigating Plastic Pollution Policies: From Awareness to Action

Plastic pollution, stemming from widespread production and improper disposal practices, presents a complex environmental challenge. Extensive scientific research has highlighted the visible consequences of plastic pollution, prompting numerous countries to enact measures aimed at reducing plastic usage. Notably, the European Commission's ban on single-use plastics reflects a global shift in addressing this concern. While primary microplastics, intentionally manufactured for various applications, garner attention, the less evident effects of secondary microplastics and Nano plastics on ecosystems and human health are gaining recognition. These minuscule particles, found ubiquitously in the environment, undergo intricate transformations, yet their dynamic impact remains insufficiently understood. With plastic entering marine environments in alarming quantities, the potential repercussions on marine fauna escalate, underscoring the need for a comprehensive approach to quantify plastic pollution. Life cycle assessment (LCA), a standardized methodology, emerges as a valuable tool for evaluating the overall impact of plastics and guiding policy decisions. Nevertheless, challenges persist in linking plastic loss to final impact, particularly concerning secondary microplastic [28]

1.5.4 Unveiling the Health Hazards of Plastics: Insights into Human Exposure and Risks

Plastics pose a multifaceted threat to human health, emanating from monomeric constituents like Bisphenol A (BPA) and additives such as plasticizers, with notable examples being antimicrobial polycarbonate. BPA, a pivotal building block of polycarbonate plastics and frequently used additive in other plastic types, exhibits concerning health implications. Released from containers into food and drinks over time, especially at elevated temperatures, BPA is prevalent in items like reusable water bottles, baby bottles, and food can linings. Research links BPA exposure through food and inhalation to disruptions in the body's hormonal messaging system, mimicking reproductive hormones. Associations have been drawn between BPA exposure and health issues such as obesity, and heightened risks of breast and prostate cancer. Additionally, phthalates, a group of compounds widely used in plastics for flexibility, contribute to hormonal imbalances and disrupt normal bodily functions. Medical exposures, ingestion of contaminated materials, and the use of phthalates in plastics like polyvinyl chloride (PVC) underscore the diverse pathways of human exposure. Both BPA and phthalates can impact newborns during pregnancy and breastfeeding, with BPA exhibiting higher damaging potential. Various plastic containers harbor harmful BPA and phthalates, collectively posing a significant risk to human health [29].

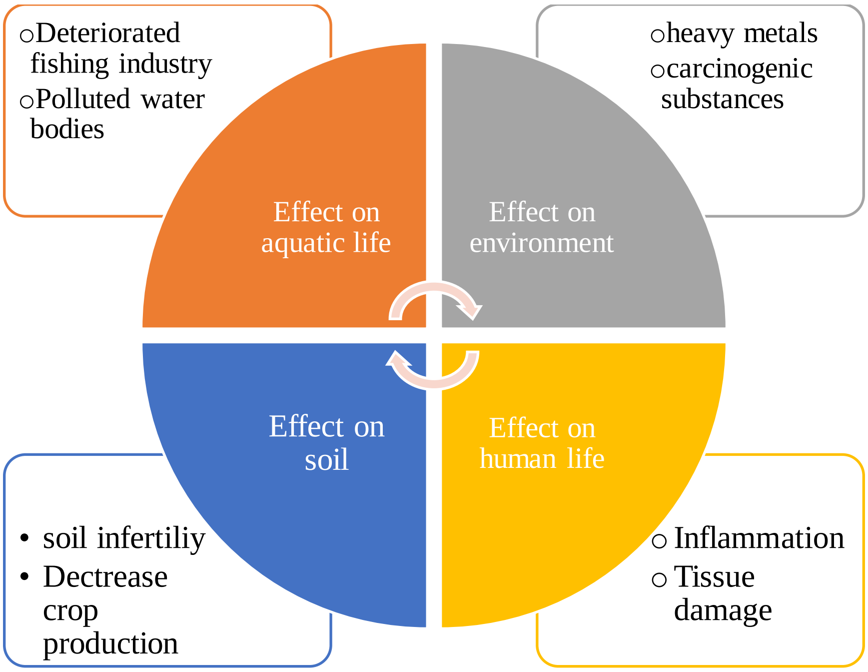


Figure 1.3 Effects of Accumulating Plastic on Ecosystems and Human Well-being.

1.6 Plastic waste management technologies

Particles of plastics may be easily found in the atmosphere, and water bodies due to over usage of plastic packaging in bottles and food containers. The techniques of plastic garbage management have become more challenging due to a persistent global condition brought on by the corona virus pandemic. The fear of transmission and international administrative rules have increased consumer demand for recyclable plastic bags, containers, and personal hygiene goods, which has contributed to an overall spike in plastic trash.

1.6.1 Incineration and landfilling:

Landfills, ubiquitous for waste disposal, have undergone regulatory advancements in developed nations, contrasting with unregulated dumping practices in rapidly urbanizing regions of less developed countries. The escalating awareness of landfill methane emissions, a potent greenhouse gas, has catalyzed endeavors to quantify and mitigate their impact. Despite challenges in accurate quantification, initiatives to reduce methane emissions from landfills have gained momentum, driven in part by international agreements like the Kyoto Protocol but landfilling is the traditionally used method of waste disposal used in most nations. Antioxidants and stabilizers are two chemicals that help waste plastic polymers dumped in landfills delay the biodegradation of plastic for an exceptionally extended period. Due to the durability of plastic, their slow biodegradation rate, the limited number of landfilling areas currently available, full utilization of starting agents, and issues arising due to pollution of groundwater and diversity of toxic chemicals and their ability to leach from landfills, landfilling does not appear to be an appropriate method for managing plastic debris. As a result, researchers do not consider this technique for waste management. Waste incineration with energy recovery plays a pivotal role in the circular economy, constituting a significant component of solid waste treatment globally. Final bottom ash, a byproduct of incineration, is crucial for evaluating combustion efficiency, with the loss on ignition (LOI) serving as an indicator of unburned material. While incineration is widely perceived as an effective method for eliminating plastic waste. [30]

1.6.2 Mechanical recycling

Recycling of plastics is a more effective method of waste management than landfilling and incineration. In broadly, recycled polymers are less expensive than new plastic, but prices vary between 20-100% depending on the kind of polymer and its percentage in the plastic. The four basic categories of recycling are primary, secondary, tertiary, and quaternary recycling. Mechanical recycling is split into Upcycling and downcycling as shown in figure 1.4 [31].

1.6.3 Down cycling and Upcycling

Polymer recycling strategies encompass downcycling, tailored for polymers of lower-grade attributes. Despite its effectiveness for certain thermoplastics, downcycling presents limitations, such as the degradation of recycled products and alterations in characteristics. Recycled plastics often lose attributes like optical clarity, making them less suitable for initial applications. The process involves collection, washing, and other physical techniques [32]. In contrast, upcycling, or creative reuse, transforms waste plastics into higher-quality materials or products for aesthetic and environmental purposes. While cost-effective, upcycling requires steps like waste segregation and thorough washing to enhance process efficiency. The narrative of polymer recycling thus explores the balance between downcycling's limitations and the creative potential in the upcycling process [33].

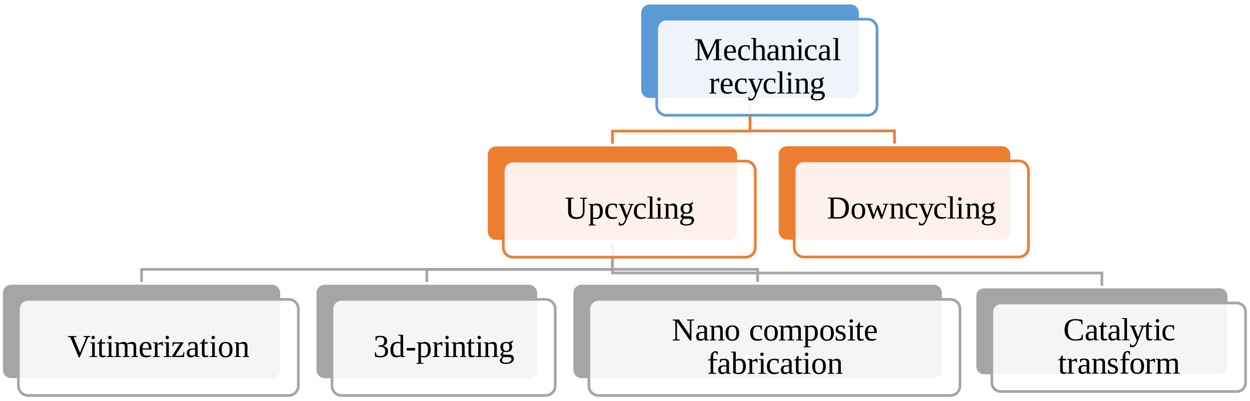


Figure 1.4 Methods involved in mechanical recycling of plastic.

1.7 Thermochemical processing:

The process of thermochemical conversion uses heat to break down organic material to create liquid, gaseous, and char products. Due to its greater energy density, which is comparable to or better than commercial diesel fuel, liquid oil is the most valuable of the three pyrolysis products (together with gas and char). Gas may be used to heat the pyrolysis reactor and the char created during the process can be utilized as fertilizer. Operating conditions can be changed and adjusted later depending on the intended product, which may be liquid oil, gas, or char. Thermochemical co-conversion represents a promising avenue for the simultaneous recycling of biomass and plastics into biochar, offering efficiencies in both time and cost compared to individual recycling processes. This review delves into the existing body of literature concerning the thermochemical co-processing of biomass and plastic wastes to generate biochar. The predominant technologies employed for this purpose were identified as co-pyrolysis and co-hydrothermal carbonization. An assessment of various biomass and plastics subjected to thermochemical conversion into biochar revealed distinctive characteristics. The resultant biochar properties were found to be influenced by factors such as feedstock composition, pre-treatment methods, blending ratios, reactor configurations, reaction temperatures, and the incorporation of catalysts [34].

1.8 Gasification and pyrolysis:

The gasification process of waste plastics emerges as a pivotal and scientifically significant avenue within the realm of energy recovery and environmental sustainability.

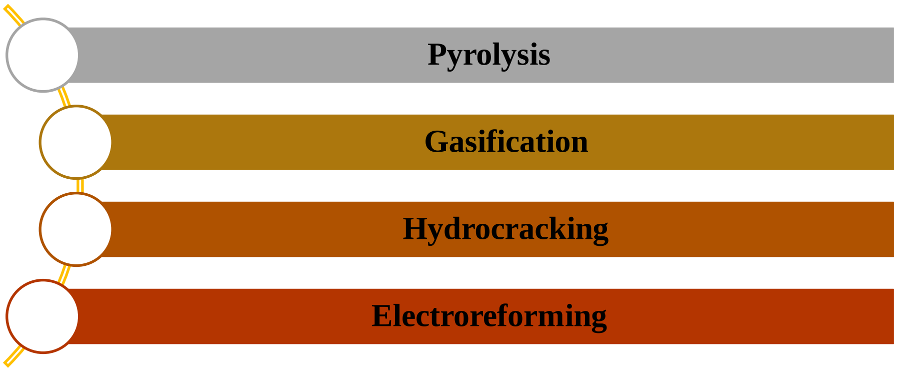


Figure 1.5 Classification of different processes involved in thermochemical processing.

Plastics, once deemed non-recyclable, pose a challenge that necessitates prudent management. In addressing this issue, the conversion of such plastics into energy or fuel through methods like incineration, pyrolysis, and gasification stands out as an instrumental choice. Gasification, characterized by the conversion of carbon-based materials into syngas through controlled heating in the presence of limited oxygen, offers distinct advantages over alternative waste-to-energy methods [35]. Hydrogen, arising as a prominent component in the produced gas, emerges as a promising clean fuel due to its environmentally friendly attributes, versatility, and potential to replace fossil fuels in various applications as shown in figure 1.6. Calcium oxide (CaO) assumes a crucial role in gasification processes, particularly in the context of the water-gas shift (WGS) reaction. The consistent removal of carbon dioxide (CO2) facilitated by the CaO sorbent serves to perpetually drive the equilibrium-limited WGS reaction in the forward direction.

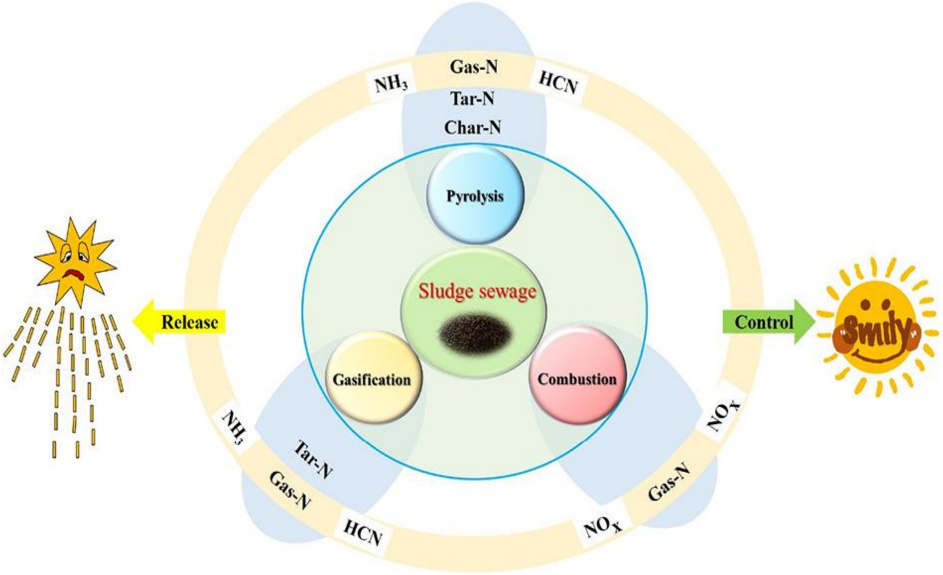


Figure 1.6 Products of different processes of conversion of plastics into energy.

This dynamic ensures a maximum yield and purity of hydrogen (H2) while maintaining a near stoichiometric balance of steam required for the reaction. The active involvement of Cao contributes significantly to the optimization of gasification processes, enhancing the efficiency and product purity in the generation of hydrogen. Gasification, referred to as "indirect combustion," entails the transformation of solid waste into fuel- or synthesis-gases through gas-forming reactions. This process involves the partial oxidation of waste using an oxidant amount below stoichiometric combustion level. In auto-thermal gasification, observed in air gasification, a portion of the fuel is combusted to generate the necessary heat for gasifying the remaining material. In allo-thermal gasification, illustrated by plasma torch utilization, external heat energy is employed. The outcome is a hot fuel gas, termed "producer gas" or "syngas," containing substantial quantities of incompletely oxidized products [36]. It is a thermal decomposition (tertiary recycling) process that creates gaseous fuel and liquid from solid plastic waste at temperatures 300-900 °C in an oxygen-free atmosphere. This process converts old and discarded plastics (polymeric compounds composed of monomers), into energy useful products e.g., fuel, monomers, and useful substances [37]. Pyrolysis, an advanced thermal decomposition process, emerges as a promising technique for efficient plastic waste disposal. It sets itself apart from conventional methods like incineration through its utilization of controlled combustion techniques, preventing oxidation with elements such as nitrogen. In the realm of waste management and sustainable energy transformation, pyrolysis highlights adaptability and effectiveness in extracting versatile oil from plastic waste.

During devolatization or pyrolysis, polymers undergo decomposition into a liquid form under heightened pressure, temperature, and within an inert atmosphere. This process facilitates the generation of essential oil from plastic wastes, with variations in yield and product distribution influenced by factors such as catalysts, feedstock proportions, residence times, temperatures, and pressures. Importantly, these variations exhibit minimal environmental impact. Specific conditions governing flash, fast, and slow pyrolysis are shaped by parameters like temperature, residence time, and particle size of the feedstock. These factors contribute to both quantitative and qualitative variations in product formation and distribution. Subsequent sections will provide detailed insights into these parameters and their consequential effects [38].

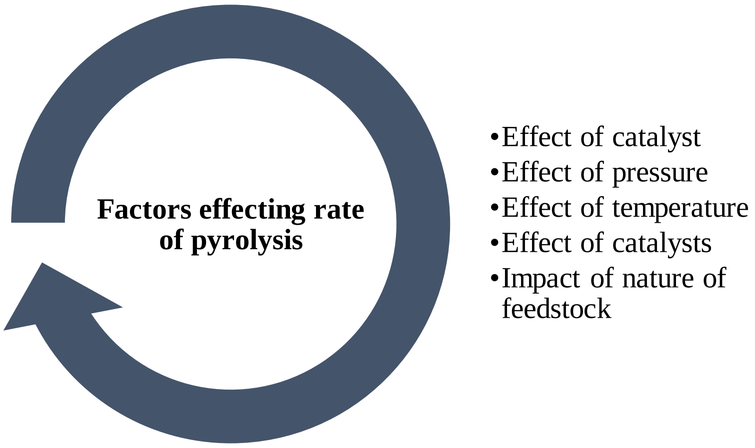


Figure 1.7 Factors responsible rate of pyrolysis.

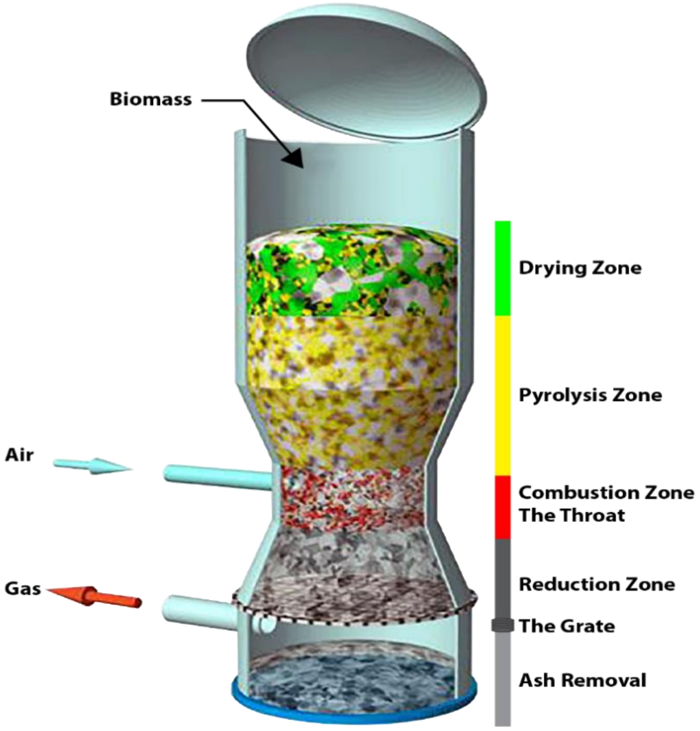


Figure 1.8 Sub-processes involved in the gasification of biomass or waste.

1.9 Waste plastic debris into useful products:

In the pursuit of environmental sustainability, the mounting global issue of plastic waste has spurred scientific exploration into converting this ecological challenge into valuable energy resources. This narrative unfolds within the context of catalytic pyrolysis, an innovative process where the effectiveness of catalysts plays a crucial role in transforming waste plastics. Distinguishing between homogeneous and heterogeneous catalysts, the former excels in quick reactions under moderate conditions. However, drawbacks such as higher energy consumption and challenges in extracting the catalyst hinder its appeal. In contrast, heterogeneous catalysts, with their large surface areas, facilitate easier separation of products and demonstrate resilience to obstacles in mass transfer [39]. Navigating through scientific advancements, this narrative introduces state-of-the-art technologies designed to convert waste plastics into high-value resources. The collaboration between catalysis and pyrolysis not only produces conventional products like gasoline but extends its transformative capabilities to generate syngas and futuristic carbon nanotubes. The narrative also explores catalytic involvement in alternative realms, shedding light on water and keratin recycling processes that underscore the broader applicability of catalytic prowess in sustainable resource management. The surge in plastic use, while offering convenience, has led to a parallel crisis in waste disposal. Traditional recycling methods have proven insufficient, and uncontrolled incineration has contributed to environmental challenges. The story reaches its zenith with the introduction of pyrolysis technology bolstered by catalytic reforming, a tertiary recycling strategy. This transformative process converts plastic waste into liquid oil and char, not just addressing waste management but offering an opportunity to harness coveted energy products [40].

2. Literature Review:

2.1 Environmental fate monitoring of plastic using EPI-Suite

Kwon et al, researchers utilized the US EPA EPI Suite program to apply in-silico methods for estimating the physicochemical attributes of styrene oligomers (SOs), persistent contaminants with global prevalence. The investigation focused on key properties like solubility, vapor pressure, Log Kow, Henry's constant, Log Koc, and fugacity-based multimedia mass balance. The in-silico analysis using the EPI Suite indicated that styrene oligomers (SOs) are expected to exhibit extremely low mobility and volatility in the environment, suggesting a tendency to accumulate in soils or sediments. The estimated values, including Log Kow, Log Koc, vapor pressure, solubility, Henry's law constant, and fugacity, all pointed towards limited environmental mobility. Notably, the study suggested a potential for high bio concentration of SOs based on Log BCF estimates. While these findings offer valuable insights into the environmental fate of SOs, the study underscores the necessity for further experimental research to validate and expand upon these predictions. The in-silico approach, exemplified by tools like the EPI Suite, emerges as a valuable tool for comprehending the behavior of emerging contaminants in the environment [41]

The paper discusses the environmental impact of organic pollutants, including persistent and emerging ones, which have gained significant attention in recent decades. It highlights the wide distribution of organic pollutants in various environmental media and their origins in industrial production and human activities. The research projects mentioned in the abstract focus on developing analytical methods, studying the distribution and concentration of organic pollutants, understanding their fate in the environment, exploring new pollutants, and conducting non-target analysis [42].

Bum Gun Kwon underscores the global concern surrounding SOs as ubiquitous contaminants and emphasizes the need for comprehensive investigations. By utilizing the US EPA EPI suite program for in-silico predictions, the study fills a significant void, revealing that SOs are anticipated to pose greater toxicity risks than well-known pollutants like biphenyl-A (BPA) and styrene monomer (SM) across various ecosystems. The slow predicted biodegradability of SOs underscores potential long-term environmental impacts, shedding light on the urgency for further understanding and regulatory measures. This study suggests that Styrene Oligomers

(SOs) exhibit lower predicted concentrations, but higher aquatic toxicity compared to BPA and SM, emphasizing their potential hazards.

While hydroxyl radicals are expected to play a significant role in SOs' atmospheric degradation, further experimental studies are imperative to precisely determine their environmental impact [43].

2.2 Polymer Repurposing and Recycling Overview:

Plastics have the ability to get recycled and converted to useful substances. Following is their repurposing of plastics in daily use.

Table 2.1 Recycling symbols and use of plastic polymers in daily usage.

Recycling symbol	Polymer name	Use	Repurposed to make	Recyclable
1 PETE	Polyethylene Terephthalate	Soda bottles Water bottles	Carpets, pillow stuffing,	yes
2 HDPE	High-Density Polyethylene	Grocery bags Trash bags	Plastic crates,	yes
3 PVC	Polyvinyl Chloride	Tile Cling films	Flooring	yes
4 LDPE	Low-Density Polyethylene	Squeezable bottles	Garbage cans	yes
5 PP	Polypropylene	Disposable cups	Battery cables	no
6 PS	Polystyrene or Styrofoam	Packing foam	Insulation	no

2.3 Multifaceted Exploration of Plastic Properties: Pyrolysis Kinetics, DFT Simulations, and Optical Characterization:

The research of *Shan et al*, explored the pyrolysis characteristics of single and mixed plastics under different atmospheres, such as nitrogen and carbon dioxide. Two kinetic models, the Kissinger-Akahira-Sunose (KAS) method and the Friedman method, were utilized to calculate kinetic parameters. The study also identifies positive and negative synergistic effects in mixed plastics under different atmospheres, providing valuable insights for environmentally friendly plastic waste recycling technologies. The study also indicates plastics experience reduced pyrolysis temperatures and activation energies under carbon dioxide compared to nitrogen atmosphere, indicating a more efficient pyrolysis process in carbon dioxide [44].*Renzi et al,* performed both experimental (Photoluminescence measurements) and computational methods (DFT simulations) to find the optical properties. Structure optimization of TFB polymer is done using the software package GAUSSIAN 09. B3PLYP, 6–31G* basis set is used similarly for obtaining Raman spectra. HOMO and LUMO band gap energy help in the identification of physiochemical properties e.g., electron affinity and ionization potential. Both experimental and DFT-calculated Raman and FT-IR results exhibited good agreement, with discrepancies in vibrational modes below 7% [45].

2.4 Upcycling of plastics via thermochemical process modeling using Aspen-plus

2.4.1 Sustainable Approaches for Plastic Waste Valorization: Catalytic Conversion and Co-Gasification:

.*Mark, L. O., Cendejas et al,* reviews recent research advances in catalytic technologies for the conversion and valorization of plastic solid waste (PSW).The methods discussed include chemical recycling via thermal and heterogeneous catalytic conversion, which have gained attention as sustainable alternatives to address the global challenge of PSW. Chemical recycling via thermal and heterogeneous catalytic conversion has gained attention as a sustainable approach to address the global challenge of PSW.These catalytic processes have the potential to convert PSW into usable monomers, fuels, synthesis gas, and adsorbents under more sustainable conditions than thermal degradation.The use of heterogeneous catalysis in PSW valorization offers the possibility of transforming waste plastics into valuable products, contributing to a circular economy and reducing environmental pollution [46].

Co-gasification process that improves overall process efficiency and reduces volume of wastes produced. It enhances quality by increasing product gas yields, HHV, and carbon conversion efficiency to gas. Polypropylene is found to be the most beneficial plastic for co-gasification. Using CO_2 as a gasifying agent reduces the quantity of H_2 due to the reverse water gas shift reaction and decreases the HHV. Air gasification decreases the HHV compared to oxygen due to the dilution effect of N_2. Steam is the most efficient gasifying agent, and a steam-to-carbon ratio of unity is recommended for high gas yield and heating value. The thermodynamic data are validated with published experimental work. Thermodynamic equilibrium simulation of biomass co-gasification with plastic was conducted using HSC Chemistry software [47].

The study investigates the co-pyrolysis of camel manure, date pits, and plastic waste using Aspen Plus® to determine the impact of waste types, blends, and temperature on pyrolysis product and plastic waste including high-density polyethylene and low-density polyethylene. Different mixing ratios of these feedstock are studied to determine their impact on pyrolysis product distribution. The pyrolysis process is analyzed at various temperatures to assess its influence on the production of pyrolysis char, pyrolysis gas, and pyrolysis oil. The production rates of these products are measured in kilograms per hour for each feedstock and mixing ratio. The results provide insights into the optimal blending ratios and temperatures for maximizing the production of pyrolysis char, pyrolysis gas, and pyrolysis oil from the co-pyrolysis process. The highest production of pyrolysis gas is observed for camel manure (623.78 kg/hr.) and date pits (555.69 kg/hr.) at a temperature of 600 °C. The maximum production of pyrolysis char is achieved for LDPE (485.43 kg/hr.) and plastic feedstock (HDPE) (618.46 kg/hr). The highest production of pyrolysis oil is observed at a temperature of 300 °C for all scenarios, with a maximum production of 309.92 kg/hr for date pits. [48]

Investigation of co-gasification of two different feeds (biomass and plastic waste) using HSC Chemistry software, assessing the efficiency of the carbon conversion to gas and production rates. The findings of the study suggest that co-gasification outperforms gasification in terms of efficiency, resulting in improved product yields and heating value. Polypropylene is identified as the most advantageous plastic, and an increase in the plastic-to-biomass ratio is observed to enhance hydrogen and CO yields, and the higher heating value of the gas. A crucial aspect highlighted in the research is the role of the gasifying agent, with steam emerging as a highly efficient choice. The study recommends a steam-to-carbon ratio of unity for optimal gas yield and heating value. Interestingly, the selection of the gasifying agent significantly influences gas composition and higher heating value. The use of as the gasifying agent leads to a reduction in hydrogen quantity due to the reverse water gas shift reaction, ultimately impacting the higher heating value. Additionally, air gasification results in a decrease in higher heating value compared to oxygen, attributed to the dilution effect of nitrogen [49].

2.4.2 Innovative Pyrolysis Strategies: From Plastics to Valuable Biochar and Fuels

The synergistic thermochemical transformation represents a promising approach for recycling biomass and plastic waste, facilitating production of biochar. This innovative method concurrently reduces the temporal and financial requirements inherent in individual recycling processes. In this process, technologies like combined pyrolysis and hydrothermal carbonation are frequently used.

Many variables, such as the feedstock's composition, pre-treatment techniques, blend ratio, the reactor layout, reaction temperature, and promoter presence, influence the characteristics of the biochar formed. They examined the impact of treating the feedstocks separately versus processing them together on the yield of biochar. Treating biomass and plastics together generally yields a higher biochar yield compared to processing them separately [50].

Thermochemical conversion of plastic waste is a potential strategy to upcycle plastic debris into valuable feedstock, but it typically requires high temperatures and can benefit from the use of promoters to improve energy and product efficiency. This review discusses the commercial implementation status and highlights the challenges and future perspectives, including sustainable and robust catalysts [51].

An intricate process simulation was developed to analyze and predict the pyrolysis of linear low-density polyethylene (LLDPE) within a fluidized bed reactor (FBR). This scientific endeavor involved a meticulous approach to model and understand the complex thermodynamic and kinetic aspects of the pyrolysis process at temperatures of 600 and 700 °C. The simulation investigates the yields of pyrolytic oil and wax, which are potential fuel and energy sources. The results showed a decrease in oil at 700 °C due to increased temperature and absorbed thermal energy. The gas yield was higher at 700 °C, excellent for controlling plastic waste. The simulation was validated with experimental data, showing less than 10% discrepancy. The pyrolysis oil yield contained 40-63% diesel fuel lumped hydrocarbons (C_{10}–C_{19}). Gas yield was higher at 700 °C, which is beneficial for controlling plastic waste. Negligible wax formation was observed at this temperature. The simulation was validated with experimental data, showing less than 10% discrepancy between the two sets of data. The pyrolysis oil yield contained 40-63% diesel fuel lumped hydrocarbons (C10–C19), indicating the potential for renewable fuel production [52].

The origins, properties, and recyclability of diverse categories of plastic waste have been examined and discusses thermochemical technologies for converting single-use plastic waste to clean fuels into liquid fuels, gases, and char are the product of pyrolysis and can effectively transform plastic residues with yield depending on different variant factors e.g. temperature, heating rate, and residence time of vapors. Microwave-assisted pyrolysis offers uniform heat distribution and higher liquid yield but requires expensive catalysts. Plastic residues are widespread in the environment, posing a threat to marine ecosystems and human health. Microplastics and Nano plastics have been found in various organisms. Thermal degradation shows promise for converting plastic waste into clean fuels. Lab-scale and small-scale demonstration studies have been conducted worldwide [53].

2.4.3 Optimizing Waste-to-Energy Processes: Kinetics, Catalysts, and Product Enhancement

The objective is to formulate a mathematical model to elucidate the pyrolysis kinetics of polypropylene (PP) utilizing a six-lump model encompassing discrete phases, namely plastic molecules, molten plastics, heavy and light fuel oil, and char. The six-lump model was used to predict an optimum temperature to produce pyrolysis oil, mass and energy balances, and carbon conversion on an industrial-scale integrated process using Aspen Plus [54].

The paper discusses the use of biomass pyrolysis to produce bio-oil and other valuable hydrocarbons, which can serve as green and renewable biofuels. It emphasizes the importance of conducting a life cycle assessment (LCA) to identify the environmental impacts of biofuel production, including feedstock collection, facility operations, and end-use. The chapter also highlights the use of kinetic modeling to determine the chemical reactions involved in the thermochemical process of biomass pyrolysis. Aspen Plus, a simulation software, is discussed as a tool for predicting pyrolysis behavior and optimizing process conditions for better yield and quality [55].

The research being investigated investigates how phosphate segregation in sewage sludge (SS) and the biochar that is produced from it is impacted by the amount of heat and chemicals used during decomposition. It explains the mechanism of phosphorus transformation and proposes channels for it. Investigations highlight that before 400 °C, the links between ester in orthophosphate diesters disintegrate to generate orthophosphate monoesters and pyrophosphate. When CaO is incorporated, Ca−P is formed more readily. The maximum Ca−P level is 2.5 times greater than when pyrolysis is done alone. Ca3(PO4)2 is the primary form of phosphorus. MgO fails to possess the same strong promoting effect as CaO on the formation of apatite phosphorus (AP) [56].

The paper investigates the pyrolysis of sugarcane bagasse and its effect on product yields, focusing on parameters such as temperature, particle size, and nitrogen flow rate. The study found that the bio-oil yield reached a maximum value at around 500 ºC and decreased at higher temperatures due to secondary cracking reactions of the volatiles. The maximum pyrolysis bio-oil yield of 45 wt. % was achieved at a temperature of 500 ºC, particle size of 0.5-1 mm, and nitrogen flow rate of 200 cm3/min. The sugarcane bagasse sample used in the study was obtained from the Nagaa Hammadi sugar factory and was sieved to different size ranges. Bagasse is commonly used for steam and power generation in sugar mills and can be used as a renewable source of energy for biofuel production through thermochemical conversion processes [57].

2.4.4 Green Energy from Waste: Co-Pyrolysis, Gasification, and Synergistic Effects

The paper discusses the co-pyrolysis mechanism of polyethylene terephthalate (PET) and polypropylene (PP) in which steam is employed to improve the yield of terephthalic acid (TPA) and reduce impurities. The optimum temperature for co-pyrolysis was found to be 450 °C, with a maximum solid yield of 85.0 wt.%. The co-pyrolysis process also reduces carbon emissions by decreasing the proportion of carbon dioxide in the gases produced. The study explores the reaction mechanism of co-pyrolysis through product analysis and predictions. It is found that TPA has a promoting effect on the pyrolysis of PP due to its thermal stability and acidic catalytic properties. A novel hydrogen transfer metabolic route between PP and PET is revealed by radioisotope mapping studies and density functional theory simulations, which increases the monomer return during joint pyrolysis. The study's conclusions have significant consequences for commercial trash plastic reclamation technologies. [58].

The paper focuses on the combined pyrolysis of sheep dunk and recycled polyethylene terephthalate (PET) as a thermochemical route for recovery of energy and disposal. The study investigates the effects of co-pyrolysis of these two-waste feedstocks. Ozawa-Flynn-Wall Analysis is the model-free method of kinetic analysis calculating dependence of activation energy E(α) on degree of conversion α for dynamic experiments with different constant heating rates β, is used for determination of combined pyrolysis. The study suggests that combined pyrolysis is a viable technique for producing green energy [59].

$$\ln\left(\beta\frac{\mathrm{d}\alpha}{\mathrm{d}T}\right)=\ln(Z)-E_a/RT+n\cdot\ln(1-\alpha)$$

The paper focuses on the degradation of waste plastic products using heat, specifically polypropylene (PP) and polystyrene (PS), through combined pyrolysis and combined gasification for synthesis gas production and energy. The study investigates the thermal degradation properties of PP and PS, as well as their blends, through thermogravimetric (TG) analysis.The study contributes to the fundamental understanding of co-processing waste plastics for enhanced syngas production and energy recovery [60].

on the entire pyrolysis process, product yield, and oil properties. The study aims to enhance the oil yield and fuel properties of the co-pyrolysis products, which is important for the development of energy sources and industrial waste with improved value. The combined pyrolysis process showed a positive effect, resulting in an increase in the oil phase and a decrease in viscosity and total acid number respectively, compared to theoretical data. The combined effects were determined by altering the compound content in the combined pyrolysis oil rather than generating cross-reaction products [61]

Previous investigations on co-pyrolysis of biomass/coal mixtures have focused on the mechanism of production of gas phase species and the impact of synergistic effects on the yield of major pyrolysis products. However, there has been less attention given to the influence of synergistic effects on the composition of pyrolysis products. Most previous studies have examined the impact of various controlling parameters in isolation, such as heating rate, temperature, and blending ratio. The objective of this study was to address these shortcomings through a comprehensive investigation of the pyrolytic behavior of woody biomass/coal blends over a wide range of heating rates and temperatures relevant to PF boilers. The fundamental knowledge gained from this project is essential for the proper understanding of co-firing in practical PF-based systems and may help prevent accidental fires and predict the impact of co-firing on combustion-related phenomena in PF boilers [62].

2.5 Gap identification

Plastics offer unparalleled versatility, durability, and lightweight properties, making them integral components in numerous products and packaging solutions. From medical devices to consumer goods, automotive parts to construction materials, the use of plastic has become deeply ingrained in modern society. The inherent qualities of plastic, such as its malleability and cost-effectiveness, contribute to its widespread adoption but plastic, ubiquitous in modern society, presents a pressing environmental challenge due to its non-biodegradable nature, leading to persistent pollution and detrimental effects on ecosystems. Improper disposal of plastic waste, such as littering and inadequate waste management practices, allows plastic to accumulate in the environment. Over time, these plastics break down into smaller particles through processes like weathering and photodegradation, forming microplastics. These microplastics can contaminate soil through direct deposition or by entering water bodies, eventually settling in agricultural areas through irrigation or precipitation and their small size allows them to be inadvertently consumed by humans through the food chain. Plastic debris may hinder water absorption, nutrient exchange, and microbial activity in the soil, affecting overall soil health and crop productivity

To date, a comprehensive examination of the intricate relationships among the monitoring and screening of microplastics' fate within ecosystems, their pathways, potential rates of biodegradation, and the subsequent structural optimization is lacking in scientific literature. Additionally, there is a notable gap in understanding the thermal degradation process, with a specific emphasis on the integration of CaO sorbent for CO2 reduction and the consequential enhancement of energy production. This study aims to address these critical aspects systematically and scientifically.

2.6 Significance of Current Research:

Density Functional Theory (DFT) stands as a sophisticated computational methodology rooted in quantum mechanics, instrumental for investigating the electronic structure of atoms, molecules, and materials at an atomic level.

This approach is characterized by its ability to provide accurate predictions of various chemical properties, offering valuable insights into the intricate behaviors of molecular and material systems.

The ongoing research endeavors to examine the environmental fate, as well as the electronic and structural properties, of plastic waste e.g. PET, PVC, PP, PE, and PS. The primary objective is to scrutinize the life cycle of plastics to enhance our understanding of the environmental trajectory of plastic and microplastics, providing valuable insights into their distribution, movement, toxicity, and behavior in natural settings.

Furthermore, the aim of the presented research work is pyrolysis or gasification, where heat induces the breakdown of complex polymer chains into simpler hydrocarbons. Concurrently, Cao, or calcium oxide, acts as a sorbent by capturing CO_2 produced during the thermal conversion process. This not only facilitates CO_2 capture for environmental considerations but also enhances the overall efficiency of the energy conversion by preventing the reformation of undesired byproducts. The result is the generation of valuable energy products, such as syngas or hydrogen, more cleanly and sustainably, effectively repurposing plastic waste and minimizing environmental impact.

2.7 Relevance to national need

Firstly, it aligns with the imperative of sustainable waste management, as plastics constitute a significant portion of the waste stream. Effective thermochemical processing provides a viable solution for reducing the environmental impact of plastic waste by converting it into valuable energy compounds. From an energy perspective, the modeling of thermal degradation contributes directly to national energy needs. By efficiently converting plastic waste into energy compounds such as syngas or hydrogen, this approach offers an alternative and cleaner source of energy. This is particularly crucial in the context of reducing dependence on fossil fuels and mitigating greenhouse gas emissions, aligning with national goals for cleaner and more sustainable energy production.

2.8 Problem Statement

Plastic, characterized by its non-biodegradable nature, poses a substantial environmental hazard with widespread implications. Inadequate disposal practices result in the pervasive accumulation of plastic waste in landfills, oceans, and ecosystems, perpetuating enduring environmental damage and adversely impacting wildlife. The prolonged decomposition period of plastics, spanning hundreds or even thousands of years, exacerbates the environmental crisis by sustaining the presence of plastic waste and associated pollutants. This slow degradation contributes to a myriad of ecological disruptions, harming diverse species across terrestrial and marine ecosystems.

2.8.1 Solution Statement

Monitoring the environmental fate of plastic waste materials and exploring their chemical structure will help in understanding and predicting their toxic effects and biodegradability in the environment and the conversion of plastic waste materials into energy-useful compounds using co-pyrolysis. Thermochemical processes, such as pyrolysis and gasification, break down the complex molecular structure of plastics into simpler compounds, generating syngas, bio-oil, or other energy-rich byproducts. It also allows for the recovery of valuable resources embedded in plastic materials. The byproducts obtained can be used as feedstocks for various industries, promoting resource efficiency and reducing the reliance on virgin material.

2.9 Aims and Objectives

This research's main aim is to explore and advance the thermochemical processing of plastic waste into energy as an innovative and sustainable solution. The overarching objective is to develop a comprehensive understanding of the thermochemical conversion processes, such as pyrolysis and gasification, for efficient and environmentally friendly transformation of diverse plastic materials into valuable energy products. This includes investigating optimal process parameters, identifying suitable feedstocks, and assessing the techno-economic feasibility of scaled-up implementations. The research seeks to contribute to the reduction of plastic pollution by diverting plastic waste from traditional disposal methods while simultaneously addressing the growing need for clean energy sources. Additionally, the study aims to evaluate the environmental impact and potential benefits of integrating thermochemical processing into waste management strategies, thereby fostering a circular economy approach to plastic utilization and energy production.

The following are objectives that need to be followed.

1) To investigate the feasibility of converting PE, PET, PS, PVC, and PP into energy.
2) Assessing the environmental durability of waste materials prior to decomposition.
3) To identify the kinetic model governing the thermochemical conversion of waste material into a sustainable energy form.

3. Methodology

3.1 Computational Chemistry modeling and Simulation

Computational chemistry, also known as Molecular Modeling or Theoretical Chemistry, is a rapidly advancing discipline widely employed across various branches of chemistry. This cutting-edge approach utilizes computer simulations and theoretical models to tackle intricate chemical challenges and forecast chemical properties [63]. The applications of computational chemistry are diverse, encompassing a broad range of areas, making it an invaluable tool in the scientific landscape some of them are given below:

- ✓ Calculate reaction kinetics to understand the rate of thermochemical conversion.
- ✓ Determine activation energy for optimizing the conversion process.
- ✓ Analyze reaction pathways to identify key steps in the conversion of plastic waste.
- ✓ Optimize parameters for efficient energy production from the thermochemical process.
- ✓ Study molecular structures to enhance the yield of energy-utilizable components.
- ✓ Utilize computational tools to model and simulate thermochemical conversion process for improved efficiency.

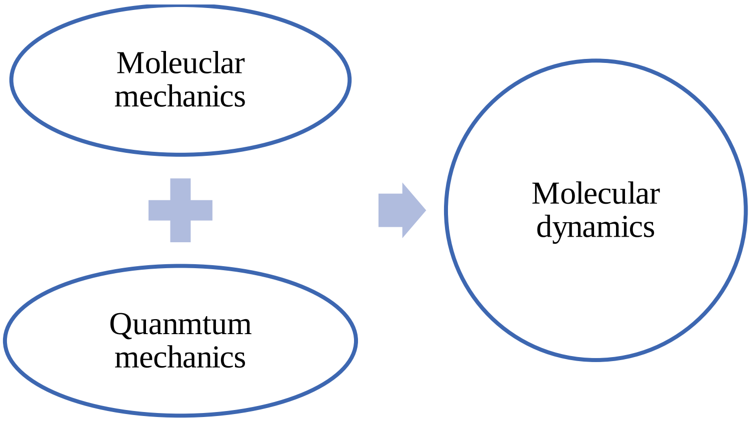


Figure 3.1 Schematic representation of methods in computational chemistry

3.2 Computational Approaches and Techniques

Amsterdam Density Functional (ADF) stands as a computational chemistry software employing advanced molecular Density Functional Theory (DFT) for the elucidation of chemical phenomena. ADF excels in predicting molecular structures, reactivity, and spectra, offering insights into the properties of diverse entities, including nanoparticles, organic materials, and transition metal complexes. Notably, ADF employs the ZORA relativistic approach and Slater

Type Orbital (STO) all-electron basis sets, ensuring accurate modeling of all elements across the periodic table.

3.2.1 Density Functional Theory

Density Functional Theory (DFT) serves as a potent single-particle method, successfully addressing the many-body Schrödinger equation through the application of the Hohenberg-Kohn and Kohn-Sham theorems [64]. DFT utilizes a functional, spatially dependent on the electron density, to characterize the properties of many-electron systems.

The Hohenberg-Kohn Theorem

The Hohenberg-Kohn theorems form the cornerstone of DFT's central theorem, grounded in two fundamental propositions:

Axiom-I

The particle density $n_{0(r)}$ of the ground state uniquely determines the external potential $V_{ext(r)}$ for any interacting many-body system of electrons subject to an external potential $V_{ext(r).}$ This implies that the ground state electron density n's ground state feature is a distinctive functional $n_{0(r).}$

Axiom-II

A global total energy function, denoted as $E_{[n],}$ incorporating the external potential $V_{ext(r).}$ and particle density $n_{(r).}$, defines the system's ground state energy for any specific $V_{ext(r).}$ The ground state energy corresponds to the global minimum value of the functional, with the minimizing density denoted as $n_{0(r).}$, precisely representing the system's ground state density. The function for total energy, denoted as $E_{[n(r)]}$ $F_{HK\,[n\,(r)]} + \int dr\, V_{ext(r)}\, n_{\,(r),}$ encapsulates the electronic kinetic energy and terms accounting for electron-electron interactions within $F_{HK[n(r)].}$ The significance of the ground-state density in determining all aspects of a system in its ground state is emphasized by Axiom-I. The universal functional $F_{HK\,[n\,(r)]}$ integral to Axiom-II and applicable to all N-electron systems plays a crucial role. The uniqueness and system-specific nature of the external potential $V_{ext(r).}$ are highlighted, wherein the Hamiltonian is fully determined by $V_{ext(r).}$ which is, in turn, entirely governed by the ground-state particle density $n_{0(r).}$

Kohen- Sham Equations

The Kohn-Sham (KS) ansatz transforms the N-particle interacting problem into a single-particle non-interacting scenario. According to the Kohn-Sham approach, non-interacting systems governed by a single effective potential are deemed to accurately describe the ground state density of the system. The electron-electron Coulomb interaction is elucidated in the second term, while the third term incorporates the exchange-correlation potential containing the manifold effects of exchange and correlation. R signifies the external potential acting on the interaction system. The distinction between the many-body problem and the single-particle problem is elucidated by the electron density function, n(r). The Kohn-Sham orbitals are contingent on the effective potential, which, in turn, relies on the electron density, thus creating an interdependence. Consequently, solving the electron density-dependent Kohn-Sham equation in a self-consistent manner is imperative to ascertain the ground state.

3.2.2 Exchange-Correlation Functional

In the formulation and solution of the exchange-correlation function, certain approximations become necessary. Electron exchange and correlations constitute the components of $E_{xc[n(r)].}$ The two prominent approximations for the exchange-correlation function are outlined below.

Local Density Approximation (LDA)

In LDA theory [35], the exchange-correlation energy of an electron is considered within a local uniform electron gas. The straightforward analytical definition is expressed as:

$$E_{LDA}(\rho)=\int n(r)\varepsilon_{xc}(\rho(r))\,dr$$

Here, ρ denotes the electronic density, and *Exc r*epresents the exchange-correlation energy per particle. The exchange-correlation energy is further decomposed into linearly combined exchange (E_x) and correlation (E_c) terms [65]

$$\mathbf{E_{xc} = E_x + E_c}$$

Generalized Gradient Approximation (GGA)

The GGA approximation incorporates details about the electron density, including its gradient.

The GGA expression can be written as:

$$E_{\mathrm{xc}}^{\mathrm{GGA}}[n] = \int n(\mathbf{r})\epsilon_{\mathrm{xc}}(n(\mathbf{r}), |\nabla n(\mathbf{r})|)d\mathbf{r}$$

In this expression, the gradient of the density $n_{(r)}$ replaces the local density in the GGA approximation. Various functions within the GGA family have been developed based on how the gradient of the density $n_{(r)}$ is treated. Notable examples include Perdew and Wang (PW91) and Perdew, Burke, and Ernzerhof (GGA-PBE) [66,67]. The GGA approach proves advantageous for systems containing hydrogen, offering superior predictions of binding and dissociation energies.

3.2.3 Semi-Empirical Methods in Computational Chemistry

Semi-empirical methods represent a blend of quantum mechanics (QM) assumptions and empirical parameters. The primary objective is to compute the electronic structure and properties of molecules while addressing computational complexity. Although these methods offer computational efficiency and speed, their accuracy tends to be lower compared to ab initio methods. Leveraging the Hartree-Fock method as a foundation allows semi-empirical methods like Austin Model-1 (AM1), Austin Model-2 (AM2), Austin Model-3 (AM3), and Parametric Method-3 (PM3) to provide rapid insights into the electronic properties of larger molecular systems [68].

3.2.4 *Ab-initio* Methods in Computational Chemistry

Ab initio methods, also known as "first principal methods," are derived directly from theoretical principles without incorporating empirical or semi-empirical parameters. Grounded solely in quantum theory, these methods aim for high accuracy without reliance on experimental data. The Hartree–Fock self-consistent field method (HF-SCF) represents a basic form of ab initio computation, neglecting electron-electron correlation. Due to their computational intensity and complexity, *ab initio* methods find application in the study of small to medium-sized molecular systems, delivering highly accurate results for the electronic structure and properties of molecules [69]. Molecular Dynamics (MD) simulations stand as a potent tool for unraveling the dynamic intricacies of molecular systems, offering insights into material properties, drug design, and bimolecular modeling. By numerically solving Newton's equations of motion, MD simulations enable the exploration of atoms' and molecules' trajectories over time, facilitating a comprehensive understanding of structural changes crucial for diverse applications [70].

3.3 Research Methodology

In the presented research work, the five most used plastics are selected PET, PP, PS, PE, and PVC. First, environmental fate properties are considered to better understand their behavior in various components of environments. By monitoring all these properties, electronic and structural properties were investigated using discrete-level simulations. Moreover, Cao sorbent will capture CO_2 produced in the gasification of waste plastics, to get energy useful products.

3.3.1 Estimation Program Interface Suit

The estimation program interface suite (Epi-Suite) is an open-source window-based estimation tool, developed by the Environmental Protection Agency (EPA) and Syracuse Research Corp. (SRC) for predicting the physical and chemical properties of compounds. These properties help in tracking the movement, and migration ability of compounds in various environmental compartments, routes of exposure, and possible health and environmental hazards. Environmental fate monitoring of 5 plastics (including PVC, PET, PP, PS, and PE) was predicted through different modules of EPI-suite. As chemical concentration in the gas phase to that in the aqueous phase at equilibrium is estimated by HENRYWIN, their biodegradability and atmospheric oxidation potential using BIOWIN and AOPWIN [71].

3.3.2 ADF Modelling Suite

ADF (Amsterdam Density Functional) program is a computational chemistry software package that uses DFT for the calculation of the electronic properties of plastics. In this research work, Quantum mechanical simulations based on the DFT approach were performed using an ADF modeling suit with GGA/BLYP functional and double zeta basis set. GGA/BLYP is one of the most popular functions in DFT studies for surface adsorption phenomenon. Initially, geometry optimization of plastics is performed to get the most stable structure with the lowest possible ground state energy. Secondly, the exploration of reactive sites was done for the identification of electrophilic and nucleophilic sites by looking into the Iso surfaces of polymers [72].

Moreover, the HOMO-LUMO gap is used to calculate all the reactivity parameters (ionization potential, electron affinity, chemical hardness, chemical softness, electronegativity, chemical potential, and electrophilicity affinity.

3.3.3 Aspen Plus

Aspen Plus is a process simulation software tool in chemical engineering, used for modeling, simulation, and optimization of complex chemical processes that help in the kinetics, transferring heat phenomena, and mass balances. Its user-accessible interface and strong simulation abilities contribute to the enhancements of sustainable and energy-efficient products. The process of producing hydrogen by gasification of waste plastics in a fluidized bed reactor was simulated using the Aspen Plus software. This section provides an explanation of each stage of the model development process, including the selection of waste plastics, setting up the simulation environment, creating the reactor, defining reaction kinetics, specifying reaction conditions, adding material streams, energy and mass balances, simulation, and analysis, optimization, and documentation. The specification of physical property techniques, the creation of the process flowsheet, the definition of initial and operational conditions, and the model validation [73].

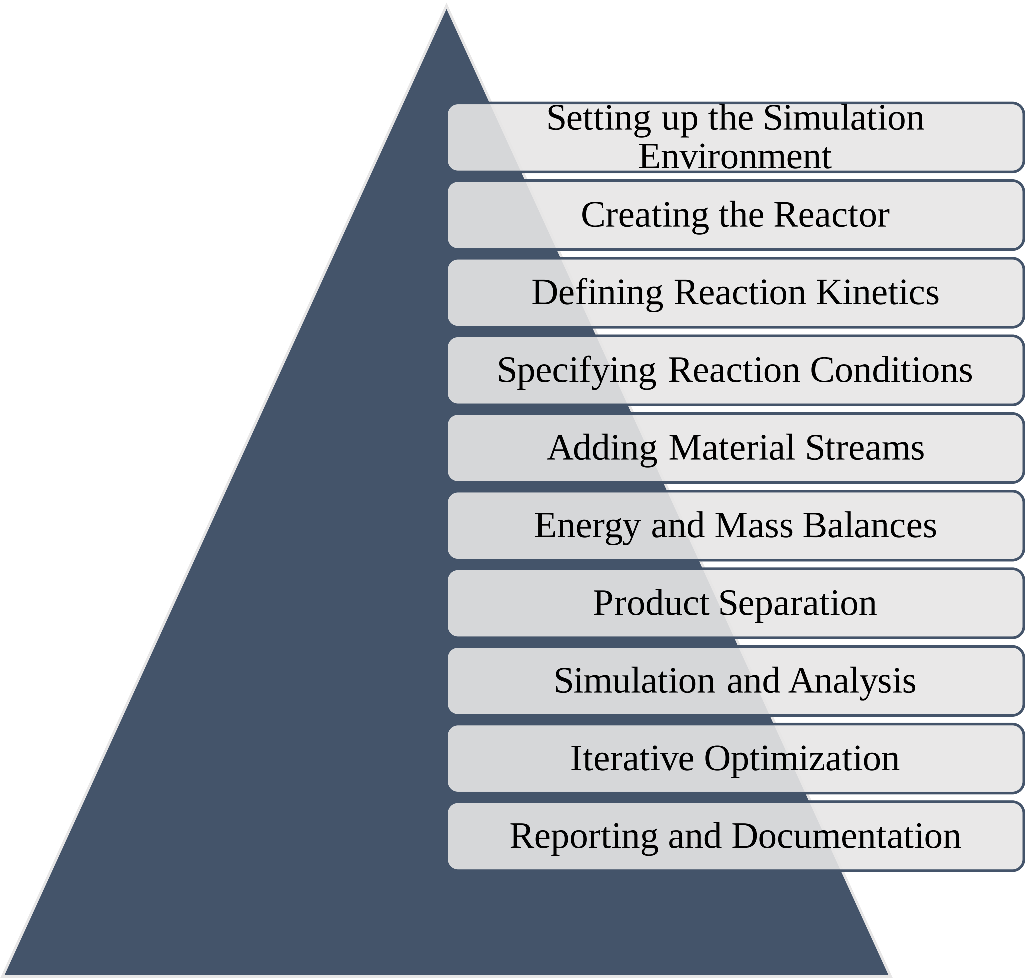


Figure 3.2 Schematic illustration of steps involved in co-gasification of plastics.

3.3.3.1 Process simulation description:

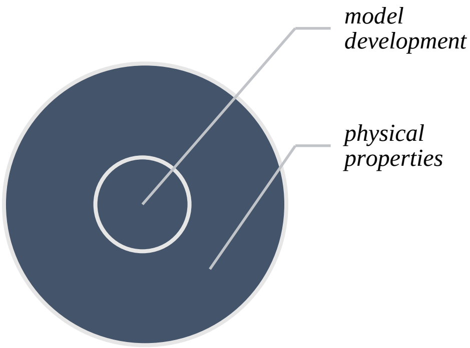


Figure 3.3 Process simulation of model flow sheet.

3.3.3.2 Model Development:

The following stages are involved in model development.

- Establishing the model flowsheet involves assembling unit blocks interconnected by material streams.
- Selection of system components is based on the ASPEN database, which provides a comprehensive range of options.
- Distinguishing between conventional and nonconventional components and categorizing stream classes accordingly.
- Defining operational parameters for unit blocks and streams entails specifying thermodynamic properties, flow rates, compositions, chemical reactions, and other relevant variables.

The proposed H_2 production system's model flowsheet, depicted in Fig. 14.3, is complemented by detailed descriptions of unit blocks outlined in Table 4.4. This gasification process encompasses four primary sub-processes: drying, pyrolysis, reduction (gasification), and oxidation (combustion). Each of these sub-processes is delineated by discrete units within the Aspen Plus simulator. Initially, the plastic stream undergoes pre-drying before entering the feed mix. The resulting plastic mixture is subsequently channeled into an RYield-type reactor, simulating yield distribution post-pyrolysis/decomposition. The reactor's output feeds into the RSTOIC reactor, where fuel-bound nitrogen, sulfur, and chlorine are transformed into H_2S, HCl, and NH_3, respectively. This stream then enters the combustion zone, COMB, via SPL to initiate the combustion reaction of char. Subsequently, the stream is directed to GASIF-3 of Gibbs, which executes gasification reactions under restricted chemical equilibrium via Gibbs free energy minimization. Finally, GASIF-4 of RGibbs fine-tunes the actual syngas composition using the temperature approach in a restricted equilibrium context. It’s noteworthy that the Gibbs reactor, owing to its operation at elevated temperatures, accelerates endothermic processes, resulting in notably lower carbon monoxide and methane concentrations compared to experimental levels. This comprehensive framework captures the intricate dynamics of H2 production through a series of interconnected processes, ensuring a scientifically rigorous representation within the Aspen Plus simulation environment.

3.3.3.3 Performance parameters:

The evaluation of a gasifier's performance in response to variations in operating conditions relies heavily on key parameters such as the syngas Lower Heating Value (LHV), Hydrogen (H2) yield, and cold gas efficiency (CGE). The syngas LHV quantifies the energy released through the complete oxidation of syngas, excluding the heat associated with water vaporization in combustion byproducts. Within Aspen PLUS, the LHV of syngas can typically be located in the stream characteristics section. These parameters serve as fundamental metrics for assessing and optimizing gasification processes, offering insights into the efficiency and effectiveness of syngas production. [74]

$$\text{Hydrogen Yield} = \frac{\text{msyngas} \times \text{LHVsyngas}}{\text{mfeedstock} \times \text{LHVfeedstock}}$$

$$\mathrm{LHV_{feedstock}} = \mathrm{a} \times (\mathrm{C}) + \mathrm{b} \times (\mathrm{H}) + \mathrm{c} \times (\mathrm{S}) + \mathrm{d} \times (\mathrm{O}) - \mathrm{e} \times (\mathrm{N}) - \mathrm{f} \times (\mathrm{ASH}) - \mathrm{hfg} \times (9 \times \mathrm{H} + \mathrm{M})$$

where C, H, S, O, and N represent the carbon, hydrogen, sulfur, oxygen, and nitrogen content of the feedstock depending on the ultimate analysis on a dry basis, respectively while HFG and M denote the water latent heat (2410 kJ/kg) and moisture content of the feedstock respectively [75]

In the provided context, the symbols *m* and *LHV* denote the mass flow rate and the lower heating value of the respective subscripts, respectively. The lower heating value of the feedstock ($LHV_{feedstock}$) in kilojoules per kilogram (kJ/kg) is determined based on the ultimate analysis of the plastics, as illustrated above.

3.3.3.4 Physical properties:

The material used for the current work is 5 different types of plastics that were collected from municipal waste. Their proximate and ultimate analysis is based on literature value [76].

Table 3.1 Proximal and ultimate analysis of commonly used plastic waste.

Proximate analysis	PP	PVC	PE	PS	PET
Fixed Carbon	0.03	2.77	0	0	13.15
Volatile Matter	99.97	97.23	94.77	99.8	86.85
Moisture Content	0	0	0.25	0	0
Ultimate analysis	PP	PVC	PE	PS	PET
C	84.14	38.64	78.18	90.02	62.5
H	14.96	4.77	12.84	8.48	4.21
N	0.23	0.11	0.06	0	0
S	0.24	0.14	0.08	0	0
Cl	0	56.03	0	0	0
O	0.43	0.31	3.61	1.3	33.29

3.3.4 Assumptions

Utilizing the Aspen Plus simulation software, a Gibbs energy minimization model is formulated to emulate the intricate process of air-steam gasification applied to biomass. This modeling framework operates within a set of carefully defined assumptions essential for achieving coherence and applicability within the realm of chemical engineering. The simulation adheres to isothermal and steady-state conditions, ensuring a consistent temperature profile throughout the gasification process. Operations are conducted at atmospheric pressure (approximately 1.01 bar) to reflect real-world scenarios accurately. Fuel-bound nitrogen, sulfur, and chlorine are presumed to undergo complete conversion into NH3, H2S, and HCl, respectively, during the simulation. Drying and pyrolysis processes are treated as instantaneous events, eliminating temporal considerations associated with these stages. The simulation excludes the formation of tar during the gasification process. The sorbent utilized in the model is assumed to be comprised entirely of calcium oxide (CaO). Heat losses from the gasifier are intentionally neglected, simplifying the model to focus on internal reactions. Similarly, pressure drops within the system are disregarded, streamlining the simulation under idealized conditions. Char produced during gasification is assumed to be composed entirely of carbon. Post-drying, the simulation omits consideration of the particle size effect, facilitating a more straightforward analysis of particle dynamics. These carefully delineated assumptions collectively underpin the Aspen Plus simulation, providing a systematic and coherent framework for the comprehensive analysis of plastics air-steam gasification within the discipline of chemical engineering.

The chosen property method for the model was the Peng-Robinson equation of state, a robust thermodynamic framework. The stream of plastics identified as a non-conventional stream in accordance underwent rigorous characterization through proximal and ultimate analyses, as detailed in Table 3.1. These analyses informed the Aspen Plus models, specifically HCOALGEN and DCOALIGT, incorporating the plastics' lower heating value (LHV). This facilitated the calculation of specific heat, enthalpy, biomass density, and capacity, all crucial parameters determined by the comprehensive proximal and final assessments. Within the Aspen Plus software for chemical engineering, the integration of proximal and ultimate analyses becomes pivotal in defining the properties of the stream. Additionally, the inclusion of LHV in HCOALGEN and DCOALIGT models enhances the accuracy of specific heat and enthalpy calculations, crucial for comprehensive plastics characterization.

3.3.5 Hydrogen production from plastic waste

The preliminary plan for producing hydrogen from waste plastic gasification entails several consecutive processes. First, the waste plastics are prepared for gasification by mechanical pretreatments such as extraction, separating, and tearing.

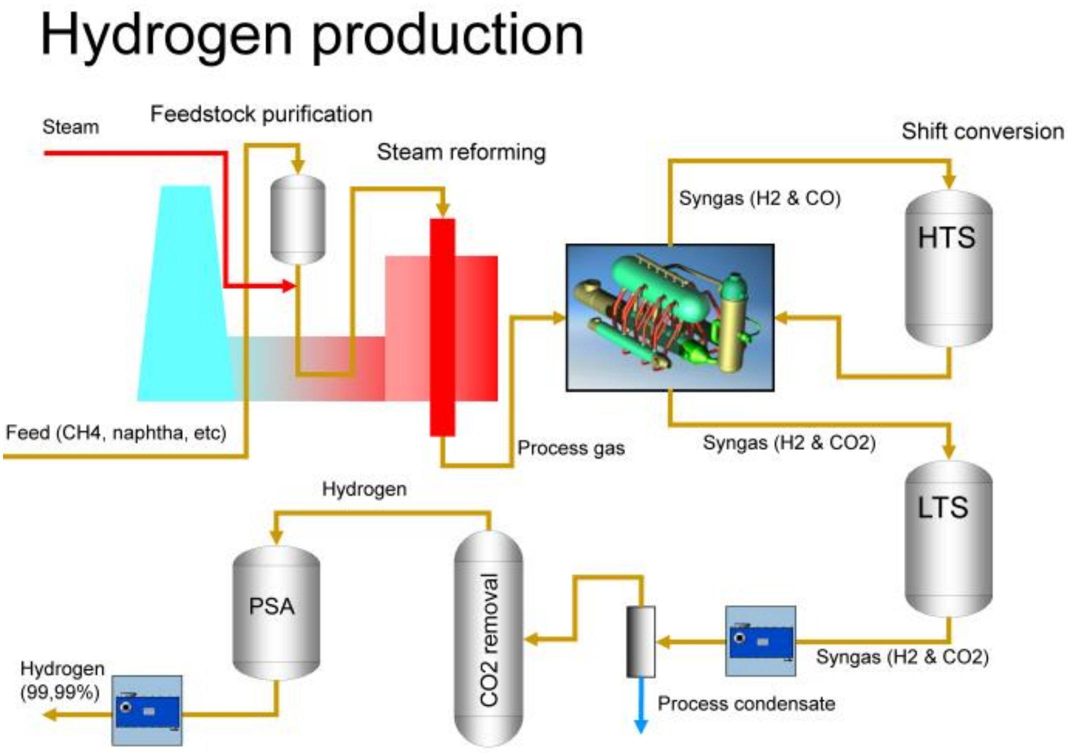


Figure 3.4 Process description hydrogen production from waste plastic.

After being ready, the waste plastic is put into the reactor and allowed to gasify with air. Important elements including H_2, CO, CO_2, CH_4, H_2O, N_2, char, ash, and other inorganic pollutants like NH_3, H_2S, and HCl are present in the resulting raw syngas. Inorganic substances and solid particulate matter, such as wasted char and ash, are eliminated from the product in the next gas cleaning unit. The water removal apparatus then extracts the water from the syngas.

Finally, the hydrogen extraction module receives the processed syngas, which is now free of impurities and moisture, to produce hydrogen with a high degree of purity. Using Aspen Plus, the full gasification process for producing hydrogen has been studied, considering chemical equilibrium and mass-energy balance factors.

4. Results and Discussion

4.1 Epi-Suite Analysis

In this study, 5 plastic polymers (including pet, pp, pe, ps, and PVC) were evaluated to estimate their persistence and bioaccumulation. The environmental behavior and distribution of chemical substances are influenced by numerous factors, of which the physical and chemical properties are of fundamental importance. Results obtained from 6 different modules of EPI-Suite were compared to monitor the environmental fate of plastics. Calculations utilizing vapor pressure (VP), water solubility (WSol or WS), and Henry's law constant (HLC) were performed to well understand the behavior of plastics in an aqueous environment i.e., their tendency to migrate, dissolve, and probability to volatilize from water bodies. Furthermore, the persistence of plastics in an aqueous environment was investigated through the atmospheric oxidation half-life model (AOPWIN) and ultimate biodegradation model (BIOWIN3).

WS models of EPI Suite were used for calculating water solubility. Among studied polymers, the highest WS was observed for polyethylene(mg/L) and polystyrene was the least soluble in aqueous environment (mg/L). The estimated WS of waste plastic polymers is given in Table 4.1, according to which very high water solubility was observed for polyethylene and polypropylene and polyvinyl chloride was slightly soluble while polyethylene terephthalates and polystyrenes were predicted to have negligible water solubility. The observed trend for WS is:

PE < PP < PVC < PET < PS

For determining persistence and toxicity BIOWIN3 models were utilized. Results obtained through BIOWIN3 also imply greater toxic behavior of waste polymers by estimating their biodegradation. According to the results, PE will take weeks to months for biodegradation, PP and PVC will take weeks while the remaining PET will take days PS may take days to weeks to biodegrade. So, we can say biodegradability of plastic is in following manner:

PET >PS >PVC >PP >PE

Table 4.1 Environmental fate monitoring of selected plastics through Epi Suite analysis.

Plastics	**WS (mg/L)**	**Log Kow**	**Log Koc**	**HLC (atm-**	**BCFBAF (Regression**	**Ultimate Biodegradation**
Styrene	0.000883	8.26	6.77	1.47×10^{-5}	3.504 (BCF=3195 L/kg wet-wt.)	Days-weeks
Ethylene	17.24	3.90	2.119	1.69×10^{0}	2.240 (BCF=173.9 L/kg wet-wt.)	Weeks-Months
Ethylene Terephthalate	0.0591	4.40	6.364	$2.68 \times 10^{-}$	0.500 (BCF = 3.162 L/kg wet-wt.)	days
Propylene	3.11	4.61	2.770	6.89×10^{0}	2.712 (BCF = 514.7 L/kg wet-wt.)	Weeks
Vinyl Chloride	22.95	3.90	2.770	2.18×10^{-5}	2.242 (BCF=174.7 L/kg wet-wt.)	Weeks

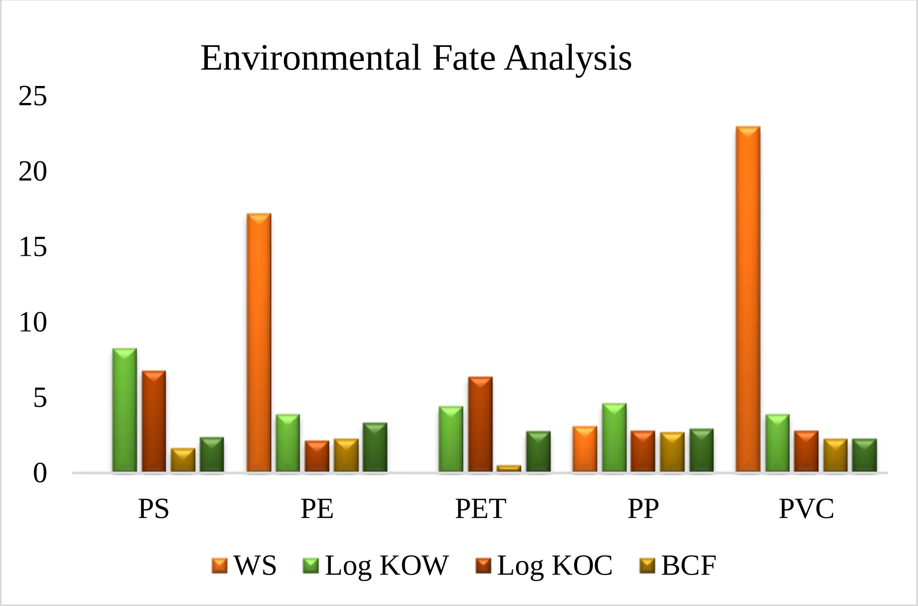


Figure 4.1 Environmental fate monitoring of commonly used plastics.

In the comprehensive evaluation conducted through the EPI (Estimation Programs Interface) Suite, five critical factors emerged from the analysis of the half-life data obtained from the model river, model lake, and wastewater treatment processes for various plastics as shown in Table 4.2, including PET (Polyethylene Terephthalate), PE (Polyethylene), PVC (Polyvinyl Chloride), PS (Polystyrene), and PP (Polypropylene). The half-life values obtained provide valuable insights into the environmental fate and persistence of these plastics in aquatic ecosystems and wastewater treatment systems.

Table 4.2 Calculated half-life of Plastic waste through epi-suite.

Plastics	**Atmospheric oxidation**	**Half-Life From Model River(Hours)**	**Half-Life From Model Lake(Hours)**	**Waste-Water Treatment**
Styrene	0.454 days with OH + No ozone estimation	72.44	938.9	94.02%
Ethylene-Terephthalate	1.960 days with OH + No ozone estimation	$5.12\text{x}10^{22}$	$5.59\text{x}10^{23}$	50.68%
Ethylene	1.205 days with OH + No ozone estimation	0.947	88.18	99.87%
Propylene	1.073 days with OH + No ozone estimation	1.156	107.6	99.95%
Vinyl Chloride	3.890 days with OH + No ozone estimation	38.38	524.1	26.48%

In the context of the model river and model lake environments, the half-life values elucidate the duration over which these plastics degrade, reflecting their potential impact on aquatic biota and ecosystems. Plastics with shorter half-lives may exhibit relatively rapid degradation,

reducing their persistence and potential for environmental accumulation compared to those with longer half-lives. Furthermore, the variations observed across different plastics underscore the diverse degradation pathways and environmental behaviors inherent to each polymer type.

Moreover, within wastewater treatment systems, the half-life values offer crucial information regarding the efficacy of treatment processes in mitigating plastic pollution. Plastics with shorter half-lives may undergo more efficient degradation or removal during wastewater treatment, whereas those with longer half-lives may pose challenges in terms of persistence within treatment facilities and potential discharge into receiving waters.

4.2 Quantum Mechanical Investigation of Plastic Waste:

4.2.1 Geometry Optimization

Quantum mechanical simulations were performed for geometry optimizations of plastics to obtain the most stable configurations with the lowest possible energies. Optimized structures were obtained by implementing GGA (Generalized gradient approximation), and BLYP (Becke-Lee-Yang-Parr) functional with a TZP (triple-zeta) basis set. Obtained optimized structures are represented in Figure 4.3 and corresponding energies are listed in Table 4.2 according to which the highest energy was observed for ethylene i.e., 7.3833. Calculated energies are listed in table 4.2.

Table 4.3 Calculated energies of Plastic waste through ADF.

Polymer	HOMO (electron volt)	LUMO (electron volt)	ΔE (electron volt)
Ethylene Terephthalate	-6.69438	-4.0419789	2.65248
Vinyl Chloride	-6.79827448	-1.092972448	5.70529
Propylene	-6.79152605	0.143621	6.93514
Styrene	-5.54219699	-0.924397924	4.6178069
Ethylene	-7.17994135	0.203187	7.383312

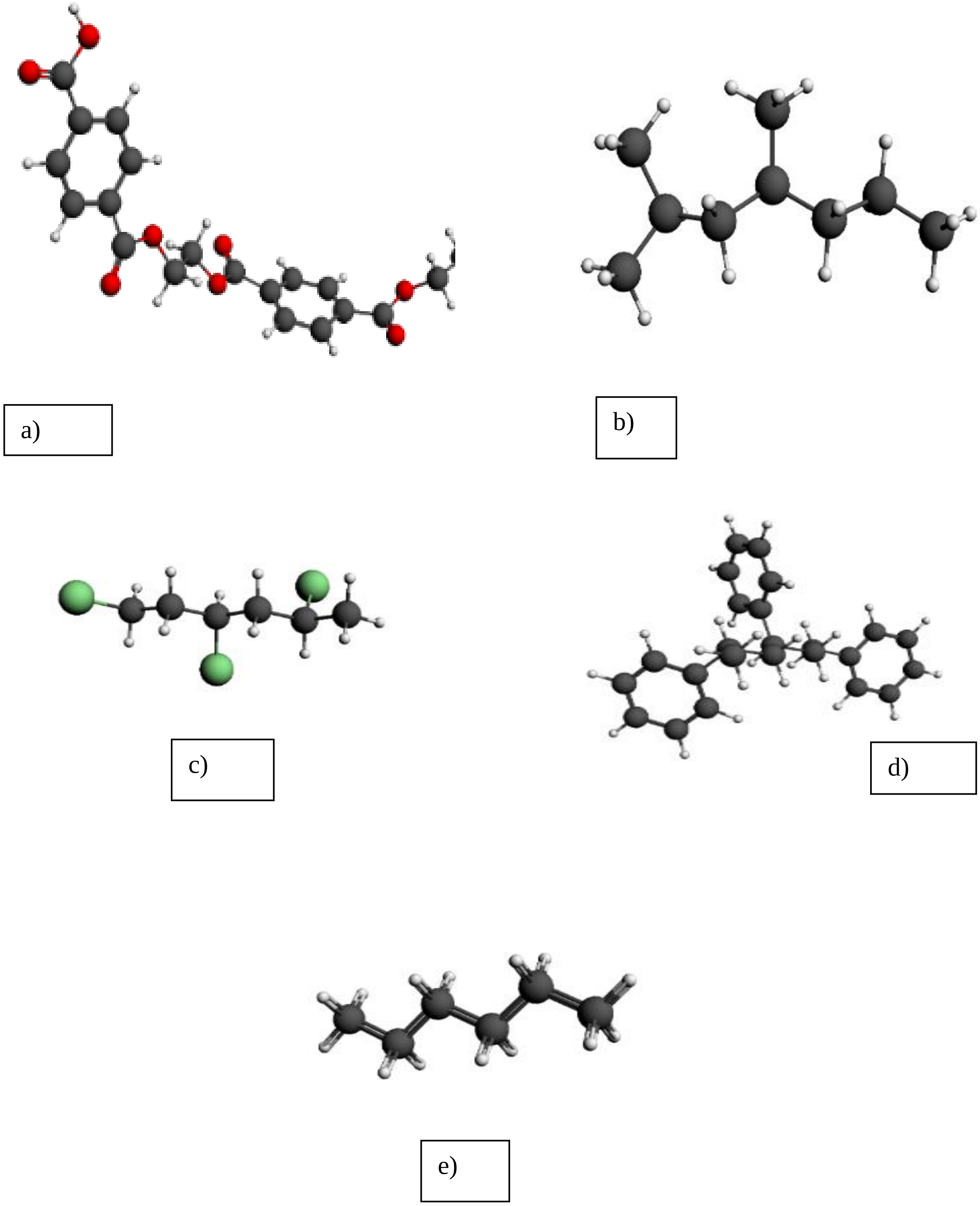


Figure 4.2 Optimized structures of plastics a) polyethylene terephthalate b) polypropylene c) polyvinylchloride d) polystyrene e) polyethylene.

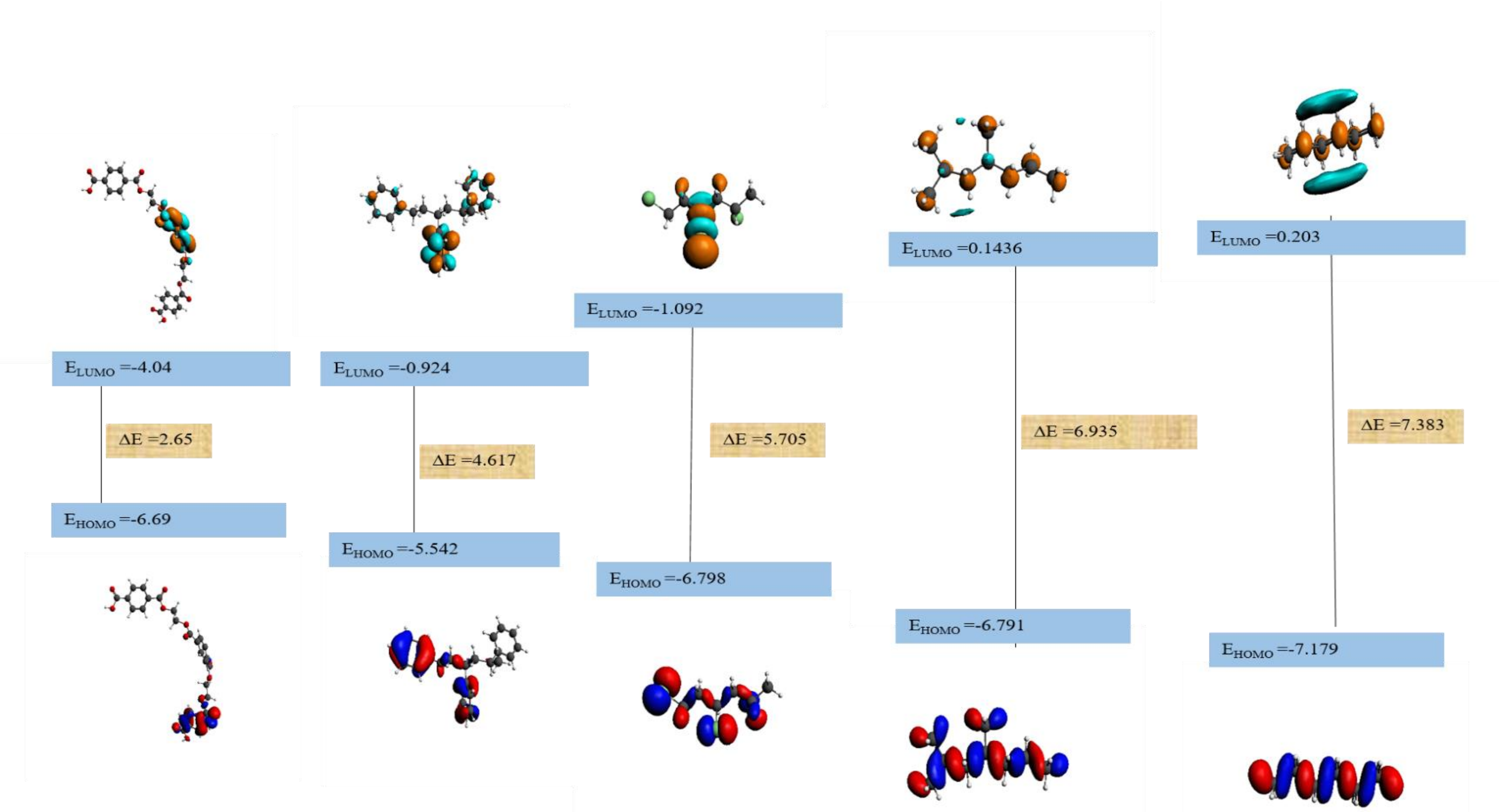


Figure 4.3 FMO analysis of plastics a) polyethylene terephthalate b) polystyrene c) polyvinylchloride d) polypropylene d) polyethylene.

4.2.2 Frontier Molecular Orbital Analysis

Frontier molecular orbital (FMO) analysis is one of the most well-known theoretical models that provide major insight into reactivity, stability, and a profound comprehension of electronic properties.This quantum technique involves the application of Molecular orbital theory for calculating HOMO (highest occupied molecular orbital), LUMO (lowest unoccupied molecular orbital), consequently describing the excitation of electrons from the HOMO to LUMO which is characterized by the energy gap (ΔE) [51]. The HOMO and LUMO energy gap is an indicator of the molecule's kinetic stability, where a large ΔE implies high chemical stability and a smaller ΔE alternatively, is attributed to high reactivity and low chemical stability. To scrutinize the energetics and electronic properties of compounds under study, FMO analyses were performed. The computed energies of HOMO, LUMO, and energy band gap are listed in table 4.3. Amongst investigated polymers maximum energy gap value is calculated for polyethylene which reflects the highest stability of this plastic.

In polymers like polypropylene (PP), polyethylene (PE), polyethylene terephthalate (PET), polyvinyl chloride (PVC), and polystyrene (PS), the distribution of the Highest Occupied Molecular Orbital (HOMO) and Lowest Unoccupied Molecular Orbital (LUMO) plays a significant role in their electronic properties. In PP, the HOMO is typically localized on carbon and hydrogen atoms, while the LUMO is on the carbon atoms of the double bond. PE exhibits a high energy difference between the HOMO and LUMO, with the HOMO distributed over the carbon atoms and hydrogen atoms, and the LUMO primarily on the carbon-carbon double bond. PET's HOMO is distributed over carbon and oxygen atoms, with the LUMO concentrated on carbon atoms of the ester group. PVC's HOMO is on carbon and chlorine atoms, with the LUMO distributed over carbon atoms. PS, being aromatic, has the HOMO spread over carbon and hydrogen atoms, while the LUMO is concentrated on the aromatic rings. In polymers like PE, a high energy difference often correlates with electro-positivity concentrated in areas contributing to the HOMO, reflecting greater electron-attracting ability and influencing electronic, chemical, and mechanical properties of these materials.

4.2.3 Global Chemical Reactivity Descriptors

In addition to conventional Frontier Molecular Orbital (FMO) analysis, molecular structures and their chemical properties can be precisely quantified through quantum chemical descriptors, namely ionization potential (I), electron affinity (A), chemical potential (μ), electronegativity (χ), electrophilicity index (ω), chemical hardness (η), and chemical softness (σ). These descriptors, derived from Koopmans' theorem, offer detailed insights into the electronic properties of molecules, facilitating quantitative descriptions of their reactivity and stability. The ionization potential (I) represents the energy required to remove an electron from a molecule's ground

state, while electron affinity (A) denotes the energy released upon capturing an electron in the ground state. Higher values of ionization potential indicate enhanced chemical resistance to oxidation and reactivity, as molecules with smaller ionization potentials tend to exhibit increased nucleophilic reactivity. Conversely, molecules with higher electron affinity possess a greater tendency to accept electrons. The energies of the Highest Occupied Molecular Orbital (HOMO) and Lowest Unoccupied Molecular Orbital (LUMO) directly correlate with ionization potential (I) and electron affinity (A) respectively, further elucidating the molecular reactivity and stability profile. This quantitative framework provides a rigorous basis for understanding the electronic behavior and chemical characteristics of studied compounds.

$$\boldsymbol{\Delta E = E_{LUMO} - E_{HOMO}} \underline{\qquad\qquad} \mathbf{(1)}$$

$$\boldsymbol{I = -E_{HOMO}} \underline{\qquad\qquad} \mathbf{(2)}$$

$$\boldsymbol{A = -E_{LUMO}} \underline{\qquad\qquad\quad} \mathbf{(3)}$$

$$\boldsymbol{\eta = \frac{I - A}{2}} \underline{\qquad\qquad} \mathbf{(4)}$$

$$\boldsymbol{\sigma = \frac{1}{\eta}} \underline{\qquad\qquad} \mathbf{(5)}$$

$$\boldsymbol{c = \frac{I + A}{2}} \underline{\qquad\qquad} \mathbf{(6)}$$

$$\boldsymbol{\mu = -c} \underline{\qquad\qquad\quad} \mathbf{(7)}$$

$$\boldsymbol{\omega} = \frac{\boldsymbol{c^2}}{\boldsymbol{2\eta}}\underline{\hspace{3cm}}(\mathbf{8})$$

The highest and lowest I was computed for PE and PS i.e.,7.17eV and 5.54Ev. The highest A was calculated for PET (4.04eV) while PE (-0.20eV) has the lowest A which indicates the least susceptibility towards electron acceptance.

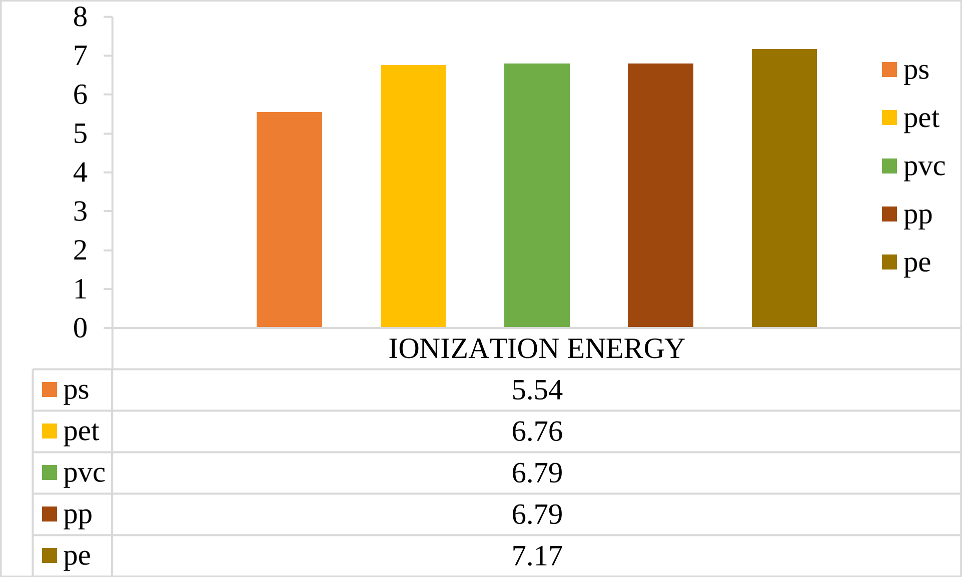
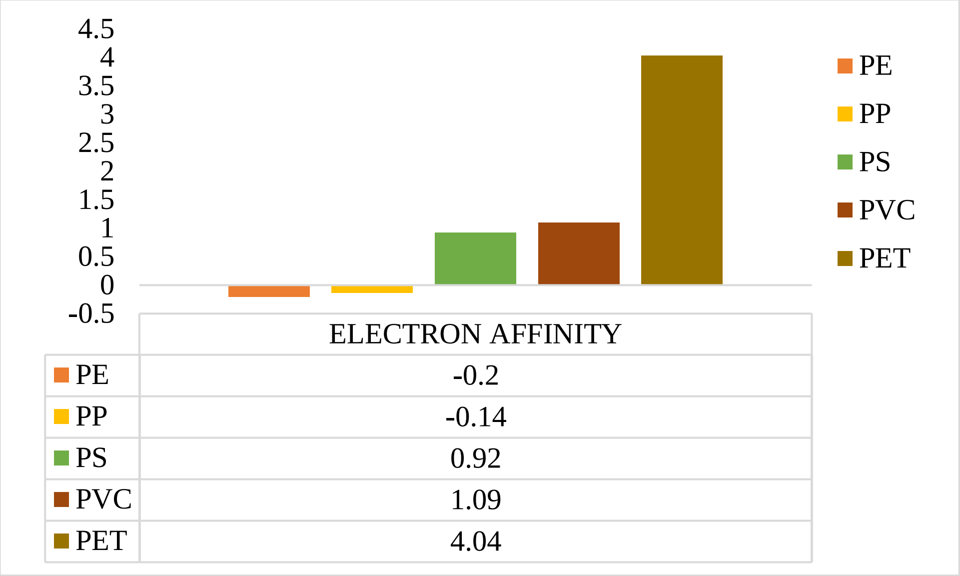


Figure 4.4 Graphical representation of calculated ionization potential for plastics.



	ELECTRON AFFINITY
🟧 PE	-0.2
🟨 PP	-0.14
🟩 PS	0.92
🟫 PVC	1.09
🟫 PET	4.04

Figure 4.5 Graphical representation of calculated electron affinity of plastics.

To gain insights into chemical interactions and the behavior of chemical species, an investigation into chemical potential (μ) was conducted. Chemical potential serves as an indicator of a molecule's propensity to engage in chemical reactions. A high value of μ, less negative in nature, suggests that the molecule is more inclined to donate electrons, thus portraying it as an electron donor. Conversely, a smaller, more negative μ indicates an enhanced capability for electron acceptance. This property of chemical potential is closely associated with electronegativity (χ), which quantifies a molecule's affinity for attracting electrons. By calculating the chemical potential and electronegativity across various molecular structures, a discernible trend was observed, as depicted in Figures 4.6 and 4.7 respectively. These findings contribute to a deeper understanding of molecular reactivity and electron dynamics in chemical systems [53]. According to Figure 4.7, pet is the most electronegative compound having an electronegativity of 5.36Ev. This observed behavior of electron attraction was confirmed by chemical potential. Both of these properties were shown to have a best-fit trend.

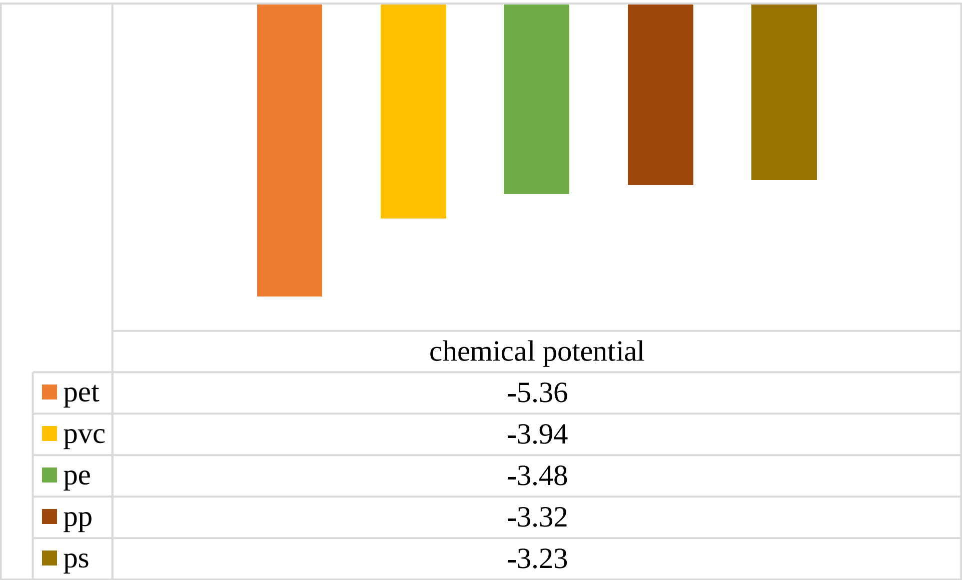


Figure 4.6 Graphical representation of calculated chemical potential of plastic wastes.

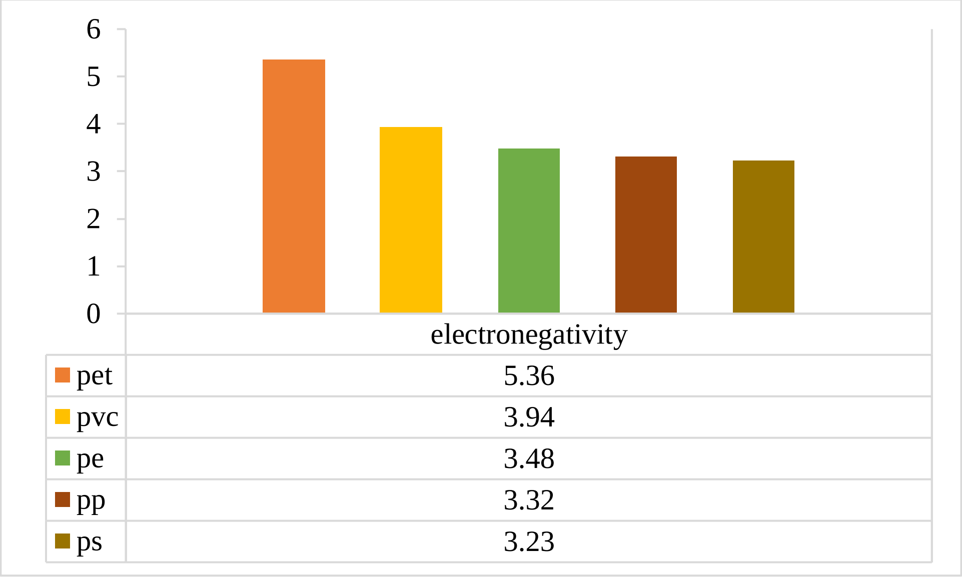
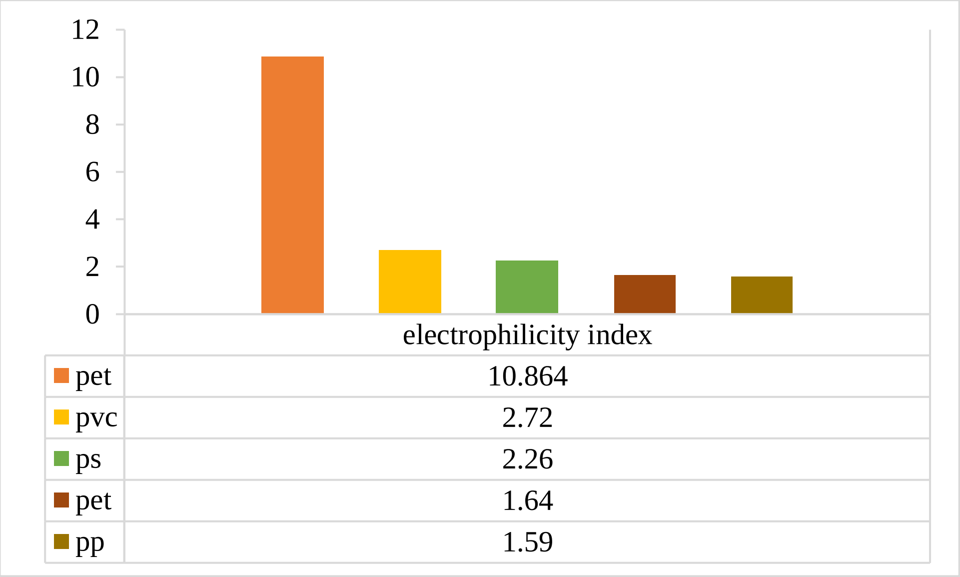


Figure 4.7 Graphical representation of calculated electronegativity of plastic wastes.

The electrophilicity index (ω) was determined through calculations involving electronegativity and chemical hardness. It serves as a predictive measure of the electrophilic tendencies exhibited by chemical species, assessing the molecule's inclination towards accepting an electron. This index offers insights into molecular behavior and reactivity, providing valuable information regarding the electron-accepting potential of the species under consideration.

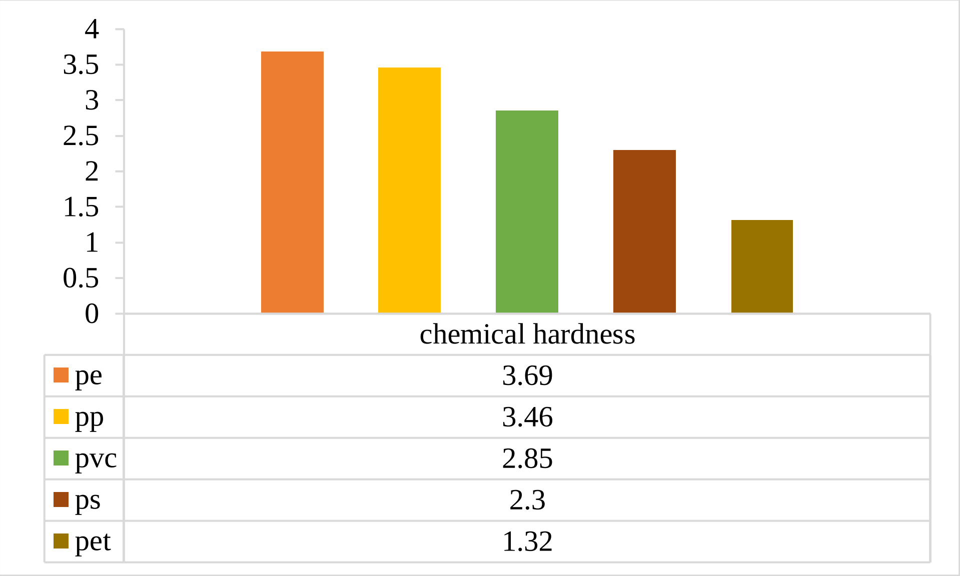
The following is a ranking of organic molecules according to the electrophilicity index; weak electrophiles have ω less than 0.8 eV, moderate electrophiles have ω in a range between 0.8 and 1.5 eV, and ω greater than 1.5 eV indicates strong electrophiles [51]. According to our results, the calculated electrophilicity value characterizes all investigated. compound as a strong electrophile. However, the comparative study is given below in Figure 4.8.



	electrophilicity index
🟧 pet	10.864
🟨 pvc	2.72
🟩 ps	2.26
🟫 pet	1.64
🟫 pp	1.59

Figure 4.8 Graphical representation of calculated electrophilicity index for plastic wastes.

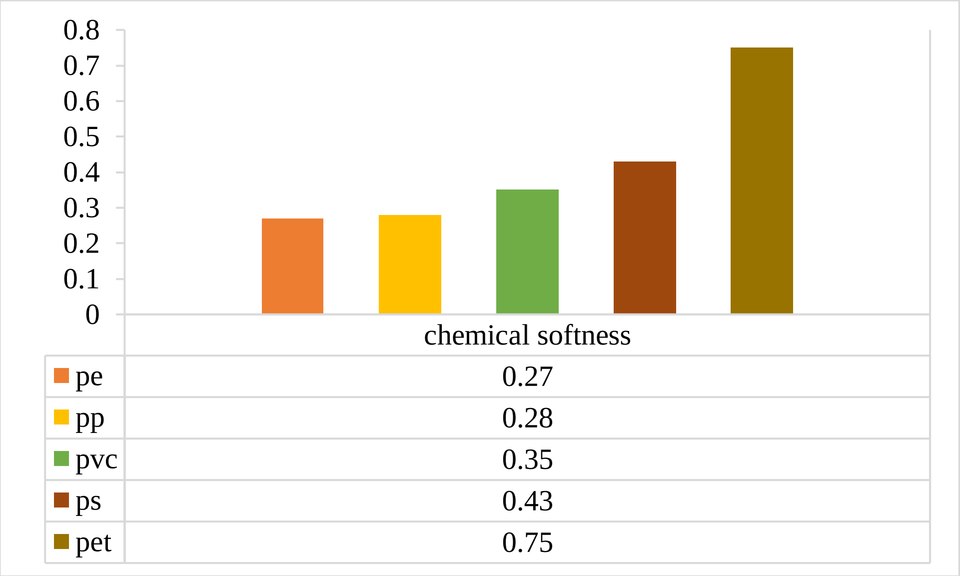
Global hardness (η) and global softness (σ) serve as pivotal descriptors for understanding a molecule's behavior in chemical reactions. Hard molecules exhibit a heightened resistance to altering their electronic distribution, whereas soft molecules display a diminished resistance to such changes during reactions. The elevated chemical hardness values observed in the investigated pesticides indicate their notable stability. Building upon our previous comprehension derived from FMO analysis, it becomes apparent that the ascending order of energy gap values exhibits a complete reversal compared to the increasing trend observed in softness values. For instance, polyethylene, identified as the least reactive component, demonstrates the lowest softness value, highest hardness, and energy gap values, as illustrated in Figures 4.9, 4.10, and 4.11, respectively. This observation underscores the intricate relationship between molecular properties and reactivity patterns in chemical systems. Meanwhile, a pet is the most reactive molecule with the greatest softness value as evident in Figure 4.11, lowest hardness and energy gap values.



	chemical hardness
🟧 pe	3.69
🟨 pp	3.46
🟩 pvc	2.85
🟫 ps	2.3
🟫 pet	1.32

Figure 4.9 Graphical representation of calculated chemical hardness for plastic waste.

Conclusively, it can be stated that the growing energy gap sequence of entitled plastics corresponds to the descending order for chemical softness and ascending order for their global hardness. Our calculations were in perfect agreement with the HOMO–LUMO bridging, thus illustrating that plastics with a significant energy gap value are hard molecules, with greater kinetic stability, lower reactivity, and high resistance against change in their electronic configurations. The values of the energy gap for the studied compounds are given in Figure 4.11.



	chemical softness
🟧 pe	0.27
🟨 pp	0.28
🟩 pvc	0.35
🟫 ps	0.43
🟫 pet	0.75

Figure 4.10 Graphical representation of calculated chemical softness for plastic wastes.

Polymer	**I** (eV)	**A** (eV)	**H** (eV)	**σ** (eV^{-1})	**χ** (eV)	***μ*** (eV)	**ω** (eV)
Ethylene Terephthalate	6.76	4.04	1.32	5.36	0.37	5.36	10.86
Vinyl Chloride	6.79	1.09	2.85	3.94	0.17	3.94	2.72
Propylene	6.79	-0.14	3.46	-3.32	0.14	3.32	1.59
Styrene	5.54	0.92	2.30	-3.23	0.21	3.23	2.26
Ethylene	7.17	-0.20	3.69	-3.48	0.13	3.48	1.64

Table 4.4 Calculated global reactivity parameters for plastic polymers.

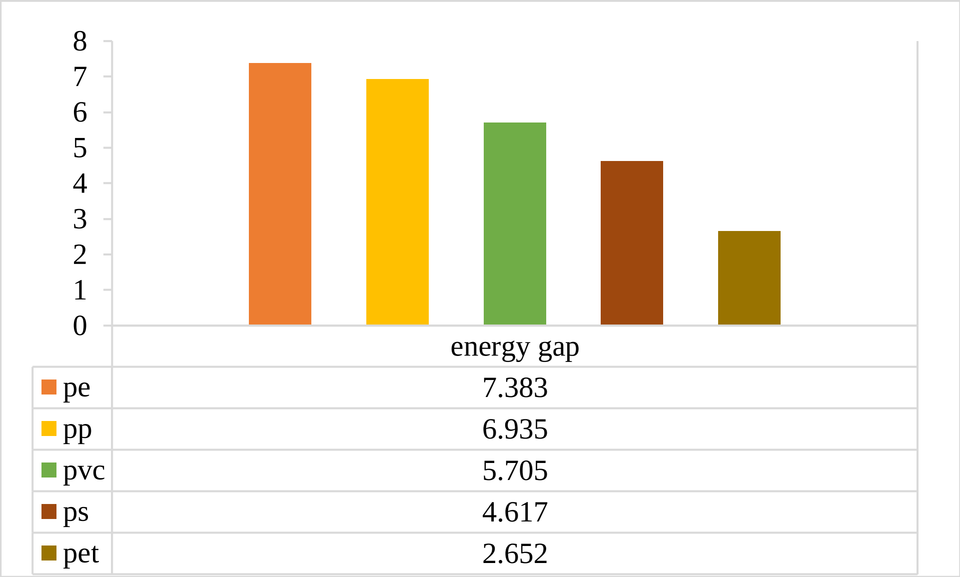


Figure 4.11 Graphical representation of calculated energy gap for plastic wastes.

4.3 Block Description in Aspen Plus Flow Sheet

Table 4.5 Block description of Process flow sheet for air–steam gasification.

Sr.No	Aspen-plus block	Block ID	Description
1	Mixer	FEEDMIX	For mixing of plastics
2	RYield	GASIF-1	Decompose the non-conventional into conventional components
3	RStoic	GASIF-2	The nitrogen, sulfur, and chlorine bound within the fuel transform, yielding ammonia, hydrogen sulfide, and hydrogen chloride, respectively.
4	RGibbs	GASIF-3	The gasification reactions are conducted under controlled chemical equilibrium conditions, optimizing Gibbs free energy to minimize the system's energy state.
5	RGibbs	GASIF-4	It adjusts the actual synthesis gas composition by manipulating temperature within the confines of a restricted equilibrium approach.
6	RStoic	COMB	Generate the combustion reaction equation for char.
7	SSplit	CYCLONE	The process involves the separation of solid components (char and ash) from hot flue gases.
8	HeatX	ECONOMIZE	Preheat the boiler feed water using syngas.

9	HeatX	HRSG	Steam is produced by heating the boiler feed water through the utilization of hot flue gas extracted from the combustion zone.
10	Sep	DRYGAS	It separates dry gas from a mixture or process stream
11	Sep	SPL	A separator is employed to partition the char between the combustion and gasification zones.
12	calculator	Yields	Gasifier-1 allocates the percentage mass yield of gasification products based on the composition of the incoming feed.
13	calculator	TCOMB	It establishes the temperature of the combustion zone relative to the gasification zone.
14	calculator	Ca-C RATIO	The function allocates the flow of sorbent (CaO) based on the calcium-to-carbon ratio.
15	calculator	S-C RATIO	Sets the steam flow rate according to the steam-to-carbon ratio.
16	calculator	A-F RATIO	Adjusts the airflow based on the rate of char flow into the combustion zone.
17	Design-spec	TG	Modulates the distribution of char to achieve the targeted gasification temperature.

4.4 Aspen plus flow sheet

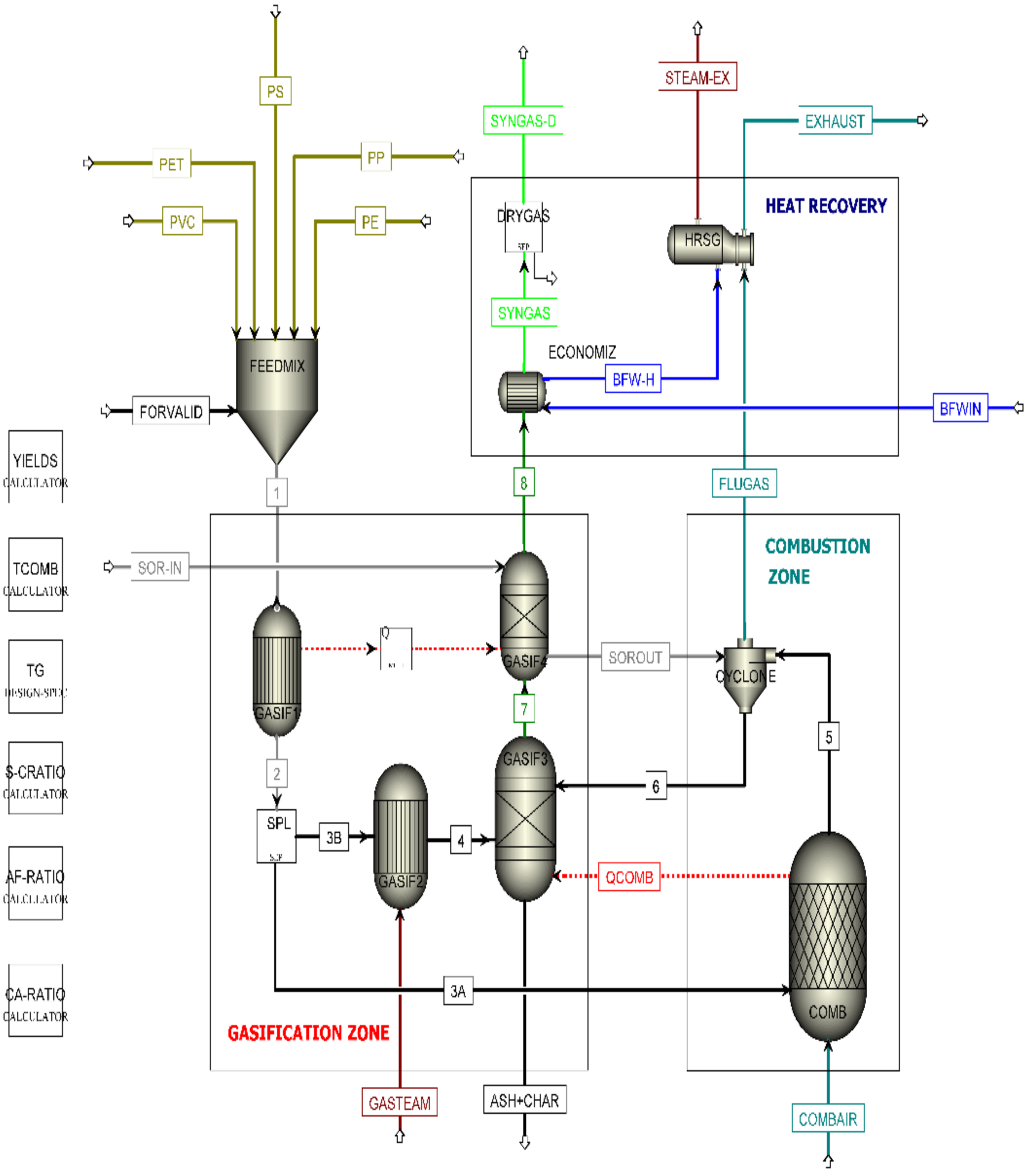


Figure 4.12 Process flow sheet for air–steam gasification.

4.4.1 Model development

Table 4.6 Chemical reaction taking place in the process flow sheet diagram.

Eq.	Reactions	Parameters
	GASIF-3 (RGibbs, restricted equilibrium mode)	
1	$C + 2H_2 \rightarrow CH_4$	Temp approach = 0°C
2	$C + H_2O \rightarrow CO + H_2$	Temp approach = 0°C
3	$C + CO_2 \rightarrow 2CO$	Temp approach = 0°C
4	$CH_4 + H_2O \rightarrow CO + 3H_2$	Temp approach = 0°C
5	$CO + H_2O \rightarrow CO_2 + H_2$	Temp approach = 0°C
	GASIF-4 (RGibbs, restricted equilibrium mode)	
6	$CH_4 + H_2O \rightarrow CO + 3H_2$	Temp approach = -115°C
7	$CO + H_2O \rightarrow CO_2 + H_2$	Temp approach = 40°C
8	$CaO + CO_2 \rightarrow CaCO_3$	Temp approach = -20°C
	GASIF-2	
9	$N_2 + 3H_2 \rightarrow 2NH_3$	Fractional Conversion = 1
10	$S + H_2 \rightarrow H_2S$	Fractional Conversion = 1
11	$Cl_2 + H_2 \rightarrow Hcl$	Fractional Conversion = 1

4.5 Sensitivity analysis

4.5.1 Sensitivity analysis on air temperature

The sensitivity analysis conducted in Aspen Plus investigates the impact of increasing air temperature on key parameters of gas composition and process efficiency in the gasification process. The temperature ranges from 250°C to 450°C to 650°C, reflecting typical operational conditions in gasification systems. Across the temperature spectrum, changes in the composition of CO_2, CO, H_2, and CH_4 are observed. Despite the temperature variation, the alterations in gas composition remain minor. This observation suggests that the influence of temperature on gas composition is negligible within the studied range. Moreover, the analysis of the Lower Heating Value (LHV) of the gas and cold gas efficiency reveals modest fluctuations with increasing temperature. Although slight variations are evident, they do not exhibit a significant trend correlating with temperature escalation. The marginal changes in LHV and cold gas efficiency underscore the limited impact of temperature on overall process performance. The findings of this study highlight the robustness of the gasification process against fluctuations in air temperature within the investigated range. While temperature influences certain aspects of gas composition and efficiency, its effect remains minimal and may not warrant substantial adjustments in operational parameters.

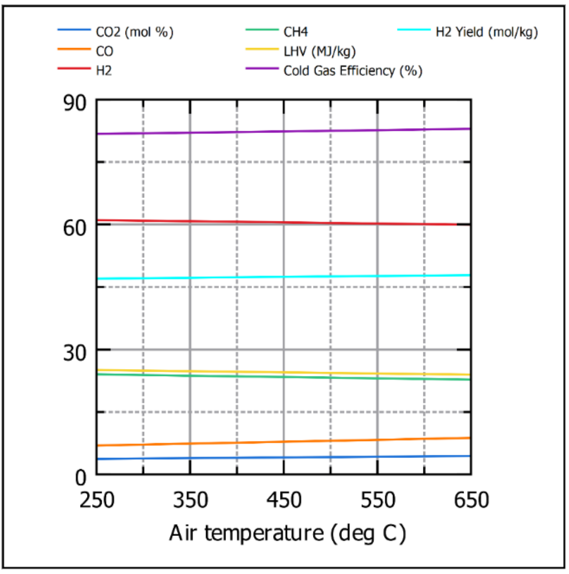


Figure 4.13 Graphical representation of sensitivity analysis on air temperature.

4.5.2 Sensitivity analysis on steam to carbon ratio

In a gasifier, steam is not only a gasification agent which takes part in the reactions, but also plays the role of fluidizing medium of the gasifier, mixing the bed particles and transferring them to the cyclone and further to the combustor. In this analysis, the influence of varying steam-to-carbon ratios on gasification parameters was explored across a range from 1 to 9. As the steam-to-carbon ratio increased, trends emerged indicating heightened CO2 production, demonstrated by an initial increase followed by stabilization, along with a substantial rise in CO and H2 fractions. These findings suggest that increased steam conditions promote CO and H2 generation during gasification. However, this was counterbalanced by a declining trend in the Lower Heating Value (LHV) of the gas, reflecting a reduction in its energy content with higher steam-to-carbon ratios. These results highlight the intricate interplay between steam conditions and gasification outcomes, underscoring the necessity for meticulous optimization strategies to achieve desired process efficiencies while balancing energy considerations.

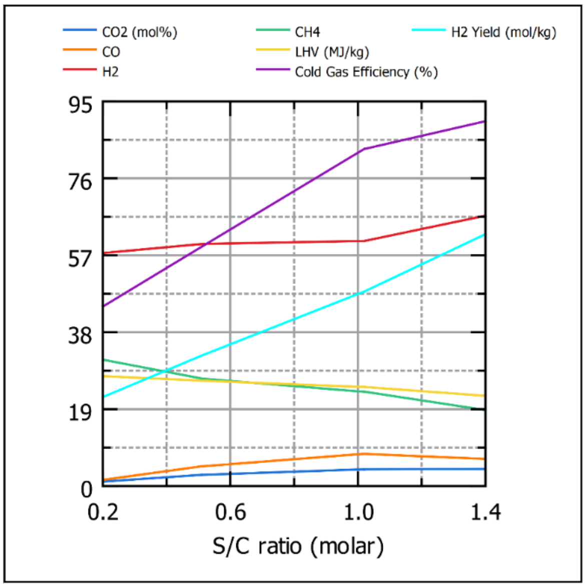


Figure 4.14 Graphical representation of Sensitivity analysis on steam to carbon ratio.

4.5.3 Sensitivity analysis on air-fuel ratio

Syngas composition was found to have a weak dependence on air-fuel ratio (mass basis). The largest change in the combustible gases was an increase from 45.7% to 47% for H2. constant. Referring to Fig. 6 a, syngas LHV remains constant. There is, however, a substantial decrease in Combustion Gas Efficiency (CGE) with increasing air-fuel ratio (CGE drops 3.35 percentage points). The decline in CGE can be attributed to the increase in char sent to the gasifier CZ and the resulting reduction in syngas mass flow rate. As the air-fuel ratio increases, the excess air lowers the temperature of the CZ, which in turn affects Tg. To maintain Tg at the desired temperature, more char must be burned. In conclusion, the air-fuel ratio should be as low as possible but high enough to ensure complete combustion of the char. Sensitivity analysis for the air-fuel ratio was conducted by varying the COMBAIR mole flow in kmol/hr from 3 to 10. This resulted in changes in the syngas composition. The CO_2 fraction varied from 4.06% to 3.24%, while the CO fraction changed from 7.78% to 5.73%. Additionally, the H2 fraction exhibited a minor increase from 60.55% to 61.7%, and the CH_4 fraction increased from 23.44% to 24.9%. The Lower Heating Value (LHV) of the syngas changed from 24.5 MJ/kg to 25.8 MJ/kg, and the Combustion Gas Efficiency (CGE) ranged from 82.27% to 80.9%. Furthermore, the hydrogen (H_2) yield decreased from 47.4% to 46.35%.

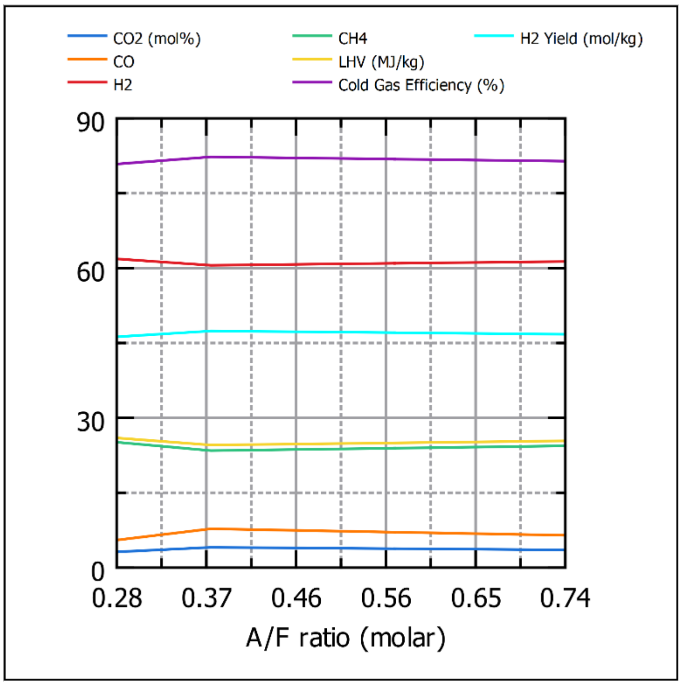


Figure 4.15 Graphical representation sensitivity analysis on air to fuel ratio.

4.5.4 Sensitivity analysis on calcium to carbon ratio

The variation of Cao sorbent from 1 to 9, with corresponding ratios of sorbent to carbon input as 0.16 to 1.52, results in changes in the gas stream composition. Initially, the CO2 fraction exhibits a decline from 6.4% to 2.44%, while CO fraction decreases from 11.91% to 4.03%. However, the H2 fraction displays fluctuations, showing an increase from 62.2% to 65.65%, and the Lower Heating Value (LHV) of gas undergoes an ascent from 19.30 MJ/kg to 27.47 MJ/kg. Moreover, the methane (CH_4) fraction escalates from 15.5% to 27.3%, resulting in a shift in Combustion Gas Efficiency (CGE) from 77% to 81%. Simultaneously, the hydrogen (H2) yield experiences a reduction from 52.9% to 44.6%. The observed decrease in CO2 production upon the addition of CaO sorbent underscores its efficacy as a carbon capture agent. As the sorbent reacts with CO2, it facilitates its removal from the gas stream, thereby diminishing its fraction. This mechanism is instrumental in mitigating greenhouse gas emissions and aligns with efforts to combat climate change. Additionally, the concurrent increase in CH_4 fraction and LHV of gas suggests a shift towards a more energy-rich gas composition, which could potentially enhance its utility in various applications. Consequently, the utilization of Cao sorbent not only contributes to environmental sustainability by reducing CO2 emissions but also enhances the energy content of the gas stream, thereby offering dual benefits towards achieving a cleaner and more efficient energy landscape.

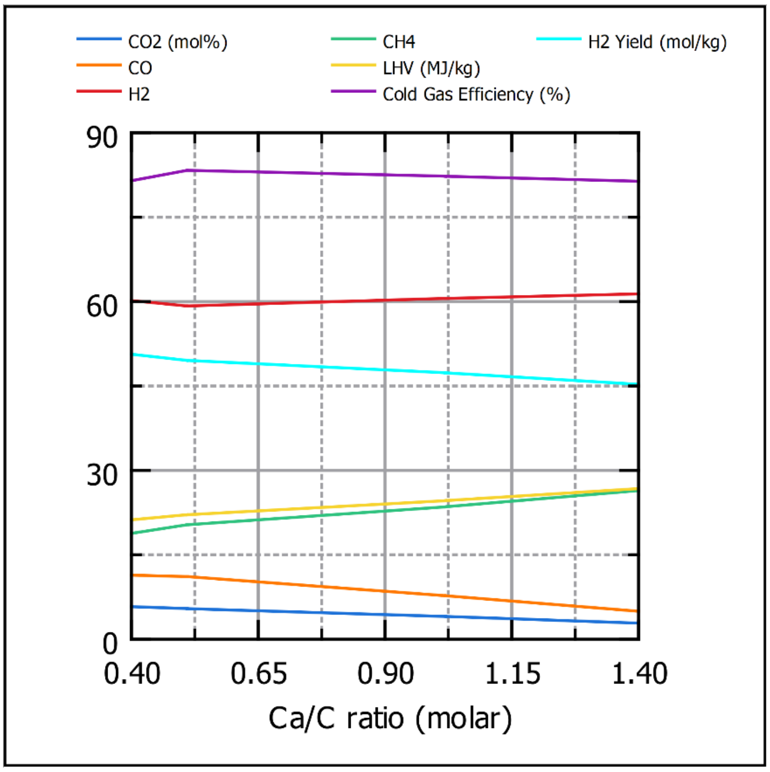


Figure 4.16 : Graphical representation of Sensitivity analysis on calcium to carbon ratio.

4.5.5 Sensitivity analysis on gasification temperature

Gasification temperature is controlled via char split which is simulated and controlled by split fraction in temperature block. By varying the char split, the gasification temperature will be varied. In the sensitivity analysis conducted using Aspen Plus, variations in gasification temperature were explored by adjusting the steam-to-carbon ratio (SPLt) and TG2 temperature. The SPL fract ranged from 0.1 to 0.9, while TG2 temperature spanned from 684.9°C to 871°C. Across this spectrum, distinct trends were observed: the CO2 fraction increased from 2.93 to 10.0%, while the CO fraction fluctuated from 5.0 to 17.7%. Conversely, the H2 fraction rose from 62 to 83.7%, while the CH_4 fraction decreased from 25 to 0.0%. Furthermore, the Lower Heating Value (LHV) of the gas decreased from 26.3 MJ/kg to 8.7 MJ/kg, reflecting changes in energy content, while cold gas efficiency (CGS) ranged from 80.5% to 36.29%, showing shifts in process efficiency. Additionally, the H2 yield fluctuated from 45.9% to 46.98%, indicating variations in hydrogen production efficiency. These results underscore the intricate relationship between gasification temperature, steam-to-carbon ratio, and process parameters, highlighting the need for meticulous optimization strategies to achieve desired gasification outcomes.

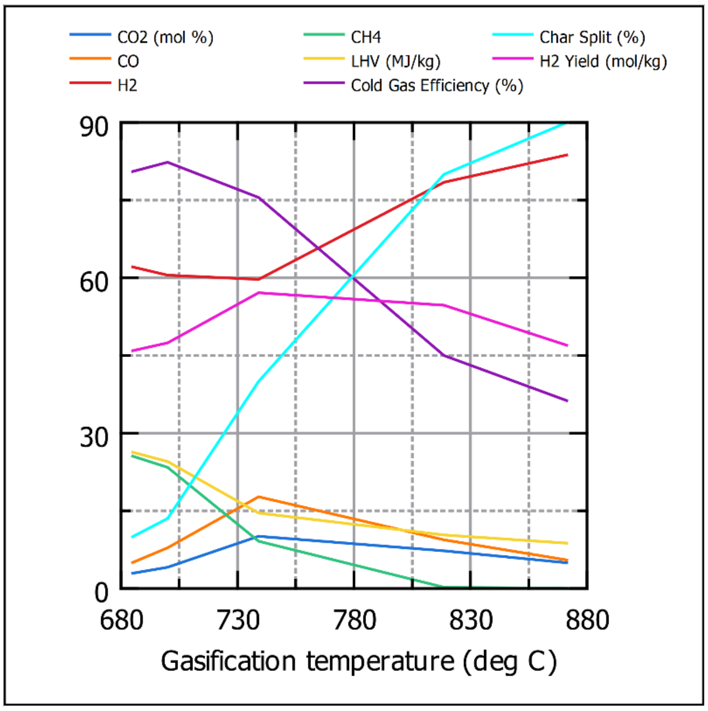


Figure 4.17 Graphical representation of Sensitivity analysis on gasification temperature.

4.5.6 Sensitivity analysis on steam temperature

In the sensitivity analysis conducted using Aspen Plus, the influence of varying gas steam mixed temperatures on key parameters of gasification processes was investigated. The temperatures ranged from 250°C to 450°C to 650°C, reflecting different thermal conditions applied during the gasification process. The results elucidated marginal changes in the parameters under study. The CO2 fraction, representing the proportion of carbon dioxide in the syngas, exhibited minor fluctuations across the temperature range, with values of 3.4, 4.7, and 5.3, respectively. Similarly, the CO fraction demonstrated slight variations, with values ranging from 6.196 to 9.59, indicating a modest increase with increasing temperature. The fraction and CH_4 fraction also displayed marginal declines with rising temperatures. Furthermore, the Lower Heating Value (LHV) of the gas exhibited a slight decrease, while cold gas efficiency experienced modest improvements with increasing temperature. These trends collectively suggest that while temperature variations exert some influence on gasification parameters, the observed changes are minimal. It is evident that increasing the gas steam mixed temperature from 250°C to 650°C yields negligible effects on the overall gasification process. This underscores the robustness of the gasification system against temperature variations within the investigated range and underscores the need for nuanced optimization strategies to achieve significant process enhancements.

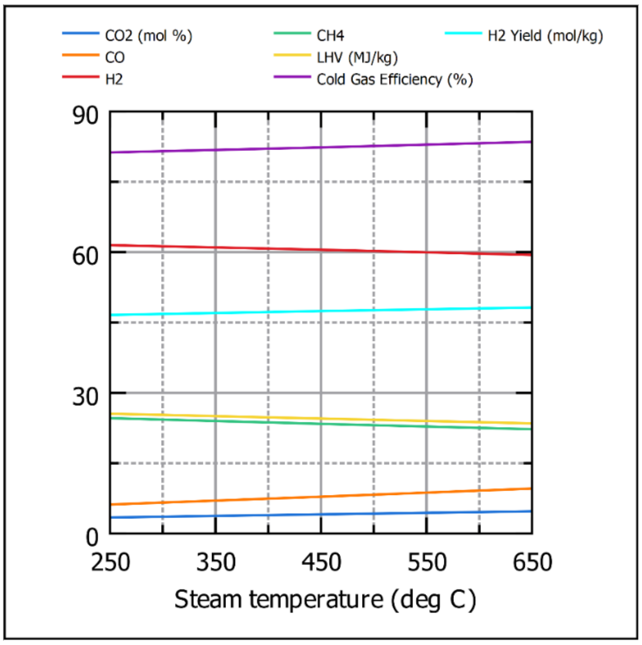


Figure 4.18 Graphical representation of Sensitivity analysis on steam temperature.

4.6 Model Validation

The comparison of syngas composition and hydrogen yield between the literature and the model results in this study shows close alignment. For woodchips, the hydrogen yield (H2) from the literature is 72.16 mol%, while the model predicts a slightly higher value of 74.48 mol%, indicating the model's robustness as shown in Table 4.3. Similarly, for municipal plastic waste (MPW), the hydrogen yield from the literature is 84.69 mol/kg_feed, closely matched by the model result of 84.74 mol/kg_feed. These results validate the model's accuracy in simulating plastic feedstock for hydrogen production using CaO-based dual bed gasification and its effectiveness in predicting syngas composition.

Table 4.7 Model validation of gasification of plastic waste materials.

	Model Feed Input	Parameters	Literature	Source	Model Results
Syngas composition (mol% dry basis) with sorbent	Woodchips	T_{Gasif} = 700^0C [S/C] =1 [Ca/C] = 1	H_2= 72.16 CO = 6.45 CH_4= 14.20 CO_2= 4.40	Simulation on hydrogen production from biomass with CaO-based chemical looping gasification	H_2= 74.48 CO = 6.18 CH_4= 14.46 CO_2= 4.70
H_2 Yield (mol/kg_{Feed})	MPW	T_{Gasif} = 800^0C [S/C] = 6.8 (assuming the process as continuous using the batch time in literature) CaO/Feed (mass) = 1	84.69	The role of CaO in the steam gasification of plastic wastes recovered from the municipal solid waste in a fluidized bed reactor	84.74

5. Conclusions and Future Perspectives

5.1 Conclusions

In the culmination of this study, a multifaceted investigation into the thermochemical processes of waste material conversion into energy and useful products was conducted. Five common plastics—PP, PS, PET, PVC, and PE—were scrutinized for their potential toxicity and long-term ecological impacts on human and environmental health. Utilizing diverse EPI-suite models facilitated the calculation of various physicochemical properties and evaluation of persistence, bioaccumulation, and toxicity (PBT) characteristics. Of the polymers mentioned, polyethylene (PE) and polypropylene (PP) are less likely to exhibit significant bioaccumulation activity compared to polyvinyl chloride (PVC), polyethylene terephthalate (PET), and polystyrene (PS). Polyethylene and polypropylene are inert and non-toxic polymers. They do not contain significant functional groups that can easily interact with biological systems, and they are not easily broken down into smaller, bioavailable molecules. On the other hand, PVC, PET, and PS may have higher bioaccumulation potential due to the presence of functional groups or aromatic rings in their structures, which can lead to interactions with biological molecules or organisms. Notably, polyethylene demonstrated the highest water solubility, followed by polypropylene, while polyvinyl chloride exhibited slight solubility, and polyethylene terephthalates and polystyrenes showed negligible water solubility as Polyethylene (PE) and polypropylene (PP) have high water solubility because they lack polar functional groups in their structure, making them hydrophobic and resistant to interactions with water molecules. Furthermore, employing BIOWIN3 models revealed insights into the persistence and toxicity of waste polymers, with PET and PS exhibiting relatively faster biodegradation rates compared to PVC, PP, and PE.

The integration of quantum chemical simulations utilizing the HOMO-LUMO gap contributed to additional understanding of the molecular-level interactions within these polymers. The maximum energy gap value calculated for polyethylene indicates its highest stability among the investigated polymers due to its relatively simple and stable molecular structure composed solely of carbon and hydrogen atoms, providing strong intermolecular interactions and resistance to degradation and PET shows maximum biodegradation because it has lowest energy gap which leads to fast biodegradation as compared to other 4 plastic polymers.

Subsequently, Using the ASPEN Plus process simulator, the dual-bed gasification process with CaO catalyst demonstrates the promising potential for efficient thermochemical conversion of plastics, as evidenced by sensitivity analyses revealing significant impacts of operational parameters on gasification performance and product yields. Optimizing parameters such as gasification and steam temperatures, catalyst-to-carbon ratio, and air-steam ratios can enhance gasification efficiency and yield valuable syngas products with reduced emissions.

In this integrated study, the examination of diverse factors elucidated the complex interplay between the characteristics of waste plastics, shedding light on their environmental fate, persistence, and potential for energy recovery and thermochemical conversion processes. The findings underscore the importance of considering multiple parameters in optimizing gasification processes for sustainable waste-to-energy conversion, while also emphasizing the necessity of continued research into the environmental impacts and efficacy of such technologies.

5.2 Future Perspectives

The future perspectives of the study encompass several avenues for further exploration and advancement. Experimental validation would be crucial to enhance the credibility and applicability of the research outcomes. Scaling up the gasification process from laboratory to pilot-scale operations would provide valuable insights into process optimization and scalability. Further optimization of gasification parameters could improve process efficiency and environmental performance. Additionally, conducting a comprehensive techno-economic analysis would evaluate the feasibility and cost-effectiveness of implementing the gasification technology on a commercial scale. Life cycle assessment would quantify the environmental impacts of the gasification process, informing sustainable decision-making. Exploring opportunities to integrate gasification technologies with circular economy principles would achieve synergistic environmental and economic benefits. Investigating novel materials and catalysts would improve the performance of gasification processes and expand the range of feedstocks for conversion. Overall, a multidisciplinary approach involving experimental validation, technological innovation, economic analysis, and environmental assessment is essential to advance gasification technologies for sustainable waste management and renewable energy production.

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