



Exploring the Potential of Transforming Sustainable Waste Thermoplastics into Liquid Petrochemicals

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Abstract

Plastics are remarkable materials in the 21st century, owing to their exceptional properties. Waste materials like PP (Polypropylene), PS (Polystyrene), and polyethylene are precious due to their composition, comprising long chains of hydrocarbon materials. A pyrolysis study explores the promising prospects of converting waste thermoplastics into green liquid petrochemicals. It is offering a sustainable solution to address both plastic waste and the growing demand for petrochemical feedstocks. Remarkably, utilizing a copper carbonate (CuCO_3) catalyst resulted in the recovery of up to 94% of liquid green petrochemicals from polyethylene waste plastics, with a carbon range spanning C_4 to C_{28} . These petrochemicals have undergone thorough analysis, encompassing physicochemical assessments, NMR (Nuclear Magnetic Resonance), FT-IR (Fourier Transform Infrared Spectroscopy), GC-MS-MS (Gas Chromatography-Tandem Mass Spectrometry), and GC \times GC/TOFMS (Two-Dimensional Gas Chromatography and Time-of-Flight Mass Spectrometry) techniques, and their chemical composition was 7.63% paraffin, 53.67% branched/cyclic hydrocarbons, 14.09% aromatics, 0.33% phenanthrenes, and 24.30% remained unclassified. Furthermore, the study explores the potential applications of these eco-friendly liquid petrochemicals across diverse industries, including fuels and chemicals, thereby exemplifying the transformative potential of this innovative approach in advancing towards a more sustainable and circular economy.

Keywords: Waste plastics; Pyrolysis; Petrochemicals; Catalysts; Sustainability.

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1. Introduction

Globally, plastics have achieved widespread prevalence due to their exceptional characteristics, encompassing high durability, lightweight, airtight, watertight properties, chemical resistance, cost-effectiveness, resistance to degradation, and ease of manufacturing. Therefore, plastics are highly sought-

after materials used in various industries, including domestic packaging, agriculture, automobile, and building construction.^[1-3] Plastic production increased significantly after World War II. The war spurred the demand for lightweight and durable materials, leading to advancements in the plastics industry. Globally, plastic production has continued increasing because the population is also growing. In 1950, global plastic production was approximately 1.7 million metric tons. By 1970, production increased to around 50 million metric tons. In 1990, it surpassed 100 million metric tons. In 2000, global plastic production reached about 200 million metric tons. By 2019,^[4] plastic production had reached 368 million metric tons and, according to 2019, produced 53.6 million metric tons of electronic waste which is estimated to exceed 1800 million tons in 2050. Waste plastic is also increasing due to virgin plastic production is also growing. In 1950, global plastic waste generation was minimal compared to production. As of 2016, the world had generated an estimated 242 million metric tons of plastic waste. Shockingly, a mere 9% of this vast plastic waste volume had been subjected to recycling, while 12% had been incinerated.

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The staggering majority, constituting 79%, had sadly found its way into landfills or the natural environment, highlighting a critical issue of waste mismanagement. Over 1 trillion plastic bags are used worldwide annually.^[5-19] The United States consumed around 100 billion plastic bags in 2019. China, Europe, and India are among the largest consumers of single-use plastic bags. In 2018, it retailed approximately 480 billion plastic bottles globally. Collected less than 50% of these bottles for recycling. An annual influx of approximately 8 to 12 million metric tons of plastic is believed to find its way into the Earth's oceans.^[1-2,5,10-15] The Great Pacific Garbage Patch, situated amidst California and Hawaii, is anticipated to reach dimensions double that of the state of Texas. Notably, the Asian region emerges as the primary source of this global plastic contamination, with China, Indonesia, the Philippines, Thailand, and Vietnam ranking among the foremost contributors. Tragically, this relentless flow of plastic waste, estimated at a staggering 8 million metric tons, exacts a toll on marine life and delicate ecosystems, presenting a grave environmental concern. Plastics only make up 4%–6% of the world's consumption of fossil fuels, even though production costs are low due to the usage of fossil feedstocks.^[16,20-21] Natural resources (such as petroleum, minerals, etc.) are used more quickly due to population expansion and improvements in life standards, which have sped up the transition from a fossil-based to a renewable-based civilization.^[22] The requirement for fossil fuel hydrocarbons like plastics, on the other hand, has resulted in an annual creation of 300 million tons of new Plastic, which added to the already existing Plastic. Furthermore, as assessed by the United Nations Environment Programme (UNEP), plastic production has outpaced all other materials since the 1970s. Projections indicate that in 2050 global primary plastic production will soar by a staggering 1,100 million tons. This disturbing trajectory coincides with a troubling shift towards disposable, single-use plastic items designed for swift disposal after just one brief use. Shockingly, a staggering 36% of all plastics produced find their way into packaging, contributing to uncontrolled waste accumulation in a staggering 85% of instances. Moreover, a striking 98% of single-use plastics originate from "virgin" feedstock, predominantly fossil fuels. Looking ahead to 2040, it is anticipated that greenhouse gas emissions linked to the production, consumption and disposal of conventional plastics derived from fossil fuels will account for a substantial 19% of the world's carbon budget.^[23] This dire situation is particularly

pronounced in India, where the stockpile of discarded plastic bottles escalates daily, exacerbated by a low recycling rate. Consequently, the responsible management and innovative utilization of these discarded materials in various sectors assume paramount importance.^[24] While plastic consumption and production typically align with market demand and supply dynamics, India exhibits a notable disparity. Here, plastic consumption averages 9.7 kg/person, reflecting a unique pattern of polymer utilization in the country.^[25] According to UNPD research, the world generates over 300 million tons of plastic trash each year, only 9% of which is recycled, 14% is collected for recycling and the remainder is dumped into the ocean.^[26] Around 300 Mt of plastic waste is thought to be produced worldwide each year.^[22] According to the World Energy Council (2013), 1.2 billion people worldwide did not have access to electricity in 2010; these people mostly belong to low-income regions of Africa, South Central Asia and Southeast Asia/Pacific. Garbage creation is increasing quickly in such nations, especially for organic and plastic waste and the uncontrolled disposal of waste is becoming a major management problem (United Nations, 2012). These factors also contribute to the expansion of the economies in those countries.^[27] According to recent data from the MNRE Report, India is predicted to generate 260 to 300 million tons of trash daily by 2047, up from 145 million tons annually. According to data from the CPCB, only roughly 49,401 MT of the 117,644 MT collected in India get treated (Central Pollution Control Board, 2016). By 2050, the globe will be expected to produce 27 billion tons of trash annually.^[28] The statistic displays the volume of plastic garbage generated in India between 2001 and 2011, with projections through 2041. Produced nearly seven million metric tons of plastic waste nationwide in 2011; by 2041, it is expected to reach over 50 million metric tons annually.^[29] The Central Pollution Control Board in Delhi has reported that a substantial 90% of plastic solid wastes (PSWs) possess the potential for recyclability. Nevertheless, the prevailing scenario reveals that a significant 80% of post-consumer plastic ends up in landfills, while 8% undergoes incineration and a mere 7% is subjected to recycling efforts.^[30] In 2018, the imposition of plastic bans by countries such as China, Malaysia and India exerted considerable pressure on Australia's recycling industry. In response, dedicated researchers have tirelessly sought effective solutions to address this mounting challenge.^[31] In addition, China's import prohibition policy exacerbated the global challenge of plastic trash. Until 2016, China was the world's top plastic importer, accounting for almost 45% of all plastic imports.^[32] In Germany in 2019, around 12 million tons of plastics were used, gathering 6 million tons of plastic garbage. Utilization is represented considerably differently in the volume of trash depending on the application. More than 95% of the consumed mass for plastic packaging, which generally has a limited lifespan, was collected as garbage. Consumption and waste volume differ dramatically for construction and automotive plastics with longer product life

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cycles. As a result, plastics are still widely used and will continue to be important for recycling ideas in the future.^[33] The COVID-19 epidemic has triggered plastic waste to increase. The use of plastics has grown due to a high reliance on takeaway and hygiene issues resulting in the usage of personal protective equipment; yet, efforts planned to minimize plastic consumption, such as the prohibition of single-use plastic bags, were postponed, rolled back and even outlawed. Single-use face masks are the most popular personal protective equipment to stop the pandemic's spread. Due to the increasing usage of single-use face masks, several local and national governments now require the public to wear them. The face mask market was worth around 0.8 billion USD in 2019, but by the end of 2020, it had grown to almost 166 billion USD. Oceans Asia predicts that 1.6 billion masks will reach the water in 2020, producing 4700–6200 tons of plastic pollution.^[34] Only 17% of the 8,600 Mt of Plastic that has ever been produced is recycled or burned to produce energy, leaving 59% of it in landfills or accumulating in natural areas like oceans. Due to COVID-19 regulations that have altered people's lifestyles, plastic waste has significantly increased recently. Over the past two years (from 2019 to 2021), the use of plastic packaging increased internationally by more than 10%. Handling waste plastic better through procedures like upcycling has never been more crucial.^[35] Waste plastic management is undoubtedly impacted by single-use plastics like masks, gloves, containers, medical packaging and utensils from the continuing COVID-19 outbreak.^[36] This issue is because plastics are not biodegradable and can persist in the environment for hundreds of years.^[37] The degradation of plastics results in the release of harmful pollutants like toluene, xylenes, benzenes and phenols into the atmosphere, water bodies and soil. This process gives rise to significant problems, including adverse effects on both humans and animals. Notably, certain microplastic particles originate from photo-degradation, leading them to drift on the surfaces of rivers, ponds and lakes. Ultimately, they find their way into the vast expanses of seas and oceans, infiltrating the food chain and eventually reaching humans.^[38] A sizable amount of PS waste is dumped in developing nations as solid pollution. Furthermore, the WEEE problem has been worsened by the rising usage of PS in electronic devices, which adds to the complexity of the matter.^[39] Plastic bags greatly contribute to floating anthropogenic marine waste, contribute to litter in urbanized regions and obstruct municipal drainage systems, aggravating localized flooding. Furthermore, plastic bags have been found as far north and south as the poles, contributing to the so-called Great Pacific Garbage Patch in the Pacific Ocean, made up of floating trash. Animals that consume or get stuck in plastic bags once they are in the environment are localized.^[40,41] Use reusable bags, water bottles and containers to reduce single-use plastic consumption. Choose products with minimal packaging or packaging made from sustainable materials. Improve recycling infrastructure and collection systems to ensure more plastics are properly recycled.

Implement regulations and policies to ban or restrict single-use plastics, such as plastic bags, straws and utensils. While reducing usage and improving recycling infrastructure is the key solution, an innovative solution such as transforming waste thermoplastic to green liquid petrochemicals through pyrolysis proposes an exciting possibility. This not only diverts plastic from landfills but converts it into valuable green petrochemicals. This can be achieved through funding research into new materials, technologies and processes that reduce plastic waste and pollution and fostering collaboration between researchers, Government and Industries.

2. Suitable Pyrolysis Feedstock for liquid petrochemicals

The pyrolysis process entails the thermal decomposition of organic materials in an oxygen-free environment, offering a means to convert various feedstocks into valuable products, including liquid petrochemicals. The feedstock selection for pyrolysis hinges on the desired outcomes and the specific pyrolysis technology employed. Several common and suitable feedstocks for the production of liquid petrochemicals via pyrolysis include polyethylene (PE), polypropylene (PP), polystyrene (PS), tires and rubber waste, all of which can yield valuable liquid petrochemicals, such as pyrolysis oil. Plastic waste pyrolysis stands as a promising approach for recycling plastic waste and deriving valuable products. Moreover, a diverse array of biomasses, including wood chips, agricultural residues, energy crops, and algae, can serve as feedstock for pyrolysis, leading to the production of bio-oil that can be further processed into liquid petrochemicals. Waste oils, including used motor oil, lubricating oil, and cooking oil, also find utility as feedstock for the pyrolysis process, allowing us to transform these waste oils into valuable liquid petrochemicals. The collection of plastic waste occurs in two primary forms: municipal and industrial.^[42-46] Water-based density separation aids in the segregation of mixed waste plastic, effectively dividing them into two groups. In the first group, plastics such as PT-ET, PVC, and PS exhibit a higher density than water, causing them to settle when submerged. Conversely, the second group includes plastics like LD-PE, HD-PE, and PP, which have a lower density than water and consequently float when placed in water.^[47,49] On a global scale, approximately 78% of thermoplastic materials within the total plastic waste stream are employed.^[50,51] The Plastic SPI codes play a pivotal role in facilitating reuse, pyrolysis, and recycling in manufacturing processes. Thermoplastics like PP, PE, and PS can be effectively recycled,^[52,53] while thermoset plastics lack the capacity for recycling into petrochemicals.^[54] Furthermore, the Kissinger method, introduced by Homer E. Kissinger in 1957, serves as a valuable tool for thermal analysis in instruments such as DTA (Differential Thermal Analysis) and DSC (Differential Scanning Calorimetry).^[14]

From a chemical perspective, waste plastics constitute a primary carbon chain. Notably, the calorific values of waste plastics closely align with those of commercial gasoline and diesel, as detailed in [Table 1](#). As a result, specific heat values

for polyolefins, such as polypropylene and polyethylene, stand at 18720 BTU/lb and 18434 BTU/lb, respectively.^[55] Assessing the thermal stability of plastic degradation, it is observed that waste HD-PE undergoes degradation within the temperature range of 410 °C to 515 °C, while PP exhibits degradation between 270 °C to 490 °C. Additionally, the analysis of waste PP, conducted through Thermogravimetric Analysis (TGA) in the presence of inert nitrogen gas flowing at a rate of 20 °C/m within the furnace chamber, reveals degradation temperatures ranging from 320 °C to 475 °C. Detailed proximate and ultimate analyses of the plastics are presented in Table 2.^[16]

Table 1. Calorific values of plastics and petroleum.^[13,14]

Types of feedstock material	Calorific values (MJ/kg)
PE	46.3
PP	46.4
PS	41.4
PVC	18.0
LPG	46.1
Petrol	44.0
Diesel	43.0
Light fuel oil	41.9
Heavy fuel oil	41.1
Waste tires	30-40
Butyl rubber	37-46

Table 2. Chemical composition of waste plastics.^[5,16]

Ultimate analysis (wt %)					
Properties	Waste HD-PE	Virgin HD-PE	PS	Waste Tyre	PP
Carbon	80.58	84.95	91	80	87
Hydrogen	13.98	14	7	5	12.70
Nitrogen	0.60	0.55	0	10	0.03
Sulfur	0.080	00	0	00	0.02
Oxygen	0.19	0.20	0.5	00	0.07
Proximate analysis (wt %)					
Moisture	00	00	0.25	0.82	0.11
Volatile matter	100	100	99.63	62.70	99.89
Fixed carbon	00	00	0.12	32.31	00
Ash contents	00	00	00	4.17	00

3. Pyrolysis methods for waste plastics

Pyrolysis is a process that involves the decomposition of organic materials at high temperatures in the absence of oxygen and it is a chemical reaction that produces char, gases, and liquid byproducts such as petrochemicals. While the concept of pyrolysis has been known for centuries, its development and application have evolved. In ancient times, early civilizations discovered the basic principle of pyrolysis through their use for fires only after that obtained charcoal and combustible gases. The term "pyrolysis" was first coined in

the 18th century by a Swedish chemist, Torbern Bergman. Pyrolysis gained more attention in the late 19th century as researchers explored its potential applications. One notable development was using pyrolysis to produce coal gas, which was used for lighting and heating purposes.^[56-58] During the early 20th century, pyrolysis processes were refined and applied to various industries, such as producing coke, coal, and fuel sources with higher carbon content. During World War II, due to fuel shortages in Germany, the Fischer-Tropsch process, a type of pyrolysis, was used to convert coal into synthetic fuels. In the 20th century, researchers began to explore the pyrolysis of waste materials for resource recovery and energy generation. This led to the development of various pyrolysis technologies, including fast and slow pyrolysis, for converting biomass, plastics, and other organic waste into valuable products such as biochar, bio-oil, and syngas. Researchers and engineers are improving pyrolysis technologies, optimizing the process parameters, and exploring new feedstock options. Today, pyrolysis is being applied in various industries and sectors, including waste management, bioenergy, agriculture, and the production of carbon-based materials. Its potential to convert organic waste into valuable products and reduce environmental impacts has positioned pyrolysis as an essential technology for a sustainable future.^[59-65] The waste-to-energy process can also reduce the volume of waste plastic garbage in landfills by 90–95%.^[66] On the other hand, the pyrolysis method seems more practical because any plastic can still be converted contained in the feedstock into liquid oil.^[67] PSW pyrolysis solvent was utilized as an engine's diesel lubricant in earlier experiments, which facilitates the recovery of thermal power and offers a means of disposing of PSW (plastic solid waste). Compared to essential diesel gasoline, PSW resulting from pyrolysis has more significant top stresses, a greater thermal release rate, and more significant pollutants. Alkanes, alkenes, and aromatics are found in PSW pyrolysis fuel, while alkanes and aromatic compounds are present in diesel fuel. Due to their double-bond structure, these alkenes are not appropriate for use as fuel in diesel-powered vehicles.^[68] The original scrap plastic significantly impacts the pyrolysis oil's biological and physical qualities. A diesel engine is the most suited energy converter for dependable engine operation and high-power generation efficiency when considering the various oil grades. It is genuinely unclear if diesel fuel or pyrolysis oil may be utilized as a 100% replacement fuel in diesel engines.^[69] The oil product yields of a lab-scale experiment in prototype copyrolysis of used lubricant oil and mixed plastic waste to produce a diesel-like fuel demonstrate the following effects of plastic waste type: In order of proximity to the PE/PP, PE/PS > PE/PP/PS > PP/PS. The yields for the gases are PP/PS > PE/PP/PS > PE/PS and the outcomes for the solids are PE/PP > PE/PS > PE/PP/PS.^[70] The quality of the pyrolysis products obtained is degraded by some undesired components that are typically found in actual waste streams (PVC, metals, PET, inert compounds, and cellulose-based materials). Depending

on where they come from, industrial waste streams have varying characteristics, which significantly impact how pyrolysis oils are produced.^[71] Scraps like WP, WCO, and WLO may be used to generate energy to create diesel-like oil, which solves the dilemma of how to dispose of trash while simultaneously recovering the energy's essential components.^[72] Olefins of different chain lengths are produced when polyethylene is pyrolyzed, while aromatic polymers yield aromatic chemicals like benzene, toluene, and styrene.^[73] PS, notably expanded polystyrene, can be obtained independently from PVC, and pyrolysis oil from PS won't be affected by chlorine-related issues, so PS appears to be a desirable fuel source.^[74] While pure PE and PP can yield acceptable pyrolysis gases for creating carbon nanotubes, municipal plastic wastes are often a blend of polymers.^[75] Waste, electrical and electronic equipment plastics, are the end-of-life materials found in WEEE trash streams, including the plastic exterior casing and edible parts of old EEE, such as refrigerators, air conditioners, televisions, and computers. The term "WEEE plastics" is used in this article following the definition given above.^[76] Chemical recycling has been recommended as an environmentally sound process of recycling electronic waste plastics for manufacturing clean fuels or chemical feedstocks, as brominated flame retardant (BFR) compounds in e-waste plastics have been the biggest hurdle for recycling treatment.^[77] After the process of distillation, the polyethylene in high-density store bag debris was pyrolyzed to create an oily hydrocarbon combination with an average structure made up of saturated aliphatic paraffinic hydrogens, aliphatic, olefinic hydrogens, and aromatic hydrogens, which corresponded to the boiling range of traditional petroleum diesel fuel.^[78] Several methods by which used polymers may be recycled or transformed into other goods. Sacks and trash cans are made from waste high-density polyethylene (HD-PE). Structures and the establishment of roads both use polymer-modified paving blocks. Scrap bags of plastic can thus be included in concrete mass in some way without significantly altering its other characteristics or slightly reducing its resilience.^[79] The conversion of two commercial-grade PE samples into higher-molecular-weight LDPE plastic bags and HD-PE water bottle caps results in overall liquid yields of 69 and 55 weight percent, respectively, with alkyl aromatic selectivity of 44 and 50 weight percent. Validates the method's applicability to real-world plastic wastes.^[80] A promising method for quickly and effectively turning waste plastics into jet fuel and hydrogen-enriched fuel gases using green, affordable, and regenerative activated carbon catalysts.^[81] Used activated carbon and MgO to catalyze the pyrolysis of waste plastic to produce jet fuel and hydrogen. Numerous research studies have looked into the variables affecting the distribution of items.^[82] According to reports, carbon nanotubes (CNTs) can be made by altering the circumstances of processing used plastics. As a result, CNTs are produced from the undesirable coke that had accumulated on the catalyst's surface.^[83] Hydrogen, methane, ethane,

propane, and butane are all present in the gas produced when plastic is burned in a pyrolysis process, giving it a high calorific value. The liquid that is created can replace traditional fuel. By pyrolyzing hydrocarbons or waste plastics, CNTs are produced from plastic waste using the chemical vapor deposition technique.^[84] Creation of various carbon-based compounds from polymers, including newly discovered materials such as tiny carbon particles, nanotubes of carbon, tiny carbon fibers, 2D graphene-based materials, fullerene graphite and composite compounds.^[85] Most existing plastics' attributes can be improved by using the helpful fraction of discarded plastics. Most of the destroyed electronics contain poly (acrylonitrile-butadiene-styrene, or ABS). Because of its high mechanical qualities and smooth surface, ABS is a favored plastic in applications across the electronics and automotive industries. By changing its components, the rates can be tailored.^[86] Throughout numerous investigations, ABS has been utilized to create blends of polymers for various uses.^[87] Polymer reformation powered by sunlight provides a quick and low-energy way to produce hydrogen from waste materials, employing low-cost CdS/CdOx quantum dots in an alkaline aqueous solution, the practical photo reformation of three widely manufactured polymers, poly(lactic acid), poly(ethylene terephthalate) and polyurethane. The waste polymers are transformed into organic compounds, including format, acetate, and pyruvate; this process runs at room temperature and pressure and produces pure H₂. The system's practical usefulness is demonstrated by transforming a PT-ET water bottle into H₂.^[88] They employed waste high- and low-density polyethylene as well as discarded computer bodies as feedstock for the pyrolysis process. The isolation of LD-PE and HD-PE was carried out from mixed plastics utilizing SPI codes 4 and 2 as reference points. Subsequently, these materials were subjected to a drying period of 4 to 5 hours in sunlight to eliminate any residual moisture. Following this, the waste materials were finely ground into small granules using a grinding machine. Fig. 1 illustrates a schematic diagram of the pyrolysis process. The experimental procedure involved the careful placement of each sample into the reactor one by one. The glass reactor was then positioned within the muffle furnace and initiated at a temperature of 23 °C. Each experiment concluded within a time frame of 3 to 4 hours. The pyrolysis process facilitated the transformation of hydrocarbons derived from waste high- and low-density polyethylene, as well as waste computer bodies, into shorter hydrocarbons or organic green petrochemicals. These environmentally friendly liquid hydrocarbons were successfully obtained within the temperature range of 340 °C to 375 °C. Any uncondensed gases resulting from the reaction were captured using a gas collection device, while residues remained following the pyrolysis process.

MV Singh employed waste polystyrene thermacol as the feedstock for the pyrolysis process, specifically isolating it using SPI code 6 as a reference point. To ensure the purity of the PS waste, it underwent a meticulous cleaning process

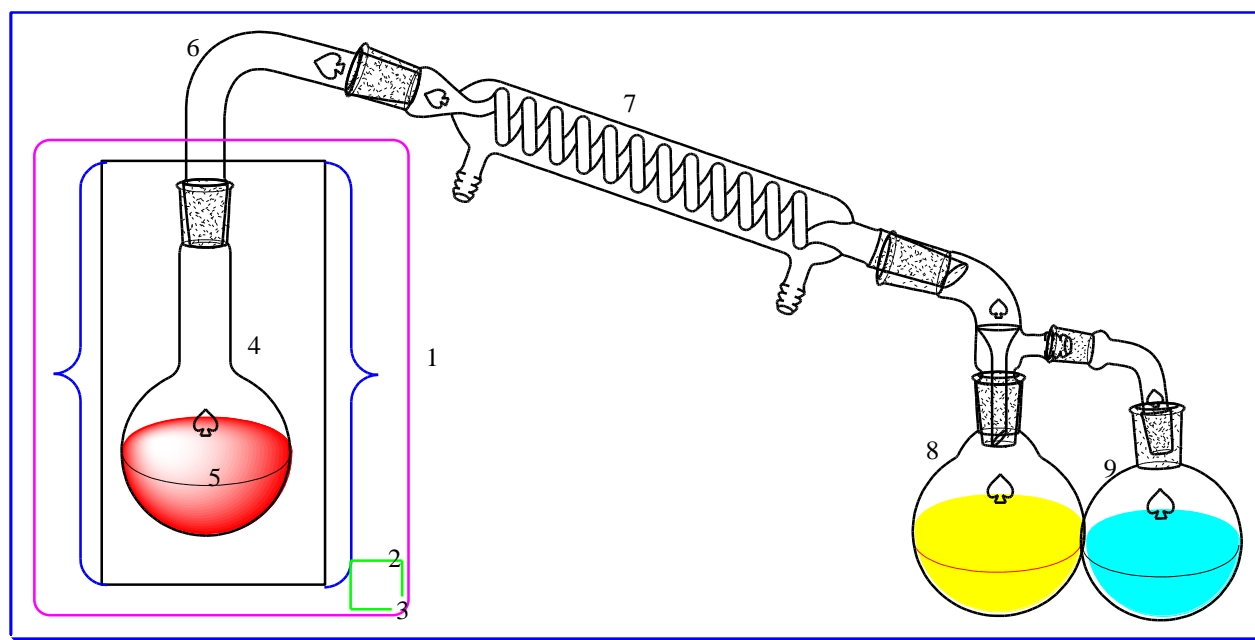


Fig. 1 Pyrolysis diagram showing the conversion of waste plastics into liquid petrochemicals. Reproduced with the permission from [15], Copyright Energy Reports.

involving the use of caustic-free soap to remove any foreign particles, followed by a thorough drying period under sunlight. The experimental setup involved placing the samples one by one into a batch reactor constructed of stainless steel. This reactor was then positioned inside a fully insulated muffle furnace. The pyrolysis apparatus featured carefully arranged components, including a coil condenser, connector, liquid petrochemical collection device, and gas collection device, as depicted in Fig. 2. Polystyrene (PS) was stored in a dedicated feedstock tank, where a continuous flow of N₂ gas was maintained at a rate of 20 °C/m to create an inert atmosphere. A sensor valve was periodically opened at 20-minute intervals

for 5 seconds. During each interval, 15 g of raw waste polystyrene thermacol (WPST) and virgin polystyrene (VPS) granules were introduced into the reactor. At a temperature of 350 °C, PS molecules transitioned from the liquid phase to the vapor phase, reaching vapor pressure equilibrium with external forces, with the boiling point varying according to the applied stress. Subsequently, the vapors were directed into a coil condenser, where they spontaneously condensed at a temperature of 21 °C due to the boiling point exceeding this threshold. The condensed product was then collected in a liquid petrochemical collection device, while any uncondensed gases were stored in a gas collection device.

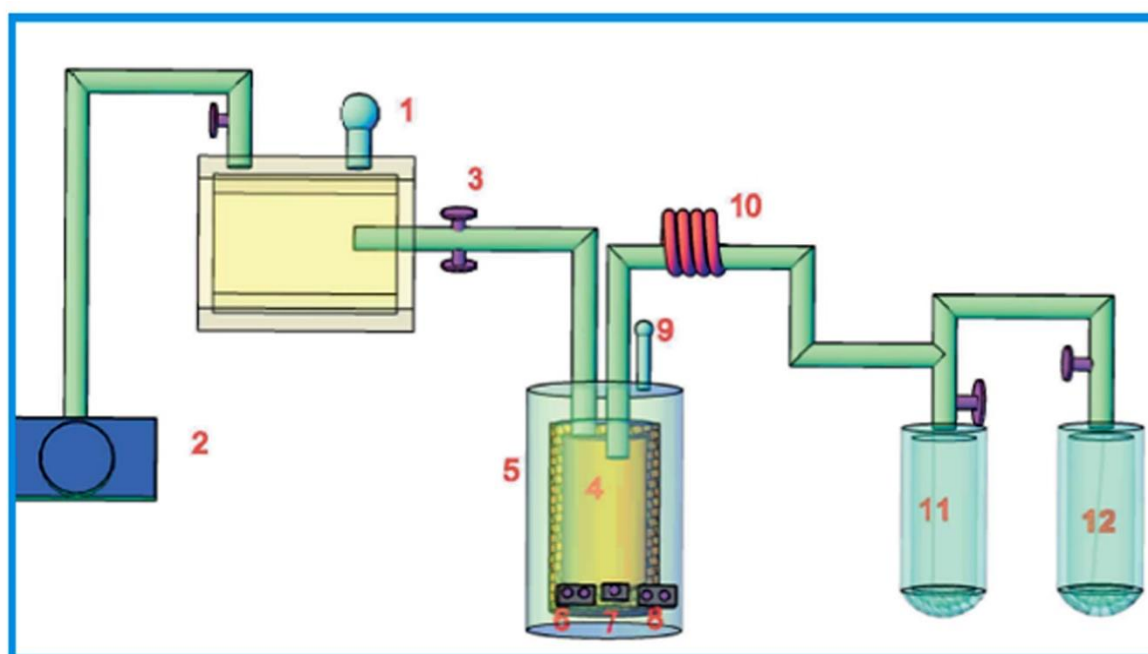


Fig. 2 pyrolysis setup diagram of PS plastics. Reproduced with the permission from [17], Copyright 2023 Wiley-VCH GmbH.

MV Singh utilized waste polypropylene and discarded tube tires as the feedstock for the pyrolysis process. The separation of waste polypropylene was achieved by referencing SPI code 5, while waste tube tires were identified by their chemical name, SBR. Both the dried waste polypropylene (WPP) and waste tube tires (WTT) were then transformed into small pieces measuring 3-4 mm² in size. Subsequently, each sample was individually placed inside a round-shaped glass reactor before initiating the experiment. This glass reactor featured dimensions of 160 mm in diameter, 158 mm in height, a reactor-neck length of 300 mm, and a reactor wall thickness of 3 mm. The glass reactor was subsequently positioned within a furnace, with a coil condenser set up at one end and the other end leading to the fuel collection device. A schematic representation of the pyrolysis setup is provided in Fig. 3. All experiments were conducted within a temperature range spanning from 23 °C to 390 °C. The pyrolysis distillation process yielded environmentally friendly liquid petrochemicals and a range of diesel products (comprising C_nH_{2n+2}, C_nH_{2n-6}/C_nH_{2n}, C_nH_{2n+1}OH, C_nH_{2n+1}CHO, RCOOR' esters). These products featured broken carbon chains, transitioning into the vapor phase inside the reactor due to their lower molecular weight. Subsequently, they traversed from the beginning to the end of the reactor neck, ultimately reaching the condenser. Liquid petrochemicals were collected in a fuel-collection device, while gases were collected in a gas-collection device. Residues were gathered in a separate glass reactor after the completion of the experimental process.

3.1 Pyrolysis temperature

The temperature at which pyrolysis is conducted exerts a profound influence on the composition of the resulting pyrolysis products. At lower temperatures, the primary products typically consist of biochar and volatile gases. However, as the temperature rises, the proportion of gases,

including methane, carbon monoxide, and hydrogen, increases, while the yield of biochar diminishes.^[89] Biochar, a solid carbon-rich product derived from pyrolysis, undergoes significant alterations in its properties based on the pyrolysis temperature. Specifically, higher pyrolysis temperatures tend to yield biochar with lower surface area, reduced porosity, and higher carbon content.^[90,91] The pyrolysis temperature also plays a pivotal role in the formation of tar, a complex mixture of organic compounds. Tar production is more pronounced at lower temperatures, leading to higher tar yields. Conversely, tar production typically diminishes as the temperature escalates, resulting in a higher proportion of gaseous products.^[92] Different temperature ranges trigger distinct thermal decomposition pathways during pyrolysis. Lower temperatures primarily induce primary pyrolysis, resulting in the generation of volatiles and biochar. In contrast, higher temperatures can initiate secondary reactions such as cracking and reforming of volatiles, further modifying the product composition. Consequently, the pyrolysis temperature directly shapes the distribution of pyrolysis products.^[93] Lower temperatures predominantly yield solid char or biochar, whereas higher temperatures yield a greater proportion of liquid products, known as bio-oil or pyrolysis oil. At elevated temperatures, a significant fraction of the feedstock may even convert into gaseous products. Notably, pyrolysis is a temperature-dependent process, with higher temperatures accelerating the reaction rate by providing the necessary activation energy. This heightened reaction rate translates into shorter residence times and increased throughput in pyrolysis systems.^[94] Moreover, the temperature at which pyrolysis is conducted influences the energy balance of the process. Higher temperatures demand more energy input to attain and sustain the desired pyrolysis temperature. However, they can also enhance energy efficiency by yielding more combustible gases that can serve as a valuable heat source or fuel for the

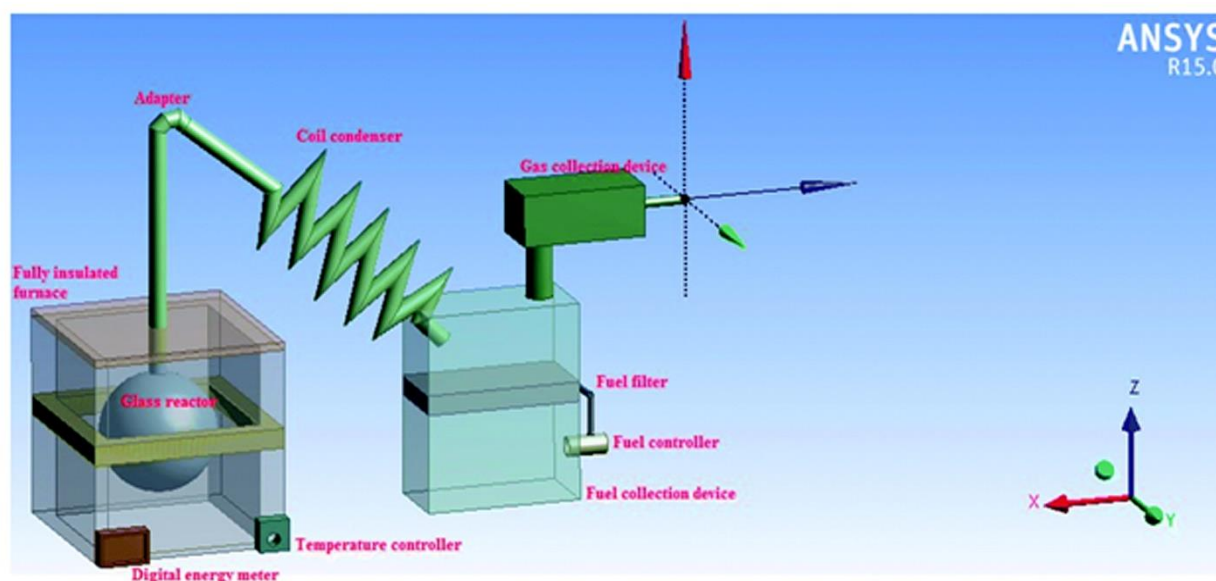


Fig. 3 Waste PP and waste tube tyre in the petrochemical diagram. Reproduced with the permission from [12], Copyright 2018 Royal Society of Chemistry.

pyrolysis process. Consequently, the chosen temperature range in pyrolysis can either favor primary pyrolysis or initiate secondary reactions, leading to variations in product composition and overall process efficiency.^[95-99]

3.2 Pyrolysis reactors

A quality pyrolysis reactor combines robust construction, efficient design, safety features, and compatibility with various feedstocks and applications. Carefully considering these qualities ensures the reactor performs effectively, contributes to waste reduction and resource recovery, and supports sustainable energy and materials production. The quality of a pyrolysis reactor is crucial for its safe, efficient, and reliable operation. A high-quality pyrolysis reactor should possess several key characteristics to ensure optimal performance and longevity. Here are some essential qualities that a pyrolysis reactor should have constructed from high-quality materials that can withstand the extreme temperatures, thermal cycling and corrosive environments associated with pyrolysis. Strong construction and proper design considerations are essential to prevent structural failures, leaks, or deformations, resistant to the corrosive effects of the feedstock and the reaction products to prevent degradation and prolong the reactor's lifespan, maintain thermal stability and to avoid heat loss, which can affect the efficiency of the pyrolysis process, essential for maintaining optimal temperature gradients within the reactor and facilitating the pyrolysis reactions, to designed to handle the pressure changes that occur during the pyrolysis process and incorporate safety features to prevent overpressure and potential ruptures, include efficient emission control systems to capture and treat harmful gases and volatile compounds produced during pyrolysis, ensuring environmental compliance, A well-designed reactor allows for easy loading and unloading of feedstock and by-products and it accommodates variations in

feedstock composition and characteristics. Numerous reactors have been employed for pyrolysis, including thermo-chemical recycling,^[100] catalytic pyrolysis cracking,^[101] fast catalytic pyrolysis,^[102] and standard pyrolysis.^[102-104] The pyrolysis process has been implemented on a commercial scale, exemplified by Brightmark's annual 100,000-ton waste-plastic processing facility currently under construction in India. Additionally, there have been instances of micro-scale pyrolysis,^[102] recycling,^[105] thermal catalytic pyrolysis,^[101] and integrated pyrolysis methods. Meanwhile, pyrolysis offers the capacity to transform waste plastics into renewable hydrocarbon fractions or petrochemicals,^[106,108] utilizing various types of reactors, including fluidized bed reactors,^[109] fixed-bed reactors,^[110] tube reactors,^[111] microwave reactors,^[112] semi-batch reactors,^[104] vacuumed fixed-bed reactors,^[105] catalytic microwave-assisted reactors,^[113] screw-type continuous reactors,^[114] rotator kiln type pyrolyzers,^[115] round shape borosilicate glass reactors,^[16,14] tube furnaces^[116] and Py-GC-MS analysis.^[117]

Table 3 presents the physicochemical properties of the green liquid petrochemicals derived from mixed waste plastics. The Total Acid Number (TAN), as calculated by the ASTM D664 method, serves as an indicator of the petrochemicals' acidic nature, falling within the range of 1.29 to 1.76 KOH/g.^[120] On the other hand, the Total Base Number (TBN) characterizes the basic properties of these liquid petrochemicals.^[121] The ash content, determining the presence of inorganic non-combustible residues after combustion, should ideally range between 0.1% and 0.2%.^[17] The flash properties of these liquid petrochemicals, distinguishing between low and high viscosity, are determined using ASTM methods D1310 and ASTM D93.^[122] Additionally, the Research Octane Number (RON) assesses their propensity for diesel knocking, while Kinematic Viscosity reflects the increase in these liquid petrochemicals' hydrocarbon chain

Table 3. Physiochemical properties of green liquid petrochemicals from waste plastics.

TAN (mg KOH/g)	TBN (mg KOH/g)	Ash Contents	RBCR (On 10% Residue)	Copper Strip Corrosion for 3 h at 100 °C	Flash point	Fire Point	Kinematic Viscosity at 40 ° (centistokes)	Kinematic Viscosity at 100 °C (centistokes)	Density at 15 °C (g/mL)	Sulfur Content (ppm)	References
2.00	0.30	0.003 % by wt	0.024 % by wt	1a	37 °C	53 °C	1.75	1.01	0.81	171.32	[13]
1.17	0.21	0.003	0.014	1a	41 °C	53 °C	2.01	104	0.872	1.394	[13]
2.02	0.32	0.002	0.021	1a	37 °C	52 °C	1.8	1.05	0.88	22.812	[11]
			0.027	1a	36 °C	50 °C	1.68	1	0.83	1000.5	[15]
2.13	0.7	0.01	0.028	1a	37 °C	52 °C	1.7	1	0.86	16.812	[12]
					65–88 °C				0.82–0.86		[118]
							3.6		0.83	10	[119]

lengths, with higher values indicating greater chain length.^[123] API gravity, a key market demand factor for high-quality liquid petrochemicals, can be categorized into four classes: light (≥ 34), medium (25–34), heavy (10–25), and extra heavy (≤ 10). The API gravity can be determined using Equation 1, where ρ represents fuel density.^[124] $API = 141.5 / \rho - 131.5$ Moreover, RON and bromine number properties play a pivotal role in determining the nature of these liquid petrochemicals. The bromine number is calculated through spectral NMR analysis of the liquid petrochemicals, employing the subsequent equation: Bromine number = $K \times HIO$ % Where $HIO = HIO/HIT \times 100$ $HIT = \text{integral of the region } 0.50\text{--}8.00 \text{ ppm}$ $HIO = \text{integral of } 4.60\text{--}6.60 \text{ ppm}$ The value of K depends on the olefin hydrocarbons (16.20 for fluid catalytic cracking and 9.30 for coker). Based on NMR data, $HIO = 1$, $HIT = 27.33$, and $K = 9.30$. Consequently, the total bromine number of the fuel is 34.03%. The knock characteristic of a fuel sample is determined under mild operational conditions, utilizing the following NMR method: $RON (NMR) = 83.14 + 0.48 (Har) + 1.02 (Holf)$

Where: Har = % aromatic hydrogen (6.50–8.00 ppm) Holf = % olefinic hydrogen (4.50–6.00 ppm)

With a percentage of aromatic hydrogen (Har) equal to 0.99 and a rate of olefinic hydrogen (Holf) at 3.66, the total RON for the fuel is calculated as 88.29^[16,97] suggesting good resistance to knocking. Overall comparison with Diesel, liquid petrochemicals shows lower density and kinematic viscosity suggesting careful consideration for engine handling. Lower flash and fire points show the requirement for safe handling. Sulfur content is higher compared to diesel and might need further processing.

3.3 Analysis of liquid petrochemicals from waste plastics

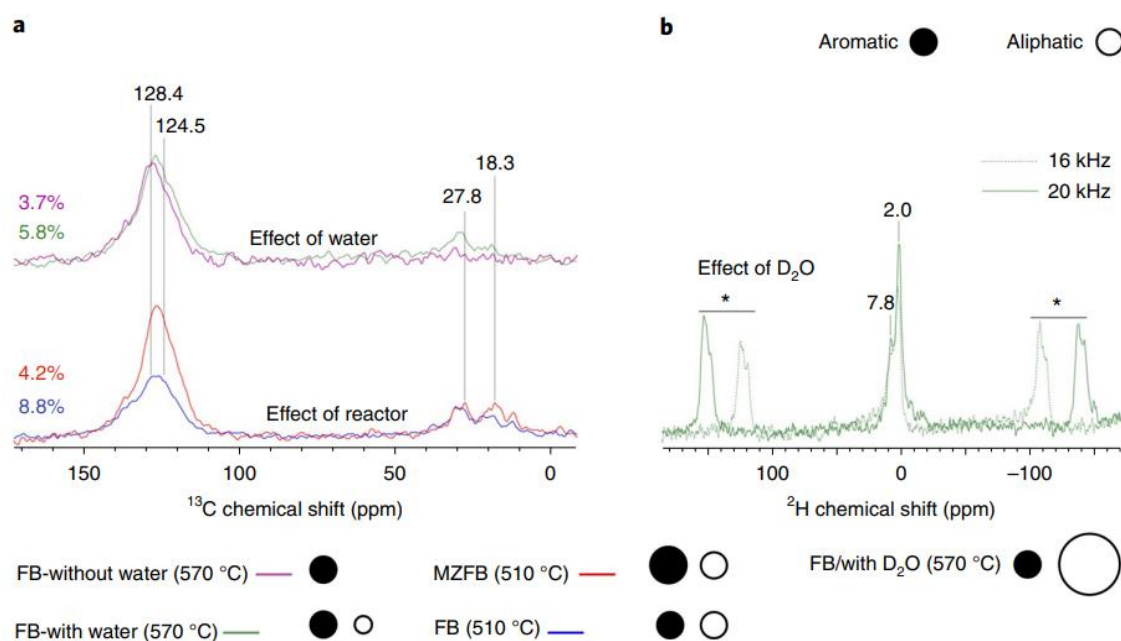


Fig. 4 (a) Effect of water and Reactor 4(b) Effect of D₂O on trapped organic compound within a hybrid-zeolite molecule using NMR Spectroscopy. Reproduced with the permission from [1], Copyright 2021 Energy Reports.

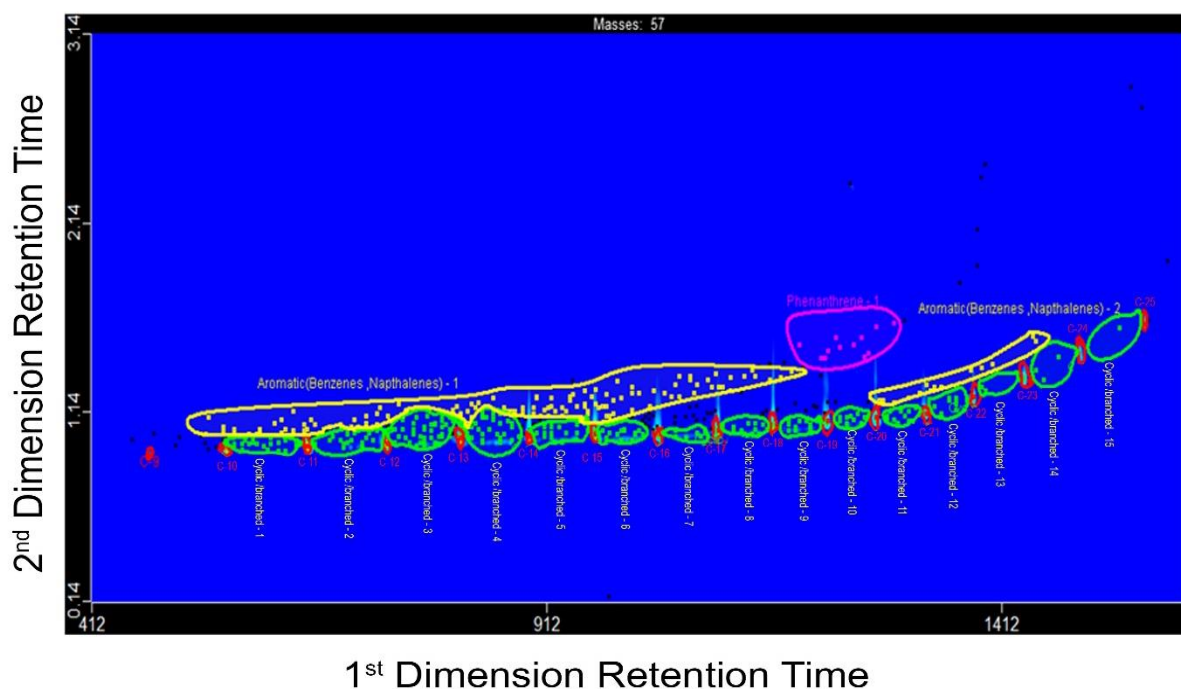


Fig. 5 Counter plot of liquid petrochemicals from polyolefins and e-components by GCxGC/TOFMS. Reproduced with the permission from [16], Copyright ICE Publishing 2022.

reactor equipped with a reflux condenser at a temperature of 480 °C. The GC-MS/FID detector identified olefin hydrocarbons with a carbon range of less than 28.^[125]

Singh *et al.* analyzed liquid petrochemicals derived from polyolefins and electronic components using cadmium carbonate (CdCO_3), as depicted in Fig. 5. Within their petrochemical samples, five distinct types of constituents were identified: 7.63% paraffins, 53.67% branched/cyclic hydrocarbons, 14.09% aromatics, 0.33% phenanthrenes, and 24.30% remained unclassified. Notably, the research octane number for these petrochemicals was determined to be 88.29, while the bromine number was found to be 34.03%.^[16] Additionally, Singh *et al.* employed copper carbonate (CuCO_3) at 390 °C to pyrolyze polyethylene into petrochemicals, revealing the presence of paraffins, aromatics, cyclic olefins, and phenanthrene moieties. An impressive 94% of the liquid green petrochemicals were obtained from polyethylene waste plastics.^[12] In a separate study, Singh *et al.* employed polyethylene in petrochemical production using a cobalt carbonate (CoCO_3) catalyst, yielding a remarkable 92% liquid yield.^[5] The above data suggest the prospect of converting thermoplastic and E-waste into liquid petrochemicals is very promising. The different catalyst and reaction conditions can influence the composition and yield of result petrochemicals.

4. Conclusion and perspectives

The prospects of converting waste thermoplastics into green liquid petrochemicals represent a transformative opportunity at the intersection of environmental sustainability, waste management, and petrochemical production. The urgent need to address plastic pollution and reduce our reliance on fossil

fuels has led to a growing interest in innovative solutions like thermos plastic-to-liquid conversion technologies. These green liquid petrochemicals have the potential to replace conventional petrochemical feedstocks, reducing greenhouse gas emissions and mitigating environmental degradation associated with both plastic waste and fossil fuel extraction. Moreover, the versatile applications of green liquid petrochemicals in industries such as transportation, chemicals, and polymers highlight their economic viability and potential for market integration. This highlights the environmental, social, and economic benefits of converting thermoplastic and E-waste to green liquid petrochemicals. The technology also faces challenges and needs researchers, Government, and industries' attention to unlock its full potential. As enterprises transition towards more eco-friendly practices, these sustainable alternatives hold promise as a valuable resource for a greener future.

Circular Economy Initiatives: Embracing circular economy principles involves designing products with recycling in mind, promoting reuse, and minimizing waste generation. This approach can create a closed-loop system for plastics. **Innovation in Material Design:** Researchers and companies are exploring innovative materials that mimic the properties of traditional plastics but are biodegradable or easier to recycle, reducing the environmental impact.

Government Regulations and Policies: Stringent regulations and policies aimed at reducing single-use plastics and promoting recycling can drive significant changes in waste management practices and encourage the adoption of more sustainable alternatives.

Public Awareness and Education: Increasing awareness

among the public about the environmental consequences of plastic waste can drive behavioral changes, leading to reduced plastic consumption and improved recycling habits.

Collaborative Industry Efforts: Collaboration among industries, governments and NGOs is crucial for developing comprehensive solutions. Joint efforts can accelerate research, innovation and the implementation of sustainable practices.

Market Demand for Recycled Plastics: Growing demand for products made from recycled plastics can create economic incentives for businesses to invest in recycling infrastructure and technologies.

Conflict of Interest

There is no conflict of interest.

Supporting Information

Not applicable.

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