INDIAN JOURNAL OF LEGAL REVIEW [IJLR – IF SCORE – 7.58]

VOLUME 6 AND ISSUE 5 OF 2026

APIS – 3920 - 0001 *(and)* ISSN - 2583-2344

Published by

Institute of Legal Education

https://iledu.in

CHEMICAL TRANSFORMATION OF POST-CONSUMER POLYMERIC WASTE INTO AUTOMOTIVE-GRADE LIQUID HYDROCARBONS

AUTHOR - MOHAMMAD ABDULLAH ASHIF* & DR.ARVIND KUMAR SINGH**

* STUDENT AT AMITY LAW SCHOOL, AMITY UNIVERSITY LUCKNOW

** PROFESSOR AT AMITY LAW SCHOOL, AMITY UNIVERSITY LUCKNOW

BEST CITATION – MOHAMMAD ABDULLAH ASHIF & DR.ARVIND KUMAR SINGH, CHEMICAL TRANSFORMATION OF POST-CONSUMER POLYMERIC WASTE INTO AUTOMOTIVE-GRADE LIQUID HYDROCARBONS, INDIAN JOURNAL OF LEGAL REVIEW (IJLR), 6 (5) OF 2026, PG. 20-27, APIS – 3920 – 0001 & ISSN - 2583-2344.

Introduction

The global accumulation of plastic waste has reached an unprecedented scale. As of 2025, approximately 130 million metric tons of plastic enter the environment annually, with projections suggesting this figure could escalate to 280 million metric tons by 2040 without aggressive global intervention. The historical reliance on mechanical recycling has proven insufficient for managing post-consumer waste, which often involves multilayer packaging and contaminated materials fundamentally unsuitable for traditional processing.

In response, chemical recycling—particularly the thermochemical conversion of plastics into liquid hydrocarbons—has emerged as a critical "molecular loop" strategy. This process involves the controlled degradation of polymer backbones into a state analogous to the crude oil from which they were originally derived, enabling regeneration of high-value fuels and petrochemical feedstocks, while diverting plastic from landfills and incinerators.

Theoretical Framework of Polymer Thermolysis

The synthesis of petrol from plastic is grounded in the science of thermolysis, or polymer cracking. This endothermic process facilitates the breakdown of long-chain macromolecules into smaller, more volatile hydrocarbon fragments in an anaerobic environment. By operating in the absence of oxygen, the process bypasses combustion, ensuring that the carbon and hydrogen content of the plastic is preserved in liquid and gaseous energy carriers rather than being released as carbon dioxide.

KEYWORDS: Plastic-to-Fuel Conversion, Pyrolysis (Thermochemical Recycling), Polymer Thermolysis, Liquid Hydrocarbon Production, Catalytic Cracking, Waste Plastic Management, Circular Economy / Molecular Loop.

Molecular Architecture and Bond Enthalpy

Polymers such as polyethylene (PE) and polypropylene (PP) consist of repeating monomer units held together by robust covalent $C-C$ and $C-H$ bonds. The thermal energy required to initiate transformation must overcome their bond dissociation energies:

Bond Type	**Bond Energy (kJ/mol)**	**Pyrolysis Implication**
C–C $C - C$	~348	Primary chain-scission site; governs cracking temperature
C–H $C - H$	~413	Controls hydrogen abstraction and formation of unsaturated products
C–Cl (PVC) $C - Cl$	~327	Early dehydrochlorination; releases corrosive HCl

The structural differences between polymers dictate their susceptibility to thermal degradation. LDPE consists of relatively linear chains with some branching, whereas PP features a methyl group on every repeating unit, creating tertiary carbon centres that are inherently less stable—making PP more susceptible to cracking at lower temperatures and producing lighter, iso-paraffin-rich oil.

Mechanisms of Polymer Chain Scission

The transition from solid plastic to liquid fuel proceeds through radical-based initiation, propagation, and termination. Four key propagation pathways govern the product distribution:

- **Random Chain Scission**: The dominant mechanism for polyolefins. Bonds cleave at random intervals along the backbone, yielding a broad distribution from light gases to heavy waxes.
- **Terminal Scission (Depolymerisation / "Unzipping")**: Cleavage begins at chain ends, thermodynamically favoured for specific polymers; ideal for monomer recovery.
- **β-Scission**: Occurs one carbon away from the radical centre, producing olefins (alkenes) and continuing the radical chain.
- **Hydrogen Abstraction and Backbiting**: Intramolecular reactions that create branched hydrocarbons and cyclic compounds, enhancing octane rating of the gasoline fraction.

Product distribution is ultimately governed by the kinetic competition between these pathways, heavily influenced by reaction temperature, residence time, and the presence of catalysts.

Kinetic Modelling and Activation Energy Analysis

The rate of degradation is modelled using the Arrhenius equation, where the activation energy (E_a) represents the energy barrier to cracking. Thermogravimetric analysis (TGA) combined with isoconversional methods such as the Kissinger-Akahira-Sunose (KAS) or Friedman models yields these parameters:

Polymer Type	Degradation Onset (°C)	Average E_a (kJ/mol)
Polystyrene (PS)	~350	192.6
Polyethylene Terephthalate (PET)	~400	197.6
High-Density Polyethylene (HDPE)	~440	202.4
Polypropylene (PP)	~380	261.2
Low-Density Polyethylene (LDPE)	~420	267.6

The low activation energy of PS explains its high liquid oil yield at lower temperatures compared to polyolefins. Conversely, the higher E_a of LDPE and PP necessitates more intensive thermal or catalytic treatment. Co-pyrolysis of mixed plastic waste often shows synergistic effects: PS-generated radicals accelerate breakdown of more stable polymers. A blend of 65 wt% PP and 35 wt% LDPE exhibits a particularly favourable combined E_a, suggesting a viable industrial strategy for polyolefin-rich municipal streams.

Catalytic Enhancement and Selectivity

Purely thermal pyrolysis requires temperatures exceeding 500 °C and yields broad, low-quality product distributions. Catalysts lower the required temperature, increase reaction rates, and improve selectivity toward the gasoline ($C_5 - C_{12}$) and diesel ($C_{12} - C_{24}$) ranges. Catalyst efficiency is determined by acidity, pore structure, and surface area:

- **ZSM-5 / MCM-41 Zeolites**: Highly acidic; shape-selective micropores crack long-chain paraffins into BTX aromatics (Benzene, Toluene, Xylene), essential for high-octane petrol.
- **Modified Bentonite Clays**: Cost-effective hierarchical porosity (micro- and mesopores) allows large polymer fragments to access active sites, reducing waxy products.
- **$AlCl_3$ on Activated Carbon**: Catalyses PP cracking at temperatures as low as 300 °C, raising oil yield from ~41% to over 54% while reducing total reaction time.

Catalyst Type	Optimal Oil Yield (%)	Key Advantage	Challenge
Thermal (None)	41.5–70.0	Simplicity; tolerates contaminants	High T; waxy products
Modified Bentonite	78.6	Efficient wax cracking; low cost	Thermal instability
ZSM-5 Zeolite	51.7–83.1	High BTX / gasoline selectivity	Rapid coking deactivation

$AlCl_3$ / Carbon	54.2	Low-temperature operation	Moisture / impurity sensitive

A significant hurdle is coke formation—solid carbonaceous deposits that build up on catalyst surfaces and block pores, driven by polymerisation and cyclisation of unsaturated intermediates. Research focuses on optimising the balance between Brønsted and Lewis acidity and developing regeneration-aware catalyst architectures.

Reactor Engineering and Operational Parameters

Temperature and Residence Time

Temperature is the primary driver of the cracking reaction. Lower temperatures favour liquid oil through controlled primary scission; higher temperatures promote light gas formation through secondary over-cracking:

Temperature Range (°C)	Primary Product	Rationale
300–450	Liquid Oil	Favours primary scission with minimal over-cracking
450–700	Mixed (Oil / Gas / Wax)	Onset of secondary reactions; shift toward lighter fractions
>700	Syngas / Light Gas	Complete breakdown to H_2, CH_4, C_2–C_4

Residence time also critically affects yield. For LDPE at 450 °C, extending residence time from zero to 120 minutes decreases oil yield from 91% to 61% as liquid hydrocarbons undergo secondary cracking. Modern reactors are designed with rapid quenching to arrest this process.

Reactor Configurations

Because molten plastic has low thermal conductivity, heat transfer is a major engineering challenge addressed by different reactor architectures:

- **Fixed-Bed Reactors**: Simple to operate but susceptible to temperature gradients and poor heat transfer.
- **Fluidised-Bed Reactors (FBR)**: A heated bed of sand or catalyst kept fluidised by inert gas provides exceptional heat and mass transfer, enabling continuous high-throughput operation.
- **Conical Spouted-Bed Reactors**: Superior blending makes them well-suited for mixed, irregular plastic feedstocks.
- **Vacuum Pyrolysis Reactors**: Reduced pressure lowers hydrocarbon boiling points, enabling faster product escape and reducing over-cracking risk.

Feedstock Variability and Its Impact on Yield

Polyolefins: Primary Fuel Feedstocks

HDPE, LDPE, and PP represent approximately 40% of plastic waste and are the gold standard for petrol and diesel production, consisting solely of carbon and hydrogen. HDPE typically yields ~82% paraffinic liquid oil resembling petroleum diesel. PP produces lighter iso-paraffin/olefin-rich oil highly beneficial for high-octane gasoline. LDPE yields are slightly lower but the resulting oil spans a broad paraffin range.

Challenges of PET, PS, and PVC

PS yields highly aromatic oil (up to 86%) rich in styrene and toluene—valuable but requiring specific refining for general automotive use. PET (oxygen-containing) yields only ~11% liquid fuel with oxygenated byproducts causing fuel acidity and equipment fouling. PVC is widely regarded as a contaminant: upon heating it releases corrosive HCl, poisoning catalysts and requiring neutralisation. Effective pre-sorting to exclude PVC and PET is critical to reactor longevity and product quality.

Feedstock	**Liquid Yield (%)**	**Gas Yield (%)**	**Char (%)**	**Major Oil Component**
HDPE	82.2	12.8	5.0	Alkanes / Alkenes
PP	61.8–82.0	15.0–35.0	~3.0	Iso-paraffins / Olefins
PS	50.0–81.0	13.0	6.0	Aromatics (Styrene)
LDPE	58.0–76.0	19.0–37.0	~5.0	Alkanes / Alkenes
PET	10.7–23.0	70.0–77.0	7.0	Oxygenates / Ethers

Refining Plastic Oil into Petrol

Raw pyrolysis oil is a "synthetic crude" that must be refined to meet automotive standards. A vertical fractional distillation column separates the crude by boiling point:

- **Gaseous fraction (<40 °C)**: C_1–C_4 hydrocarbons (methane, ethane, butane)—often recycled to power the reactor itself.
- **Gasoline / Petrol fraction (40–200 °C)**: The C_5–C_{12} range—the primary target for petrol production.
- **Kerosene / Jet Fuel fraction (200–250 °C)**: C_{10}–C_{16} hydrocarbons.
- **Diesel fraction (250–350 °C)**: C_{13}–C_{20} range, suited for tractors, generators, and heavy machinery.
- **Residue (>350 °C)**: Heavy oils and waxes—further cracked or used as industrial fuel/bitumen.

Purification and Upgrading

Post-consumer pyrolysis oils contain impurities requiring removal before use in modern engines: filtration and de-dusting removes char particles and inorganic additives; hydrorefining uses hydrogen and catalysts to eliminate sulfur, nitrogen, and oxygen, ensuring compliance with environmental standards; adsorption on silica gel or alumina removes residual nitrogen compounds and organic acids.

Characterisation of Plastic-Derived Gasoline

Research Octane Number (RON)

One of the most significant findings is that gasoline-range hydrocarbons from PP pyrolysis possess a naturally high RON—the fuel's resistance to "knocking" under compression:

Fuel Type	**Measured RON**	**Context**
Standard Gasoline (EU)	95.0	Typical commercial requirement
Pure PP Pyrolysis Oil	95.2	Direct thermal cracking product

Purified PP Fuel (100 °C distillate)	96.7	High-purity fraction
PP Waste Pyrolysis Oil	90.3	Post-consumer contamination effects
Mixed Plastic Fuel (PP/PE)	91.1	Linear PE chains lower the average

The high RON of PP fuel is attributed to its concentration of branched alkanes (iso-paraffins) and olefins, which resist auto-ignition under compression. Testing in spark-ignition engines showed a measurable decrease in fuel consumption compared to commercial 95 RON gasoline, alongside a slight increase in NOx emissions. A critical advantage is the ultra-low sulfur content of polyolefin-derived fuel—since PE and PP monomers are sulfur-free, no costly desulfurisation step is required.

Property	**Pyrolysis Gasoline (C_5–C_{12})**	**Commercial Gasoline (EN228)**
Density (kg/m³)	730–820	720–775
Viscosity (mm²/s)	1.4–1.7	~1.5
Calorific Value (MJ/kg)	35–46	~44
Sulfur Content (ppm)	<10 (polyolefins)	<10 (Tier 3 standard)
Aromatic Content (vol%)	Variable 3–35%	Max 35%

Techno-Economic Assessment and Industrial Scaling

The transition to commercial plastic-to-fuel plants requires a robust financial model accounting for the volatility of both waste plastic supply and fossil fuel prices. For an industrial-scale plant at 10 TPD capacity in India:

Economic Factor	**Typical Range (India / 10 TPD)**	**Major Components**
CAPEX	₹3.0–₹15.0 Crores	Reactors, distillation columns, land, shredders, logistics
OPEX	40–50% of revenue	Feedstock procurement and transport is the single largest cost
Feedstock Cost	₹5–₹25 per kg	Dependent on local sorting and municipal contracts
Gross Profit Margin	40–50%	Strong viability when off-take agreements are secured

A 10 TPD plant is often cited as the "sweet spot" for municipal clusters in developing economies. At this scale, the cost of producing one litre of diesel or petrol can fall to approximately ₹50, provided feedstock is available for less than ₹10/kg or subsidised through municipal waste management fees.

Case Studies: Ayodhya and Jhansi

Uttar Pradesh has become a leader in implementing these technologies through Public-Private Partnerships (PPP). The Ayodhya MK Aromatics project—North India's largest at 20 TPD—processes 7,300 tonnes of plastic annually, operating as a "mini-refinery" producing automotive-grade diesel sold at subsidised rates to local farmers for generators and tractors. The Jhansi municipal initiative (10–15 TPD) relies on "Waste Exchange Centres" to formalise the informal sector (ragpickers) through a profit-sharing mechanism for low-commercial-value plastics, and was estimated to reach self-sustainability within three years.

Analysis of decentralised pyrolysis plants indicates a payback period of 2–6 years depending on feedstock purity and automation. When feedstock cost is borne by municipal disposal budgets (zero net cost to plant operator), the Internal Rate of Return (IRR) can reach 48%. Even accounting for feedstock costs, the system remains economically viable at an IRR of approximately 33% annually.

Life Cycle Analysis and Environmental Impacts

LCA studies indicate that GHG emissions can be reduced by 50–60% when chemical recycling replaces incineration of plastic waste. Fossil resource depletion is reduced by 30–75% by retaining carbon in a molecular loop rather than destroying it through combustion. However, some LCAs show conflicting results depending on boundary conditions—whether the analysis includes pre-treatment energy, the heat source for the reactor, and credits for avoiding landfill methane emissions.

To maximise environmental benefits, the pyrolysis process itself must be decarbonised. The emerging bio-plastic plant in Balrampur, Uttar Pradesh, sets a benchmark by targeting 100% renewable energy operation. When the reactor's thermal load is met by renewables or by efficiently burning its own off-gases, the carbon handprint of the resulting fuel becomes significantly more favourable than conventional fossil fuel production.

Operational Challenges and Safety

Post-consumer plastics frequently contain contaminants that create severe industrial challenges:

Contaminant	Typical Level in Oil	Industrial Limit	Risk
Chlorine	~2,300 ppm	3 ppm	Corrosion; hazardous HCl emission
Nitrogen	~1,650 ppm	100 ppm	Catalyst poisoning; NOx pollutants
Oxygen	~1,250 ppm	100 ppm	Organic acid formation; fuel instability
Iron / Metals	~33 ppm	0.001 ppm	Fouling of downstream catalytic units

Addressing these contaminants requires effective pre-sorting and post-distillation upgrading. Process safety hazards include flammable syngas and high-temperature liquids; inert nitrogen atmosphere creates asphyxiation risk in confined spaces; residual tars and ash contain concentrated heavy metals requiring hazardous waste disposal; and pressure spikes from highly branched plastics can create reactor hotspots. Robust temperature profiling and process control systems are essential for safe 24/7 industrial operation.

Future Directions: Machine Learning and Molecular Optimisation

Machine learning—including neural networks and support vector regression trained on TGA and GC-MS data—enables real-time optimisation of pyrolysis plants. Control systems can dynamically adjust temperature, residence time, and catalyst feed rates to compensate for fluctuations in the incoming waste stream composition, maximising liquid yield and octane quality.

On the pre-treatment side, automated deinking of plastic films, microwave-assisted drying, and mechanical crushing improve heat transfer and reduce energy consumption. Multi-stage reactor designs that dehalogenate PVC-contaminated streams at low temperatures before high-temperature cracking offer a scalable path to handling real-world mixed waste without damaging the primary reactor or downstream catalysts.

Conclusion: The Path Toward Circularity

The synthesis of petrol from plastic waste represents a convergence of chemical engineering, environmental necessity, and economic opportunity. By leveraging the fundamental principles of thermolysis and catalysis, it is possible to transform a global pollutant into a high-grade energy resource chemically indistinguishable from its fossil-derived counterparts. The high research octane numbers observed in PP-derived gasoline, coupled with the ultra-low sulfur profiles of polyolefin oils, position plastic-derived fuels not merely as "alternatives" but as high-performance energy carriers in their own right.

Industrial projects in Ayodhya and Jhansi demonstrate that the technology has moved beyond the pilot phase into the commercial mainstream. The success of this transition depends on continued refinement of catalyst selectivity, decarbonisation of the pyrolysis process through renewable energy, and the implementation of robust Extended Producer Responsibility policies. Ultimately, by "closing the loop" at the molecular level, this approach can significantly reduce reliance on virgin crude oil while resolving one of the most pressing environmental crises of the 21st century.