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Unlocking Hydrocarbon Potential from Metallized Multi-Layer Plastics: A Kinetic and Product Evolution Study

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Abstract: This study explores the thermal decomposition behavior, kinetic parameters, and product evolution of metallized multi-layered plastics (MLPs). Thermogravimetric analysis (TGA) revealed a three-stage, diffusion-controlled decomposition process, best described by the three-dimensional Ginstling–Brounshtein model, attributable to the complex layered structure of MLPs. The apparent activation energy ranged from 183.47 to 218.42 kJ mol^{-1}, higher than that of polypropylene (PP), high-density polyethylene (HDPE), polystyrene (PS), and polyurethane (PU), but lower than polyamide (PA) and polyethylene terephthalate (PET). The maximum decomposition rate occurred between 457.10°C and 486.63°C, following first-order kinetics. Pyrolysis at 500°C yielded a fuel oil, which, after hydro-processing, produced hydrocarbons in the C_5–C_{40} range, with 97.55% falling within the C_5–C_{18} fraction, comprising 45.72% paraffins and 37.80% aromatics. Densification of MLPs effectively suppressed the carry-over of metallized layers, while chemical treatment removed suspended carbon and reduced fuel oil viscosity before hydro-processing. These findings elucidate the decomposition and product formation mechanisms of metallized MLPs and offer a comparative evaluation against conventional plastics (types 1–7) concerning fuel oil yield and composition.

Key words: Multi-Layer Plastic (MLP); Fast Moving Consumer Goods (FMCG) Waste; Pyrolysis; Fuel Oil; Chemical and Hydro-processing

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1. Introduction

Managing plastic waste is one of the major concerns worldwide as it impacts the environment and releases pollutants and toxic chemicals[1]. In particular, multi-layered plastic (MLP) is one of the categories which is widely used in the food and packaging industries. MLP packaging is generally made from 3-7 thin layers consisting of aluminum foil with a cascade of paper, polyethylene (PE), polyethylene terephthalate (PET), polypropene (PP), polyamide (PA), polystyrene (PS), polyvinylchloride (PVC). The tentative representation of constitutes in MLP is shown in **Fig. 1(a).** MLPs are generally made through co-extrusion and/or lamination and have a thickness of 200 µm with barrier properties capable of protecting the goods from light, moisture, oxygen, and carbon dioxide. Specific properties are achieved through additives such as adhesives, fillers, plasticizers, flame-retardants, colorants, stabilizers, lubricants, foaming agents, and antistatic agents[2]. These additives restrict recycling due to the cross-linkage between the layers[3]. Degradation in natural conditions takes a long time and leads to adverse effects on the environment like microplastics, and lose in fertility of soil. Thus, MLPs are generally disposed of in landfills or incineration resulting release of dioxins and toxins (fly-ash) chemicals in the process of breakdown, which in turn cause a way into contaminate the groundwater and food chain, air pollution and global warming aswell.

Upcycling/recycling of MLPs has been reported in recent studies utilizing primary recycling: mechanical recycling, secondary recycling: solvolysis/chemical and tertiary recycling: pyrolysis/energy recovery[4]. The low recycling rate, energy consumption, CO_2 emissions, and consumption of a lot of chemicals are the problems associated with chemical and mechanical treatments. Solvent-targeted recovery and precipitation is an emerging technology for deconstructed into their constituent resins before being co-fed into processing equipment to produce reconstituted multilayer films, but it still, has a long way to become commercially viable technologies. A thermal treatment especially using pyrolysis wherein polyolefins are decomposed at an elevated temperature of 400-500°C in the absence of oxygen is technology that has the capability to convert the MLPs into high-added-energy products such as liquid oil, gas, and char[5]. The challenge associated with MLP pyrolysis is the high wax content of C_{21}-C_{30} in oil with significant car-

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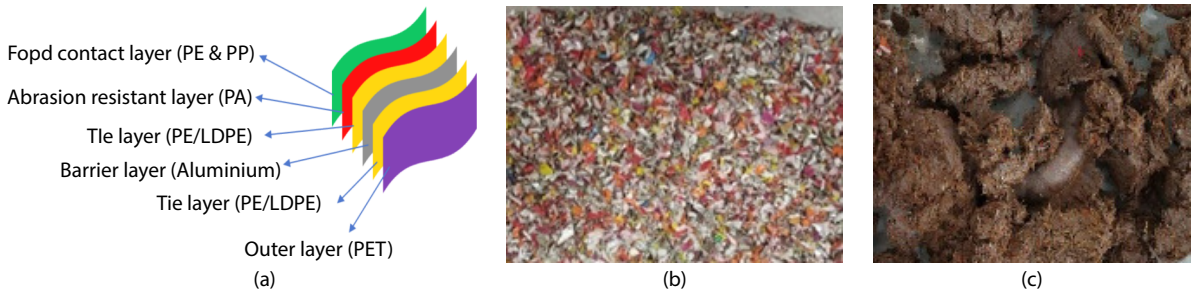

Fig. 1. (a) Representation of constitutes in MLP Pre-processing of MLP waste (b) Shredded MLPW (c) Extruded MLPW

bon and aluminums carryover in downstream operation[6]. Utilization of catalysts such as Zeolite, ZSM-5, HZSM-5, FCC, clay during in-situ or ex-situ pyrolysis plastic waste (MPW) process has shown to improve the properties of oil through cracking, oligomerization, cyclic, aromatic compounds formation and isomerization reactions[7,8]. Additionally, such catalysts have been shown to improve the stability of oil with the reduction in carbon/solid deposition (higher molecular weight fraction) in the pyrolysis oil over storage/handling or during ageing. Sivagami et al.,[6] investigated catalytic pyrolysis of multilayer packaging-based waste plastics of PET/MET/PET in the presence of commercial zeolite catalyst and showed an oil yield of 17.8%. Velghea et al.,[9] studied MSW as a mixture of carpet disposal, residues of plastic/metal/drinking cartons and obtained oil fraction is rich in C_8–C_{28} aliphatic carbons (63.5% with 44.1% alkenes) besides 23.5% of aromatic compounds. Juliastuti et al.,[10] reported the microwave pyrolysis of MLP using a zeolite catalyst and reported a solid yield of 2.88% with a 28.12% of liquid yield.

Martínez-Narro et al.[11] investigated the thermal decomposition and kinetics of plastic waste to support optimal reactor design and scale-up of pyrolysis for chemical recycling. Using thermogravimetric analysis, kinetic parameters were determined for both individual polymers and mixed plastic waste samples representative of major waste stream components such as polyolefins and polyesters. The study revealed strong conversion-dependent variations in activation energy for mixtures, indicating a multistep process with significant interactions between plastic components that lower their decomposition energy. While PP and LDPE decomposed through two distinct steps, the other polymers followed single-step pathways, and plastic mixtures exhibited three dominant, partially overlapping stages. Kinetic deconvolution analysis enhanced the accuracy of the models, allowing the contributions of individual steps to be resolved. These models successfully predicted experimental behavior under different heating rates and plastic compositions, providing insights into the complex thermal decomposition of mixed plastic. Mahapatra et al.[12] investigated the kinetics and batch pyrolysis behavior of multilayered waste milk packets with the aim of optimizing their conversion into valuable products. Thermogravimetric analysis was carried out at heating rates of 5, 10, 15, and 20°C/min, and the kinetics were evaluated using both model-free methods (Kissinger–Akahira–Sunose, Flynn–Wall–Ozawa, and Kissinger) and model-fitting approaches. The decomposition was best described by an F1 order-based mechanism, with an activation energy of 304 kJ/mol and a pre-exponential factor of 2.60×10^{12} min^{-1}. The highest weight loss (97.2%) was observed at a heating rate of 5°C/min. The calculated thermodynamic parameters included an average Gibbs free energy change of 814.939 kJ/mol, enthalpy change of 135.698 kJ/mol, and entropy change of -903.846×10^{-3} $kJK^{-1}mol^{-1}$. Batch pyrolysis experiments further showed that the maximum pyrolytic oil yield of 66.92% was achieved at 450°C.

Plastic waste management, particularly for multilayer plastics (MLPs), remains a major challenge, and only limited studies have reported on their decomposition mechanisms, product yields, and oil characterization. During MLP pyrolysis, the carryover of metal particulates and suspended carbon into the oil phase is a critical issue, as these impurities trigger side reactions and wax formation during storage and complicate hydroprocessing. To address these challenges, this study investigates the use of thermal densification of feedstock to achieve controlled decomposition and acid–base pretreatment to improve pyrolytic oil quality. The resulting fuels are characterized and benchmarked against those derived from other plastic wastes to evaluate their potential.

The novelty of this work lies in presenting a comprehensive kinetic and behavioral understanding of metallized MLPs, an especially complex and underexplored waste stream compared to conventional polymers. Unlike earlier reports focused on single-component plastics, this study establishes the three-dimensional diffusion model as the most appropriate descriptor of MLP decomposition, emphasizing the role of layered structures and polymer–metal interfaces. The higher activation energies highlight the thermal stability of MLPs, while pyrolysis coupled with extrusion-based densification reduces metal carryover, and subsequent chemical treatment with hydroprocessing produces a C_5–C_{18} hydrocarbon fraction enriched in paraffins and aromatics. Together, these steps demonstrate a scalable pathway for the sustainable valorization of MLP waste into fuel-grade hydrocarbons.

2. Materials and Methods

2.1. Material

The metallized multi-layered plastics (MLPs) sourced from Waste Ventures were subjected to mechanical preprocessing to facilitate subsequent thermal treatment. Initially, the MLPs were shredded into small fragments measuring approximately 2-4 mm using a plastic shredder, achieving a bulk density of 0.11 g/cc. This material was then densified using a batch extruder, operated at 80°C for 10 minutes, resulting in extrudates with an approximate density of 0.31 g/cc. This densification process is illustrated in **Fig. 1(b, c).**

2.2. Catalyst Materials and Preparation

The aluminosilicate zeolite catalyst utilized in the pyrolysis experiments was commercially sourced from Innova Engineer-

ing, featuring a silica-to-alumina (Si/Al) molar ratio of approximately 2:1. Prior to use, the catalyst underwent calcination at 550°C with a heating rate of 10°C/min for 4 hours, followed by cooling to ambient temperature. The elemental composition of the catalyst was characterized via Energy Dispersive X-ray Fluorescence (EDXRF), with detailed results provided in **Table S1**.

For the subsequent oil upgrading through hydrogenation, a nickel (Ni)-supported aluminosilicate catalyst was prepared using the wet impregnation method. In this process, a nickel nitrate ($Ni(NO_3)_2{\cdot}6H_2O$) solution was impregnated onto the aluminosilicate support (spent FCC, procured from MRPL), followed by drying and calcination steps to achieve the desired catalyst structure. The preparation details are comprehensively outlined in the study by Kathula et al.[13].

2.3. Feedstock Characterization Methods

The proximate analyses of metallized multi-layered plastics (MLPs) were conducted in accordance with ASTM standards: ASTM E790 for moisture content, ASTM E897 for volatile matter, and ASTM E830 for ash content. The ultimate analysis was performed using a LECO TruSpec Micro CHNS/O analyzer (Model 209-190), which provides precise measurements of carbon, hydrogen, nitrogen, sulfur, and oxygen in solid or liquid micro samples. Functional group identification in the MLP samples was carried out using Fourier Transform Infrared Spectroscopy (FTIR), following ASTM E168 and ASTM E1252 standards. This technique enables the identification of molecular species and functional groups within the sample. The elemental composition of metals present in the MLP samples was determined using Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES), in accordance with ASTM D5185 standards. All analyses were performed in triplicate, and the average values were reported to ensure the accuracy and reliability of the results.

2.4. Thermogravimetric Analysis

Seiko 220TG/DTA analyzer (Tokyo, Japan) was used to measure the thermal behavior of the MLP. Extruded MLP material was used for the TGA analysis wherein material was heated from 30°C to 800°C at a different heating rate (10, 30, and 50°C min^{-1}) under a controlled N_2 atmosphere with a flow rate of 50 mL min^{-1} to remove the oxidative gas present in the chamber. The baseline correction was performed for each sample using blank runs with an empty aluminum crucible. Additionally, in between sample analyses an oxidative condition (1000°C) was maintained to remove the trace material of the previous material.

2.4.1. Kinetics Estimation

To investigate the thermal decomposition behavior of metallized multi-layered plastics (MLPs) during pyrolysis at varying heating rates, it is essential to analyze the process kinetics and underlying mechanisms. Solid-state kinetic studies were conducted under isothermal conditions, as detailed by Munagala et al.[14]. Various linear and nonlinear isoconversional methods-including Starink, Kissinger-Akahira-Sunose (KAS), Flynn-Wall-Ozawa (FWO), Friedman, Budrugeac differential, and Vyazovkin integral approaches-were employed to estimate the activation energy across different conversion levels. These methods are widely recognized for their effectiveness in determining kinetic parameters in pyrolysis studies.

To elucidate the reaction mechanisms, several model-fitting approaches were applied, encompassing diffusion models, geometric contraction models, nucleation and growth models, and reaction order models. Additionally, the master plot and Popescu methods were utilized to estimate the kinetic triplets-comprising activation energy, pre-exponential factor, and reaction model function[15]. These comprehensive analyses provide a deeper understanding of the complex thermal degradation behavior of MLPs. Further details regarding the kinetic estimations are presented in **Section S1** of the supplementary information.

In this study, well-established isoconversional methods (Starink, KAS, FWO, Friedman, Budrugeac, and Vyazovkin) and model-fitting approaches (master plot and Popescu) were selected because they provide reliable activation energy estimates without assuming a fixed reaction order, making them suitable for the heterogeneous and multi-component nature of MLPs. These models are widely benchmarked in polymer pyrolysis studies, allowing direct comparison with conventional plastics reported in the literature. While more advanced approaches such as distributed activation energy models (DAEM) or data-driven methods could further refine the analysis, the chosen models offer a robust and reproducible mechanistic baseline that is both experimentally tractable and consistent with the scope of this work.

2.5. Pyrolysis Experiments

Pyrolysis experiments were conducted in a vertical fixed-bed reactor operating in batch mode, as previously detailed by Munagala et al.[14]. To determine the optimal conditions for maximizing oil yield from metallized multi-layered plastics (MLPs), the experiments were performed at three different temperatures: 400°C, 500°C, and 600°C, both with and without the addition of a catalyst. Prior to the pyrolysis process, MLP films were densified to a bulk density of 0.31 g/cm^3 and introduced into the reactor from the top. This densification step was crucial in minimizing the entrainment of metal particulates into the vapor phase during pyrolysis. In experiments involving a catalyst, a catalyst-to-feedstock ratio of 1:20 was maintained. The system was heated to the target temperature over a period of 20 minutes, followed by a 120-minute pyrolysis reaction time. These experimental parameters were selected to assess the influence of temperature and catalytic presence on the pyrolysis behavior and oil yield of MLPs.

2.6. Upgradation of Pyrolytic Oil

The pyrolytic oil (PO) derived from metallized multi-layered plastic (MLP) pyrolysis underwent a two-step upgrading process to enhance its physicochemical properties and suitability as a fuel.

(a) Acid-Base Pretreatment

Initially, the PO contained finely dispersed carbon particles, which were removed through chemical treatment. The oil was treated with 5 wt.% sulfuric acid (H_2SO_4) relative to the PO mass and stirred for 30 minutes. After settling, the mixture separated into layers, allowing for the removal of the carbon-rich sludge. Subsequently, the oil layer underwent neutralization via the dropwise addition of a base (3–5 wt.% of the oil mass) until the color changed from dark brown to pale yellow, indicating the reduction of residual impurities.

(b) Hydro-Processing

The pretreated oil was then subjected to hydro-process-

ing in a 100 mL high-pressure autoclave reactor (Amar Equipment Pvt. Ltd., India). The reactor was purged with hydrogen to eliminate any oxidative environment after loading the PO and catalyst. A modified fluid catalytic cracking (FCC) catalyst, doped with 10% nickel, was used at a catalyst-to-oil mass ratio of 1:10. The reactor conditions were maintained at 240°C and 70 bar pressure for 6 hours under continuous stirring at 350 rpm. These conditions were selected based on previously optimized parameters to facilitate effective hydro-processing and improve the quality of the resulting hydro-processed oil (HPO)[7]. This comprehensive treatment approach effectively upgraded the PO, enhancing its thermal stability and fuel properties.

2.7. Product Characterization

The PO and non-condensable gases analysis was carried out through GC–MS, Agilent 6850 GC (coupled with an Agilent 7890 MS) and Agilent 7890A GC, respectively, and details reported in our previous work[14]. The physicochemical properties of the pyrolysis fuel oil obtained were estimated by following the ASTM methods.

2.8. Techno-Economic Assessment

The economic assessment is to assess the competence of the plastic pyrolysis plant, which can generate profit before its applicability to the actual market. For carrying out economic analysis, the percentage of delivered equipment cost method is selected, and the detailed procedure is discussed in the following section. Furthermore, breakeven analysis is carried out to determine the payback period for a given process plant and to determine the economic viability of the proposed project. The economic assessment at 1 ton per day is carried out, and its effect on the net profit, rate of return, and the payback period is analyzed.

3. Result and Discussion

3.1. Physicochemical Characterization

The proximate and ultimate analyses of metallized multi-layered plastics (MLPs) were conducted and compared with those of other common plastics, as summarized in **Table 1**. The results indicate that MLPs contain higher fixed carbon (FC) content (2.78%) and ash content (1.01%) compared to their constituent precursors such as polyethylene (PE), polypropylene (PP), and polyethylene terephthalate (PET), etc. These characteristics suggest that MLPs are more likely to produce solid residues (char) during pyrolysis, as opposed to plastics with higher volatile matter (VM) and lower ash content, which tend to yield higher liquid oil fractions.

The presence of fillers and additives in MLPs contributes to their higher ash content and lower-quality fuel oil with reduced calorific value. Densification of MLPs enhances the pyrolysis mechanism, improving product quality and yields. Without densification and catalyst use during pyrolysis, wax formation occurs over time, attributed to the presence of higher hydrocarbons and metal traces in the pyrolytic oil (PO). Although the catalyst did not significantly increase overall oil yield, it played a key role in improving product quality. The complex composition of MLPs, including aluminum layers and adhesives, limits catalyst–polymer interactions, reducing its apparent activity compared to single-polymer systems. However, the catalyst improved oil stability, lowered heteroatom content, and shifted hydrocarbons toward lighter C_5–C_{18} fractions, demonstrating qualitative rather than quantitative benefits.

The higher heating value (HHV) of MLPs was estimated to be 35.67 MJ/kg, which is lower than that of PE and PP (48.74 MJ/kg) but higher than that of PET (31.11 MJ/kg) and polyurethane (PU) (29.86 MJ/kg). These findings underscore the potential of MLPs as a feedstock for fuel oil production, with appropriate processing to mitigate challenges associated with their composition.

The ultimate analysis of metallized multi-layered plastics (MLPs) reveals a significant carbon content of 66.51%, underscoring their potential as a viable feedstock for pyrolytic conversion into fuel oil. Notably, the nitrogen and sulfur contents are relatively low, at 0.27 wt.% and 0.072 wt.% respectively, suggesting that subsequent thermal processing would result in minimal emissions of nitrogen oxides (NO_x) and sulfur dioxide (SO_2), thereby reducing environmental pollutants.

Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) analysis tabulated below in **Table 2** indicates the presence of various metals within the MLP samples, with sodium (Na), calcium (Ca), and aluminum (Al) being predominant. These elements are commonly introduced during the manufacturing process of MLPs, serving as fillers and flame retardants to enhance material properties such as thermal stability and barrier performance. For instance, aluminum comes from the metal layer or the compounds like aluminum hydroxide are widely used as flame retardants due to their ability to act as heat sinks and form protective char layers during combustion. The presence of sodium and barium are attributed to their application in food packaging materials to enhance various properties like strength, opacity, and resistance to chemicals and heat. The enhancement in the levels of sodium and barium can be explained by the reduction of the overall mass of the sample, but the composition of these elements remained same.

Table 1. Proximate, Ultimate Analysis and Calorific value of MLPs and other plastics

Sample	C (%)	H (%)	N (%)	S (%)	O (%)	Moisture (%)	Ash (%)	VM (%)	FC (%)	HHV (MJ/Kg)	LHV (MJ/Kg)
PP	84.98	13.91	0.99	0.02	0.08	0.4	1.06	98.54	0	45.43	42.44
PET	64.22	4.65	0.05	0.55	30.53	0	0	88.61	11.39	31.11	30.09
LDPE	83	16.75	0	0.25	0	0.199	0.148	99.653	0	48.74	45.08
PU	62.69	6.32	6.37	0.63	24.01	0	6.2	83.2	10.6	31.47	29.86
HDPE	83.29	13.93	0.2	0.07	2.51	0	0.08	99.92	0	45.75	42.72
PE	85.81	13.86	0.12	0.06	0	0.02	0.15	99.85	0	46.29	43.27
PS	89.1	8.02	0.22	0.01	2.65	0.21	0	99.3	0.59	40.83	39.08
MPW	82.33	13.92	2.71	0.33	0.67	15.9	9.8	74.2	0.1	41.12	38.51
MLP	72.76	10.05	0.29	0.07	16.8	1.12	1.01	95.08	2.78	35.67	33.66

Table 2. ICPOES analysis of the MLP and its pyrolyzed char.

(PPM)	AL	Ba	Ca	K	Mg	Na	Si	Pb	Ti
MLP	3.43	0.2167	10.13	1.74	2.54	20.87	4.49	BD	0.062
MLP Char	1632	47.56	98.18	34.87	87.49	140.9	BD	1.37	1.93

Fourier Transform Infrared (FTIR) spectroscopy was employed to analyze the polymer composition of metallized multi-layered plastics (MLPs) compared with its constituent layers present in **Table S4**. Key peaks confirmed the presence of multiple polymers. Peaks at 1376, 1455, and 2875 cm^{-1} indicated methyl and C–H vibrations characteristic of polypropylene (PP). A strong absorption at 1711 cm^{-1} and additional bands at 1407, 870, and 721 cm^{-1} identified polyethylene terephthalate (PET). LDPE was suggested by CH_2 bending peaks in the 1400–1330 cm^{-1} range, while distinct peaks at 2955, 905, and 730 cm^{-1} confirmed HDPE. Polystyrene (PS) was identified through aromatic C–H bending at 1082 and 875 cm^{-1}. Peaks at 2280 and 1729 cm^{-1}, corresponding to isocyanate and carbonyl stretching, indicated the presence of polyurethane (PU). The detection of these diverse polymers highlights the complex, co-extruded nature of MLPs, compounded by adhesives and additives. This heterogeneity underscores the recycling challenges and the need for advanced characterization methods for effective material recovery.

3.2. Thermogravimetric Analysis

The thermal decomposition behavior of metallized multi-layered plastics (MLPs) was investigated using thermogravimetric analysis (TGA) and differential thermogravimetric (DTG) analysis under a nitrogen atmosphere at heating rates of 10, 30, and 50°C min^{-1}. The TGA curves (**Fig. 2 (a)**) revealed an overall weight loss ranging from 83% to 90%, indicating substantial thermal degradation parameters reported in **Table 3**. DTG analysis identified three distinct decomposition stages, as plotted in **Fig. 2 (b)**

It is observed that the decomposition characteristics at 30°C/min differ from those observed at 10°C/min and 50°C/min. At lower heating rates (10°C/min), heat transfer is uniform and decomposition proceeds gradually, allowing sufficient time for volatile species to evolve without significant secondary reactions. At higher heating rates (50°C/min), decomposition is dominated by rapid volatilization and diffusion-limited mass transfer, leading to sharp weight loss and a high decomposition rate. In contrast, at the intermediate heating rate (30°C/min), partial overlap of primary polymer degradation and secondary vapor–solid interactions, resulting in elevated maximum decomposition temperatures and higher decomposition rates. This effect is amplified in MLPs due to their heterogeneous polymer-metal interfaces, which create localized thermal lag and uneven volatilization compared to single-polymer plastics.

Initial Stage (40–200°C): Minimal weight loss occurred, primarily due to the moisture removal without significant decomposition. Intermediate Stage (200-390°C): A gradual decomposition was observed, attributed to the breakdown of organic components within the layers. Main Decomposition Stage (390-500°C): This phase exhibited the highest mass loss, corresponding to the volatilization, thermal cracking, and vaporization of polymer constituents. Final Stage (500-700°C): A slower decomposition rate was noted, associated with char formation and the degradation of more stable components.

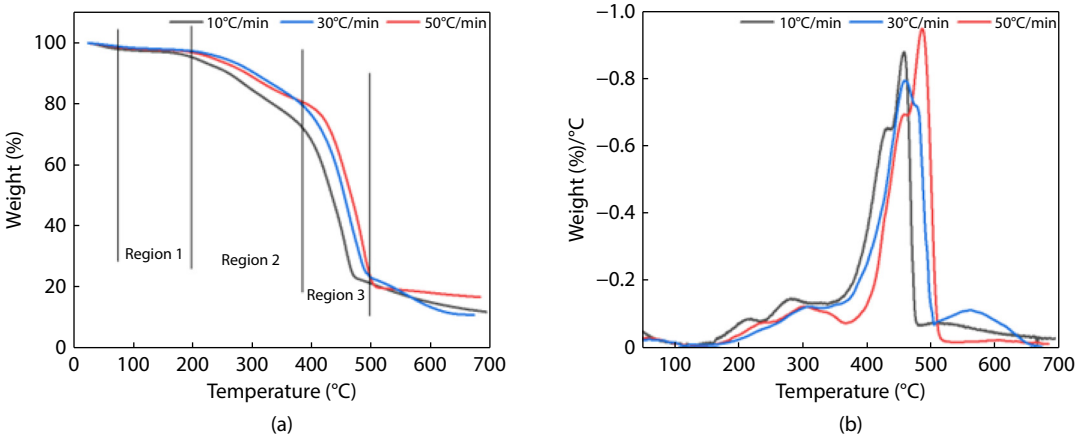

Fig. 2. (a) TGA and (b) DTG curves of MLP at different heating rates, 10°C/min, 30°C/min, and 50°C/min

Table 3. Pyrolysis characteristics for MLP at different heating rates

Pyrolysis Parameters	10 (°C/min)	30 (°C/min)	50 (°C/min)
Initial decomposition temperature, T_i (°C)	373.12	400.45	380.33
Temperature at max rate of decomposition, T_m (°C)	457.10	486.63	459.21
final decomposition temperature, T_f (°C)	474.78	509.61	500.96
Max rate of decomposition, R_{max} (%/min)	21.58	28.02	171.46
Temperature at which R_d/R_{max}=0.5, $T_{1/2}$ (°C)	59.50	65.85	70.10
Devolatilization index, D_i (% min^{-1} $°C^{-3}$)	2.13E^{-6}	2.19E^{-6}	1.4E^{-5}
Final percentage of mass remaining, M_f (%)	11.84	16.73	10.88

The peak decomposition temperatures, as indicated by DTG curves, were 457.10°C, 459.21°C, and 486.63°C, for heating rates of 10, 30, and 50°C min^{-1}, respectively. An increase in heating rate led to higher maximum decomposition rates, with the highest rate of 171.46% min^{-1} observed at 50°C min^{-1}. These findings suggest that a pyrolysis temperature range of 400-600°C is optimal for maximizing fuel oil yield from MLPs.

3.2.1. Estimation of kinetic triplets

The energy required for the thermal decomposition of metallized multi-layered plastics (MLPs) was assessed by determining the activation energy (E) using various isoconversional methods. These methods estimate E across different degrees of conversion (α), providing insights into the decomposition kinetic. **Table 4** reports activation energy for linear isoconversional methods and nonlinear isoconversional methods.

These methods yielded nearly parallel fitting lines, indicating consistent activation energy values across the main reaction zone (α = 0.3 to 0.8). The variation in activation energy values among these methods reflects the complex decomposition behavior of MLPs, influenced by their heterogeneous composition and layered structure. The consistency of results across different methods enhances the reliability of the kinetic analysis. These results were compared with activation energies reported for individual polymers: High-Density Polyethylene (HDPE): 177.58–197.35 kJ/mol; Low-Density Polyethylene (LDPE): 215–229 kJ/mol; Polypropylene (PP): 199–250 kJ/mol; Polystyrene (PS): 170–190 kJ/mol; Polyurethane (PU): 119–176 kJ/mol; Polyamide (PA): 111–276 kJ/mol; Polyethylene Terephthalate (PET): 145–218 kJ/mol. The activation energy for MLPs falls within the range of these polymers, reflecting the composite nature of MLPs. Notably, the activation energy for MLPs increases with the degree of conversion, as depicted in Fig. 3(a), suggesting a complex, multi-step decomposition process.

The decomposition mechanism of metallized multilayer plastics (MLPs) was investigated using the Popescu method across three temperature regions: (a) 200–300°C, (b) 300–400°C, and (c) 400–500°C. In the first region (200–300°C), the D3 and D4 diffusion models exhibited high correlation coefficients (R^2) and near-zero intercepts, indicating a good fit. However, in regions (b) and (c), none of the tested mechanisms achieved R^2 values above 0.9, suggesting that the Popescu method is less effective at higher temperatures, to further elucidate the decomposition behavior, the master plot method was employed (**Fig. 3**) The analysis revealed that MLP pyrolysis aligns closely with the D4 diffusion model in the conversion range of 0.1–0.5, transitions to the D2 model between 0.5–0.65, and approximates the D1 model from 0.65–0.8. These findings suggest that the overall pyrolysis process of MLPs is governed by diffusion-controlled mechanisms, likely due to their complex, layered structure which impedes mass transfer and leads to sequential layer-by-layer degradation.

Table 4. Summary of linear and nonlinear Iso-conversional methods free methods

Method	Expression	Activation Energy (kJ/mol)	Pre exponential factor (1/min)
Starink	$\ln\left(\frac{\beta}{T^{1.92}}\right) = \ln\left(\frac{AR}{E_a g(\alpha)}\right) - \frac{E_a}{RT}$	183.47	1.46×10^{12}
KAS	$\ln\left(\frac{\beta}{T^{2}}\right) = \ln\left(\frac{AR}{E_\alpha g(\alpha)}\right) - \frac{E_\alpha}{RT}$	182.99	1.33×10^{12}
FWO	$\ln(\beta) = \left(\frac{\ln AE_\alpha}{Rg(\alpha)}\right) - 5.335 - \frac{1.0516E_\alpha}{RT}$	185.31	1.92×10^{12}
Friedmann	$\ln\left(\beta_i\left(\frac{d\alpha}{dT}\right)_{\alpha,i}\right) = \ln(A_\alpha f(\alpha)) - \frac{E_\alpha}{RT_{\alpha,i}}$	218.42	7.78×10^{14}
Differential (Budrugeac)	$\sum_{i=1}^{n}\sum_{j\neq i}^{n}\frac{\beta_i\left(\frac{d\alpha}{dT}\right)_i\left[\exp\left(\frac{E_\alpha}{RT_i}\right)\right]}{\beta_j\left(\frac{d\alpha}{dT}\right)_j\left[\exp\left(\frac{E_\alpha}{RT_j}\right)\right]} - n(n-1)$	177.41	5.88×10^{11}
Integral (Vyazovkin)	$\sum_{i=1}^{n}\sum_{j\neq i}^{n}\frac{\beta_j I(E_\alpha, T_i(t_\alpha))}{\beta_i I(E_\alpha, T_j(t_\alpha))} - n(n-1)$	218.40	7.78×10^{14}

Where n is the number of heating rates at which TGA experiment has been performed.

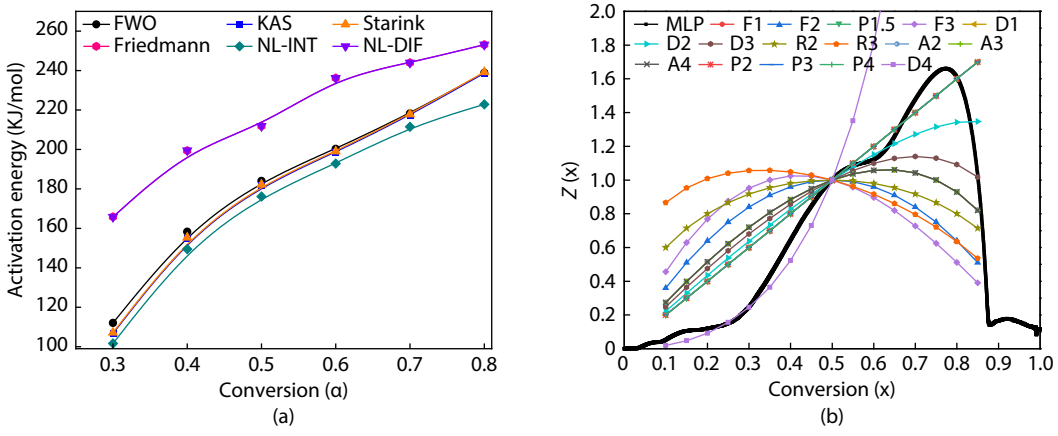

Fig. 3. (a) Variation in Activation energy and (b) Master plots for investigation of reaction mechanism and with conversion for different methods

Compensation parameters were calculated (as detailed in **Section S1.1**), confirming that the D4 model aptly describes the kinetics of MLP pyrolysis within the conversion range of 0.3 to 0.8. The pre-exponential factors (A) for the D4 mechanism, derived using average activation energies from various isoconversional methods are reported in **Table 4** these kinetic parameters reinforce the conclusion that MLP pyrolysis is predominantly governed by diffusion-controlled mechanisms, particularly the D4 model, across a significant portion of the conversion range.

It is important to note that the linearity of the kinetic fitting plots (Fig. S1) appears less ideal compared to single-polymer systems. This effect arises from the heterogeneous composition of MLPs, where multiple polymers, fillers, and metallized layers decompose over slightly different temperature windows, causing overlap and minor scatter in the isoconversional plots. Nevertheless, within the main conversion region (α = 0.3–0.8), the correlation coefficients (R^2 = 0.997–0.998 for D1, D2, and D4 models) indicate statistically reliable fits. Moreover, validation against experimental data (Fig. S3) confirmed that the diffusion-controlled Ginstling–Brounshtein model accurately reproduces the decomposition profile, supporting the robustness of the kinetic triplets despite apparent deviations in linearity.

3.2.2. Model Development and Validation

The kinetic triplets-activation energy (E), pre-exponential factor (A), and reaction order (n)-for the pyrolysis of metallized multilayer plastics (MLPs) were validated by numerically solving the governing differential equation using MATLAB's ODE45 solver, which is based on the adaptive Runge-Kutta 4th-order method. The conversion rate (α) of MLPs during pyrolysis is described by the following equation:

$$\frac{d\alpha}{dt} = Ae^{\frac{-E}{RT}} \times \frac{3}{2}\left[\left((1-\alpha)^{-\frac{1}{3}} - 1\right)^{-1}\right] \quad (1)$$

This expression corresponds to the D4 diffusion-controlled reaction mechanism. For the accuracy of model parameters, the simulation results were compared with experimental data across different heating rates, as illustrated in **Fig. S3**. At a heating rate of 50°C/min, the simulated conversion closely matched the experimental observations within the conversion range of 0.3 to 0.8, exhibiting errors less than 3% for differential methods and less than 2% for integral methods. However, at heating rates of 10°C/min and 30°C/min, larger discrepancies were noted, with integral methods maintaining errors below 5%. These findings indicate that the D4 diffusion model, when applied with the derived kinetic parameters, effectively predicts the pyrolysis behavior of MLPs, particularly at higher heating rates. The model's accuracy diminishes at lower heating rates, suggesting the need for further refinement or alternative modeling approaches under those conditions.

In validation of the developed models of MLP pyrolysis, kinetic analysis revealed that the decomposition behavior conforms primarily to the Ginstling–Brounshtein (D4) diffusion model, with a gradual D4→D2→D1 transition observed across the conversion range. This model transition is closely linked to the layered structure and sequential degradation behavior of MLP components. At lower conversion levels (α = 0.3–0.5), the dominance of the D4 model corresponds to the initial decomposition of the outer polyolefin (PE/PP) layers, where the intact multilayer configuration restricts volatilization, resulting in diffusion-controlled mass transport across the polymer–metal interfaces. As degradation progresses, the exposure and partial breakdown of intermediate layers reduce diffusion resistance, leading to a transition toward the D2 (two-dimensional diffusion) regime. Beyond α > 0.65, the D1 (one-dimensional diffusion) model becomes dominant, representing the late-stage decomposition of the inner PET and metal foil layers, where the structural collapse and increased pore formation facilitate simpler gaseous diffusion pathways. The main weight loss between 390–500°C can be attributed to the degradation of polyolefins, while the residual decomposition between 500–700°C is associated with PET degradation and metal-layer stabilization. This correlation between layered structure evolution, diffusion pathway transformation, and model fitting provides a mechanistic basis for understanding the complex degradation kinetics of MLPs[14,15].

3.3. Pyrolysis product yield

The pyrolysis of metallized multilayer plastics (MLPs) under inert conditions, both with and without catalysts, across various temperatures (400°C, 500°C, and 600°C), has demonstrated lower pyrolysis oil (PO) yields compared to single-polymer plastics such as polypropylene (PP), low-density polyethylene (LDPE), high-density polyethylene (HDPE), polyethylene terephthalate (PET), polyurethane (PU), and polyamide (PA) (**Fig.4**). This disparity is primarily attributed to the complex, layered structure of MLPs, which includes diverse polymers,

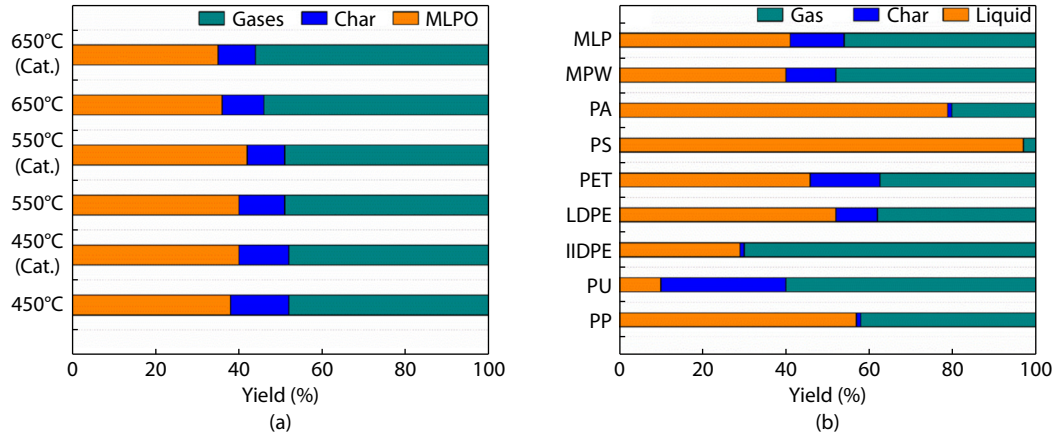

Fig. 4. Comparison of Yields of (a) MLP pyrolysis with and without catalyst (b) Different plastics waste

fillers, and additives that hinder efficient thermal degradation.

Introducing a catalyst, such as zeolite, during the pyrolysis of MLPs enhances the PO yield, achieving up to 42%, compared to a lower yield of 24% observed in non-catalytic processes. In contrast, single-polymer plastics exhibit significantly higher PO yields under similar conditions. For instance, PP can yield approximately 57% at 400°C[7]. LDPE bags have been reported to produce oil yields as high as 52% at 500°C when catalyzed with zeolite[6]. HDPE and polystyrene (PS) also demonstrate high oil yields, with HDPE and PS achieving up to >70% at 500°C[8]. In the case of MLPs, the presence of catalysts tends to stabilize char yield across varying temperatures due to the inherent metals, fillers, and additives in the material. However, increasing the pyrolysis temperature leads to a decrease in oil yield and an increase in non-condensable gas production. This is attributed to more intense cracking and secondary decomposition of pyrolysis vapors at higher temperatures, particularly around 600°C. Interestingly, at a constant temperature, non-catalytic processes may yield higher PO than catalytic ones, as catalysts can promote cracking that favors gas formation over liquid products.

Although the overall oil yield from catalytic pyrolysis of multilayer plastics (MLPs) showed only modest improvement over the non-catalytic process, zeolite addition primarily enhanced product quality rather than yield. The zeolite catalyst (Si/Al = 2:1) promoted hydrocracking, cyclization, and hydrogen transfer reactions, leading to a higher paraffin fraction (17.77% - 33.87%) and reduced oxygenates (43.36% - 40.79%) (Table 6). This reflects the stronger Brønsted acidity of low Si/Al ratio zeolites, which favor β-scission and hydrogenation pathways that enhance paraffin formation while suppressing aromatic condensation[22,23]. The limited yield improvement is attributed to MLP heterogeneity-fillers, adhesives, and metal layers partially neutralize catalytic sites and restrict polymer-catalyst interaction. Nevertheless, the catalyst stabilized char production and shifted product composition toward fuel-relevant fractions. Literature further suggests that lower catalyst dosages (e.g., 1:10) yield more aromatics due to reduced cracking intensity, whereas higher dosages (⩾1:20) increase hydrogen transfer and paraffin selectivity[13, 24]. Thus, while catalytic pyrolysis of MLPs is less yield-sensitive, it is highly effective in steering product composition, emphasizing zeolite's role in improving the quality and suitability of derived fuel oils, hence the zeolite with Si/Al 2:1 is considered with dosage of 1:20 in this study.

Therefore, while catalysts can enhance the quality of the pyrolysis oil by increasing the production of desirable compounds, they may also reduce the overall oil yield. Consequently, evaluating the effectiveness of pyrolysis processes should consider not only the quantity of oil produced but also its quality. Further characterization of the PO and char obtained at 500°C is essential to comprehensively understand their properties and potential applications. The obtained PO was further hydro-processed, and the results are discussed in the subsequent session.

3.4. Product Characterization

3.4.1. Pyrolytic Oil Characterization

The physicochemical properties of the product obtained are reported in **Table 5**. The C content in oil was found to be 72.7% and 76.56% for non-catalytic and catalytic oil processes, and it was lower than that of PP (83.74%)[7] and LDPE (89.44%), while higher than PET (64.22%) and Mixed Plastic waste (MPW) (72.7%). The HPO enhanced the C content to 86.96%. The H and N content in the CPO was found to be 10.70% and 0.24%, respectively, with a minimum amount of sulfur content of 0.075%. Similar behavior was observed in the HPO. The Cl content is found to be 0.9% in PO and reduced to 0.43% in CPO and not detected in HPO. A significant reduction in O content was observed after the hydro-processing. The density of crude pyrolysis oil (PO) was measured as 0.7965 g/cm^3, which further decreased to 0.784 g/cm^3 upon hydro-processing. This value is slightly higher than that of polypropylene-derived oil (0.775 g/cm^3) but lower than commercial diesel (0.835 g/cm^3), indicating that hydro-processed pyrolysis oil (HPO) falls within a workable range, though still marginally lighter than the EN 590 and ASTM D975 diesel density specification of 0.820–0.845 g/cm^3 and pyrolytic oil obtained from LDPE, HDPE, MPW, PS and PS. The S content in ultimate analysis was

Table 5. Physiochemical Properties of the fuel oil and its comparison with others.

Parameters	MLP PO	MLP CPO	MLP-HPO	PP[6]	HPPO[7]	LDPE[7]	HDPE[5]	PS[6]	MPW[16]	Diesel[7]	EN 590	ASTM D975
Density (kg/m3)	836	796.5	784	775.2	855	798.5	814	940.5	930.9	835	820–845	820–860
K Viscosity cSt	2.1	1.89	1.03	1.82	3.90	4.98	1.89	1.83	3.20	3.02	2.0–4.5	1.9–4.1
Pour Point°C	6	−3	−4	−30	−25	+ 26	−8	< −30	-	−20	−5 to −15	−12 to −15
Flash Point°C	32	10	10	30	78	20	57.5	32	34	80	⩾55	⩾52
Fire Point°C	35	15	14	55	80	30	62.7	42		82		
HHV (MJ/Kg)	37.41	39.66	45.14	40.80	42.36	48.14	46.31	38.86	44.75	42.04	~42.0	~42.0
Water Content (mg/kg)	148	81	62	80	75	-	-	-	-	200	200	
Carbon Residue (%)	0.10	0.10	0.01	0.10	0.10	0.06	1.88	1.38	0.27	0.18	0.30	
Sulphur Content (%)	0.01	0.0075	0.005	0	0	-	0	0.102	0.178	0.002	⩽0.001	⩽0.0015
Chlorine Content (%)	0.90	0.43	-	-	-	-	0	-	-	0.06		
Ash Content (%)	0.10	0.092	0.058	0.01	0.01	0.01	-	0.01	-	0.01	0.01	
C (%)	72.7	76.56	86.96	82.49	81.46	74.88	84.97	81.34	21.40	90.06		
H (%)	8.19	10.70	12.71	14.31	14.74	12.36	14.49	7.79	1.96	9.72		
N (%)	0.30	0.24	0.09	1.31	1.01	0.45	0.27	0.38	0.08	0.0681		
S (%)	0.072	0.075	0.05	-	-	-	-	-	0.38	0.0398		
O (%)	12.3	5.48	0.19	1.87	0.36	12.29	0.27	10.50	12.34	0.2560		

reduced through the catalytic process and was found to be less than 0.1%. Higher S content was found in the pyrolytic oil derived from PS and MLP waste.

The kinematic viscosities of crude pyrolysis oil (CPO) and hydroprocessed oil (HPO) were measured 1.89 cSt and 1.03 cSt, respectively, both lower than that of other plastic-derived oils such as those from mixed plastic waste (MPW), high-density polyethylene (HDPE), and low-density polyethylene (LDPE). With respect to calorific value, the higher heating values (HHVs) of CPO and HPO are lower than those of most plastic-derived oils; however, the HHV of HPO exceeds that of polypropylene, mixed plastic waste (MPW), and even diesel, though it remains lower than LDPE and HDPE derived oils. In terms of flash point, CPO exhibited a much lower value than diesel, consistent with previous reports for unrefined pyrolysis oils.

After hydro-processing, the flash point significantly increased, meeting the EN 590 requirement of ⩾55°C and aligning with ASTM D975 standards, thereby ensuring safe storage, handling, and transportation. This enhancement not only mitigates fire hazards but also positions HPO closer to diesel-grade fuels in terms of compliance with international standards for density, calorific value, and flash point, demonstrating its potential as a sustainable diesel substitute.

The pH values of CPO and hydroprocessed oil (HPO) were measured at 4.69 and 6.00, respectively, indicating their acidic nature. GC–MS analysis of PO obtained with and without a catalyst at temperatures ranging from 400°C to 600°C revealed significant compositional changes as shown in **Table 6**. At 400°C without a catalyst, the oil contained 33.9% olefins and 43.36% oxygenated compounds. Catalytic pyrolysis reduced olefins to 23.74% and decreased aromatic content to 1.78%.

Increasing the pyrolysis temperature to 500°C without a catalyst resulted in a reduction of olefins to 26.49% and oxygenated compounds to 30.5%, with an increase in paraffins to 33.85% and aromatics to 9.1%. With catalytic pyrolysis at the same temperature, aromatic content significantly increased to 21.38%, attributed to hydrocracking, hydro-isomerization, cyclization, and hydro-aromatization processes. At 600°C with a catalyst, aromatic content decreased to 4.71% due to further cracking leading to non-condensable gas formation, as evidenced by the reduced oil yield. Therefore, 500°C was identified as the optimal pyrolysis temperature, with subsequent hydrogenation enhancing the oil's quality.

The hydro-processing of the CPO at 500°C enables the increase in paraffin content to 45.72% and lowers the olefins to 15.01%. The increase in the aromatic (37.80%) content with a significant decrease in oxygenated (1.47%) compounds due to the hydrodeoxygenation makes this fuel similar to that obtained through PP pyrolysis. The composition analysis is also confirmed through NMR analysis (**Section S2**). The GCMS analysis in terms of carbon range for the obtained oil with and without catalyst at different temperatures is also reported in **Table 6.** The CPO at 500°C contains 52.59% C_5–C_{12} range, 33.59 wt.% in the C_{13}-C_{18} range, and 7.04 wt.% in the C_{19}-C_{40} range. The hydro-processing enhanced the content to 75.86% in C_5–C_{12} while C_{13}-C_{18} range, and C_{19}-C_{40} was found to be 21.69% and 3.65%, respectively. This result clearly shows that the major fraction in hydro-processed oil is C_5–C_{12} range.

3.4.2. Pyrolytic gas analysis

At a pyrolysis temperature of 500°C, the non-condensable gas produced exhibits the following composition by volume of 27.80% H_2, 19.89% CH_4, 0.92% CO, 11.32% CO_2, 16.91% Ethylene, and 12.56% Ethane. This gas mixture is notably rich in hydrogen, contributing to a high heating value (HHV) of 18.08 MJ/Nm^3. Such a composition makes it a valuable energy source, suitable for combustion processes that generate heat for applications like liquid fuel production. Utilizing this pyrolytic gas to supply process heat can enhance the overall energy efficiency of the system.

3.4.3. Pyrolysis char characterization

The ultimate analysis of char produced from multilayer plastic (MLP) pyrolysis at varying temperatures indicates a notable increase in carbon content compared to the original MLP feedstock, as shown in **Table 7,** highlighting its carbon-rich nature. Comparative analysis between MLP and the resulting char reveals significant variations in carbon and oxygen contents, while hydrogen, nitrogen, and sulfur levels exhibit minimal changes. This pattern implies that pyrolysis effectively expels oxygen and volatile components from MLP, thereby increasing the fixed carbon proportion in the char.

Proximate analysis of char obtained at 500°C demonstrates a volatile matter (VM) content of 12.25%, a high fixed car-

Table 6. Compositional and fractionation of the MLP oils and comparison with other plastics fuel oil.

Fuel oil precursor With temp.	Paraffins	Olefins	Aromatics	Others/Oxygenates	Gasoline (C_5-C_{12})	Light Diesel (C_{13}-C_{18})	Heavy Diesel (C_{19}-C_{40})	Ref.
PP-460°C	30	40	28	2	92.89	7.01	0.1	[5]
PU-550°C	-	2	14	84	36.93	54.93	8.13	[17]
HDPE-460°C	82.11	6.4	11.49	-	56.55	37.79	5.66	[5]
LDPE-450°C	36	42	22	-	92.04	7.95	0.01	[18]
PET-600°C	20	16	41	23	90.4	6.95	2.65	[19]
PS-550°C	39.8	41.1	-	19.1	24	69	6	[20]
MPW-450°C	55	23	22	-	99.13	0.87	0	[18]
MLPPO-400°C	17.77	33.9	4.98	43.36	55.38	35.14	8.98	Present Study
MLPCPO-400°C	33.87	23.74	1.78	40.79	50.82	37.59	11.77	Present Study
MLPPO-500°C	33.85	26.49	9.19	30.5	45.62	35.66	18.74	Present Study
MLPCPO-500°C	27.87	23.12	21.38	27.17	52.59	33.59	7.04	Present Study
MLPPO-600°C	10.56	15.15	22.34	51.95	37.53	47.64	13.24	Present Study
MLPCPO-600°C	33.46	47.18	4.71	14.63	28.24	37.23	34.52	Present Study
MLPHPO	45.72	15.01	37.80	1.47	75.86	21.69	3.65	Present Study

bon (FC) content of 63.57%, and an ash content of 23.88%. These values align with typical trends observed in biochar production, where elevated pyrolysis temperatures lead to decreased volatile matter and increased fixed carbon and ash contents.

Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) analysis confirms the presence of inherent metallic elements in the char, including aluminum (Al), barium (Ba), calcium (Ca), potassium (K), magnesium (Mg), sodium (Na), silicon (Si), lead (Pb), and titanium (Ti). The densification process of MLP prior to pyrolysis appears to mitigate the transfer of these metals into the pyrolytic oil, concentrating them within the char residue.

Furthermore, the char exhibits an alkaline nature, with a pH ranging between 8 and 9. This alkalinity is attributed to the reduction of organic content during pyrolysis, which is consistent with observations in biochar studies where increased pyrolysis temperatures result in higher pH values due to the concentration of basic mineral components.

The inherent metal content of MLPs, as analyzed through OCP OES analysis (**Table 2**), such as Al, Ca, Na, Ba, and Pb, is predominantly retained in the char by densification and pyrolysis rather than in the oil fraction, thereby minimizing the direct impact of metals on fuel quality. The immobilization of metals, as a result of densification, reduces the risk of fuel contamination; direct disposal of char could lead to leaching of toxic metals if not managed properly. The high fixed carbon (63.6%) and alkaline nature (pH 8-9) of the char suggest potential for beneficial reuse as an adsorbent, catalyst support, or supplementary fuel in cement kilns. To ensure environmental safety, stabilization strategies such as vitrification, incorporation into construction composites, or controlled recovery of metals may be required, thereby aligning char management, and for the non-condensable gases present, trade-offs between risks and opportunities for reuse. The gaseous byproducts, rich in H_2 and light hydrocarbons, exhibit a HHV (~18 MJ/Nm^3) and can be used as an internal process fuel, reducing the load of external energy demand. Therefore, appropriate management strategies are essential to transform these byproducts from environmental liabilities into valuable co-products, aligning the process with sustainability goals.

Though this study includes significant characterisation data, its objective was not confined to publishing parameter values, but also to establishing the underlying kinetic and behavioural principles that control MLP disintegration. The study demonstrated that the thermal degradation of metallised multilayer polymers occurs via a three-stage diffusion-controlled pathway best represented by the Ginstling-Brounshtein model. This isoconversional model fit demonstrates the influence of multilayer polymer-metal interfaces on heat and mass transmission, which contrasts with conventional plastics. Furthermore, integrating densification and chemical treatment stages results in a technological breakthrough in tackling MLPW-specific issues (metal entrainment, viscosity, and oil quality).

3.5. Techno-Economic Assessment

3.5.1. Total Capital Investment (TCI)

The total capital investment (TCI) for the plant comprises the fixed capital investment (FCI) and the working capital investment (WCI). The FCI is divided into two categories: direct and indirect costs. Direct costs include purchased equipment, installation, instrumentation and controls, piping, buildings, yard improvements, service facilities, land, and electrical systems. Indirect costs cover know-how and technology fees, engineering and supervision, construction expenses, contractor fees, legal charges, contingencies, and start-up costs. Since many of these components are difficult to estimate precisely, their values were chosen from established ranges reported in the literature (Munagala et al.,[14]; Razak et al.,[21]) and normalized for the present case. Based on equipment cost data provided by an engineering company for setting up a full-scale process plant with a maximum capacity of 1 TPD of raw material, the total equipment cost was estimated at ₹18,00,000. The WCI is typically considered as a fraction of FCI, and in this study, it was taken as 17.6% of FCI. Accordingly, the total capital investment (TCI) for a 1 TPD MLP pyrolysis plant with an assumed oil yield of 60% was estimated to be ₹56,92,690 as detailed in **Table 8**.

3.5.2. Total Production Cost (TPC)

The total production cost comprises both manufacturing costs and general expenses. Manufacturing costs are further divided into variable production costs, fixed charges, and plant overheads. Variable costs include raw material, operating labor, utilities, office and clerical expenses, maintenance and repairs, operating supplies, and laboratory charges, while the feed MLPW was taken as free of cost. Fixed charges account for depreciation, local taxes, insurance, and plant overhead, while general expenses cover administrative overhead, marketing/distribution and selling costs, and research and development activities. For the present case, the process plant operates 330 days per year, producing approximately 600 ton of oil. A detailed breakdown of the annual production cost is presented in **Table 9**. Under the given conditions, the total production cost was estimated at ₹37,47,028. Based on market specifications, the assumed selling prices of the products are ~₹60 L^{-1} for oil.

3.5.3. Economic Analysis

The economic performance of the present process was evaluated using key indicators such as net profit, rate of return (ROR), and payback period for two scenarios of 42% and 60%

Table 7. Ultimate analysis of the MLP pyrolytic char at different conditions

Char samples without catalyst (%)	C (%)	H (%)	N (%)	S (%)	O (%)
400°C	75.96	8.719	0.59	0.084	5.729
500°C	75.96	8.675	1.21	0.131	7.758
600°C	56.98	1.451	1.26	0.116	8.138
Char samples with catalyst					
400°C	64.13	10.103	7.89	0.232	8.128
500°C	68.42	10.320	7.26	0.145	6.062
600°C	54.66	2.706	7.66	0.575	6.469

Table 8. Components of total capital investment (TCI) and their estimated cost for the MLPW pyrolysis plant for a capacity of 1 TPD

Total capital investment (TCI)	**Estimated Cost** (₹)
Fixed capital investment (FCI)	
A. Direct Cost	
Purchased equipment	1800000
Purchased equipment installation	239931
Instrumentation and controls	479863
Piping	400057
Electrical	279577
Building (Including Services)	400057
Yard Improvements	20080
Service Facilities	400057
Land	79805
Total Direct Cost	4099428
B. Indirect Cost	
Engineering and Supervision	199771
Construction Expenses and Contractor fee	160126
Legal expense	20080
Contingency	199771
Start-up Expenses	159611
Total Indirect Cost	739359
Total Fixed capital investment (FCI)	4838787
Working Capital (WCI)	853903
Total Capital Investment (TCI)	**5692690**

Table 9. Components of total production cost (TPC) per year for 1TPD MLPW pyrolysis plant to fuel oil.

Total production cost (TPC)	Estimated Cost (₹)
A. Manufacturing or Operating cost	
(i) Variable production cost	
Raw Materials	-
Operating Labour(Plant Manager - 1Operator-2Skilled Labour-2Unskilled Labour-2)	1440000
Utilities	329670
Maintenance and Repairs	96776
Operating Supplies	9677
Laboratory Charges	144000
(ii) Fixed charges	
Depreciation	491879
Local taxes	-
Insurance	19355
(iii) Plant overhead	720000
B. General Expenses	
Administrative Cost	216000
Distribution and Selling cost	279670
Total product cost (TPC)	**3747028**

Table 10. Parameters for economic analysis at 1 ton/day of plastic waste processing with 330 days plant operation.

Parameters	**Cost** (₹)	
	42% Yield	**60% Yield**
Manufacturing/Operating costs	20,20,123	20,20,123
Total production costs	3747028	37,47,028
Profit before tax	4568972	81,32,972
Net profit (30% tax)	3198280	56,93,080
Rate of return (ROR)	56	100
Payback period [Y]	2-3	1-2

overall yield of the fuel oil. Where in the 42% yield is considered from the experimental findings and the 60% is assumed for the ideal case for the high ROR and less payback period. Net profit was calculated as the difference between total annual sales and production costs, ROR as the ratio of net profit to total capital investment, and payback period as the ratio of fixed capital investment to annual profit. These parameters were estimated using the data from the capital investment and production cost analysis at different operating capacities, as summarized in **Table 10** for a 1 TPD MLP pyrolysis plant. The results in two scenarios indicate that at full operational capacity, the plant achieves a rate of return of nearly 56% with a payback period of 2-3 years in the case of 42% overall yield, while in the other case with an overall yield of 60%, a rate of return of nearly 100% with a payback period of 1–2 years. At 1 TPD operation, the net annual profit from the combined sale of oil is estimated at ₹56,93,080 INR. Overall, the assessment confirms that the MLP pyrolysis plant is economically viable and capable of generating value-added products with strong commercial potential.

4. Conclusion

This study establishes the viability of converting multilayer plastics (MLPs) into liquid fuels through pyrolysis and hydro-processing, offering a sustainable route for managing complex plastic waste. MLPs exhibit high volatile content (95.08%) and significant heating value (35.67 MJ/kg), confirming their suitability for thermal conversion. Thermogravimetric analysis revealed multi-stage decomposition between 250–500°C, with kinetic modeling indicating diffusion-controlled pyrolysis and activation energies of 177–218 kJ/mol, comparable to conventional polymers. Pyrolysis at 500°C yielded up to 42 wt.% oil, while subsequent hydro-processing improved fuel quality by raising car-

bon content (86.96%), calorific value (45.14 MJ/kg), and lowering heteroatoms (S < 0.1 wt.%, Cl < 0.03 wt.%). The upgraded crude oil shows a rich hydrocarbon characteristic mainly composed of alkanes and aromatics, and its physical and chemical properties are very close to those of diesel standards. The techno-economic assessment further confirmed process feasibility at scale. A 1 TPD MLP pyrolysis plant was estimated to generate a net annual profit of ₹56.93 lakh, with a rate of return of ~100% and a payback period of 1–2 years. These results indicate that MLP pyrolysis is technically effective and economically attractive, providing a theoretical basis for industrial-scale conversion of complex plastic waste into fuel-grade hydrocarbons.

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Declaration of competing interest

The authors declare no conflict of interest.

Credit authorship contribution statement

Chandan K Munagala: Experimental Investigation, Writing-original draft., Syed Md Razak: Methodology, Naresh Kathula: Formal analysis., Harsha Nagar: Validation, Analysis & Writing-Editing; Pravin R Likhar: Resources, Vineet Aniya: Conceptualization, Writing – Review & Editing.

Electronic Supplementary Material (ESM)

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