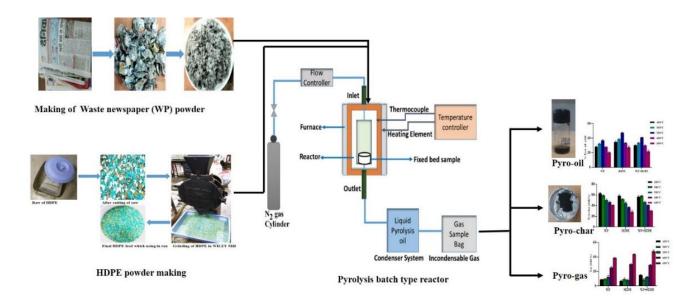
Co-pyrolysis of waste newspaper and high-density polyethylene for pyro-oil production and parameter optimization Pritam Kumar Patel ¹, Ankit kumar ¹ # These authors contributed equally Pritam Kumar Patel Department of Chemical Engineering Indian Institute of Technology Varanasi, India Keywords: Pyrolysis, Co-polymers, HDPE, Waste Newspaper (WP), Oil phase, Aqueous phase, Synergistic effect, Cross reaction product *Correspondence to: Ankit Kumar Department of Chemical Engineering Indian Institute of Science Bangalore Malleswaram Bangalore 560012 Phone: +91-8118089992

Email: ankitkumar16@iisc.ac.in

Abstract

High-density polyethylene (HDPE) and waste newspapers (WP) have the potential to revolutionize waste management and energy issues. To increase oil production, high-density polyethylene (HDPE) was initially co-pyrolysis with feedstock generated from waste newspapers (WP). Using thermo-gravimetric analysis (TGA), elemental analysis, Fourier transform infrared spectroscopy (FTIR), and scanning electron microscopy (SEM), the yield as well as the characteristics of liquid products (oil phase) have been researched and studied. Based on the physical property study and elemental analysis results, we found that HDPE had a high carbon content along with volatile matter content. Contrary to theoretical projections, experimental results indicated that significant pyrolytic activity occurred within the temperature range of 450–650 °C, resulting in a marked enhancement of the oil-phase yield. While pyrolysis of HDPE predominantly produces hydrocarbon-rich fractions, the pyrolysis of WP alone primarily generates oxygenated compounds within the oil phase.

Graphical abstract



Keywords: Pyrolysis, Co-polymers, HDPE, Waste Newspaper (WP), Oil phase, Aqueous phase, Synergistic effect, Cross reaction product

1. Introduction

India faces significant environmental challenges due to the accumulation of waste materials, such as high-density polyethylene (HDPE) and discarded newspapers. The country generates approximately 9.46 million tonnes of plastic waste annually, with around 40% remaining uncollected. HDPE, commonly used packaging and containers, constitutes a substantial portion of this waste[1]. Its non-biodegradable nature leads to long term persistence in landfills and natural environments, contributing to soil and water pollution[2]. Similarly, when waste newspaper not recycled, it accumulates in landfills where it starts to decompose anaerobically, releasing methane and becoming a potential source of greenhouse gases[3].

Population growth and economic development have increased the global demand of energy[4]. Currently, approximately 85% of global energy demand is met by fossil fuels, leading to significant economic and environmental challenges[5,6]. The extensive combustion of coal, petroleum, and natural gas results in substantial greenhouse gas (GHG) emissions, contributing to global warming and its associated socio-environmental impacts[7,8].

To address these issues, pyrolysis has emerged as a promising technology[9,10]. This thermochemical process converts organic materials, including HDPE and paper waste, into valuable products like pyrolytic oil, gas, and char in the absence of oxygen[11–13]. By transforming waste into fuel, pyrolysis not only reduces the volume of pollutants entering the environment but also provides an alternative energy source, thereby mitigating reliance on fossil fuels[14]. Implementing pyrolysis on a larger scale could play a crucial role in managing India's waste problem while contributing to sustainable energy production[15,16].

This research paper extends the scope of pyrolysis research beyond the conventional focus on single feed system by investigating the thermal decomposition behaviour of both individual and heterogeneous mixture of HDPE and waste newspaper[4,16,17]. Specifically, it aims to

characterize and compare the pyrolytic product obtained from three types of feed stocks. The first two involve homogeneous waste newspaper and HDPE which involves the pyrolysis of isolated, single waste streams. The second involves heterogeneous waste feed focusing on copyrolysis of mixed waste streams that more accurately reflect complex and varied composition found in real-world waste. Copolymerization of Waste newspaper (WP), HDPE, and a blend of WP and HDPE (1:1 ratio) was performed to understand the effect of operating temperature on the yield of liquid product, known as pyro-oil. The highest yield of pyro-oil was obtained in the case of HDPE at 550°C temperature compared to other feedstock, but it is higher than pristine waste newspaper.

2. Materials and method

2.1Chemicals used

We have started converting the waste newspaper into powder, we cut the newspaper into small pieces. We have washed the powder to remove the dust and finally converted into fine powder after more grinding. Dry the powder in an oven at 50°C for 4 hours and store it in airtight containers to maintain freshness. Recycling non-disposable plastic waste like HDPE into useful powder involves collecting and selecting HDPE from mixed plastics. After washing with ethanol, HDPE is cut into chips, ground using a WILLY MILL, and screened to less than 1mm size which is shown in supplementary information **fig. S1.** The HDPE powder is dried at 50°C for 8 hours, then stored in sealed containers for future use in crafting, composting, or as a raw material for products.

2.2 Experimental procedure

The process of thermally breaking down materials at high temperatures, frequently in an inert atmosphere, is called pyrolysis (sometimes called devolatilization). Typically, when the pyrolysis of organic materials is being performed volatile compounds are released along with

char, which is a solid residue abundant in carbon and some aqueous product. Pyrolysis is the process of breaking down organic compounds in the absence of oxygen in a fixed batch type of reactor for 2.30 hours at temperatures between 450° and 650° C with 50 ml/min of N_2 and a heating rate of 5 to 15° C/min.

The pyrolysis of pure waste newspaper (WP), high-density polyethylene (HDPE), and a 1:1 mixture of waste newspaper and HDPE was carried out in a 250 mL batch pyrolysis reactor. A schematic of the batch reactor and the product separation setup is presented in Fig.1.

Each experimental run utilized 8 g of powdered feedstock: either WP, HDPE, or a 1:1 mixture consisting of 4 g of WP and 4 g of HDPE. Prior to heating, the reactor was purged with nitrogen gas for 5 minutes at a flow rate of 50 mL/min to remove entrapped air. The feedstock was then heated to the target operating temperature and held for a specified residence time. All reactor valves were sealed during the process to maintain system integrity.

The furnace was programmed to ramp the temperature at a rate of 15 °C/min until reaching the desired operating temperature, ranging from 450 to 650 °C. Temperature control was achieved using a PID controller. The reactor was connected to a condensation system, where the evolved gases were cooled to condense the liquid fraction. The condensed liquid was collected as the bio-oil, while non-condensable gases were collected separately as gaseous products.

The operating temperature was systematically varied, and product yields were quantified as described in the Results section. The liquid fraction is referred to as pyro-oil, and the solid residue remaining in the reactor is termed pyro-char. All experiments were performed in triplicate to guarantee repeatability.

2.3 Product characterization

The functional group was examined using Fourier transform infrared spectroscopy. These measurements are performed with a spectrometer (NICOLET iS5, THERMO Electron

Scientific Instruments, produced in Japan) to determine the functional groups and type of bonding present in nanomaterials in terms of transmission % within the wavenumber range of 4000-500cm⁻¹. All these characterizations were conducted at room temperature.

WP and HDPE were pyrolyzed in a nitrogen atmosphere using a TGA system (STA 8000 & 8500 Perkin Elmer Ltd.; temperature precision: ± 0.1 K, microbalance sensitivity: ± 0.1 µg) to measure weight loss over time or temperature during the pyrolysis process. An alumina crucible containing about 5 mg of powdered WP&HDPE samples were maintained at room temperature or 18 °C[18,19]. To assess the kinetic triplets, the thermal study for WP & HDPE were conducted from 18 to 900°C utilizing three distinct heating rates of 15°C/min. Superficial microstructure and morphology and composition of elements in the solid residue were determined by EVO - SEM MA15 / 18 (Carl Zeiss Microscopy Ltd.) scanning electron microscope. Gas Chromatography–Mass Spectrometry (GC–MS) analysis was performed using a PerkinElmer Clarus 680 system equipped with two capillary columns: Elite-1 and Elite-5MS, each with dimensions of 30 m × 0.25 mm × 0.25 µm. This setup was employed to identify and characterize the molecular constituents present in the pyro-oil samples.

Nuclear Magnetic Resonance (NMR) spectroscopy was conducted using a Bruker AVANCE III 500 MHz spectrometer (AV 500) operating at a frequency of 500 MHz for both ¹H and ¹³C nuclei. Deuterated chloroform (CDCl₃) was used as the solvent for sample preparation. The spectrometer was configured with 5 mm TXI and BBO probes for the acquisition of ¹H and ¹³C spectra at ambient temperature[20]. Spectral data were processed and analyzed using TopSpin software, version 2.1, to determine the relative abundance and distribution of hydrocarbon species present in the pyro-oil.

2.4 Performance Parameter

Proximate and ultimate analysis

The ASTM-defined process is used to carry it out. This analysis determined the biomass's moisture content (MC), volatile matter (VM), ash content (AC), and fixed carbon (FC)[2].

Fixed Carbon

FC (wt. %) =
$$[100- (MC\% +VM \% + AC \%)]$$
(I)

Fixed Carbon on a dry basis.

$$FC_{db} = \frac{FC \times 100}{100 - MC} \tag{II}$$

Where FC_{db} represents fixed carbon on a dry basis.

Ultimate Analysis:

The elemental analysis composition (C, H, N, S, and O) is determined by ultimate analysis. The elemental composition of C, H, N, S, and O was determined[21].which is based on proximate analysis that yields acceptable accuracy because biomass has relatively low S and N content in the current study.

The equations for elemental compositions are given below.

$$C \text{ (wt. \%)} = [0.635*\text{FC} + 0.460*\text{VM} - 0.095*\text{Ash}] \qquad \qquad \text{(III)}$$

$$H \text{ (wt. \%)} = [0.059*\text{FC} + 0.060*\text{VM} + 0.010*\text{Ash}] \qquad \qquad \text{(IV)}$$

$$O \text{ (wt. \%)} = [0.340*\text{FC} + 0.469*\text{VM} - 0.023*\text{Ash}] \qquad \qquad \text{(V)}$$

$$Pyro\text{-Oil (\%)} = \text{(Weight of oil/ Weight of feed)*100} \qquad \qquad \text{(vi)}$$

$$Pyro\text{-char (\%)} = \text{(Weight of solid residue/ Weight of feed)*100} \qquad \qquad \text{(vii)}$$

$$Gas \text{ (\%)} = 100\text{-} \text{ (Oil (\%)} + \text{Solid char (\%))} \qquad \qquad \text{(viii)}$$

3. Results and discussion

The pyrolysis of waste newspaper (WP), high-density polyethylene (HDPE), and a 1:1 (w/w) mixture of both was conducted at varying temperatures within the range of 450–650 °C. The yields of pyro-oil, pyro-char and gas were quantified and compared across all temperature conditions. Each experiment was carried out with a fixed residence time of 120 minutes. Process performance was evaluated by determining the pyro-oil yield for each feedstock composition at each operating temperature.

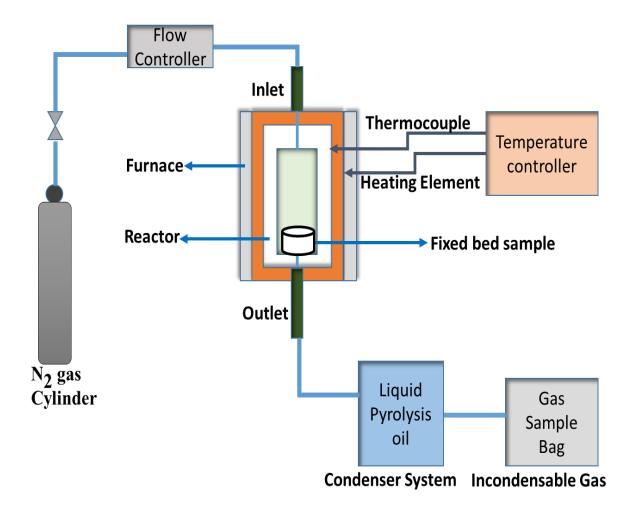


Fig.1. Schematic illustration of Pyrolysis batch type reactor

3.1 Physicochemical Properties Analysis

Table 1 shows the moisture content, volatile matter, ash content, and fixed carbon of waste newspaper (WP) and high-density polyethylene (HDPE). After analyzing the data below, we found that HDPE contains a significant level of volatile matter (92.4%). Therefore, the conclusion is that although the volatile matter trend is opposite, WP has higher fixed carbon and moisture content than HDPE. Table 2 presents the elements carbon (C), hydrogen (H), nitrogen (N), and sulphur (S). According to the CHNS study, HDPE has a maximum carbon content of 85.43%. Additionally, Table 02 displays the C/H ratios for WP and HDPE, which are 7.17 and 6.01, respectively.

Table 1Proximate analysis of waste newspaper (WP) and HDPE

	WP (wt. %)	HDPE (wt. %)
Volatile matter	79.8	92.4
Moisture Content	3.1	1.2
Ash Content	2.5	4.3
Fixed Carbon	14.6	2.1

Table 2
CHNS analysis of waste newspaper (WP) and HDPE

Component	WP (wt. %)	HDPE (wt.%)
С	59	85.43
Н	8.23	14.21
N	-	-
S	0.33	-
0	32.44	0.36

3.2 Impact of operating temperature

The operating temperature has very dominant effect on the yield of various products obtained during pyrolysis, as shown in figure 2 (A), (B) and (C). As the pyrolysis temperature rises, the oil yield first rises and subsequently falls, as the graph illustrates. Figures also show that while gas yield increased gradually as temperature increased, as the pyrolysis temperature rose from 450°C to 650°C, it climbed noticeably. The results demonstrated the effect of temperature on the fractional yields of volatiles and char under the current experimental settings. An increased devolatilization of the solid hydrocarbons in the char is responsible for the char yield reduction with pyrolysis temperature. Following the examination of all three types of feed, we obtained

a high yield from HDPE because, according to CHNS analysis, the material has a high carbon content.

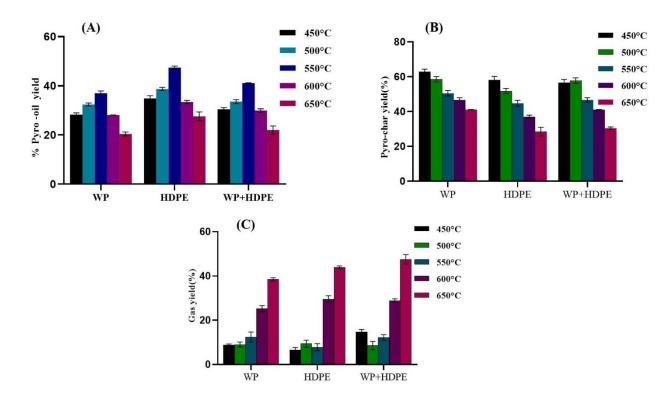


Fig. 2. Effect of operating temperature on pyrolysis products: (A) Pyro-oil, (B) Pyro-Char, and (C) Gas. All these experiments have been done in triplicates, and mean ±SD deviations of results have been plotted.

The pyrolysis oil yield depends largely on the chemical composition and thermal behaviour of feedstocks used. In this work three types of feedstocks were used -Waste newspaper (WP), HDPE and the blend of WP & HDPE (1:1) while varying the temperature to observe their oil yield.

HDPE is a synthetic polymer composed of long chains of saturated hydrocarbon. During pyrolysis these chains break down thermally into smaller hydrocarbon molecules, which readily vaporize and condense into oil. Since, HDPE lacks moisture, oxygen, and inorganics, it has high volatile content and produces fewer solid residues, leading to higher oil yield.

WP is rich in cellulose, hemicellulose, and lignin, which are oxygenated biopolymers. During pyrolysis, these compounds decompose into gases, water, and char with relatively less oil. The

presence of moisture and oxygen-rich compounds results in lower oil yield and higher solid char residues. Lignin degrades over a wider temperature range and forms complex aromatics (which is confirmed by NMR and GCMS analysis), contributing to increased char formation.

When WP is mixed with HDPE, a synergistic effect can occur. The hydrogen-rich HDPE can donate hydrogen radicals to stabilize oxygenated intermediates formed from WP decomposition. This interaction can suppress char formation and enhance liquid production. However, due to the presence of WP, the oil yield is still less than pure HDPE but higher than WP alone.

Table3Effect of operating temperature on yield (%) of pyrolysis oil.

Temperature(°C)	WP	HDPE	WP+HDPE (1:1)
450	20	22.00	21.25
450	28	33.98	31.25
500	32.18.	37.96	33.19
550	37	47.16	41.23
330	37	47.10	41.23
600	27.89	33.12	30.56
650	20.56	25.63	22.75

3.3 Pyro char characterization

3.3.1 FTIR analysis

FTIR was used to examine the chemical makeup of the supporting material. Newspaper samples were subjected to FTIR analysis, with findings displayed in Fig.3. The wide absorption band at 3438 cm⁻¹ (caused by intermolecular hydrogen bonding and –OH group stretching) is home to the peaks that represent the cellulose molecule's backbone. A large absorbent peak is detected at around 3336 cm⁻¹ for paper, which is linked to the hydroxyl group of cellulose's -

OH stretching and the absorbed water's intra-hydrogen bond stretching [22]. The newspaper and HDPE show the peaks at 2908 cm⁻¹ and 2916 cm⁻¹ wave number peaks which are associated with the C-H stretching vibrations of methyl and methylene groups [23]. The newspaper FTIR curve shows the peak at 2126 cm⁻¹ corresponds to the CEC stretching of weak alkyne and monosubstituted present and other peaks like 1635 cm⁻¹ correspond to the C=C stretching of medium alkene and disubstituted (cis) present, the C-H bending of medium alkane and methyl group present is represented by both of them, respectively, by 1434 cm⁻¹ and 1450 cm⁻¹; the C-O stretching of strong alkyl aryl ether present (CH-O-CH₂ stretching) is represented by 1265 cm⁻¹; the C-O stretching of strong primary alcohol present is represented by 1054 cm⁻¹ of newspaper and 1055 cm⁻¹ of HDPE; the C=C bending of strong alkene and vinylidene present is represented by 895 cm⁻¹ of newspaper and 883 cm⁻¹ of HDPE

.

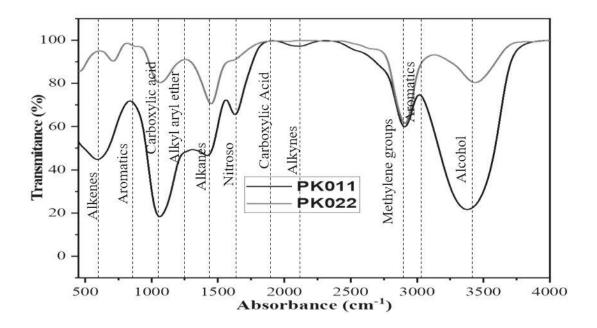


Fig. 3. FTIR of feed of WP(PK011) and HDPE(PK022)

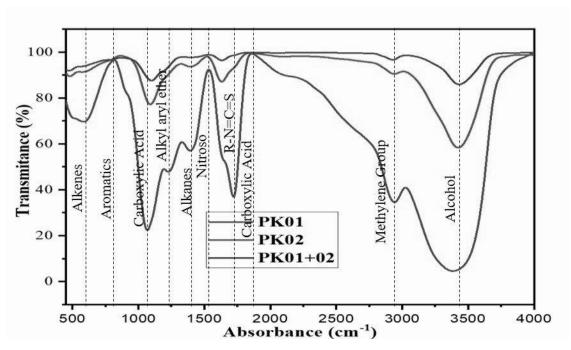


Fig. 4: FTIR of pyro char of WP(PK01), HDPE(PK02) and WP+HDPE(PK01+02)

FTIR analysis was done on newspaper oil product, HDPE, and newspaper and HDPE combined. Fig.4 shows the results. The three plots (Fig.4) include maxima at 3380, 3424, and 3430 cm⁻¹, which correspond to the hydroxyl group of cellulose's -OH stretching and the intrahydrogen bond stretching of the absorbed water [13]. Other peaks on all three figures are wave number peaks of 2854, 2925, and 2942 cm⁻¹, corresponding to the C–H stretching vibrations of the methyl and methylene groups. Strong C=O stretching peak PK01 of the conjugated anhydride is situated at wave number 1720 cm⁻¹. The strong C=O stretching of the carboxylic acid is connected to PK02's wave number of 1714 cm⁻¹, which takes the form of a dimer. The functional group medium C=C stretching of the conjugated alkene is correlated with wave numbers 1631 and 1633 cm⁻¹, which show peaks of PK02 and PK03. Aldehyde exhibits mild C–H bending, as indicated by additional wave values of 1390 and 1384 cm⁻¹, respectively, collected from graphs PK01 and PK02. The alkyl aryl ether with a strong C-O stretching is indicated by the graph PK01's peak wave number of 1225 cm⁻¹. The absorbance peak of wave numbers 1105 and 1093 cm⁻¹ (PK02 & PK03) indicates a substantial C–O stretching of

secondary alcohol. The last peak, measured at 1059 cm⁻¹, which has a low wave number (PK01), exhibits a substantial C–O stretching of the main alcohol.

3.3.2 FESEM and energy dispersive X-ray (EDX) analysis

FESEM-EDX (Field Emission Scanning Electron Microscopy) analysis is employed to examine the morphological structure and quantify the dispersion of various elements in pyrochar. Scanning Electron Microscopy (SEM) analysis of waste newspaper (WP) and high-density polyethylene (HDPE) was performed at magnifications of 100X, 500X, 1000X, 5000X, 10000X, 20000X, and 30000X, as shown in Fig.5 and Fig.6. The surface morphology of WP indicates that pyrolysis led to a considerable reduction in structural heterogeneity compared to HDPE. Fig.6 clearly illustrates the morphological deformation and surface disruption noted in HDPE. Additionally, both materials demonstrated significant ash content, with HDPE and WP containing approximately 18 wt% and 12 wt%, respectively.

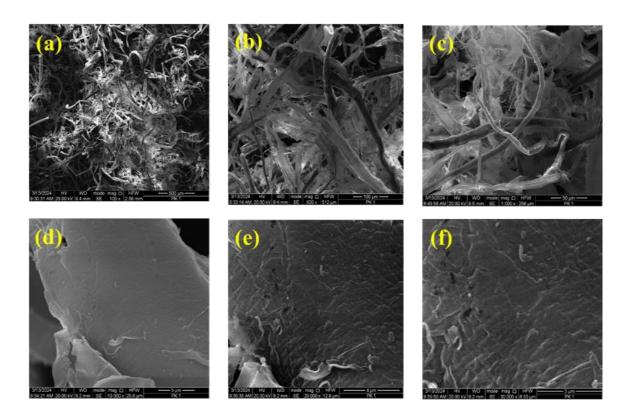


Fig. 5. SEM analysis of WP at different magnifications (a)100X, (b)500X, (c)1000X (d) 10000X, (e) 20000X and (f) 30000

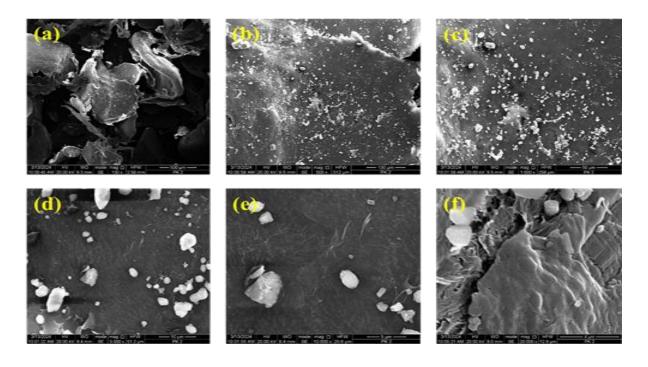


Fig.6. SEM analysis of HDPE at different magnifications (a)100X, (b)500X, (c)1000X (d) 10000X, (e) 20000X and (f) 30000

Identifying the inorganic constituents in each sample was essential, as the ash content and elemental composition of biomass significantly influence its thermal degradation behaviour, as reported in previous studies[24]. To elucidate the elemental profiles, Energy-Dispersive X-ray Spectroscopy (EDX) analysis was performed on both waste newspaper (WP) and high-density polyethylene (HDPE) samples. The EDX results, summarized in Table 04, indicate the presence of elements such as silicon (Si), antimony (Sb), and calcium (Ca) in the WP sample. Similarly, the HDPE sample revealed the presence of potassium (K), silicon (Si), calcium (Ca), titanium (Ti), and iron (Fe). A quantitative distribution of the detected elements is also presented in Table 4.

Table 4Composition of elemental species taken from EDX

Elements	WP (wt %)	HDPE (wt %)
С	39	84

0	43	4	
Si	5	3	
S	4	3	
Sb	3	-	
Fe	-	1	
Ca	6	4	
Ti	-	1	

3.3.3 TGA and DTG Analysis

Thermogravimetric Analysis (TGA) was conducted to evaluate the thermal decomposition behaviour of waste newspaper (PK011), HDPE (PK022), and their 1:1 blend (PK011+022) under a nitrogen atmosphere at a constant heating rate of 10 °C/min. The temperature was ramped from ambient to 900 °C, with a nitrogen flow rate maintained at 100 mL/min. fig. 7 presents TGA curves illustrating mass loss profiles for PK011, PK022, and the blend. Corresponding DTG curves, depicting the derivative of mass loss concerning temperature, are shown in fig8.

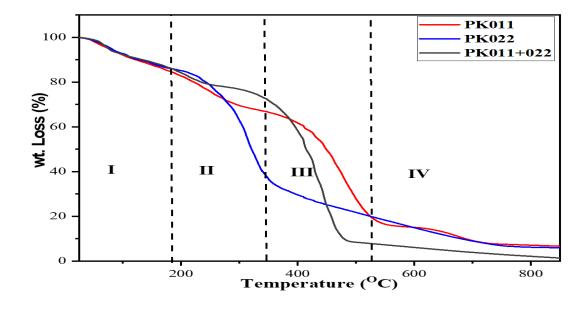


Fig.7. TGA of feed of WP (PK011), HDPE (PK022) and WP+HDPE (PK011+022)

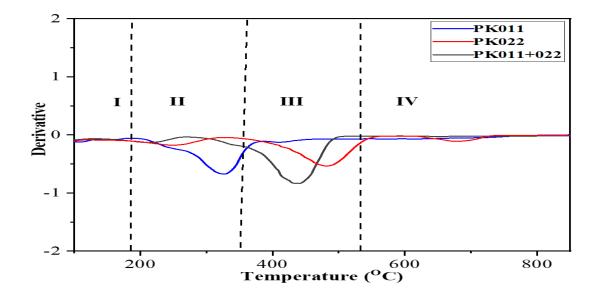


Fig.8. DTG of feed of WP (PK011), HDPE (PK022) and WP+HDPE (PK011+022)

The thermal decomposition of waste newspaper (WP), HDPE, and their 1:1 blend was characterized by three distinct stages, as evidenced by the TGA and DTG profiles. In the initial stage (up to ~180 °C), dehydration and the removal of surface moisture and light volatiles occurred, resulting in a minor mass loss of approximately 3.4% to 7%[25].

The second stage (180–380°C) exhibited the most significant mass loss, ranging from 47% to 51%, as indicated by the steep slope in the TGA curve[26]. This region corresponds to active pyrolysis and is characterized by the thermal degradation of hemicellulose (247–290 °C), observed as a shoulder on the DTG curve, followed by cellulose decomposition (290–380 °C), marked by a pronounced DTG peak. Similar decomposition behaviour has been reported[27,28].

The third stage (above 380 °C) is marked by a slower degradation rate. Lignin decomposition, occurring within 360–650 °C, is facilitated by the presence of inorganic alkali and alkaline earth metals, which reduce its thermal stability. This phase involves complex multistep reactions, including both parallel and sequential mechanisms, leading to overlapping peaks in

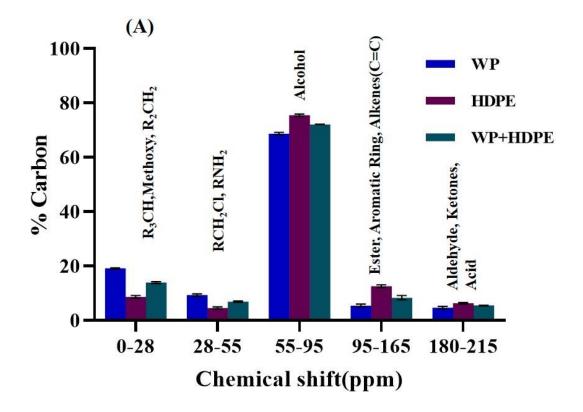
the DTG curves[29]. These reactions result in the formation of condensable and non-condensable volatiles, commonly referred to as pyro-condensation and carbonization processes. Beyond 590°C, the mass loss rate approaches zero, indicating the completion of devolatilization and the onset of char formation. This stage is associated with the final conversion of WP, HDPE, and their blend into stable carbonaceous residues.

3.4 Pyro-oil characterization

3.4.1 NMR analysis

Nuclear Magnetic Resonance (NMR) analysis of pyro-oil obtained from pyrolysis at 550 °C was conducted to identify the protons present in various functional groups. The ¹H NMR spectra shown in Figure 9(B) reveal that the highest percentage of protons appears in the spectral region of 0–1.5 ppm, confirming the presence of aliphatic protons attached at the β and γ positions relative to double bonds, with a maximum aliphatic content of 83.17% observed in HDPE. The spectral region from 1.5–2.5 ppm indicates the presence of protons attached to heterocyclic amines. Protons observed in the region between 2.5–4 ppm confirm the presence of alcohol, ether, and methoxy functional groups in the pyro-oil, which is also supported by GC-MS analysis[30].

The region from 6–7.5 ppm suggests the presence of aromatic protons and protons bonded to double-bonded carbon atoms in alkenes. A high percentage of aromatic protons is particularly evident in waste newspaper (WP), attributed to phenolic groups present in lignin. A very low percentage of protons is observed in the 7.5–10.5 ppm range, indicating a low abundance of aldehydes and carboxylic acids in the oil sample due to retro-aldol reaction.



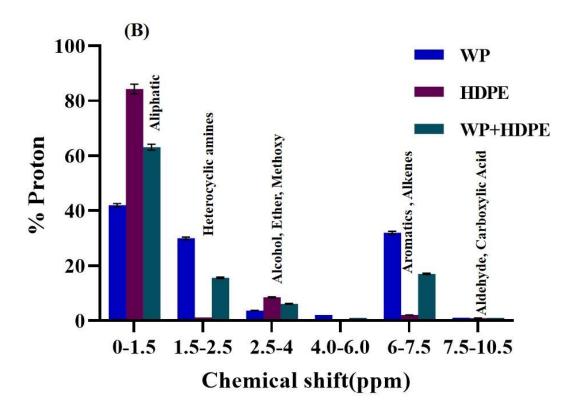


Fig.9. 13C NMR (A) and 1H NMR(B) of pyro oil obtained from the pyrolysis of WP, HDPE, and WP+ HDPE (1:1)

The ¹³C NMR spectra shown in Figure 9(A) display a chemical shift range of 0–215 ppm, representing the distribution of carbon atoms in various functional groups present in the oil samples obtained after the pyrolysis of all feedstocks at 550 °C.

The graph indicates the presence of aliphatic and methoxy groups in the spectral region of 0–28 ppm. The region between 28 and 55 ppm confirms the presence of alkyl halide and amine groups in the oil sample. The highest percentage of carbon appears in the 55–95 ppm region, indicating the presence of carbon atoms bonded to alcohol, phenolic, methoxy, and ether groups. The extreme downfield region of 180–215 ppm suggests the presence of carbon atoms associated with aldehyde, ketone, and carboxylic acid groups. The lower percentage of carbon in the 95–165 ppm and 180–215 ppm regions indicate limited dissociation of higher molecular weight compounds into esters, aromatic compounds, and aldehydes.

3.3.2 GC-MS analysis

The pyro-oil samples obtained at optimal temperature(550°C) were analysed by GC-MS to detect the compound present in it. GC-MS peak of pyro oil from all samples has been shown in Fig.S2 (Supplementary image), and the compounds present in the oil have been shown in Table 5.

Table 5

Identification of compounds present in pyro-oil at 550°C using GC-MS spectra

S. No	Retention	Compound name	Chemical	MW	Area (%)
	time		formula		
1	1.41	1-Penethyl-5	C ₁₄ H ₁₉ N ₅	257	27.12
		Pyrrolidine-1-methyl-			
		1H-Tetrazole			

1	3.39	Pyrocatechol	C ₉ H ₁₀ O ₃	199	0.047
		-			
		monomethyl ether			
2	3.05	4-Methoxyheptan-3-	C ₈ H ₁₈ O	130	0.177
		ol			
3	7.16	Tert-Butyl-(2,2-	C ₉ H ₁₆ Cl ₂	194	0.031
) 10 <i>2</i>		
		dichloro-1-			
		methylcyclopropyl)			
		methane			
4	9.47	Trans-2-Methyl-4-	C10H ₂₀ O ₂ S	204	2.022
		butyl-1-			
		thiacyclohexane			
5	10.43	1-(2,3,3-	C ₁₃ H ₂₀ O ₂	208	12.89
		trimethylcyclopentyl)-			
		2-pentene-1,4-dione			
6	10.55	Oleic acid	C ₁₈ H ₃₄ O ₂	282	2.543
7	11.75	Bendiocarb	C ₁₁ H ₁₃ O ₄ N	223	0.0529
8	11.92	Vanillin	C ₈ H ₈ O ₃	153	0.324
9	12.41	2,6-	C ₁₇ H ₁₇ O ₅ N	315	0.199
		Pyridinedicarboxylic			
		Acid			
10	13.52	m-Nitroaniline	C ₆ H ₆ O ₂ N ₂	138	0.089
11	14.34	Aspisospermidin-17-	C ₂₃ H ₃₀ O ₅ N ₂	414	1.023
		ol			

The results of the GC-MS analysis of pyro oil, shown in Table 5, indicate that the oil primarily consists of alcohols, ethers, and esters. However, the mass spectra confirm the presence of esters and carboxylic acids[24]. Pyro oil contains the major compound tetrazole, which has an area percentage of 27.12, along with other significant compounds such as vanillin, oleic acid, Dione, and Thiacyclohexane, extracted from the NIST library of mass spectra[31]. Higher temperatures promote the decomposition of WP and HDPE, leading to the breaking of ether aryl bonds, producing phenolic compounds, and limiting the recombination of intermediates. Esterification is one of the primary reaction pathways that generates esters in the reaction between acid and alcohol. Waste paper is rich in lignocellulosic materials, particularly lignin, which serves as the primary precursor for vanillin formation during pyrolysis. However, HDPE does not contribute to the production of vanillin[4,30]. The pyro-oil produced during the pyrolysis of waste paper and HDPE contains some higher molecular weight compounds that are non-volatile and can not be detected by GC-MS.

4. Conclusion

The present study investigates the effect of operating temperature (450–650 °C) on the yield of pyro-oil obtained from the pyrolysis of waste newspaper (WP), high-density polyethylene (HDPE), and a 1:1 blend of WP and HDPE. The results demonstrate that the yield of pyro-oil increased with temperature for all feedstocks up to 550 °C, beyond which it began to decline. The maximum pyro-oil yields were recorded as 38.03% for WP, 47.16% for HDPE, and 41.11% for the WP+HDPE blend.

The temperature exhibited a synergistic effect in enhancing the yield of pyro-oil. The oil obtained from pyrolysis was found to contain aliphatic and aromatic hydrocarbons, alcohols, phenolic compounds, aldehydes, ethers, ketones, and trace amounts of carboxylic acids, as confirmed by NMR, FTIR, and GC-MS analyses.

FESEM-EDX (Field Emission Scanning Electron Microscopy with Energy Dispersive X-ray

Spectroscopy) analysis of the WP surface morphology revealed a significant reduction in

structural heterogeneity after pyrolysis compared to HDPE. EDX results, presented in Table

04, showed the presence of elements such as silicon (Si), antimony (Sb), and calcium (Ca) in

the WP sample. In contrast, the HDPE sample contained potassium (K), silicon (Si), calcium

(Ca), titanium (Ti), and iron (Fe). Overall, the study confirms that HDPE produces the highest

pyro-oil yield among the three feedstocks examined.

Author Information

Corresponding author

*E-mail: ankitkumar16@iisc.ac.in. Phone: +91-8118089992.

Author Contributions

Pritam: MTech. student; conducted experiments data interpretation.

AK: Developed the research concept, supervised pyrolysis experiments, prepared figures,

tables, the manuscript, analyzed generated data, and contributed to manuscript editing.

Notes

The authors declare no competing financial interest.

Acknowledgment

The author thanks the ministry of Education and Science govt of India and IIT Roorkee and

IIT BHU for financial and technical assistance for this work.

5. References

- [1] A. Locaspi, A. Frassoldati, T. Faravelli, Reduced-order condensed-phase kinetic models for polyethylene, polypropylene and polystyrene thermochemical recycling, Chemical Engineering Journal 500 (2024) 156949. https://doi.org/10.1016/j.cej.2024.156949.
- [2] A.C. Johansson, L. Sandström, O.G.W. Öhrman, H. Jilvero, Co-pyrolysis of woody biomass and plastic waste in both analytical and pilot scale, J Anal Appl Pyrolysis 134 (2018) 102–113. https://doi.org/10.1016/j.jaap.2018.05.015.
- [3] J. Akhtar, N.A.S. Amin, A review on process conditions for optimum bio-oil yield in hydrothermal liquefaction of biomass, Renewable and Sustainable Energy Reviews 15 (2011) 1615–1624. https://doi.org/10.1016/j.rser.2010.11.054.
- [4] A.K. Varma, P. Mondal, Pyrolysis of sugarcane bagasse in semi batch reactor: Effects of process parameters on product yields and characterization of products, Ind Crops Prod 95 (2017) 704–717. https://doi.org/10.1016/j.indcrop.2016.11.039.
- [5] A.R.K. Gollakota, N. Kishore, S. Gu, A review on hydrothermal liquefaction of biomass, Renewable and Sustainable Energy Reviews 81 (2018) 1378–1392. https://doi.org/10.1016/j.rser.2017.05.178.
- [6] R. Olcese, V. Carré, F. Aubriet, A. Dufour, Selectivity of bio-oils catalytic hydrotreatment assessed by petroleomic and GC*GC/MS-FID analysis, in: Energy and Fuels, 2013: pp. 2135–2145. https://doi.org/10.1021/ef302145g.
- [7] Y. Cao, C. Zhang, D.C.W. Tsang, J. Fan, J.H. Clark, S. Zhang, Hydrothermal liquefaction of lignin to aromatic chemicals: Impact of lignin structure, Ind Eng Chem Res 59 (2020) 16957–16969. https://doi.org/10.1021/acs.iecr.0c01617.
- [8] H. Chen, Z. He, B. Zhang, H. Feng, S. Kandasamy, B. Wang, Effects of the aqueous phase recycling on bio-oil yield in hydrothermal liquefaction of Spirulina Platensis, A-cellulose, and lignin, Energy 179 (2019) 1103–1113. https://doi.org/10.1016/j.energy.2019.04.184.
- [9] M. Sekar, V.K. Ponnusamy, A. Pugazhendhi, S. Nižetić, T.R. Praveenkumar, Production and utilization of pyrolysis oil from solidplastic wastes: A review on pyrolysis process and influence of reactors design, J Environ Manage 302 (2022). https://doi.org/10.1016/j.jenvman.2021.114046.
- [10] M. Sogancioglu, G. Ahmetli, E. Yel, A Comparative Study on Waste Plastics Pyrolysis Liquid Products Quantity and Energy Recovery Potential, in: Energy Procedia, Elsevier Ltd, 2017: pp. 221–226. https://doi.org/10.1016/j.egypro.2017.07.020.
- [11] S.M. Al-Salem, Thermal pyrolysis of high density polyethylene (HDPE) in a novel fixed bed reactor system for the production of high value gasoline range hydrocarbons (HC), Process Safety and Environmental Protection 127 (2019) 171–179. https://doi.org/10.1016/j.psep.2019.05.008.
- [12] S.M. Al-Salem, P. Lettieri, Kinetic study of high density polyethylene (HDPE) pyrolysis, Chemical Engineering Research and Design 88 (2010) 1599–1606. https://doi.org/10.1016/j.cherd.2010.03.012.

- [13] W. Chen, S. Shi, J. Zhang, M. Chen, X. Zhou, Co-pyrolysis of waste newspaper with high-density polyethylene: Synergistic effect and oil characterization, Energy Convers Manag 112 (2016) 41–48. https://doi.org/10.1016/j.enconman.2016.01.005.
- T. Suresh, N. Sivarajasekar, K. Balasubramani, Enhanced ultrasonic assisted biodiesel production from meat industry waste (pig tallow) using green copper oxide nanocatalyst: Comparison of response surface and neural network modelling, Renew Energy 164 (2021) 897–907. https://doi.org/10.1016/j.renene.2020.09.112.
- [15] Z. Tang, W. Chen, Y. Chen, H. Yang, H. Chen, Co-pyrolysis of microalgae and plastic: Characteristics and interaction effects, Bioresour Technol 274 (2019) 145–152. https://doi.org/10.1016/j.biortech.2018.11.083.
- [16] K. Ding, Z. Zhong, J. Wang, B. Zhang, L. Fan, S. Liu, Y. Wang, Y. Liu, D. Zhong, P. Chen, R. Ruan, Improving hydrocarbon yield from catalytic fast co-pyrolysis of hemicellulose and plastic in the dual-catalyst bed of CaO and HZSM-5, Bioresour Technol 261 (2018) 86–92. https://doi.org/10.1016/j.biortech.2018.03.138.
- [17] E. Lazzari, T. Schena, C.T. Primaz, G.P. da Silva Maciel, M.E. Machado, C.A.L. Cardoso, R.A. Jacques, E.B. Caramão, Production and chromatographic characterization of bio-oil from the pyrolysis of mango seed waste, Ind Crops Prod 83 (2016) 529–536. https://doi.org/10.1016/j.indcrop.2015.12.073.
- [18] B. Biswas, D. Sahoo, R.K. Sukumaran, B.B. Krishna, J. Kumar, Y.S. Reddy, V.P. Adarsh, A. Puthiyamadam, K.K. Mallapureddy, S.B. Ummalyma, T. Bhaskar, Co-hydrothermal liquefaction of phumdi and paragrass an aquatic biomass: Characterization of bio-oil, aqueous fraction and solid residue, Journal of the Energy Institute 102 (2022) 247–255. https://doi.org/10.1016/j.joei.2022.03.013.
- [19] N. Shimizu, B. Zeng, K. Kushima, Hydrothermal liquefaction of wood chips under supercritical and subcritical water reaction conditions, SN Appl Sci 3 (2021). https://doi.org/10.1007/s42452-021-04561-0.
- [20] Y. Miyata, K. Sagata, M. Hirose, Y. Yamazaki, A. Nishimura, N. Okuda, Y. Arita, Y. Hirano, Y. Kita, Fe-Assisted Hydrothermal Liquefaction of Lignocellulosic Biomass for Producing High-Grade Bio-Oil, ACS Sustain Chem Eng 5 (2017) 3562–3569. https://doi.org/10.1021/acssuschemeng.7b00381.
- [21] P. Yadav, S.N. Reddy, Reaction kinetics for hydrothermal liquefaction of Cu-impregnated water hyacinth to bio-oil with product characterization, Ind Crops Prod 198 (2023). https://doi.org/10.1016/j.indcrop.2023.116677.
- [22] S. Das, Mechanical and water swelling properties of waste paper reinforced unsaturated polyester composites, Constr Build Mater 138 (2017) 469–478. https://doi.org/10.1016/j.conbuildmat.2017.02.041.
- [23] M.K. Hossain, M.W. Dewan, M. Hosur, S. Jeelani, Effect of surface treatment and nanoclay on thermal and mechanical performances of jute fabric/biopol 'green' composites, Journal of Reinforced Plastics and Composites 30 (2011) 1841–1856. https://doi.org/10.1177/0731684411430426.

- [24] P. Yadav, S.N. Reddy, Catalytic hydrothermal liquefaction of water hyacinth: An investigation into bio-oil generation and co-synthesis of Cu core-shell carbon hybrids, Int J Green Energy (2023). https://doi.org/10.1080/15435075.2023.2253872.
- [25] P. Yadav, S.N. Reddy, Experimental and Kinetic modeling of In-situ Catalytic (Fe/Cu) Pyrolytic Degradation of Water Hyacinth, J Therm Anal Calorim 148 (2023) 12761–12780. https://doi.org/10.1007/s10973-023-12573-8.
- [26] X. Zhang, H. Lei, L. Zhu, X. Zhu, M. Qian, G. Yadavalli, J. Wu, S. Chen, Thermal behavior and kinetic study for catalytic co-pyrolysis of biomass with plastics, Bioresour Technol 220 (2016) 233–238. https://doi.org/10.1016/j.biortech.2016.08.068.
- [27] A.H. Faris, A.A. Rahim, M.N. Mohamad Ibrahim, M.H. Hussin, A.M. Alkurdi, A. Salehabadi, Investigation of oil palm based Kraft and auto-catalyzed organosolv lignin susceptibility as a green wood adhesives, Int J Adhes Adhes 74 (2017) 115–122. https://doi.org/10.1016/j.ijadhadh.2017.01.006.
- [28] S. Xu, B. Cao, B.B. Uzoejinwa, E.A. Odey, S. Wang, H. Shang, C. Li, Y. Hu, Q. Wang, J.N. Nwakaire, Synergistic effects of catalytic co-pyrolysis of macroalgae with waste plastics, Process Safety and Environmental Protection 137 (2020) 34–48. https://doi.org/10.1016/j.psep.2020.02.001.
- [29] S. Nanda, J. Mohammad, S.N. Reddy, J.A. Kozinski, A.K. Dalai, Pathways of lignocellulosic biomass conversion to renewable fuels, Biomass Convers Biorefin 4 (2014) 157–191. https://doi.org/10.1007/s13399-013-0097-z.
- [30] A. Kumar, P. Yadav, S.N. Reddy, Catalytic (copper) hydrothermal liquefaction for lignin to produce high quality bio-oil and nano Cu carbon hybrids material, Chem Eng Sci 270 (2023). https://doi.org/10.1016/j.ces.2023.118548.
- [31] V.B.F. Custodis, C. Bährle, F. Vogel, J.A. Van Bokhoven, Phenols and aromatics from fast pyrolysis of variously prepared lignins from hard- and softwoods, J Anal Appl Pyrolysis 115 (2015) 214–223. https://doi.org/10.1016/j.jaap.2015.07.018.